CONNECTICUT RESOURCES RECOVERY AUTHORITY

ADDENDUM NO. 1
Issued March 20, 2013

TO

"REQUEST FOR BIDS
FOR
ENVIRONMENTAL MONITORING, LABORATORY ANALYSIS AND REPORTING SERVICES FOR CRRA LANDFILLS"
(RFB Number 13-EN-002)
(RFB Issued February 25, 2013)

Note: **Bidders are required to acknowledge this and all Addenda in Section 6(a) of the Bid Form.**

1. ANSWERS TO SUBMITTED QUESTIONS

This Addendum consists of the Connecticut Resources Recovery Authority's responses to written questions that were received by CRRA by 3:00 p.m., Friday, March 15, 2013.

1.	Question	Are bid bonds required?
	Answer	There is not a bid bond associated with this RFB.
2.	Question	Are Connecticut firms preferred? Will CRRA consider a bid from a firm that does not currently operate an office within the state?
	Answer	CRRA's procurement policy states that: "In its Contract selection process, CRRA shall insofar as is practicable and assuming all things are comparable between price and quality, give preference to entities or persons based in Connecticut."
3.	Question	Is CRRA currently performing monitoring and laboratory services at the landfills included in this procurement? If so, who is currently providing this service to CRRA? Can we get a copy of the bidder's list from the previous RFP that was issued for this scope of work? We would be interested in seeing the list of bidders, the winning firm and any price-related information you can provide.
	Answer	The RFB via which CRRA previously procured monitoring and laboratory services at the landfills included in this procurement was issued in 2010 as RFB10-EN-002. A copy of that RFB, including the applicable Scopes of Services and a copy of the Board of Directors Resolution which specifies the firms and prices selected at that time is available at http://www.crra.org/pages/busi_opp_closed.htm#em10.
4.	Question	When doing business with CRRA, is there a pre-qualification or pre-registration requirement?
	Answer	Any of the documents anticipated to be required as part of this RFB are contained in the RFB Package Documents, although that in no way limits CRRA's right to issue addenda to this RFB as specified in article 8 of the Instructions to Bidders (Section 2 of the RFB Package Documents).
5.	Question	Will CRRA require the services of a Connecticut Licensed Environmental Professional (LEP) under this contract?
	Answer	Services of a Connecticut Licensed Environmental Professional (i.e., conducting and verifying remediation under the Remediation Standard Regulations) are not required under this contract. When evaluating a Bidder's qualifications to perform the Scope of Services, however, CRRA does consider LEP licensure to be one manner for a Bidder to demonstrate its knowledge and capabilities.

6.	Question	Will the contractor be required to coordinate activities on this contract with the landfill operator, with CRRA, or both?
	Answer	Please refer to Sections 2.3 and 2.4 of the Form of the Agreement (Section 6 of the RFB Package Documents)
7.	Question	Are there any changes anticipated to the scope of work at any of the sites?
	Answer	No, there are no changes anticipated to the scope of work at any of the landfills during the term of the anticipated Agreements.
8.	Question	Are there any restrictions to the type of vehicles used on the landfills or on the flood control levee at the Hartford Landfill?
	Answer	All main roads and access roads are accessible by two-wheel drive vehicles at each of the landfills. It is not necessary to drive any vehicle over the caps of the landfills. Any damage that is caused is the responsibility of the Consultant to repair. Four-wheel drive and All Terrain Vehicles may be used at each landfill at the Consultant's discretion. Vehicles may be driven on top of the flood control levee at the Hartford Landfill, as well as along the gravel road at the base of the flood control levee.
9.	Question	At the Hartford Landfill, are any of the surface water collection points within the radius of the 500-ft buffer around the existing eagle's nest?
	Answer	As stated by CRRA during the pre-bid conference and site tour, when developing their bid prices for the Hartford Landfill, Bidders should <u>not</u> consider potential delays and the need to potentially conduct supplemental sampling events due to the potential presence of nesting bald eagles in the vicinity of some Hartford Landfill monitoring locations. If sampling of some monitoring locations needs to be delayed until after June 1st due to the presence of nesting bald eagles, then the sampling delay for those specific monitoring locations would be considered outside of the Scope of Services, and CRRA would seek to enter into an RFS with the Consultant to complete the supplemental sampling event and its associated reporting.
10.	Question	Regarding the Hartford Police Department shooting range next to the Hartford Landfill, is there someone at the Hartford Police Department that the contractor should contact to arrange for clearance or schedule the testing at the sites near the shooting range?
	Answer	The Hartford Police Department has a Range Master who is the point of contact for sampling notification.
11.	Question	Are all of the testing wells at the Ellington Landfill roughly the same 2" PVC construction? Are there any micro-wells?

	Answer	As summarized in Table 1 of the Ellington Landfill Scope of Services, all monitoring wells are 2" diameter. There are no micro-wells at the Ellington Landfill.
12.	Question	Does CRRA want to see a draft of all reports first?
	Answer	Yes, the Consultant must provide a draft of every report to CRRA for review and comment before the report is finalized for submission. Per each scope of services, an electronic copy of the draft is due 10 business days prior to the due date of the report. CRRA prefers a Word version of the report text in order to be able to provide a "red-line" mark-up of the draft with CRRA's questions, comments and suggested revisions. All other components of the draft report (drawings, analytical reports, tables, etc.) can be sent as PDF documents.
13.	Question	Would you please provide a list of analytical laboratories that are covered by the Connecticut Department of Administrative Services ("CTDAS") contract number 09PSX0054, "Environmental Laboratory Testing Services"?
	Answer	CTDAS contract number 09PSX0054 can be accessed through the CTDAS internet site at the following URL: http://www.biznet.ct.gov/SCP_Documents/Results/6062/Contract%20Supplement4.pdf
14.	Question	Several of the scopes of service require collection of equipment blanks when completing surface water sampling. Are equipment blanks required if we plan to only use disposable equipment/supplies?
	Answer	Equipment blanks are required if the sampling equipment requires decontamination between sample points. If sampling personnel utilize new, disposable sampling equipment at each surface water sample location, equipment decontamination would not be required between sample points, and collection and analysis of equipment blanks would be unnecessary.
15.	Question	Stormwater monitoring is no longer included as one of the tasks under the Environmental Monitoring, Laboratory Analysis and Reporting Services for CRRA Landfills bid for any of the landfills?
	Answer	No, the stormwater component is not included in the RFB. If the consultant awarded the bid for a landfill expresses interest in stormwater monitoring, CRRA may extend a Request for Services (RFS) to the consultant for the required work. Otherwise, CRRA will procure the stormwater monitoring services via a different solicitation..
16.	Question	Do individual appointments need to be set-up for sampling of the private domestic wells for the Ellington Landfill, or can the sampling contractor simply notify the property owner that it will conduct sampling on a specific day and the

		sampling location will be made accessible?
	Answer	All third-party domestic well samples are obtained from outdoor spigots. Therefore, it is generally not necessary to have a specified appointment time to collect the samples. It is imperative, however, that the sampling contractor contact each property owner prior to each scheduled event to ensure that there are no conflicts associated with the scheduled event, to ensure that the outdoor spigot is accessible and functional (for example, make sure that the spigot has not been turned off during the month of January to prevent freezing) and to verify that no water treatment equipment has been placed prior to the sampling point.
17.	Question	Is access to the landfills limited to normal operating hours?
	Answer	Each successful bidding consultant will be provided with keys to the locks placed on the access gates. Consultants may access the property during off-hours such as weekends. CRRA does not encourage consultants to conduct contracted work during unsafe conditions, so this should be taken into consideration when scheduling the time of the work.
18.	Question	Is there access to restrooms at the closed landfills?
	Answer	There is no restroom access at the Ellington Landfill. The Hartford Landfill and Shelton Landfill have restroom facilities. There is a restroom inside the town-operated scalehouse for the Wallingford Landfill Transfer Station that a consultant could request to use during normal operating hours, but CRRA does not control this scalehouse.
19.	Question	For Ellington Landfill, recent samples collected from MW-16 for VOC analysis have been collected in unpreserved VOA vials and submitted for laboratory analysis within 24 hours of collection due to the "foamy" characteristic of the groundwater. Is the successful bidder going to be required to meet these requirements?
	Answer	Yes. For quarterly samples collected from monitoring well MW-16 for VOC analysis, collection of the samples in unpreserved VOA vials and submission to the analytical laboratory for analysis within 24 hours of collection is required.
20.	Question	Why did CRRA purchase properties adjacent to the Ellington, Shelton and Wallingford Landfills?
	Answer	CRRA purchased properties in order to obtain control of the groundwater within the zone of influence of the plume.
21.	Question	Why did CRRA purchase properties adjacent to the Ellington, Shelton and Wallingford Landfills?

	Answer	CRRA purchased properties in order to obtain control of the groundwater within the zone of influence of the plume.
22.	Question	Is the consultant responsible financially for revising the Quality Assurance Project Plan (QAPP) after the Task as described in the Scope of Services is completed?
	Answer	If QAPP revisions are necessary due to a program change that is under the Consultant's control (e.g., changing project management, changing analytical laboratory, etc.) , then the required revisions will be the financial responsibility of the Consultant. If QAPP revisions are necessary due to a program change that is not under the Consultant's control (e.g., changes to approved monitoring locations, monitored parameters, monitoring frequency, etc.), then CRRA may extend a Request for Services (RFS) to the consultant for the required QAPP revisions if CRRA cannot make the revisions in-house.
23.	Question	If high turbidity is encountered during sampling of a groundwater monitoring well, and < 5.0 NTU cannot be achieved, how should the Consultant proceed?
	Answer	Well purging, field parameter monitoring and sample collection requirements are all described in the Scope of Services (Exhibit A) for each Landfill, as well as in the QAPPs for the Shelton Landfill and the Wallingford Landfill.
24.	Question	For Hartford Landfill and Shelton Landfill, is it possible to launch boats from the landfill sites to collect surface water samples or do public boat launches need to be utilized?
	Answer	For both Hartford Landfill and Shelton Landfill, sampling personnel will have to utilize public boat launches. It will be the successful bidder's responsibility to pay any and all applicable fees for use of the boat launches and to verify access during the respective sampling months.
25.	Question	If private property owners forbid access to sampling sites, or are hostile to field personnel how will CRRA address this issue?
	Answer	CRRA expects that field personnel will immediately remove themselves from the private property and then notify CRRA of the issue. CRRA will then contact the property owner to discuss their concerns and attempt to resolve the issue.

26.	Question	With respect to surface water sampling at Hartford Landfill and Shelton Landfill, what if the contractor is unable to collect samples during the specified sampling month due to reasons outside of the contractor's control (for example, due to unsafe river conditions associated with ice floes in January; or due to the frequency of rainfall events in Shelton occurring less than 72 hours apart)?
	Answer	If sampling personnel are unable to conduct surface water sampling during the specified sampling month due to conditions outside of their control, CRRA expects that the contractor will continue to monitor conditions into the following month, and conduct surface water sampling by the 15th day of the following month if the opportunity presents itself. For example, if conditions during January preclude sampling, CRRA expects that the contractor will continue to monitor conditions until February 15th and conduct the surface water sampling if the opportunity presents itself. If the contractor is unable to sample by the 15th day of the following month, then the applicable quarterly report must discuss the reason(s) why sampling could not be conducted and include appropriate documentation. When scheduling each sampling event, CRRA encourages its Consultants to take the weather and availability of watercraft into consideration such that surface water samples can be collected as early during the specified sampling month as possible, when feasible.

2. QAPP FOR SHELTON AND WALLINGFORD

The Quality Assurance Project Plan (QAPP) for the Shelton and Wallingford landfills are attached hereto this Addendum 1.

The Scope of Services for the Shelton Landfill and for the Wallingford Landfill includes a task for revising the QAPP prior to the October 2013 groundwater monitoring event. The Consultant will be responsible for any revisions that CT DEEP may require in order to approve the final QAPP developed by the Consultant.

3. SIGN IN SHEETS

Attached hereto this Addendum 1 is the sign in sheet for the pre-bid meeting and site tours on Wednesday March 13, 2013 and Thursday March 14 is attached (attendees_at_pre-bid_site_tours.pdf)

END OF ADDENDUM 1

QUALITY ASSURANCE PROJECT PLAN (QAPP-GEN)

CRRA STEWARDSHIP PROGRAM

CRRA- Shelton Landfill
EPA ID No. CTD000604546
River Road
Shelton, Connecticut

March 12, 2010

Prepared For:

Connecticut Resources Recovery Authority
100 Constitution Plaza
Hartford, Connecticut 06106

Prepared By:

HRP Associates, Inc
197 Scott Swamp Road
Farmington, Connecticut

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CRRA STEWARDSHIP PROGRAM QUALITY ASSURANCE PROJECT PLAN (QAPP)
SHELTON LANDFILL, RIVER ROAD
SHELTON, CONNECTICUT

Stewardship Permit Number: DEP/HWM/CS-126-005

Prepared By: HRP Associates, Inc.
197 Scott Swamp Road
Farmington, Connecticut 06032

Preparer: _____
Signature

Tom Sicilia
Print Name/Date

Project Manager: _____
Signature

Brian P. Washburn, P.E., LEP
Print Name/Date

Project QA Officer: _____
Signature

_____
Print Name/Date

CRRA Representative: _____
Signature

Christopher R. Shepard, P.E.
Print Name/Date

CT DEP: _____
Signature

_____
Print Name/Date

2. Project Organization and Responsibility

(Refer to Site Specific QAPP-ENG Addendum)

3. Problem Definition

The Shelton Landfill covers approximately 110 acres and is located on the east side of River Road (Rte. 110) in the southeast portion of Shelton, Connecticut. The landfill is located in the Housatonic River Valley, immediately upstream and north of the confluence of the Housatonic and Farmill Rivers. The landfill is owned and managed by the Connecticut Resources Recovery Authority (CRRA). The landfill property is bordered by the following properties and features (Figure 1).

North- miniature golf course/driving range,

South- Farmill River and United Technologies-Sikorsky Aircraft property,

East- Housatonic Lagoon and River, and

West- River Road/commercial properties.

The topography of the property rises from near mean sea level (MSL) in the east along the Housatonic River to 170 feet above MSL at the peak of the landfill. From this point, the land slopes downward to the west to an elevation of approximately 60 feet above MSL along River Road.

Site Activities

The Shelton Landfill consists of the four following parts (Figure 2).

1. Municipal Solid Waste Landfill (MSW)/Interim Ash Residue Landfill

2. Southeast Expansion Area (SEEA)

3. Northeast Expansion Area (NEEA)

4. Hazardous Waste Disposal Area

The MSW/Interim Ash Residue Landfill includes 37 acres located along the western edge of the property. The initial permit to operate the municipal solid waste landfill at this location was issued to CRRA by the CTDEP in August 1983. In February of 1988, this permit was modified to allow CRRA to dispose of ash residue on top of the existing municipal solid waste. From February of 1988 to August of 1994, only ash residue was landfilled on-site in a roughly 22-acre parcel atop the 37-acre footprint (Figure 2). The interim ash residue landfilling operations ceased in August of 1994 and final cover was applied in the winter of 1996/1997, with CTDEP approval of the final closure on March 30, 1999.

The Southeast Expansion Area (SEEA) consists of about 6.5 acres in the southeast corner of the landfill property, near the confluence of the Housatonic and Farmill Rivers, and adjacent to the Housatonic River Lagoon (Figure 2). According to previous consultant reports, the SEEA base pad (beneath the liner layers) was constructed partly of dredge spoils from Bridgeport Harbor, which were contaminated with VOCs. The SEEA consists of four (4) lined cells equipped with a leachate collection system on top of the primary liner and between the primary and secondary liners. Landfilling of ash residue in this lined area began in August 1994 and

ended in November 1996. The SEEA is covered to prevent erosion, lined, and has a leachate collection system. In October 1999, the HDPE geomembrane was completely installed over the area. Final cover soils (18 inches protective cover plus 6 inches topsoil) and hydroseed was completed at the SEEA in the end of May 2000. CRRA continues to maintain and monitor the leachate collection system.

The Northeast Expansion Area (NEEA) comprises approximately 3.1 acres in the northeastern corner of the landfill, adjacent to the Housatonic River and the Housatonic River Lagoon. The NEEA consists of three lined cells and a leachate collection system that serves both the primary and secondary cell liners. Ash residue was landfilled in the NEEA from November 1996 to February 1998 when capacity was reached (with a temporary diversion of the ash to the Hartford Landfill beginning in October 1997; re-depositing of ash in the NEEA restarted in December 1997). The NEEA received final cover at the end of October 1999 and closure of the ash expansion area was approved by CTDEP in October 2001.

The closed hazardous waste disposal area consists of about 2 acres, located atop the 37-acre footprint, in the north central corner of the MSW Landfill area. The hazardous waste disposal area was certified closed by the CTDEP in October of 1989.
All disposal activities at the Shelton Landfill have ceased and all disposal units have been closed. The only activities currently performed at the Shelton Landfill are listed below.

- Post-closure activities including regular landfill inspections to ensure the integrity of all landfill caps,
- Operation and maintenance of the ash leachate collection and pretreatment system, and
- Operation and maintenance of the landfill gas collection and flaring system.

An active residential drop-off center/transfer station for municipal solid waste, bulky waste, and scrap metal is also operated on the landfill property. The residential drop-off center/transfer station is permitted and operated by the City of Shelton, and is located outside of all disposal units at the landfill.

Future use of the Shelton Landfill property is governed by a "Future Use Plan" that has been developed by CRRA with input and approval from both the CTDEP and the City of Shelton. Proposed future site uses would include the post-closure activities that are currently conducted, as well as passive recreation areas, such as a walking trail, wildlife viewing areas, and a boat launch onto the Housatonic River lagoon for non-motorized boats.

4. Project Description

Monitoring well completion details are summarized in Table 1. Wells to be sampled include

MW-Qb	MW-Td	MW-Cd	MW-BR7	MW-BR-18
MW-BR5	MW-100	MW-Cs	MW-D2d	MW-BR-19
MW-GP4	MW-BR1	MW-I3s	MW-16s	
MW-BR4	MW-A	MW-BR8	MW-104s	
MW-Rs	MW-BR2	MW-17d	MW-BR6	
MW-Rd	MW-Bd	MW-105	MW-Ed	

Well locations are presented on Figure 2

A synoptic groundwater measurement will be completed on the first day of each semi-annual monitoring event to determine the groundwater elevations at all sampled monitoring wells prior to any purging and sampling activities. At each monitoring well, the depth to groundwater and the depth to the bottom of the will be measured with either an electronic water level indicator or a steel tape accurate to within 0.01 feet. All measurements will be made relative to the surveyed measurement point at each well, i.e., the top of the PVC casing.

The water level measuring device will be decontaminated between monitoring wells to ensure that cross-contamination of the monitoring wells does not occur. The decontamination will consist of rinsing the measuring device with deionized water.

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TABLE 1
Summary of Monitoring Well Construction
Shelton Landfill
Shelton, Connecticut

Well Number	Dedicated Sampling Apparatus	Measuring Point Elevation (Top of PVC) (feet)	Top of Screen Elevation (feet)	Measured Well Depth (feet)	Well Bottom Elevation (feet)
MW-Qb	Bladder Pump	71.48	2.16	74.43	-8.16
MW-BR5	Bladder Pump	69.02	30.02	NA	NA
MW-GP4	Bladder Pump	56.72	42.52	36.12	22.52
MW-BR4	Bladder Pump	55.32	-4.45	70.62	-14.45
MW-Rs	Tubing	17.17	7.1	20.04	-3.1
MW-Rd	Bladder Pump	16.22	-17.3	37.82	-22.3
MW-Td	Bladder Pump	12.68	-41.32	64.05	-46.32
MW-100	Bladder Pump	14.08	-2.2	26.43	-12.2
MW-BR1	Bladder Pump	13.26	-57.43	80.62	-67.43
MW-A	Bladder Pump	16.22	-6.6	32.59	-16.6
MW-BR2	Bladder Pump	10.26	-28.38	50.03	-38.38
MW-Bd	Bladder Pump	11.50	-5.33	26.62	-15.33

TABLE 1
Summary of Monitoring Well Construction
Shelton Landfill
Shelton, Connecticut

MW-Cd	Bladder Pump	22.33	-54.08	85.83	-64.08
MW-Cs	Bladder Pump	22.34	-3.78	40.88	-18.78
MW-I3s	Bladder Pump	9.98	0.96	21.43	-10.96
MW-BR8	Bladder Pump	11.98	-99.02	123.98	-109.02
MW-17d	Bladder Pump	14.43	-36.79	65	-46.79
MW-105	Bladder Pump	14.15	4.80	25	-6.80
MW-BR7	Bladder Pump	19.96	-34.3	103.85	-54.3
MW-D2D	Bladder Pump	21.62	-9.81	42.49	-19.81
MW-16s	Bladder Pump	8.16	-83.95	100.5	-93.95
MW-104s	Bladder Pump	9.64	4.48	12	-6.48
MW-BR6	Bladder Pump	9.06	-66.46	84.2	-76.46
MW-Ed	Bladder Pump	8.97	-52.66	71.31	-62.66
MW-BR18*	Bladder Pump	N/A	N/A	N/A	N/A
MW-BR19*	Bladder Pump	N/A	N/A	N/A	N/A

* = Proposed

N/A = Not Available

Groundwater Sample Collection Methods

The following sample collection procedures will be followed during each sampling event:

- A “Monitoring Well Field Data Sheet” which summarizes well elevation data, well condition, purge data, observed water yield and quality comments, sampling data, and results of measured field parameters will be completed for each monitoring well sampled.
- Measure well’s water depth using decontaminated equipment (depth to water, depth to bottom, depth of sample) referenced to top of PVC (or casing) and record on the data sheet.
- Provide an in-line meter (or equivalent methodology which mitigates exposure to the atmosphere) to concurrently measure pH, temperature, specific conductivity, dissolved oxygen (DO), and redox potential (RP), as applicable, during purging. Also, provide a device to measure turbidity. A minimum of four (4) readings of each parameter shall be taken and recorded during purging.
- Perform purging using dedicated bladder pump equipment at all wells at low flow rates, not taking the first reading until at least one pump volume plus one discharge tubing volume have passed. (Note: Due to its shallow depth and typically low water column height, MW-RS is equipped with dedicated tubing that is

connected to a peristaltic pump for purging.) The purged groundwater may be discarded to the ground. Sampling personnel are to monitor the drawdown in the wells and ensure that the drawdown is maintained at less than or equal to 0.3 feet during the entire purging and sampling process. Wells shall be purged at a rate of less than or equal to 300 ml/minute. Field parameter readings shall be recorded at a minimum of three minute intervals, until turbidity is stabilized such that three consecutive reading are within 10% of each other for readings >10 NTU, or readings are within 2 NTU of each other for readings <10 NTU. Per US EPA Region I Standard Operating Procedure GW-0001 – "Low Stress (Low Flow) Purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells" (January 19, 2010 – Revision 3), if the turbidity has not stabilized after four hours of purging or after at least five well volumes have been purged, collect samples and provide full explanation of attempt to achieve stabilization. Provide a summary of periodic readings and time of reading for all parameters.

- Sample collection should proceed from high parameter volatility to low parameter volatility at a low flow rate. Samples for volatile parameters should be transferred slowly to the sample container to eliminate creation of air bubbles. Samples are to be collected in proper containers and properly preserved in the field, as summarized in Table 4.
- All observations relating to the well sampling, well conditions and any deviations from the sampling plan are to be recorded on the Monitoring Well Data Sheet.

Surface Water Sample Collection Methods

The surface water samples will consist of grab samples collected from the middle of the water column at locations SW-1 and SW-2; and one composite sample of top, middle, and bottom depths from each point SW-3, SW-4, and SW-5. The following sample collection procedures will be followed during each sampling event:

No filtering of samples is to occur.

Untreated Ash Residue Leachate Sample Collection Methods

The untreated ash residue leachate samples will consist of grab samples collected from the NEEA lift station and the SEEA lift station. The following sample collection procedures will be followed during each sampling event:

- A Field Data Sheet will be utilized at each ash residue leachate sample location to record all applicable field observations and data, such as weather conditions, field measurements, and sample collection times.
- Disposable or decontaminated bailers and clean rope will be utilized to collect each untreated ash residue leachate sample.

- Field measurements of pH, specific conductance, dissolved oxygen, turbidity, and leachate temperature shall be recorded.
- The appropriate sample containers will be filled from the bailer and properly preserved in the field, as summarized in Table 4.
- No filtering of samples is to occur.

4a. Project Timeline

Activities (list products)	Dates	
	Activity Start	Activity End
Sampling (Groundwater, Surface water & Untreated Leachate)	Semi-annual to occur first week of April and October each year	Approximately two to three working days after activity start date
Reporting to CTDEP	Immediately following sampling	Within sixty calendar days following the last day of sampling

5. Sampling Design and Site Figures

In order to fulfill the requirements of the Stewardship Permit, CRRA will sample groundwater and untreated leachate from various locations to monitor the leachate plume at the site on a semi-annual basis. The scope of sampling is described in the table below. Each well location is presented on Figure 2.

MONITORING PARAMETERS

SHELTON LANDFILL
SHELTON, CONNECTICUT

(1)	(2)	(3)	(4)
Parameters	**Surface Water**	**Groundwater**	**Leachate**
Description: **Number of Sample Locations:**	**5 ea + 1 QA/QC**	**Wells** **26 ea + 1 QA/QC**	**Untreated** **2 ea**
Field Measured			
Time of Collection	X	X	X
Sample Depth	X	X	X
Total Water Column Depth	X	X	X
Water Level Elevation		X	
Water Temp.	X	X	X
Air Temp.	X		X
PH	X	X	X
Spec. Cond.	X	X	X
Salinity	X		X
Dissolved Oxygen (D)	X		X
ORP		X	
Turbidity - (NTU)		X	
Water Clarity-Secchi Disk	X		X
Lab Measured			
Spec. Cond.		X	X
PH			X
TDS			X
TSS			X
Chloride			X
Alkalinity			X
Hardness as CaCO3		X	X
BOD - 5-day			X
COD			X
Ammonia - (T)			X
TKN (T)			X
Nitrate (T)			X
Nitrite (T)			X
Phosphorus (T)			X
Aluminum (T)			X
Arsenic (T)		X	X
Barium (T)		X	X
Cadmium (T)		X	X
Chromium (T)		X	X
Copper (T)	X	X	X
Iron (T)	X	X	X
Lead (T)		X	X
Manganese (T)		X	X

MONITORING PARAMETERS

SHELTON LANDFILL
SHELTON, CONNECTICUT

(1)	(2)	(3)	(4)
Parameters	**Surface Water**	**Groundwater**	**Leachate**
Description: **Number of Sample Locations:**	**5 ea + 1 QA/QC**	**Wells** **26 ea + 1 QA/QC**	**Untreated** **2 ea**
Mercury (T)			X
Nickel (T)		X	X
Potassium (T)		X	
Selenium (T)		X	
Silver (T)		X	X
Zinc (T)		X-1	X
Additional Parameters to be monitored only at listed locations:			
Radium (Radium-226 and Radium-228 combined via EPA Method 9320 of SW-846)		X-1	
Gross Alpha		X-1	
Gross Beta		X-1	
Dioxins and Furans via EPA Method 8280			X

NOTES:

The minimum detection limit (MDL) must be at least as low as the SWPC, if a criteria has been established for the compound.

Surface Water

Column 2 - Samples will be collected as a composite of top, mid and bottom from SW-3, sW-4, SW-5. A mid-depth sample will be collected from SW-1 and SW-2

Ground Water

Column 3– The well designations in Groundwater Discharge Permit LF0000052 are as follows:

MW-100 MW-Cs MW-D2d MW-BR-19 MW-Ed
MW-GP4 MW-BR1 MW-I3s MW-16s MW-BR4
MW-Td MW-BR8 MW-104s MW-Rs MW-BR2
MW-17d MW-BR6 MW-Rd MW-Bd MW-105
MW-Cd MW-BR7 MW-BR-18

X-1 Radionuclide monitoring wells
MW-Qb MW-BR5 MW-A

Untreated Leachate

Column 6 –The following 2 locations represent the sample locations for untreated ash residue leachate from the SEEA and the NEEA, respectively:
L-1S (SEEA Lift Station) L-1N (NEEA Lift Station)

6. Sampling and Analytical Methods Requirements

The following tables summarize sampling and analytical protocols that may be utilized during the monitoring events. Refer to the Site Specific QAPP-LAB Addendum for the details regarding sample and QC quantities, containers per sample, preservation requirements, and maximum holding time.

					Containers per Sample			Preservation Requirements			
Parameter	**Matrix**	**Number of Samples (including Field QC)**	**Prepara-tion Method**	**Analyti-cal Method***	**No.**	**Size**	**Type**	**Temp.**	**Light Sensi-tive**	**Chemi-cal**	**Maximum Holding Time**
Trace metals by ICP-AES	Aqueous	-LAB	-LAB	SW-846 Method 6010B	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Mercury by Cold Vapor AAS	Aqueous	-LAB	-LAB	SW-846 Method 7470A	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Alkalinity (Total)	Aqueous	-LAB	-LAB	SM2320 B	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Total Dis-solved Solids (TDS)	Aqueous	-LAB	-LAB	SM2540 C	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Hardness	Aqueous	-LAB	-LAB	EPA 200.7	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Biologica Oxygen De-mand (BOD)	Aqueous	-LAB	-LAB	SM5210 B	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Chemical Oxygen De-mand (COD)	Aqueous	-LAB	-LAB	SM5220 D	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Nitrate	Aqueous	-LAB	-LAB	EPA 300.0; 9056	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Nitrite	Aqueous	-LAB	-LAB	EPA 300.0	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Ammonia (N)	Aqueous	-LAB	-LAB	EPA 350.1	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Cyanide (Total)	Aqueous	-LAB	-LAB	SW9014	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Sulfate (To-tal)	Aqueous	-LAB	-LAB		-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Total Sus-pended Sol-ids (TSS)	Aqueous	-LAB	-LAB	SM2540 D	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Phosphorus	Aqueous	-LAB	-LAB	EPA 365	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Total Kjeldahl Nitrogen (TKN)	Aqueous	-LAB	-LAB	EPA 351	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Gross Aplha	Aqueous	-LAB	-LAB	EPA 9310; 900.0	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Gross Beta	Aqueous	-LAB	-LAB	EPA 9310; 900.0	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Radium	Aqueous	-LAB	-LAB	EPA 9320, 903.0, 904.0	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB
Diox-ans/Furans	Aqueous	-LAB	-LAB	EPA1613 B; 8280B, 8290A	-LAB	-LAB	-LAB	2-6º C	-LAB	-LAB	-LAB

Notes: *In accordance with RCPs where applicable
-LAB = refer to Lab Addendum

7. Method and SOP Reference Tables

The contract engineer will adhere to the following ASTM standards that apply to the scope of work. Laboratory SOPs are provided in the QAPP-LAB Addendum.

Document Title	Date
D2113-06 Practice for Rock Core Drilling and Sampling of Rock for Site Investigation	2006 (Revised 2008)
D4750-87R01 Test Method for Determining Subsurface Liquid Levels in a Borehole or Monitoring Well (Observation Well)	1987 (Reapproved 2001)
D5088-02 Practices for Decontamination of Field Equipment Used at Waste Sites	2002 (Reapproved 2008)
D5092-04E01 Practice for Design and Installation of Ground Water Monitoring Wells	2004
D5299-99R05 Guide for Decommissioning of Ground Water Wells, Vadose Zone Monitoring Devices, Boreholes, and Other Devices for Environmental Activities	1999 (Reapproved 2005)
D5784-95R06 Guide for Use of Hollow-Stem Augers for Geoenvironmental Exploration and the Installation of Subsurface Water-Quality Monitoring Devices	1995 (Reapproved 2006)
D5978-96R05 Guide for Maintenance and Rehabilitation of Ground-Water Monitoring Wells	1996 (Reapproved 2005)
D6089-97R03E01 Guide for Documenting a Ground-Water Sampling Event	1997 (Reapproved 2003)
D6452-99R05 Guide for Purging Methods for Wells Used for Ground-Water Quality Investigations	1999 (Reapproved 2005)
D6517-00R05 Guide for Field Preservation of Ground-Water Samples	2000 (Reapproved 2005)
D6634-01R06 Guide for the Selection of Purging and Sampling Devices for Ground-Water Monitoring Wells	2001 (Reapproved 2006)
D6771-02 Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations	2002
D6911-03 Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis	2003

Document Title	Date
D7069-04 Guide for Field Quality Assurance in a Ground-water Sampling Event	2004
D0888-05 Test Methods for Dissolved Oxygen in Water	2005
D1067-06 Test Methods for Acidity or Alkalinity of Water	2006
D1125-95R05 Test Methods for Electrical Conductivity and Resistivity of Water	1995 (Reapproved 2005)
D1293-99R05 Test Methods for pH of Water	1999 (Reapproved 2005)
D1498-07 Test Method for Oxidation-Reduction Potential of Water	2007 (Revised 2008)
D4453-02R06 Practice for Handling of Ultra-Pure Water Samples	2002 (Reapproved 2006)
D4840-99R04 Guide for Sample Chain-of-Custody Procedures	1999 (Reapproved 2004)
D6764-02R07 Guide for Collection of Water Temperature, Dissolved-Oxygen Concentrations, Specific Electrical Conductance, and pH Data from Open Channels	2002 (Reapproved 2007)
D4448-01R07 Guide for Sampling Ground-Water Monitoring Wells	2001 (Reapproved 2007)
D6009-96R06 Guide for Sampling Waste Piles	1996 (Reapproved 2006)
D6232-08 Guide for Selection of Sampling Equipment for Waste and Contaminated Media Data Collection Activities	2008
D6699-01R06 Practice for Sampling Liquids Using Bailers	2001 (Reapproved 2006)
D6759-07 Practice for Sampling Liquids Using Grab and Discrete Depth Samplers	2007
D7353-07 Practice for Sampling of Liquids in Waste Management Activities Using a Peristaltic Pump	2007

Document Title	Date
D5358-93R03 Practice for Sampling with a Dipper or Pond Sampler	1993 (Reapproved 2003)

8. Field Equipment Calibration and Corrective Action

Instrument	Activity	Frequency	Acceptance Criteria	Corrective Action
pH meter	Calibration	Daily	N/A Compare to historical data when applicable	Recalibrate
Specific Conductance Meter	Calibration	Daily	N/A Compare to historical data when applicable	Recalibrate
ORP Meter	Calibration	Daily	–400 mV to 800 mV	Recalibrate
DO Meter	Calibration	Daily	Between 0 and 4 mg/l unless historically shown to be above 4 mg/l. Should not be negative.	Recalibrate Change Membrane
Turbidity Meter	Calibration	Between Each Rental Checked Daily	Appendix C Should NEVER be negative	Appendix C Cease use and Contact Rental Company to Recalibrate or Replace

N/A – Not Applicable

9. Laboratory Equipment Calibration and Corrective Action

(Refer to Site Specific QAPP-LAB Addendum)

10. Sample Handling and Custody Requirements

(Refer to Site Specific QAPP-LAB Addendum)

11. Analytical Sensitivity and Project Criteria

If a compound is regulated by the CT DEP surface water protection criteria (SWPC), the minimum reporting limit will be equal to or less than the SWPC standard.

(Refer to Site Specific QAPP-LAB Addendum)

12. Field Quality Control Requirements

QC Sample	Frequency	Acceptance Criteria	Corrective Action
Duplicate (Groundwater)	1 per sampling event	Duplicate concentra-tions are within 30%.	Flag in data report
Duplicate (Surface Water)	1 per sampling event	Duplicate concentra-tions are within 30%.	Flag in data report

13. Laboratory Quality Control Requirements

(Refer to Site Specific QAPP-LAB Addendum)

14. Data Management and Documentation

Field Data

Low-flow groundwater sampling data will be recorded on Monitoring Well Data Sheets. All other field data will be recorded in a permanently bound waterproof notebook. All notes will include the date, sampling location, weather conditions, any measurements taken, and any problems encountered in the field. Monitoring Well Data Sheets will be scanned and archived in the project file.

The sampling labels and the chains-of-custody will be clearly written and consistent with one another.

Laboratory Data

The following deliverables will be provided by the laboratory:

1. Client's Name
2. Project Number
3. Laboratory Sample ID
4. Client Sample ID
5. Collection Date
6. Sample Matrix
7. Analyses
8. Analytical Results/Data Results Sheets
9. Reporting Limits
10. Reporting Units
11. Dilution Factor
12. Date Analyzed
13. Method Blank Results
14. Surrogate Recoveries and Acceptance Limits
15. Matrix Spike/Matrix Spike Duplicate Results and Acceptance Limits
16. Spike/ Duplicate Results and Acceptance Limits
17. Laboratory Control Sample Results and Acceptance Limits
18. Project Narrative which contains all observations and deviations

Types of information the laboratory will provide include:

1. Analytical Summary Sheets
2. QC Summary Sheets

The following will be maintained by the laboratory:

- All raw data including chromatograms
- Copies of Instrument Logbooks
- Copies of internal chains-of-custody
- PE sample results
- ICP Serial Dilution Results
- ICP Interference Check Sample Results

The laboratory will provide analytical reports in a hard-copy form and electronic data deliverables (Excel format).

Project Files

Working files will be stored via hard copy and electronically with the Project Staff during the operation of the Scope of Work. Subsequent to the completion of the project and issuance of all final documents, all pertinent information will be stored electronically in archive files for future reference.

15. Assessment and Response Actions

All field personnel will be provided with a copy of the QAPP to review prior to commencement of field activities. Subsequent to the review and prior to beginning any site work, the Project Manager (or designated alternate) will review the QAPP with field personnel. At the conclusion of each field day, field personnel will provide a verbal report to the Senior Technical Staff member, Project Manager, and/or Project QA Officer. Any deviations from the QAPP will be documented. If significant, the client will be contacted.

Following completion of field activities, the Project QA Officer will perform a final review of the scope of sampling activities and sample handling practices to ensure that the activities are consistent with the QAPP. Any previously unidentified discrepancies will be reported to the Project Manager for review. All discrepancies and deviations from the QAPP will be documented in the final report.

16. Project Report

The results of each semi-annual sampling event will be summarized in a separate report. Each report will include the following items.

- A narrative summarizing the sampling event and any anomalous test results
- Groundwater contour maps for the overburden and bedrock aquifers
- Tabulated data summary of analytical results, field parameters, and ground water elevations
- Data Quality Assessment and Data Usability Evaluation completed in accordance with *Laboratory Quality Assurance and Quality Control Data Quality Assessment and Data Usability Evaluation Guidance Document* (CTDEP, May 2009)
- Evaluation of test results with respect to the SWPC
- Field sampling data sheets
- Laboratory analytical report

The October semi-annual monitoring report prepared for each year will also include the additional items listed below.

- Graphs depicting Plume monitoring parameters since closure of the various landfill parts in 2001.
- A brief narrative reviewing the current data trends relative to the applicable SWPC will also be included
- Any proposed changes to the monitoring program that can be supported by site data.

Laboratory

The laboratory will provide CRRA with an electronic copy of the analytical results. The Engineer will incorporate the analytical results into a database using the format provided by CRRA.

In an effort to reduce paper usage, CRRA will no longer submit paper copies of the lab reports. CRRA will maintain the paper copies at its office; however, a hard copy of the RCP documentation and an electronic copy (CD) of the laboratory reports will be submitted with the report. Per the Stewardship Permit, surface and groundwater reports will be submitted within 60 days of the sampling event.

17. Field Data Evaluation

All field screening and sampling procedures will be reviewed with the field personnel. All personnel that perform field screening and sampling activities have been trained in the use of the SOPs to be utilized pursuant to the QAPP. Field personnel will be given a copy of this QAPP to read prior to performing any field screening and sampling activities. The field sampling team will speak to the Project Manager and/or Senior Project Technician on a daily basis to verify that the screening and sampling procedures specified in the QAPP are being followed. These managerial controls will confirm that the field screening and sampling procedures contained in this QAPP are utilized. The project manager will be responsible to ensure that the appropriate field screening and sampling procedures are utilized to attain the objective of the proposed investigations.

18. Laboratory Data Evaluation

The laboratory will perform internal validation procedures as per their SOPs. The contract laboratory will follow the CTDEP's Final Reasonable Confidence Protocols, approved on August 21, 2006.

The engineer will perform a review of the laboratory data deliverables received from the Connecticut Certified Laboratory. The following tasks will be performed.

A Summary of Technical Usability

The engineer will identify and document the following:

- Laboratory and laboratory project number
- Number of samples and sample field identifications (IDs) submitted to the laboratory by comparing the laboratory narrative to the chain-of-custody
- The laboratory sample IDs
- List parameters analyzed by comparing the laboratory narrative to the chain-of-custody

B Technical Issues Affecting Accuracy

The engineer will review, document, and comment on:

- Whether CT RCP protocols were met
- Sample holding times compared to acceptable holding times
- Sample minimum detection limits are below applicable RSR criteria
- Laboratory control sample recoveries compared to acceptable laboratory control sample recoveries as established by the method standard operating procedures of the laboratory internal procedures
- Matrix spike recoveries compared to acceptable matrix spike recoveries as established by the method standard operating procedures of the laboratory internal procedures

C Technical Issues Affecting Precision and Representativeness

The relative percent differences (RPD) will be calculated between samples and sample duplicates and between matrix spikes and matrix spike duplicates. The acceptable RPD for water is an RPD<30% (see Section 13).

D Technical Issues Affecting Sensitivity

The engineer will review and comment on any contaminants identified in the following:

- Method Blanks

The engineer will review the laboratory report's minimum detection limits (MDLs).

E Summary of Completeness, Documentation, and Chain-of-Custody Issues

The engineer will review the deliverable package for the following components:

- Laboratory Narrative
- RCP Forms
- Data Results Sheets
- Method Blank Results
- Surrogate Recoveries and Acceptance Limits
- Matrix Spike/Matrix Spike Duplicate Results and Acceptance Limits
- Laboratory Control Sample Results and Acceptance Limits
- Project Narrative which contains all observations and deviations

If any sample or QC issues are documented in the narrative that are not included as part of the data package deliverables, the laboratory will be contacted, copies of the relevant information obtained, and a discussion of any limitations on the use of the data will be presented in the validation section of the final report. If the data deliverables package is incomplete, the laboratory will be contacted and requested to provide the missing documentation.

The laboratory will perform internal validation procedures as per their SOPs.

19. Data Usability and Project Evaluation

Present Field Duplicate Results

All field duplicate results will be presented in tables throughout the corresponding reports. Relative Percent Difference (RPD) will be calculated for select compounds on all sample/dupe pairs using the formula below

$$RPD = 100 \times \frac{|difference|}{Average}$$

Any RPD greater than 30% will be noted, and the affect on data usability evaluated.

Representativeness

All samples will be collected in accordance with this document and the Water Quality Monitoring Plan. Data will be compared to historical results and the following actions will be taken in the event of a significant anomaly.

- Any unexpected and/or anomalous results will be discussed in the corresponding report.
- Field personnel will be asked for clarification on any anomalous data. Field personnel will also be asked to provide any missing data. All findings will be presented in the final report
- The laboratory will be contacted to confirm results

Comparability

In order to ensure comparability from location to location and event to event, the engineer will follow the same sampling procedures and request the same laboratory protocols throughout the project. The engineer will also review field notes and laboratory data to ensure the QAPP has been adhered too. The engineer will consult with the field technician or laboratory personnel if any missing anomalous data is encountered. Deviation in the field duplicates will be compared to the criteria specified in the QAPP. If necessary, the laboratory will be asked to reanalyze samples to verify results.

Groundwater results will be compared to the Surface Water Protection Criteria of the Connecticut Remediation Standard Regulations (RSR). Surface water will be compared to the Chronic Aquatic Life Criteria from the State's Surface Water Quality Standards

Where possible, the engineer will present data in table and graph format. If historical data is available, such as multiple groundwater monitoring events, it will be discussed in reports to evaluate the contaminant trends.

Sensitivity

If reporting limits are above the SWPC, the laboratory will be contacted to rerun the sample at a reporting limit below the standard. If it is not possible to achieve reporting limits below the RSR criteria the analyte will be flagged in the report.

Usability Summary

Data will be reviewed in accordance with the *Laboratory Quality Assurance and Quality Control Data Quality Assessment and Data Usability Evaluation Guidance Document* (CT DEP, May 2009) in order to identify deviations from RCP QA/QC performance criteria and their potential impact on the project objectives. Any deviations will be discussed in a Data Usability Evaluation (DUE) section of the corresponding report.

QUALITY ASSURANCE PROJECT PLAN (QAPP) – LAB ADDENDUM

CRRA STEWARDSHIP PROGRAM

CRRA- Shelton Landfill
EPA ID No. CTD000604546
866 River Road
Shelton, Connecticut

March 12, 2010

Prepared For:

Connecticut Resources Recovery Authority
100 Constitution Plaza
Hartford, Connecticut 06106

Prepared By:

HRP Associates, Inc
197 Scott Swamp Road
Farmington, Connecticut

TABLE OF CONTENTS

CRRA Corporate Stewardship QAPP
Shelton Landfill

Title and Approval Page

CRRA STEWARDSHIP PROGRAM QUALITY ASSURANCE PROJECT PLAN (QAPP)
SHELTON LANDFILL, RIVER ROAD
SHELTON, CONNECTICUT

Stewardship Permit Number: DEP/HWM/CS-126-005

Prepared By: HRP Associates, Inc.
197 Scott Swamp Road
Farmington, Connecticut 06032

Preparer: _____
Signature

_____
Print Name/Date

Project Manager: _____
Signature

_____
Print Name/Date

Project QA Officer: _____
Signature

_____
Print Name/Date

CRRA Representative: _____
Signature

Christopher R. Shepard, P.E.
Print Name/Date

CT DEP: _____
Signature

_____
Print Name/Date

2. Project Organization and Responsibility

(Refer to Site Specific QAPP-ENG Addendum)

3. Problem Definition

(Refer to Generic QAPP-GEN)

4. Project Description

(Refer to Generic QAPP-GEN)

5. Sampling Design and Site Figures

(Refer to Generic QAPP-GEN)

6. Sampling and Analytical Methods Requirements

The following table summarizes sampling and analytical protocols that may be utilized during the monitoring events.

Parameter	Analytical Method	Matrix	Number of Samples (number of QC samples in parentheses)	Sampling SOP	Container	Preservation	Hold Time
Metals	6010B	Water	33 (2)	EPA 6010-200.7	200 mL Plastic	HNO_3 (pH<2) 4ºC	14 days extraction 6 months
Mercury	7470A	Water	2	EPA 245.1	200 mL Plastic	HNO_3 (pH<2) 4ºC	14 days extraction 28 days
Ammonia (N)	350.1	Water	2	EPA 350.1	100 mL Plastic	H_2SO_4 pH<2, 4ºC	28 days
Conductivity	SM2510B	Water	28 (1)	-LAB	250 mL Plastic	4ºC	28 days
Total Dissolved Solids (TDS)	SM2540C	Water	2	SM2540C	500 mL Plastic	4ºC	7 days
Total Suspended Solids (TSS)	SM2540D	Water	2	SM2540D	500 mL Plastic	4ºC	7 days
Alkalinity	SM2320B	Water	2	SM2320B	200 mL Plastic	4ºC	14 days
Hardness	200.7	Water	28 (1)	EPA 200.7	250 mL Plastic	HNO_3 (pH<2) 4ºC	14 days extraction 6 months
BOD	SM5210B	Water	2	SM5210B	1000 mL Plastic	4ºC	48 hours
COD	HACH 8000	Water	2	SM5220D	250 mL Plastic	H_2SO_4 pH<2, 4ºC	28 days
Chloride	SM 4500-Cl E	Water	2	-LAB	250 mL Plastic	4ºC	28 days
Nitrate (N)	SM4500-NO_3	Water	2	EPA 300.0	100 mL Plastic	4ºC	48 hours
Nitrite (N)	SM4500-NO_2	Water	2	-LAB	100 mL Plastic	4ºC	48 hours

Parameter	Analytical Method	Matrix	Number of Samples (number of QC samples in parentheses)	Sampling SOP	Container	Preservation	Hold Time
Phosphorus, Total	365.1	Water	2	-LAB	250 mL Plastic	H_2SO_4 pH<2, 4ºC	28 days
TKN	351.2	Water	2	-LAB	200 mL Plastic	H_2SO_4 pH<2, 4ºC	28 days
pH	SM4500-H^+B	Water	2	-LAB	100 mL Plastic	4ºC	Immediate
Gross Beta	-LAB	-LAB	-LAB	-LAB	-LAB	-LAB	-LAB
Gross Alpha	-LAB	-LAB	-LAB	-LAB	-LAB	-LAB	-LAB
Radium 226	-LAB	-LAB	-LAB	-LAB	-LAB	-LAB	-LAB
Radium 228	-LAB	-LAB	-LAB	-LAB	-LAB	-LAB	-LAB
Dioxans/Furans	-LAB	-LAB	-LAB	-LAB	-LAB	-LAB	-LAB

-LAB To be provided by Laboratory

7. Method and SOP Reference Tables

The following table presents all of the analytical methods, as well as the contract Standard Operating Procedures (SOPs) and sample preparation SOPs for all of the listed parameters. A copy of each of the laboratory SOP referenced below is included in Appendix A.

Analytical Method	Document Title	Revision Number	Date
EPA 9310	"EPA 9310: Gross Alpha and Gross Beta"	17	October 2008
ICP 6010B	""Recommended Reasonable Confidence Protocols Quality Assurance and Quality Control Requirements Determination of Trace Metals By SW-846 Method 6010 Inductively Coupled Plasma-Atomic Emission Spectrometry"	2.0	July 2006
Radium-226	" EPA 9315- Alpha Emitting Radium Isotopes	20	February 2009
Radium-228	"EPA 9320 Radium-228"	20	January 2010

8. Field Equipment Calibration and Corrective Action

(Refer to Generic QAPP-GEN)

9. Laboratory Equipment Calibration and Corrective Action

Premier Laboratory is currently the contract laboratory that analyses the groundwater and leachate samples for the project. Copies of all of Premier SOPs have been provided in Appendix A.

Frequencies and Triggering Events for Maintenance

Purge and Trap Devices

Frequency or Triggering Event	Maintenance Required	Procedure
1) Trap contaminated 2) Sensitivity to gasses or ketones decreases below acceptable levels.	Change Trap	PT001

Gas Chromatographs

Frequency or Triggering Event	Maintenance Required	Procedure
1) Annually 2) Baseline becomes elevated 3) Area counts become inconsistent	have ECD cleaned	GC000
Resolution becomes poor	Clip column	GC002
Annually or when indicated	Change gas filter	GC003
Loss of sensitivity	Change PID lamp	GC004
1) Column becomes too short for acceptable resolution 2) Column cannot be cleaned by bake out 3) Loss of sensitivity	Change column	GC005
Baseline becomes elevated	Bake out ECD detector	GC006

Mass Spectrometers

Frequency or Triggering Event	Maintenance Required	Procedure
Semi-Annually	Change rough pump oil	MS000
1) Instruments cannot be tuned or tunes are erratic 2) Sensitivity decreases below acceptable levels	Clean ion source	MS001

ICP Spectrophotometers

Frequency or Triggering Event	Maintenance Required	Procedure
Daily As needed: loss of linearity or sensitivity	Clean the torch	IP001
Clogging or drop in sensitivity	Clean the nebulizer end cap	IP002
Every two weeks	Replace the peristaltic pump tubing	IP003
Every month	Clean the autosampler	IP004

Cold Vapor AA

Frequency or Triggering Event	Maintenance Required	Procedure
Daily	Clean the quartz cell	CV001
Every month	Replace the reagent tubing	CV002
Every six months	Clean the liquid/gas separator	CV003

Maintenance SOPs	
Procedure No.	**Activity**
GC000	<u>Gas Chromatograph Maintenance to be performed by Contractors</u> ECD: Hydrogen cleaning shall be performed by a certified vendor.
GC001	<u>Changing Septa</u> 1. Allow the injector port to cool. 2. Remove the injector cap. 1. Remove and replace the septum. 2. Replace the injector cap and heat the injector. 3. Pierce the septum with a syringe.
GC002	<u>Clipping Capillary Columns</u> 1. Allow the injection port to cool. 2. Loosen the fitting on the injector end of the column. 3. Inspect and replace the ferrule if necessary. 4. Use a capillary column cutter to clip approximately one loop from the column. Inspect the cut end with a magnifier to ensure the cut is perpendicular to the tubing wall and is free of chips, burrs, or uneven areas. Make a new cut if necessary. 5. Inert the column into the injector so that the end of the column will be about 2 cm below the tip of the syringe when an injection is being made. 6. Tighten the fitting (DO NOT OVERTIGHEN!) and heat the injector.
GC003	<u>Changing Gas Filters</u>

Maintenance SOPs	
Procedure No.	**Activity**
	7. Turn off the gas supply. 8. Loosen the nut at each end of the filter. 1. Remove the filter and replace it with a new filter. 2. Tighten the nut at each end of the filter. 3. Turn the gas supply on. 4. Check for leaks
GC004	<u>Changing the PID Lamp</u> 1. Turn the lamp power supply off and allow the detector to cool. 2. Remove the lamp shield by depressing and turning it counter-clockwise. 3. Remove the two lamp ring retaining screws. 4. Remove the lamp by lifting it straight up. The lamp retaining ring, wave spring, and contact ring will also be removed. 5. Replace the lamp followed by the contact ring, wave spring, and retaining ring 6. Tighten the two retaining screws. 7. Replace the lamp shield by pressing it into place and turning it clockwise. 8. Heat the detector and turn on the lamp power supply.
GC005	<u>Changing GC Columns</u> 1. Allow the oven, injector, and detector to cool. **GC/MS**: Cool the ion source. When cool, turn the pumps off and vent the source. 2. Loosen the retaining nut at each end of the column and remove the column. 3. Place the nuts on the new column with new ferrules. 4. Use a capillary column cutter to clip a few cm from each end of the new column. Inspect the cut ends with a magnifier to ensure the cut is perpendicular to the tubing wall and is free of chips, burrs, or uneven areas. Make a new cut if necessary. 5. Insert the column ends into the injector and detector and tighten the fittings **<u>(Do Not Over Tighten)</u>**. 6. Heat the detector, injector, and oven. 7. GC/MS: Turn the pumps on and heat the ion source. 8. Condition the column per manufacturer's specifications.
GC006	<u>Cleaning the ECD Detector</u> **1. Perform this procedure only in the event of a sever signal problem.** 2. Bake the detector at 350°C for 12 - 24 hours.
MS000	<u>Mass Spectrometer Maintenance to be Performed by Contractors</u> 1. Turbo Pumps: All service shall be performed by a certified vendor. 2. Rough pumps: Change the oil every 6 months.
MS001	<u>Cleaning the Ion Source</u> 1. Allow the mass spectrometer to cool. 2. Turn the pumps off. 3. Remove the analyzer. 4. Clean the ion source according to the directions in the Hewlett-Packard HP5970B MSD Hardware Manual section 4-15. 5. Replace the analyzer. 6. Turn the pumps and mass spectrometer heater on.
PT001	<u>Changing the Purge Trap</u> 1. Remove the trap door. 2. Set the purge and trap device to Purge Ready.

Maintenance SOPs	
Procedure No.	**Activity**
	3. Loosen the nut at the bottom of the trap while holding the bottom fitting in place. 4. Loosen the top nut. 5. Pull the trap straight down through the furnace sleeve. 6. Insert a new trap. 7. Replace the ferrules if necessary. 8. Tighten the top nut. 9. Tighten the bottom nut while holding the bottom fitting in place. 10. Replace the trap door. 11. Follow the directions in the applicable analytical procedure to condition the trap before use.
IP001	**Cleaning the Torch** 1. Remove the nebulizer and spray chamber. 2. Gently remove the torch. 3. Place the torch, inverted, in a beaker containing aqua-regia (1 part conc. HNO_3 : 3 parts conc. HCl) being careful not to submerge the ceramic base. Soak for one hour. Do not soak for extended periods of time, the torch is held in place only with adhesive. 4. Rinse with reagent water. 5. Sonicate in a beaker of 10% nitric acid in a water bath for at least 2 hours. 6. Rinse with reagent water and dry thoroughly with compressed air. 7. Replace the torch.
IP002	**Cleaning the Nebulizer** 1. Disconnect the nebulizer from the spray chamber. 2. Rinse with reagent water and soak in a laboratory detergent solution. 3. Rinse with reagent water and 20% nitric acid solution. 4. Reattach the nebulizer to the spray chamber. 5. High salt build ups may be removed by soaking the nebulizer in 1:1 HCl, being careful to rinse all traces of HCl from the nebulizer afterwards.
IP003	**Replacing the Peristaltic Pump Tubing** 1. Loosen the tension on the pump windings. 2. Remove the tensioning plates from the peristaltic pump. 3. Remove and discard the old windings. 4. Install new windings. 5. Align the tensioning barbs on the tensioning plates and reattach the plates. 6. Adjust the tension for maximum flow. 7. Run the pumps for at least 30 minutes in order to condition the new windings prior to sample analysis.
IP004	**Cleaning the Auto Sampler** 1. Remove all autosampler racks. 2. Rinse the reservoir with deionized water. 3. Wipe the autosampler tray with a cloth dampened with a laboratory detergent solution. 4. Spray light penetrating oil on all moving assemblies as necessary to facilitate motion. 5. Reassemble the autosampler.
CV001	**Cleaning the Quartz Cell** 1. Remove the mercury vapor tube and ventilation tube from the cell. 2. Remove the quartz windows from the cell.

Maintenance SOPs	
Procedure No.	**Activity**
	3. Pipette about 10 mL of methanol into the cell and swirl. Discard the methanol. Repeat this rinse 3 times. 4. Dry the quartz cell with compressed air. 5. Replace the cell and reconnect the tubes.
CV002	**Replacing the Reagent Tubing** 1. Disconnect the tubing. 2. Discard the old tubing. 3. Replace with the appropriate Tygon tubing.
CV003	**Cleaning the Liquid/Gas Separator Cell** 1. Disconnect all tubing. 2. Remove the cell. 3. Flush the cell with 10% HCl, repeat until all stannous chloride and debris is cleared. 4. Replace cell and attached tubing and flush with method reagents prior to use.

10. Sample Handling and Custody Requirements

All samples will be clearly labeled with the company name, job number, date, time, sampler's initial and sample identification (i.e., location, depth, etc.). Samples will be stored in coolers with ice until arrival at the laboratory. Holding times for various parameters are specified in the most recent SW-846 promulgated method for the requisite analytical parameter. Questions on holding times will be directed to the analytical laboratory.

All samples will be tracked via a chain-of-custody (COC). The chain of custody will include job number, date, time, sample identification (i.e., location, depth, etc.), and parameters to be analyzed. Each individual handling the sample must sign the COC. The original COC will remain with the sample through out the duration of the sampling event and will be kept in the permanent project file. Copies of the COC will be distributed to the working project file, laboratory manager, and the data package.

Upon receiving samples at the laboratory, the chain of custody must be signed and dated by the person relinquishing the custody of the samples (client or courier) in the space provided on the bottom of the chain of custody. The person accepting the samples (client services personnel) must sign and date the received by section of the chain of custody, located on the bottom of the chain of custody next to the relinquished by signature. The pink copy (or a photo copy if a non multi-copy form is used) should be given to the client. The samples now remain in a secure area, not accessible to unescorted non-employees.

The sample coolers are opened and the cooler internal temperature is determined by either reading the cooler thermometer or by measurement using a calibrated IR thermometer and recorded on the COC. All samples which require thermal preservation shall be considered acceptable if the arrival temperature is either within ± 2 °C of the required temperature or the method specific range. The exceptions to this are the UCMR2 samples, which must meet the following temperature requirements or be recollected:

- **a.** ≤ 10 °C if received within 48 hours of collection
- **b.** ≤ 6 °C if received more than 48 hours after collection.

Temperature deviations of all other samples are noted in the final analytical report.

The samples **must** be unpacked and inspected for damage, proper sample volume and preservation, (absence of air bubbles in water volatile containers); all custody seals are not broken (if used), and accuracy of the chain of custody. The sample custodian will immediately notify the project management team of any unclear or incorrect chains of custody. The project management staff will then contact the client to clarify any confusion or to correct any improperly filled in COC. Any alterations to the COC will be verified with the client and documented on the COC, signed, and dated by the project manager.

Samples are then lined up in order listed on the chain of custody. The individual containers for each site are lined up front to back in the line. For aqueous samples, multiple containers are usually required. The sample volume and preservation guide can be used for assistance.

Samples must then be checked for proper preservation by measuring the pH, except for those samples for oil & grease, volatile organics, 525 and all UCMR2 tests. All of the sample containers that have been preserved with acid (HCl, HNO_3, H_2S0_4) must have a pH of less than 2. All samples preserved with a base (NaOH) must have a pH greater than 12. All pHs are

recorded on the COC. If the pH is not correct (i.e. pH of 12 for an acid preserved container), the client must be informed. If the client then directs the pH be correctly adjusted this must be noted on the Chain of Custody.

Follow the BLISS manual for step-by-step directions for logging in samples.

The batch of samples will then be assigned a job number based on the following code:

(i.e.) = E107234
E = Premier Laboratory Code
1 = year 199(1)
07 = month (July)
243 = sequential number of jobs for the month.

This job number must be clearly marked across the top of the chain of custody. The job number must be legible on all copies. The sample fractions must be numbered with a sequential two digit code, i.e.: 01, 02, 03 etc. A letter is also assigned to further separate fractions based on preservative or field filtering when applicable.

Labels are printed through LIMS and placed on all sample containers. If possible do not cover the client's sample identification with the label.

For soil/solid waste sample matrixes, all of the analysis may be performed from one container with the exception of volatile analysis. **Any sample which requires volatile analysis must have its own properly preserved container.**

All samples are then moved to the appropriate refrigerator (environmental, volatile or drinking water, bacteria) and stored in a secured area accessible only to authorized individuals. All storage locations must be locked when unattended.

Samples are stored in one of the following designated areas:

Aqueous Volatiles	VOA Refrigerator
Metals	Walk-in Refrigerator
Wet Chemistry	Walk-in Refrigerator
All soils	Walk-in Refrigerator
Profiles	DW Refrigerator
Bacteria	BAC Refrigerator

11. Analytical Sensitivity and Project Criteria

If a compound is regulated by the CT DEP surface water protection criteria (SWPC), the minimum reporting limit will be equal to or less than the SWPC standard.

Analyte	Analytical Method	Quantitation Limit [1]	Detection Limit	Precision (water) ** %RPD	Accuracy (water) ** %R	SWPC
Metals	6010B			Varies by lot		
Aluminum	6010B	50.0	5.23			NE
Arsenic	6010B	5.0	3.70			4
Barium	6010B	2.0	0.51			NE
Cadmium	6010B	2.0	0.45			6
Chromium	6010B	2.0	1.07			NE
Copper	6010B	2.0	0.87			48
Iron	6010B	50.0	2.07			NE
Lead	6010B	2.0	1.59			13
Manganese	6010B	2.0	0.19			NE
Nickel	6010B	2.0	1.83			880
Potassium	6010B	200.0	4.79			NE
Selenium	6010B	5.0	4.96			50
Silver	6010B	2.0	1.25			12
Zinc	6010B	2.0	1.42			123
Mercury	7470A/7471A	0.20	0.018	varies by lot		0.4
Gross Alpha	EPA 900.0	N/A	3 pCi/L	NAD ≤ 3	± 43 %	NE
Gross Beta	EPA 900.0	N/A	3 pCi/L	NAD ≤ 3	± 17 %	NE
Radium 226	EPA 903.0	N/A	1 pCi/L	NAD ≤ 3	± 26 %	NE
Radium 228	EPA 904.0	N/A	1 pCi/L	NAD ≤ 3	± 43 %	NE
pH (Lab Analysis)	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Specific Conductance (Lab Analysis)	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Total Dissolved Solids (TDS)	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Total Suspended Solids (TSS)	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Alkalinity, Total	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Hardness	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Biochemical Oxygen Demand (BOD5)	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Chemical Oxygen Demand (COD)	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Chloride	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Nitrate (N)	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Nitrite (N)	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Ammonia (N)	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Total Kjeldahl Nitrogen (TKN)	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Phosphorus, Total	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Total Organic Carbon (TOC)	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab
Polychlorinated Dibenzo-*p*-Dioxins and Polychlorinated Dibenzofurans	-Lab	-Lab	-Lab	-Lab	-Lab	-Lab

1 Detection and quantitation limits given in µg/L.
NE- Not Established
-LAB information to be provided by Lab

12. Field Quality Control Requirements

(Refer to Generic QAPP-GEN)

13. Laboratory Quality Control Requirements

Required QA/QC Parameter	Frequency	Performance Standard	Recommended Corrective Action
Quality Assurance and Quality Control Requirements-Method 6010B			
Quality Control Standard (second source)	▪ Once at the beginning of the run, immediately following the calibration.	▪ The QCS recovery must be +/-5% for all elements of interest.	If the QCS fails for any element of interest, inspect the instrumentation for problems and correct any abnormal conditions, and re-calibrate prior to rerunning the QCS.
Instrument Performance Check (same source as the calibration, at mid-point)	▪ Once at the beginning of the run, immediately following the QCS and bracketing every 10 samples analyzed.	The IPC recoveries must be +/-10% for all elements of interest.	The IPC may be run one additional time if the specified recoveries are not met, however if the second analysis fails, corrective action must be taken and any samples analyzed after the previous valid IPC must be re-analyzed.
Initial Calibration Blank/ Continuing Calibration Blank	▪ ICB-Once at the beginning of the run, immediately following the IPC. ▪ CCB- After each IPC	▪ The concentration for each element of interest must be less than the reporting limit.	Investigate the source of the contamination and rerun the blank. If no laboratory contamination is found, recalibrate and any samples analyzed after the previous valid CCB must be re-analyzed.
Interference Check Solution (ICSA-interferences only)	▪ Once prior to samples being introduced and once at the end of the sample run.	▪ The concentration of each element of interest must be less than twice the reporting limit.	Review the inter-element correction factors and recalculate if required. Recalibrate and restart the run sequence.
Interference Check Solution (ICSAB-interferences & elements of interest)	▪ Once prior to samples being introduced and once at the end of the sample run.	▪ The concentration of each element of interest must be within +/- 20 of the true value.	Review the inter-element correction factors and recalculate if required. Recalibrate and restart the run sequence.
Matrix Spike/MSD	▪ One pair per analytical batch of 20 samples or less analyzed, per matrix.	▪ The MS/MSD spiked elements of interest must be within 75-125% recovery or established laboratory control limits.	Evaluate the laboratory control sample to determine if the cause is matrix or preparation related. If the LCS is acceptable, note in the case narrative for the associated samples.
Laboratory Reagent Blank	▪ One per analytical batch of 20 samples or less analyzed, per matrix.	▪ The concentration for each element of interest must be less than the reporting limit.	Investigate the source of the contamination and rerun the blank. If the rerun fails to meet the criteria, re-process the effected samples for the failing elements if the sample concentrations are <10 times the reporting limits.

Required QA/QC Parameter	Frequency	Performance Standard	Recommended Corrective Action
Sample Duplicate	▪ Analyze one duplicate sample for every 20 samples. (A duplicate sample is a sample brought through the entire sample preparation and analytical process.)	▪ A control limit of ±20% for RPD shall be used for sample values greater than 5 times the method detection limit. Samples less than 5 times the detection limit should be within +/- the method detection limit.	Investigate the cause of the control failure. If the spiked samples for the batch duplicate within the control limit of +/-20% note in the case narrative. If duplication is not proven, re-process all samples in the batch.
Laboratory Fortified Blank	▪ One per analytical batch of 20 samples or less analyzed, per matrix.	▪ Percent recoveries must be between within 80-120% for each element of interest.	Re-process any associated samples requiring the elements that were recovered outside of the limits.
Low Level Check Standard	▪ Once at the beginning of the run prior to samples being introduced and once at the end of the sample run.	▪ Recovery should be within +/-20% of the true values of the elements of interest.	Note variances in the case narrative.
Quality Assurance and Quality Control Requirements-Method 7470/7471			
Initial Calibration Verification (second source)	▪ Once at the beginning of the run, immediately following the calibration.	▪ The ICV recovery must be +/-10%.	If the ICV fails, inspect the instrument for problems and correct any abnormal conditions, and re-calibrate prior to rerunning the ICV.
Continuing Calibration Verification (same source as the calibration, at mid-point)	▪ Bracketing every 10 samples analyzed.	▪ The CCV recovery must be +/-20%.	The CCV may be run one additional time if the specified recovery is not met, however if the second analysis fails, corrective action must be taken and any samples analyzed after the previous valid CCV must be re-analyzed.
Initial Calibration Blank/ Continuing Calibration Blank	▪ ICB-Once at the beginning of the run, immediately following the ICV. ▪ CCB- After each CCV	▪ The results of the calibration blank are to agree within +/- the PQL. If not, repeat the analysis two more times and average the results.	If the average is not within +/- the PQL, terminate the analysis, correct the problem; re-calibrate; and reanalyze the previous 10 samples.
Matrix Spike/MSD	▪ One pair per analytical batch of 20 samples or less analyzed, per matrix.	▪ The MS/MSD must be within 75-125% recovery or established laboratory control limits.	Evaluate the laboratory control sample to determine if the cause is matrix or preparation related. If the LCS is acceptable, note in the case narrative for the associated samples.

Required QA/QC Parameter	Frequency	Performance Standard	Recommended Corrective Action
Method Blank	▪ One per analytical batch of 20 samples or less analyzed, per matrix.	▪ The concentration must be less than the reporting limit.	Investigate the source of the contamination and rerun the blank. If the rerun fails to meet the criteria, re-process the effected samples if the sample concentrations are <10 times the reporting limits.
Laboratory Control Sample	▪ One per analytical batch of 20 samples or less analyzed, per matrix.	▪ Percent recovery must be between within 80-120%.	Re-process the associated samples.
Low Level Check Standard	▪ Once at the beginning of the run prior to samples being introduced and once at the end of the sample run.	▪ Recovery should be within +/-20% of the true value.	Note variances in the case narrative.
Sample Duplicate	▪ Analyze one duplicate sample for every 20 samples. (A duplicate sample is a sample brought through the entire sample preparation and analytical process.)	▪ A control limit of ±20% for RPD shall be used for sample values greater than 5 times the method detection limit. Samples less than 5 times the detection limit should be within +/- the method detection limit.	Investigate the cause of the control failure. If the spiked samples for the batch duplicate within the control limit of +/-20% note in the case narrative. If duplication is not proven, re-process all samples in the batch.
Quality Assurance for Quality Control Requirements-Method 8082			
Calibration Verification Standard (Aroclor 1016/1260 mix)	▪ Every 12 hours or, once every 20 samples or less (10 sample intervals will result in fewer reruns in the case of the criteria not being met.), and at the end of the run sequence.	▪ The calibration factor must not exceed +/-15% difference. ▪ All samples must be bracketed with passing calibration verification standards.	If the calibration does not meet the ±15% limit, check the instrument operating conditions, and if necessary, restore them to the original settings, and inject another aliquot of the calibration verification standard. If the response for the analyte is still not within ±15%, then a new initial calibration must be prepared.
Method Blank	▪ 1 per batch of samples per matrix extracted, not to exceed 20 samples per batch	▪ The concentration for each target compound must be less than the reporting limit.	Locate the source of contamination, correct the problem; re-extract the effected samples.

Required QA/QC Parameter	Frequency	Performance Standard	Recommended Corrective Action
Solvent Blank	▪ Whenever a new lot of solvent is used.	▪ The concentration for each target compound must be less than the reporting limit and no significant interferences are present.	Investigate the source of the contamination and rerun the solvent blank. If no laboratory contamination is found, isolate a solvent that is free of contamination.
Matrix Spike/MSD	▪ One pair per 20 samples or less extracted per matrix ▪ At least every 30 days for each matrix ▪ Alternately an unspiked duplicate sample and MS may be evaluated if the sample is expected to contain target analytes.	▪ The MS/MSD spike compounds must be recovered within the established laboratory control limits. ▪ The sample duplicate must be recovered within the established laboratory control limits.	Evaluate the laboratory control sample to determine if the cause is matrix or extraction efficiency related. If the LCS is acceptable, review alternate cleanup techniques for the MS/MSD associated samples.
LCS	▪ Extracted with each batch of 20 samples or less per matrix	▪ Percent recoveries must be between within established control limits.	Re-extract the associated samples if recovered outside of the limits.
Surrogates	▪ All sample and QC injections	▪ Compare to laboratory control limits, which must be generated annually.	Re-analyze the sample, if still outside of recovery limits then re-extract the sample.
Quality Assurance for Quality Control Requirements-Method 8260B			
BFB	▪ Every 12 hours	▪ Compare to the criteria listed in table 2 of the method.	Retune and recalibrate the GC/MS. It may be necessary to clean the ion source and/or the quadrapoles before retuning.

Required QA/QC Parameter	Frequency	Performance Standard	Recommended Corrective Action
Continuing Calibration (CCAL)	▪ Every 12 hours	▪ If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater than 20% difference or drift), for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion. ▪ Specific SPCC compounds must the minimum response requirements in the method SOP.	Perform instrument maintenance; retune instrument
Method Blank	▪ 1 per batch of samples per matrix, not to exceed 20 samples per batch	The concentration for each target compound must be less than the reporting limit (RL). Except common laboratory contaminates such as acetone, methylene chloride, and MEK which must be <5x the RL.	Locate the source of contamination, correct the problem; reanalyzed the method blank and all effected samples.
Matrix Spike/MSD	▪ One pair per 20 samples or less extracted per matrix batch. ▪ At least every 30 days for each matrix	▪ The MS/MSD spike compounds must be recovered within the established laboratory control limits.	Evaluate the laboratory control sample. If the LCS is acceptable, proceed with the method, note MS/MSD recoveries in the case narrative.
LCS	▪ Prepared with each batch of 20 samples or each new tune clock.	▪ Percent recoveries must be within established control limits.	Reanalyze the LCS. If the LCS continues to not meet the criteria, correct the problem and reanalyze the LCS and associated samples.
Surrogates	▪ All sample and QC injections	▪ Compare to laboratory control limits which must be generated	Re-analyze the sample, if still outside of recovery limits then report the results of both analyses, unless obvious interferences are present.

Required QA/QC Parameter	Frequency	Performance Standard	Recommended Corrective Action
Internal Standards	▪ All sample and QC injections	▪ Area counts must be within 50-200% of those in the associated CC. ▪ Retention times must be within +/- 30 seconds of those in the associated CC.	Re-analyze the sample, if still outside of recovery limits then report the results of both analyses, unless obvious interferences are present.

14. Data Management and Documentation
(Refer to Generic QAPP-GEN)

15. Assessment and Response Actions
(Refer to Generic QAPP-GEN)

16. Project Report
(Refer to Generic QAPP-GEN)

17. Field Data Evaluation
(Refer to Generic QAPP-GEN)

18. Laboratory Data Evaluation
(Refer to Generic QAPP-GEN)

19. Data Usability and Project Evaluation
(Refer to Generic QAPP-GEN)

APPENDIX A

LABORATORY STANDARD OPERATING PROCEDURES (SOPS)

Benchmark Analytics, Inc.

EPA 900.0: Gross Alpha and Gross Beta Radioactivity in Drinking Water
EPA 9310: Gross Alpha and Gross Beta

Document No. RA 001

Revision No. 17

October 30, 2008

Written By_____ Date:_____

Routing:_____ Date:_____

Reviewed By:_____ Date:_____

Management Approval:_____ Date:_____

Note: The date of management approval is the effective date of this SOP.

CHANGES

Section 7.8 changed to reflect new criteria for verification of attenuation curve.

TABLE OF CONTENT

REFERENCES

EPA Method 900.0, EPA Method 9310, SW 846 Revision 0, SOP RA006 Eclipse Software settings, SOP G-029 Labware washing procedures, SOP G-039 Definitions, SOP G-009 Method validation, SOP G-032 Acronyms, SOP G-016 Calibration and method validation, SOP G-033 Preparation of a final Report under NELAP, SOP IN-041 TCLP Extractions, and NELAC Standard latest issue as well as CHP, RSPM and QAPM.

Canberra Eclipse LB Technical Reference Manual, Canberra S550 Eclipse LB User's Manual for the Software controlling the S5XLB gas flow proportional counter hardware, and the installation guide.

Standard Methods for the Examination of Water and Wastewater 20th edition 1998 pp 8-9 for the preparation of Reconstituted Fresh Water, SM#19: 7110 B., EPA-600/4-80-032, 40CFR141 on drinking water, Federal Register Vol. 65, No. 236 pp. 76708 Rules and Regulations.; US EPA SOW for Radiochemistry; National Primary Drinking Water Regulations: Radionuclides Final Rule 40 CFR Parts 9,

141, 142, Dec 7 2000 pp 76708 – 76753.

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1.0 GENERAL

1.1 INTRODUCTION

1.1.1 This method covers the measurement of gross alpha and gross beta particle activities in drinking water, surface water, and ground water. The method is applicable to the measurement of alpha emitters having energies above 3.9 mega electronvolts (MeV) and beta emitters having maximum energies above 0.1 MeV.

1.2 DEFINITIONS

1.2.1 Batch = refers to a preparation batch which is 20 samples or less not including QA samples and blanks.

1.2.2 Beta rate = 1.29 * gamma rate (for Cs-137).

1.2.3 Ci = Curie (One curie = $3.7x10^{10}$ disintegrations per second = $3.7x10^{10}$ becquerels = $2.22x10^{12}$ disintegrations per minute.)

1.2.4 Counting efficiency (efficiency factor) = counts per minute / disintegrations per minute or cpm/dpm.

1.2.5 MDA = minimum detectable activity. The calculation for the MDA is in SOP Ra006.

1.2.6 MeV = megaelectronvolt = 10^6 Volt.

1.2.7 Rem = is the special unit of any of the quantities expressed as dose equivalent. The dose equivalent in rems is equal to the absorbed dose in rads multiplied by the quality factor (1 rem = 0.01 Sievert).

1.2.8 RSPM = Radiation Safety Program Manual.

1.2.9 Source = in this SOP this word refers to original material. It does not specifically refer to radioactive source material of U and Th.

1.2.10 Spillover = the number of erroneous counts in a counting channel (alpha or beta). See instrument manual for more detail.

1.3 QUANTITATION LIMITS

1.3.1 The minimum limit of quantitation depends on sample size, counting system characteristics, background, and counting time. The minimum detection limit or minimum detectable activity (MDA) is defined as the concentration which can be counted with a precision of plus or minus 100 percent at the 95 percent confidence level (1.96 sigma, where sigma is the standard deviation of the net counting rate of the sample). The National Primary Drinking Water Regulations require a gross alpha detection limit of 3 pCi/L and a gross beta detection limit of 4 pCi/L. If gross alpha is to be used as a measurement of alpha plus radium 226 then the MDA must be 1 pCi/L.

1.4 METHOD SUMMARY

An aliquot of a preserved drinking water, surface water, or ground water sample is evaporated to a small volume and transferred quantitatively to a tared 2-inch stainless steel counting planchet. The sample residue is dried for a minimum of 2 hours, reweighed to determine dry residue weight, then counted for alpha and/or beta radioactivity. Counting efficiencies for both alpha and beta particle activities are

determined according to the amount of sample solids from counting efficiency vs. sample solids standard curves.

1.5 INTERFERENCES

1.5.1 The solids concentration is very much a limiting factor in the sensitivity of the method for any given water sample. Sample density on the planchet area should not be more than 5 mg/cm^2 for gross alpha and not more than 10 mg/cm^2 for gross beta.

1.5.2 Moisture absorbed by the sample residue is interference as it affects counting and self-absorption characteristics. Planchets must be stored in a desiccator when not being counted.

1.5.3 Non-uniformity of the sample residue in counting planchet interferes with the accuracy and precision of the method. It is very difficult to spread the sample solids uniformly. Achieve uniformity as much as possible.

1.5.4 For counting with a gas-flow proportional counting system, counting at the alpha plateau discriminates against beta particle activity, whereas counting at the beta plateau is sensitive to alpha particle activity present in the sample. This latter effect should be compensated for during the calibration of the instrument.

1.6 SAFETY

1.6.1 The analyst must have completed the radiation safety-training program prior to handling radioactive material. The training must be documented. Refer to the RSPM and the Radiation Safety Officer for details.

1.6.2 Radioactive standards are to be stored in a properly labeled area.

1.6.3 Radioactive standards and samples must be prepared in an area specifically designated for those purposes.

1.6.4 Personal protective equipment for handling radionuclide standards includes gloves, safety glasses and laboratory coat.

1.6.5 Preparation of radioactive standards must be carried out on a tray with adsorbent liner to absorb any spilled radioactive liquid.

1.6.6 Due to the nature of the low intensity radiation and the low dose rate of the radionuclide standards, radiation monitoring is not necessary.

1.6.7 The analyst should take appropriate precautions when using HNO_3.

2.0 LABWARE WASHING PROCEDURES

2.1 Beakers should be acid washed to assure removal of any solids. Read the corresponding SOP on glassware washing procedures.

2.2 Planchets should be disposed after use and not be reused.

3.0 APPARATUS

3.1 Gas-flow proportional counting system - Canberra Tennelec Model 5S-XLB.

3.2 Tray(s) for radioactive standard preparation are to be constructed of stainless steel, plastic, or fiberglass and lined with absorbent paper to avoid contamination.

3.3 Adsorbing liners with plastic backing

3.4 Stainless steel counting planchets

3.5 Electric hot plate

3.6 Drying oven

3.7 Glass desiccator

3.8 Glassware: various size beakers and volumetric flasks

3.9 Analytical balance with 0.1 mg precision

3.10 Digestion Block, recommended model SC150 Hot Block from Environmental Express.

3.11 100 mL Disposable Digestion Cups, recommended catalog number SC490 from Environmental Express.

3.12 TCLP tumbler (for solid sample extraction).

3.13 Nalgene Extraction bottle (or equivalent).

3.14 142 mm Whatman glass microfiber filter

4.0 REAGENTS AND STANDARDS

4.1 General Comments

4.1.1 All reagents used must be analytical grade or better, whenever they are commercially available.

4.1.2 Materials of substandard reactivity or deterioration should not be used.

4.1.3 All reagents and reagent solutions should be properly labeled for identity, titer, strength or concentration, recommended storage, preparation and expiration dates, and any other relevant information.

4.1.4 Any expired reagent or reagent solution should be discarded or revalidated.

4.1.5 All reagents are prepared using volumetric flasks, unless otherwise specified.

4.2 Deionized (DI) water having a resistance value between 0.5 and 2.0 megaohms (2.0 to 0.5 micromhos)/cm at 25^{o}C. (1 micromhm = 1 megohm)

4.3 Nitric acid, 16 M HNO_3 (conc.)

4.4 Nitric acid, 1 M: Mix 64 ml 16 M HNO_3 with DI water and dilute to 1000 ml, or use an equivalent dilution. This solution has 6 months stability at room temperature.

4.5 Nitric acid, 0.1 M: Mix 10 ml 1 M HNO_3 with DI water and dilute to 100 ml, or use an equivalent dilution. This solution has 6 months stability at room temperature.

4.6 Hydrochloric acid, 12 M HCl (conc.)

4.7 Hydrochloric acid, 1 M: Mix 8.3 ml 12 M HCl with DI water and dilute to 100 ml, or use an equivalent dilution. This solution has 6 months stability at room temperature.

4.8 Hydrochloric acid, 0.1 M: Mix 8.3 ml 12 M HCl with DI water and dilute to 1000 ml, or use an equivalent dilution. This solution has 6 months stability at room temperature.

4.9 Sodium Bicarbonate - $NaHCO_3$

4.10 Calcium Sulfate - $CaSO_4 \times 2H_2O$

4.11 Magnesium Sulfate - $MgSO_4$

4.12 Potassium Chloride - KCl

4.13 Salt Mixture to represent Reconstituted Fresh Water (SM20:8010)

4.13.1 Mix in a beaker 384 mg $NaHCO_3$, 240 mg $CaSO_4 \times 2H_2O$, 240 mg $MgSO_4$ and 16 mg KCl with 1000 ml DI water, or use an equivalent dilution. This solution has 6 months stability at room temperature.

4.14 Radioactive Stock Standard Solutions

4.14.1 NIST traceable radionuclide reference standards are obtained

- Reference standards have to have a certificate of analysis for their activity.
- The decay corrected certified value is to be used at all times.

4.14.2 Expiration Date of Secondary Radioactive Standards

a. Radioactive standards will decay over time, which will decrease the radioactivity of the standard. The half-lives of the standards used in this SOP are as follows:

Th-230	alpha	75,000 years
Am-241	alpha	432.2 years
Cs-137	beta	30.17 years
Sr-90	beta	29 years

b. The impact of this is minimal: For example, the decay of Cs-137 with a half life of 30 years loses 1 percent of the activity in 15 years.

c. It is therefore practical, economical and environmentally responsible to assign the secondary standard solutions a shelf life equal to that of the primary standards. It is important to keep the solutions in a tightly closed container, as evaporation may change the concentration.

4.14.3 Radioactive Standard Solutions

a. Thorium-230 standard will be used for gross alpha testing as the test calibration standard in screening for the presence of all alpha-emitting radionuclides. Prepare secondary calibration standards as follows.

i. Purchase primary standard in the range of 0.1 uCi/5ml in 0.1 M HNO_3.

ii. Prepare the working standard, used in all alpha spiked solutions, by making a 1:100 dilution of the primary standard, or using a similar dilution. This solution is in the range of 200 pCi/mL.

b. Cesium-137 standard will be used for gross beta testing as the test calibration standard in screening for the presence of all beta-emitting radionuclides. Prepare secondary calibration standards as follows.

i. Purchase primary standard in the range of 0.1 uCi/5ml in 0.1 N HCl.

ii. Prepare the working standard, used in all beta spiked solutions, by making a 1:100 dilution of the primary standard, or using a similar dilution. This solution is in the range of 200 pCi/mL.

c. The standards will be revalidated every five years. Analyzing a known concentration of the secondary standard may revalidate the primary standard. The recovery must be within 10% of the known concentration.

4.14.4 Radioactive Sealed Source Calibration Standards

a. The instrument is calibrated for counting efficiency and for alpha and beta plateaus according to instrument manufacturer instructions for gross alpha using a sealed source of Th-230 or a similar alpha source element and for gross beta using a sealed source of Sr-90 or a similar beta source element.

b. A suggested supplier is Isotope Products Laboratory. The geometry for the solid standard must be the same as that of the prepared samples and QC samples. A suggested geometry is 45 mm on stainless steel backing with an aluminized mylar cover or electroplated onto the stainless steel planchet.

- Th-230 Cat. # EAB-230-PL at about 40,000 dpm total alpha activity.
- Sr-90 Cat. #EAB-090-PL at about 30,000 dpm activity for Sr-90 only, as Y-90 exists in equilibrium in the standard.

4.15 P-10 Counting Gas containing 10 % methane in 90% argon. The counting gas should contain no water vapor. The calibration plateau, background and efficiency must be verified whenever the gas is changed. To stabilize background, order the gas 1-week prior to using it. Cylinder changes must be noted in the maintenance manual.

5.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIMES & STORAGE

5.1 Collect 1L of sample.

5.1.1 For drinking water, the sample must be collected from a free-flowing source.

5.1.2 Ground water or surface water samples must have been collected in a manner which addresses the considerations discussed in SW 846 Revision 0, chapter 9

5.2 The samples should be preserved at the time of collection by adding enough HNO_3 to the sample to bring it to pH less than 2 (15 ml 1N HNO_3 or 1 ml of conc. nitric acid per liter of sample is usually sufficient). This step eliminates the formation of insoluble material, which could contain radioactive material and falsely lower the result.

5.3 Samples collected with preservative can be analyzed without additional waiting.

5.4 Samples collected without preservation should be brought to the laboratory within 5 days, then preserved and held in the original container for a minimum of 16 hours before transfer or analysis.

5.5 The container of choice should be plastic rather than glass to prevent loss due to breakage during transportation and handling.

5.6 The holding time is six months. Samples should not be stored in the same room as the counter. Samples are stored at room temperature.

6.0 QUALITY ASSURANCE

6.1 GENERAL

6.1.1 Setup the Canberra Tennelec Model 5S-XLB following the instrument manual, controlled document T402A. This includes alpha and beta plateau, spillover and deadband regions. Be sure to use the same sample geometry for samples as well as QC samples.

6.1.2 All radiochemical instruments are to be kept in good repair.

6.1.3 Permanent records of preventive maintenance, testing, and calibration for the proper operation of radiation instruments, and actions taken to detected defects are kept in the instrument maintenance manual.

6.1.4 Quality control performance records for the instrument are maintained on a daily

or day-of-use basis.

6.1.5 Before beginning analyses, determine the alpha efficiency, beta efficiency and background.

6.1.6 The counting instrument may not be located in a room where samples and standards are being prepared, and may not be located in a room where other types of chemical analyses are being performed.

6.2 INITIAL INSTRUMENT CALIBRATION

6.2.1 Calibration of the instrument is required when purchased, serviced, moved, change of gas cylinder and when the instrument's response has changed as determined by a performance check or when the instrument's response exceeds predetermined acceptance criteria for the instrument quality control.

6.2.2 Reference standards described in section 4.14.4 will be used.

6.2.3 Instrument calibration is recorded.

6.2.4 Determine the background, and the calibration plateau, and the counting efficiency, also called the efficiency factor (cpm/dpm) for gross alpha as well as for gross beta according to instrument manufacturer specification. This determines the absolute gross alpha and gross beta measurement. The background count must be for 1000 minutes.

6.2.5 The methods in the Eclipse software to be used are ALPHA PLATEAU, BETA PLATEAU, AB BKG, WEEKLY BKG, DAILY ALPHA EFFICIENCY, and DAILY BETA EFFICIENCY. These are contained in the sequence: AutoCal1. Copies of the methods and sequence are found in SOP RA006.

6.2.6 The background for alpha must be less than 1.0 cpm and for beta must be less than 4.0 cpm. The efficiency must be greater than 30 % for alpha and greater than 40 % for beta. If these criteria are not met then the root cause must be investigated and the instrument recalibrated before use.

6.3 CONTINUING INSTRUMENT CALIBRATION VERIFICATION

6.3.1 The calibration verification is monitored on a day of use basis to ensure that the instrument is operating appropriately and that the calibration has not changed. This includes alpha efficiency, beta efficiency and background monitoring. These parameters are charted on a monthly basis by the Eclipse software.

6.3.2 For batches of samples that uninterruptedly count for more than a day a performance check can be performed at the beginning and end of the batch as long as the time interval is no greater than one week.

6.3.3 A weekly background count must be performed once a week. These results are subtracted from the sample CPM to give the NCPM. The weekly background should be run at 360 minutes. The Eclipse program to use is WEEKLY BKG.

6.3.4 The Eclipse programs to use for the performance check are DAILY ALPHA EFFICIENCY, DAILY BETA EFFICIENCY and DAILY BACKGROUND. These programs are contained in the sequence: Daily QC. Copies of the methods and sequence are found in SOP RA006.

6.3.5 The sealed check source described in section 4.14.4 shall be used for the continuing calibration verification.

6.3.6 The background for alpha must be less than 1.0 cpm and for beta must be less

than 4.0 cpm. The efficiency must be greater than 30 % for alpha and greater than 40 % for beta. If these criteria are not met then the root cause must be investigated and the instrument recalibrated before use.

7.0 SELF-ADSORPTION CALIBRATION

7.1 The presence of solids in the sample has an impact on the counting efficiency. Therefore, prepare alpha and beta particle self-absorption graphs showing water sample residue weight (mg) vs. the efficiency factor (cpm/dpm), using standard alpha and beta emitter solutions and known amounts of salt on planchets. The self-adsorption calibration is done initially and whenever there is an indication that the solids impact on the counting efficiency needs to be reestablished. Count each sample until at least 10,000 counts have been accumulated.

7.2 Prepare about 1 liter artificial hard water as in SM20:8010 to approximately 880 mg/L total solids, see section 4.13.

7.3 Add the artificial hard water plus DI water to achieve the target final concentration of total solids in each aliquot covering a range of 0 to 150 mg.

7.4 To each aliquot add the same amount of both alpha and beta isotopes to approximately 300 pCi final amount for each. For example in the initial study, 1.5 ml of solution was added, for alpha and beta each, described in section 4.14.3 a and b.

7.5 Process these similar to a routine sample. However, adjust the counting time to ensure that at least 10,000 counts have been accumulated.

7.6 Count on the simultaneous mode. The Eclipse methods for counting are: ALPHA ON SIMULTANEOUS 1.5 ML STD and BETA ATTENUATION 1.5 ML STD. Copies of the methods and sequence are found in SOP RA006.

7.7 The attenuation curves must be fit to a specific model. A recommended choice for the alpha curve is an exponential fit. The zero mass efficiency should be in the range of 25%.

7.8 The self-adsorption calibration curve must be verified at least annually by preparing and counting standards at three different solids levels. The efficiency must be the expected efficiency plus/ minus 5.0 %. For example if the expected efficiency is 24.2%, the acceptable range is 19.2 % to 29.2 %. If at least one of the standards is not acceptable, the curve must be redone. Planchets prepared for the original attenuation curve may be reused for this verification. Alternately, the calibration curve may be re-done annually by re-using the planchets from the original calibration curve or preparing a new set. See section 14.0 for the information on the original planchets.

8.0 DEMONSTRATION OF CAPABILITY/MDA

8.1 Detection limits must be determined prior to sample analysis. They also must be established annually by each qualified analyst for each analyte.

8.2 It must be done initially and done again if there is a significant change in instrument type, personnel, or method.

8.3 Prepare 4 samples at approximately 30 pCi/L gross alpha and approximately 30 pCi/L gross beta, or equivalent if spike is > 5 time MDA. Both activities are added to the 4 samples. The samples are carried through the sample preparation steps and counted on the simultaneous mode.

8.4 To 100 ml DI water add 15 uL of solution from section 4.14.3a for gross alpha, and 15 uL of solution from section 4.14.3b for gross beta.

8.5 It is also acceptable to use 4 or more sample batches and generate the MDA from the

LCS data of those batches.

8.6 Calculate the gross alpha, and gross beta.

8.7 Determine the recovery and the relative standard deviation for gross alpha and gross beta as pCi/L

8.8 The recovery of the gross alpha and gross beta must be at or below the following criteria:

8.8.1 for gross alpha +/- 43 % precision and +/- 25% relative standard deviation (RSD).

8.8.2 for gross beta +/- 17 % precision and +/- 25% relative standard deviation (RSD).

8.9 Proficiency Sample Results

8.9.1 The laboratory will use the results of proficiency samples as an evaluation of the ability to produce accurate data.

9.0 SOLID SAMPLE PREPARATION

9.1 Weigh out the sample into a Nalgene plastic extraction bottle (or equivalent). The sample to extraction fluid ratio must always be 0.05 g/mL. The amount of extraction fluid is directly proportional to the sample weight; 1 g sample = 20 mL fluid. Example: 50 g of solid needs 1000 mL of extraction fluid.

9.2 Unless specified by the client, the extraction fluid typically used is DI water acidified with HNO3. Add the appropriate extraction fluid to the extraction bottle (using the ratio in section 9.1). A blank container must also be analyzed. Fill an empty extraction bottle with an equal amount of extraction fluid. See SOP IN041 for more details on types of extraction fluids.

9.3 Seal the extraction bottle tightly and rotate sample for 18 + 2 hours. Record the rotation period.

9.4 Filter samples through a 142 mm Whatman glass microfiber filter into a 1000 mL (or larger) sidearm flask. Pour filtrate into a clean sample bottle.

9.5 Analyze the filtrate and the blank following the regular sample procedure. For reporting as a solid (example: pCi/Kg) use the 0.05 g/mL ratio for converting mL's to grams.

10.0 SAMPLE PREPARATION

10.1 Verify that the sample pH is < 2 and record the information. If the pH is higher than 2, the sample must be acidified. Add 1 ml of concentrated nitric acid to the 1 L sample in the collection container, mix and allow to set for 16 hours before the sample aliquot is remove for evaporation.

10.2 Transfer to a beaker or a disposable digestion cup an aliquot of water sample of a volume size that contains

10.2.1 No more than 100 mg of total water solids for alpha only or alpha and beta determination.

10.2.2 No more than 200 mg of total water solids for beta only determination.

10.2.3 Typically 100 ml of drinking water, surface water, or ground water is used.

10.3 Evaporate the aliquot to near dryness (about 10-25 ml remaining) on a hotplate or digestion block. If the sample goes to dryness, discard and begin again.

10.4 If sample is known to or suspected to contain chloride salts, those chloride salts should be converted to nitrate salts before the sample residue is transferred to a stainless steel planchet. Chloride salts can be converted to nitrate salts by adding 5 ml portions of 16N

HNO_3 to the sample residue and evaporating to near dryness. Two treatments will accomplish this. BE SURE TO PERFORM THIS STEP IN THE HOOD.

10.5 Allow samples to remain on the hotplate or digestion block to near dryness. Do not allow complete evaporation! If the sample goes to dryness, discard and begin again.

10.6 Add 10 ml 1N HNO_3 to the beaker and swirl to dissolve the residue. Quantitatively transfer the aliquot concentrate in small portions (not more than 5 ml at a time) to a tared and marked planchet. The sample needs to be evaporated to dryness on the hotplate before drying at 105° C. Analyst should use discretion.

10.7 Dry sample residue to in drying oven at 105° C for at least 2 hours. Cool in a desiccator.

10.8 Weigh the sample residue.

10.9 If there is evidence of hygroscopic salts in sample counting planchets, they should be flamed to a dull red heat for a few minutes to convert the nitrate salts to oxides before weighing and counting. It is possible to have loss of cesium during the flaming of these samples. If a stable weight cannot be attained on the balance it can be assumed that hygroscopic salts are present.

10.10 Store sample residue in desiccator until ready for counting.

10.11 Count for alpha and beta activity at their respective voltage plateaus. Counting time is based from the current weeks background measurement. A sample may not be counted for longer than the weekly background (360 minutes). If the MDA can not be achieved for this reason it must be noted in the final report along with the appropriate data qualifying code.

10.12 If beta alone is being analyzed it can be counted immediately after evaporation. Alpha counting must be delayed 72 hours for drinking water samples only. Surface and ground water samples have no delay in counting.

10.13 If sample is to be recounted for reverification, store it in a desiccator.

11.0 QUALITY CONTROL SAMPLES

11.1 METHOD BLANK (MB)

11.1.1 The frequency of a method blank is one method blank per preparation batch. The batch is defined as 20 samples or less (excluding the method blank, LCS, and spike).

11.1.2 Prepare a method blank by using 100 ml of DI water and treat it the same as all of the samples. Add 0.1 ml of 16 N HNO_3. If a batch of 200 ml samples is used, then the Method Blank should also be 200 ml sample size with 0.2 ml of 16 N HNO_3. The method blank must be prepared with similar aliquot size to that of the routine samples. If this is not possible, the method blank must be calculated in a way that compensates for sample results based upon differing aliquot size.

11.1.3 The result of this analysis is recorded as a quality control measure to assess the batch.

11.1.4 The result of the blank must be below the MDA for gross alpha and/or gross beta measurements.

11.1.5 When the acceptance criteria for the method blank are not met the specified corrective action and contingencies must be followed; results must be reported with the appropriate data qualifying codes. The corrective action may include some or all of the following:

- check planchet holder for contamination
- check for area contamination
- Assure that the instrument background is in control. For specifications see section 6.2.4.

11.1.6 Note in the laboratory report if a method blank fails. The corrective actions will be recorded in the raw data.

11.1.7 NOTE: The method blank must not be subtracted from the sample results.

11.1.8 NOTE: The weekly background is applied to all analyzed samples and QC and does not depend on the method blank result associated with the analytical batch.

11.1.9 Management is notified when out-of-control or unacceptable data occurs.

11.2 LABORATORY CONTROL SAMPLES (LCS)

11.2.1 One LCS is prepared for each preparation batch. The batch is defined as 20 samples or less (excluding the method blank, LCS, and spike).

11.2.2 The LCS must be of similar aliquot size to that of routine samples.

11.2.3 A practical level for the LCS is about 30 pCi/L for gross alpha and about 30 pCi/L for gross beta, which is greater than five times the detection limit. Choose a level comparable to the level of the samples if the samples exceed five times the detection limit.

11.2.4 Prepare a solution with approximately 30 pCi/L of alpha and / or beta and test as a sample. To 100 ml DI water add 15 uL of both solutions from section 4.14.3 a and b.

11.2.5 Calculate the relative bias = (observed)/(known). The result is recorded as a quality control measure to assess the batch and must be within 43 % of the expected value for gross alpha and within 17 % for gross beta.

11.2.6 The LCS acceptance criteria will be re-evaluated and adjusted (if necessary) at least once a year. QC charting of the LCS data will be done to facilitate this.

11.2.7 When the acceptance criteria for the LCS are not met, follow the specified corrective action and contingencies. The corrective actions may involve but are not limited to recount the LCS and assure that the instrument calibration parameters are in control.

11.2.8 Occurrence of a LCS failure will be noted in the laboratory report. The corrective actions will be recorded in the raw data.

11.2.9 Management is notified when out-of-control or unacceptable data occurs.

11.3 MATRIX SPIKE/DUPLICATE

11.3.1 Gross alpha and gross beta require matrix spikes as well as duplicates for aqueous samples at a frequency of one for every ten samples. The batch is defined as 20 samples or less (excluding the method blank, LCS, and spike).

11.3.2 The matrix spike and the matrix spike duplicate are spiked after subsampling but before any chemical treatment.

11.3.3 A sample aliquot is spiked at approximately 60 pCi/L with gross alpha and /or gross beta, which is greater than five times the detection limit. For example, a 100 ml sample is spiked with 30 uL of the solutions from section 4.14.3 a and b.

11.3.4 Repeat for the matrix spike duplicate sample.

11.3.5 Prepare and read the samples along with the other QC samples and field samples.

11.3.6 Calculate the normalized absolute difference (NAD) between the sample and the laboratory duplicate. This result is recorded as a quality control measure to assess the batch and must be < or = 3.

$$NAD = (S-D) / [(TPU_S)^2 + (TPU_D)^2]^{1/2} = or < 3$$

Where,

S = sample result

D = duplicate result

TPU_S = 1s total propagated uncertainty of the sample

TPU_D = 1s total propagated uncertainty of the duplicate

11.3.7 Calculate the spike recovery = (spiked result – sample result)/(spike amount). The result is recorded as a quality control measure to assess the batch and must be within 43 % of the expected value for gross alpha and within 17 % for gross beta.

11.3.8 The acceptance criteria will be re-evaluated at least annually. QC charting of the MS/MSD data will be done to facilitate this.

11.3.9 If the specified criteria are not met for the spikes or duplicate calculations, specified corrective action and contingencies will be followed. The RPD of the total solids may be used as an acceptance criterion to prove reproducibility. The acceptance criteria is < or = 10%. To Calculate the RPD: [((MS-MSD)*2)/(MS+MSD)]*100

11.3.10 Occurrence of a matrix spike and duplicate failure, as well as the actions taken, must be noted in the laboratory report.

11.3.11 The analyst must make a note in the laboratory report if there is not enough sample to perform the matrix spike and duplicate.

11.3.12 Management is notified when out-of-control or unacceptable data occurs.

11.4 NONCONFORMANCE

11.4.1 Root cause of nonconformance must be done. Check appropriate count times, dilutions, aliquot size, detector efficiency, and detector background. If the nonconformance is due to inadequate sample volume, elevated radioactivity levels, sample matrix interference such a high amount of suspended solids, etc., explain these factors in the report.

11.4.2 To address nonconformance of QC results consult the troubleshooting section of the instrument manual. It addresses the following problems: gas flow, plateau, background, efficiency and spillover, count timer incrementing and data reproducibility.

11.5 QC SAMPLE SUMMARY

11.5.1 For each batch of 20 or less samples there will be:

- 1 solid standard for alpha counting efficiency
- 1 solid standard for beta counting efficiency

- 1 instrument background
- 1 MB in DI water
- 1 LCS at approximately 30 pCi/L alpha and / or 30 pCi/L beta activity
- 1 MS and 1 MSD for every ten samples at approximately 60 pCi/L alpha and / or 60 pCi/L beta activity

10.5.2 The cover page for the data packet includes a QC checklist, which shows criteria for the QC in section 11.5.1. The reviewer of the data pack is responsible to check that all criteria are met, and that if a criterion is not met that the appropriate notation is made in the raw data. The reviewer should also review and QA the batch in the Omega LIMS. This cover page also has an analyst checklist, items that the analyst who ran the batch is responsible for.

12.0 CALCULATIONS

12.1 CALCULATE ALPHA RADIOACTIVITY

12.1.1 The instrument will give the results in pCi/L after all of the required information is added in the ECLIPSE software. Enter sample volume, dry weight, and reference the attenuation data to be used.

12.1.2 For understanding the relationships of the results these are the calculations from the reference procedure EPA 900.0. It uses the following equation:

$$\text{Alpha (pCi/L)} = (A \times 1000) / (2.22 \times C \times V)$$

Where:

A = net alpha count rate (gross alpha count rate minus the background count rate) at the alpha voltage plateau

C = alpha efficiency factor, read from graph of efficiency versus mg of water solids per cm^2 of planchet area, (cpm/dpm)

V = volume of sample aliquot, (ml)

2.22 = conversion factor from dpm/pCi

12.2 CALCULATE BETA RADIOACTIVITY

12.2.1 Use the following equation(s):

12.2.2 If there are no significant alpha counts when the sample is counted at the alpha plateau:

$$\text{Beta (pCi/L)} = (B \times 1000) / (2.22 \times D \times V)$$

Where:

B = net beta count rate (gross count rate minus the background count rate at the beta voltage plateau)

D = beta efficiency factor, read from the graph of efficiency versus mg of water solids per cm^2 of planchet area, (cpm/dpm)

V = volume of sample aliquot, (ml)

2.22 = conversion factor from dpm/pCi

12.2.3 When counting beta activity in the presence of alpha radioactivity by gas-flow proportional counting systems (at the beta plateau) alpha particles are also

counted.

12.2.4 The alpha amplification factor (E) from that curve is used to correct the amplified alpha count on the beta plateau. The following equation s then used:

$$\text{Beta (pCi/L)} = [(B - A \times E) \times 1000] / (2.22 \times D \times V)$$

Where:

B = net beta count rate (gross count rate minus the background count rate at the beta voltage plateau)

D = beta efficiency factor, read from the graph of efficiency versus mg of water solids per cm^2 of planchet area, (cpm/dpm)

A = net alpha count rate (gross alpha count rate minus the background count rate) at the alpha voltage plateau

E = alpha amplification factor, read from the graph of the ratio of alpha counted at the beta voltage / alpha counted at the alpha voltage vs. sample density thickness

V = volume of sample aliquot, (ml)

2.22 = conversion factor from dpm/pCi

12.3 REPORTING

12.3.1 The customer report must contain the calculated value for gross alpha and / or gross beta, the MDA for each and the counting error.

12.3.2 Error Reporting. Each result must be reported with the measurement of uncertainty, also called error reporting. The counting error must be established and reported at the 95 % confidence level. The ECLIPSE software calculates the error as uncertainty with all results. The documentation is in the Canberra Technical Reference Manual. Copies of the methods, calculations and sequence are found in SOP RA006.

12.3.3 MDA Reporting: The Eclipse software has an MDA calculator. Use the calculator to determine the counting time required to reach the MDA of 3 pCi /L for gross alpha (1 pCi/L if the data is to be used for compliance with Radium 226 and gross alpha) and 4 pCi/ L for beta. The MDA calculator equations are described in detail in SOP RA006.

12.3.4 If a MDA is unable to be achieved, for example due to high solids, the sample should be reported with the appropriate data qualifier.

12.3.5 If reanalysis is not possible the sample should be reported with the appropriate data qualifier.

12.3.6 The full sample ID must be used throughout the entire procedure. At no point during preparation or reporting is an abbreviated sample ID used.

13.0 QC Summary Table (approximate values)

	Gross Alpha	Gross Beta	Specification	Reference
LCS	30 pCi/L	30 pCi/L	+/- 43 % GA; +/- 17% GB	At least 5 x MDA
MS/MSD	60 pCi/L	60 pCi/L	< 3 NAD; +/- 43 % GA & +/- 17% GB	>5 x MDA

MS/MSD total solids			+/- 10 % GA +/- 10 % GB	Used when NAD > 3
Attenuation curves			Verified annually	
DOC/MDA study	30 pCi/L or equivalent	30 pCi/L or equivalent	Annually by analyst +/- 43 % GA; +/- 17% GB and 25% RSD	>5 x MDA
Background	< 3 or <1 pCi/L	< 4pCi/L	Verified daily and weekly	< MDA
MDA specs	3 / 1 pCi/L	4 pCi/L	Each sample	40 CFR 141, 142

14.0 Original Attenuation Planchets

14.1 The original attenuation planchets are kept in the dessicator in the radiation counting room. Please handle with extreme care!

14.2 The original data can be found in book 719, page 6.

Planchet #	Residual Mass (mg)
75	0.00
76	9.00
77	17.80
78	35.70
79	54.00
80	70.70
81	90.60
82	109.80
83	126.80
84	145.30
85	161.30

15.0 Pollution Prevention & Waste Management

15.1 See Benchmark Analytics QAPP.

Attachment A:

Benchmark Analytics Page_____

Gross A/B Worksheet: EPA 900.0

SOP RA 001 Revision _____

(72 Hours from Evaporation)

COUNT AFTER:

Prep Analyst: _____

Start Date & Time: _____

Evaporation Date & Time : _____ **Omega Run # :** _____

Th-230 Standard Lot# : _____ **Exp.** _____ **Balance used:** _____

Cs-137 Standard Lot# : _____ **Exp.** _____ **Book # :** _____

16N HNO_3 Lot # : _____ **Exp.** _____ **Beaker or Digestion Cup ?** _____

#	Sample ID	Volume ml	Planchet # A	Initial wt. g	Final wt. g	Delta wt. mg	Count Time min
1	MB						
2	LCS						
3							
4							
5							
6							
7							
8							
9							
10							
11							
12							
13							
14							
15							
16							
17							
18							
19							
20							
21							
22							
23							
24							
25							
26							

Notes: _____

All Sample pH < 2 ? _____

Reviewed by: _____

Attachment B: **Page # _____**

Solution: Nitric acid, 1 M

SOP RA001 Instructions: Mix 64 ml 16 M HNO_3 with DI water and dilute to 1000 ml, or use an equivalent dilution. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment C: **Page # _____**

Solution: Salt Mixture to represent Reconstituted Fresh Water (SM20:8010)

SOP RA001 Instructions: Mix in a beaker 384 mg $NaHCO_3$, 240 mg $CaSO_4$ x $2H_2O$, 240 mg $MgSO_4$ and 16 mg KCl with 1000 ml DI water, or use an equivalent dilution. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment D: **Page # _____**

Solution: Nitric acid, 0.1 M

SOP RA001 Instructions: Mix 10 ml 1 M HNO_3 with DI water and dilute to 100 ml, or use an equivalent dilution. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment E: **Page # _____**

Solution: Hydrochloric acid, 1 M

SOP RA001 Instructions: Mix 8.3 ml 12 M HCl with DI water and dilute to 100 ml, or use an equivalent dilution. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment F: **Page # _____**

Solution: Hydrochloric acid, 0.1 M

SOP RA001 Instructions: Mix 8.3 ml 12 M HCl with DI water and dilute to 1000 ml, or use an equivalent dilution. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment G:

Benchmark Analytics
Radiochemistry Data Package Review
Last Revision: 04-18-07

GROSS ALPHA & BETA

Date: 07/25/07 Instrument: Canberra Tennelec S5-XLB
Method: EPA 900.0 LIMS # : _____
SOP: RA001 Latest Revision

Instrument (circle one)	1	2	3	4	5
0-Mass Alpha Efficiency	27.40%	26.65%	28.28%	26.62%	27.54%
0-Mass Beta Efficiency	52.16%	54.02%	55.56%	52.71%	55.23%

CHECKLIST

Analyst

- Daily QC Done
- Sample Reports Printed
- Custom Reports Printed
- All Alpha MDAs < 3pCi/L
- All Beta MDAs < 4 pCi/L
- Work Book Complete and Copied
- Spike Inventoried
- All QC recorded in Excel

QC	Criteria
❑ Daily Alpha Efficiency	1) 35.8% 2) 35.8% 3) 38.3% 4) 36.4% 5) 38.5% at +/- 5%
❑ Daily Beta Efficiency	1) 46.0% 2) 45.2% 3) 46.0% 4) 43.7% 5) 48.0% at +/- 5%
❑ Daily Background	Alpha < 1 CPM, Beta < 4 CPM
❑ Alpha Method Blank	< or = 3.0pCi/L
❑ Beta Method Blank	< or = 4.00pCi/L
❑ Alpha LCS	+/- 43%
❑ Beta LCS	+/- 17%
❑ Alpha Matrix Spike	+/- 43%
❑ Beta Matrix Spike	+/- 17%
❑ Alpha Duplicate	NAD < or = 3 or RPD < or = 10%
❑ Beta Duplicate	NAD < or = 3 or RPD < or = 10%
❑ Alpha MDAs	< or = 3pCi/L
❑ Beta MDAs	< or = 4pCi/L

STANDARDS USED

Solid	Source Ref. #	Half Life	Reference Date	Contained Radioactivity
Instruments #3 and #4				
Th-230	4979-S	75,400 years	04/01/2005	19.38 nCi / 43020 dpm
Sr-90	4979-S	28.5 years	04/01/2005	14.05 nCi / 31190 dpm
Instruments #1 and #2				
Th-230	4223-S	75,400 years	12/15/2002	19.56 nCi / 43420 dpm
Sr-90	4223-S	28.5 years	01/01/2003	13.38 nCi / 29700 dpm
Instruments #5				
Th-230	20002-S	75,400 years	07/01/2007	14.35 nCi / 31860 dpm
Sr-90	20002-S	28.5 years	07/01/2007	14.35 nCi / 31860 dpm

Preparation Analyst: _____ **Date:** _____

Instrument Analyst: _____ **Date:** _____

LIMS Entry By: _____ **Date:** _____

Reviewed and LIMS QA By: _____ **Date:** _____

Note: Reviewer is responsible for checking the entire data package and may choose to sign only the front cover sheet.

ICP Metals
Method 6010B

Prepared by: Melisa Montgomery, Quality Assurance Officer
Approved by: Robert Stevenson, Laboratory Director
Reviewed and Implemented by: Ronald Warila, General Manager

Reference

Test Methods for Evaluating Solid Waste, SW-846, Revision 2, December 1996, Method 6010B.

I. Applicability

Analyte: Refer to ICP manual for installed spectral lines

Matrix: Digestates from procedures 3005A, 3010A, 3015, 3040A, 3051

Regulation: RCRA

II. Important Notes

The proper identification of interferences encountered while performing ICP analysis is vital to producing sound analytical data. The following is a brief summary of some of the major interferences that may produce either false positive or false negative results.

Spectral interferences are caused by (1) overlap of a spectral line from another element; (2) unresolved overlap of molecular band spectra; (3) background contribution from continuous or recombination phenomenon and (4) stray light from the line emission of high-concentration elements. Computer-correcting the raw data after monitoring and measuring the interfering element can compensate for spectral overlap. Unresolved overlap requires selection of an alternate wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Users of simultaneous multi-element instruments must verify the absence of spectral interference from an element in a sample for which there is no instrument detection channel. Potential spectral interferences for the recommended wavelengths are given in Table 2. The data in Table 2 are intended as rudimentary guides for indicating potential interferences; for this purpose, linear relations between concentration and intensity for the analytes and the interference can be assumed.

The interference is expressed as analyte concentration equivalents (i.e. false analyte concentrations) arising from 100 mg/L of the interference element. For example, assume that As is to be determined

(at 193.696 nm) in a sample containing approximately 10 mg/L of Al. According to Table 2, 100 mg/L of Al would yield a false signal for As equivalent to approximately 1.3 mg/L. Therefore, the presence of 10 mg/L of Al would result in a false signal for As equivalent to approximately 0.13 mg/L. The interference effects must be evaluated for each individual instrument since the intensities will vary with operating conditions, power, viewing height, argon flow rate, etc.

Generally, interferences were discernible if they produced peaks, or background shifts, corresponding to 2 to 5% of the peaks generated by the analyte concentrations.

At present, information on the listed silver and potassium wavelengths is not available, but it has been reported that second-order energy from the magnesium 383.231-nm wavelength interferes with the listed potassium line at 766.491 nm.

Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample, by using a peristaltic pump or by using the standard additions method. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. The problem can be controlled by wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rate improves instrument performance; this is accomplished with the use of mass flow controllers.

Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally, these effects are not significant with the ICP technique. If observed, they can be minimized by careful selection of operating conditions (incident power, observation position, and so forth), by buffering of the sample, by matrix matching, and by standard addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

III. Procedure

Preliminary treatment of most matrices is necessary due to the complexity of sample matrices. The use of an internal standard or matrix matching must be used to determine concentrations of unknowns. The internal standard used is Yttrium.

Set up the instrument with proper operating parameters established by the instrument manufacturer. The instrument must be allowed to become thermally stable before beginning (usually requiring at least 30 minutes of operation prior to calibration).

Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures, using the typical mixed calibration standard solutions described in Table 3. Flush the system with a reagent blank between each standard. Use the average intensity of multiple exposures for both standardization and sample analysis to reduce random error. In the case of multi-level calibrations the correlation coefficient must be > 0.995 for all elements.

NOTE: For boron concentrations greater than 500 mg/L, extended flush times >1 minute may be required.

The validity of the calibration must be verified by analyzing a second source standard (ICV) with concentrations of all elements of interest at or near the midpoint of the calibration.

The CCV and ICB must be run and meet the QC requirements before proceeding. Each may be rerun once before having to initiate corrective actions and recalibration.

Flush the system with the calibration blank solution for at least 1 minute before the analysis of each sample. Rinse time may be reduced if data will support the absence of analytes above the stated MDLs. Analyze the instrument performance check and the calibration blank after every 10 samples.

An Interference Check solution (ICS) containing the major interferences must be run prior to analysis of samples. An ICSA and ICSAB must also be run at the beginning and end of each analytical sequence, this solution contains parts A (major interferences) only and A (major interferences) plus B (elements of interest), respectively.

A low-level check standard (or project required detection limit standard, however named) must be run at the beginning of each run and at the end. Unsatisfactory recoveries must be narrated in the final report based on project specific limits and requirements.

IV. Standards Preparation

Standard Concentrations: **Enviro 61E**

Standard 1

10mL HNO_3
490mL reagent H_2O
total vol.= 500mL

This standard serves as the CCB/ICB

Standard 2

2.5mL (1000ppm) Ag stock
5.0mL (1000ppm) As stock
5.0mL (1000ppm) B stock
2.0mL (10,000ppm) Ba stock
1.0mL (1000ppm) Be stock
5.0mL (1000ppm) Cd stock
5.0mL (1000ppm) Co stock
2.5mL (1000ppm) Cr stock
2.5mL (1000ppm) Cu stock
5.0mL (1000ppm) Mn stock
5.0mL (1000ppm) Mo stock
5.0mL (1000ppm) Ni stock
5.0mL (1000ppm) Pb stock
5.0mL (1000ppm) Sb stock
5.0mL (1000ppm) Se stock
5.0mL (1000ppm) Si stock
5.0mL (1000ppm) Sn stock
5.0mL (1000ppm) Ti stock
5.0mL (1000ppm) Tl stock
5.0mL (1000ppm) V stock
5.0mL (1000ppm) Zn stock

10mL HNO_3
399.5mL reagent H_2O
total vol.=500mL

This sample serves as an initial calibration standard for the above analytes.

Standard 3

2.5mL (10,000ppm) Al stock
5.0mL (10,000ppm) Ca stock
1.0mL (10,000ppm) Fe stock
5.0mL (10,000ppm) Mg stock
5.0mL (10,000ppm) K stock
5.0mL (10,000ppm) Na stock

10mL HNO_3
466.5mL reagent H_2O
total vol.=500mL
This sample serves as an initial calibration standard for the above analytes.

ICV

20mL *CLPP-CAL 1
10mL *CLPP-CAL 2
10mL *CLPP-CAL 3
10mL (1000ppm) Mo stock
10mL (1000ppm) Ti stock

40mL HNO_3
1920mL reagent H_2O
total vol.=2000mL

***(Certified vendor.)**

***CLPP-CAL 1**	***CLPP-CAL 2**	***CLPP-CAL 3**
5000ppm Ca, Mg, K, Na	1000ppm Sb	1000ppm As, Pb, Se, Tl
1000ppm Al, Ba, Fe		50ppm Cd
500ppm Co, Mn, Ni, V, Zn		
250ppm Ag, Cu		
200ppm Cr		
50ppm Be		

CCV

The CCV solution must be made from the same stock solutions as the calibration standards.
CCV solutions can be made using the corresponding 61E Standards at a dilution of 1:5. In the instances where instability is not an issue, a combination of 61E Standards is acceptable.

ICSAB

100mL **CLPP-ICS-A
10.0mL **CLPP-ICS-B
2.0mL (1000ppm) As stock
1.0mL (1000ppm) B stock
1.0mL (1000ppm) Mo stock

ICSA

100mL **CLPP-ICS-A
10.0mL **CLPP-ICS-B

100mL HNO_3
790mL reagent H_2O

1.0mL (1000ppm) Sb stock
1.0mL (1000ppm) Se stock
1.0mL (1000ppm) Si stock
1.0mL (1000ppm) Sn stock
1.0mL (1000ppm) Ti stock

total vol.=1000mL

20mL HNO_3
861mL reagent H_2O
total vol.=1000mL

****(Certified Vendor.)**

**CLPP-ICS-A	**CLPP-ICS-B
5000ppm Al, Ca, Mg	100ppm Cd, Pb, Ni, Ag, Zn
2000ppm Fe	50ppm Ba, Be, Cr, Co, Cu, Mn, V

Yttrium internal standard

Stock solution
0.39g Yttrium solid (Yttrium Nitrate Tetrahydrate, 99.999% or Yttrium Oxide, 99.9999%)
2 mL HNO_3
98mL reagent H_2O
(Note: Use of Yttrium oxide requires that the solution be gently heated.)

Working solution
50mL stock solution
20mL HNO_3
930mL reagent H_2O
total vol.=1000mL

This solution is not used to determine a specific concentration but a constant absorbance, therefore has no QC required recovery limits.

61E Profile solution
1.0mL (1000ppm) Cu stock
2mL HNO_3
97mL reagent H_2O
total vol.=100mL

This solution is used to generate a peak on the copper line in order to profile the instrument, the final solution is ≈ 10ppm.

61E Table 3

All values are in (ppb)

Element	STD1	STD2	STD3	CCV	ICV	ICSA	ICSAB	LFB
Ag	BLANK	5,000	-	1,000	2,500	-	1,000	500
Al		-	50,000	10,000	20,000	250,000	250,000	10,500
As		10,000	-	2,000	5,000	-	2,000	500
B		10,000	-	2,000	5,000	-	1,000	500
Ba		40,000	-	8,000	20,000	-	500	500
Be		2,000	-	400	500	-	500	500
Ca		-	100,000	20,000	50,000	250,000	250,000	10,500
Cd		10,000	-	2,000	2,500	-	1,000	500
Co		10,000	-	2,000	5,000	-	500	500
Cr		5,000	-	1,000	2,000	-	500	500
Cu		5,000	-	1,000	2,500	-	500	500
Fe		-	20,000	4,000	10,000	100,000	100,000	500
K		-	100,000	20,000	50,000	-	-	25,000
Mg		-	100,000	20,000	50,000	250,000	250,000	10,500
Mn		10,000	-	2,000	5,000	-	500	500
Mo		10,000	-	2,000	5,000	-	1,000	500
Na		-	100,000	20,000	50,000	-	-	10,500
Ni		10,000	-	2,000	5,000	-	1,000	500
Pb		10,000	-	2,000	5,000	-	1,000	500
Sb		10,000	-	2,000	5,000	-	1,000	500
Se		10,000	-	2,000	5,000	-	1,000	500
Sn		10,000	-	2,000	5,000	-	1,000	500
Ti		10,000	-	2,000	5,000	-	1,000	500
Tl		10,000	-	2,000	5,000	-	1,000	500
V		10,000	-	2,000	5,000	-	500	500
Zn		10,000	-	2,000	5,000	-	1,000	500

Multipoint calibration is performed using the listed standards as is, @1:2 dilutions, and @1:4 dilutions.

A low level standard is run for all elements of interest at or near specific project reporting limits when applicable.

Standard Concentrations: **TRACE**

TRACE 1

10mL HNO_3
490mL reagent H_2O
total vol.= 500mL

This standard serves as the CCB/ICB

TRACE 2

0.5mL (1000ppm) Ag stock
0.5mL (1000ppm) As stock
2.5mL (1000ppm) B stock
0.25mL (10,000ppm) Ba stock
0.5mL (1000ppm) Be stock
0.5mL (1000ppm) Cd stock
0.5mL (1000ppm) Co stock
0.5mL (1000ppm) Cr stock
0.5mL (1000ppm) Cu stock
0.5mL (1000ppm) Mn stock
0.5mL (1000ppm) Mo stock
0.5mL (1000ppm) Ni stock
0.5mL (1000ppm) Pb stock
2.5mL (1000ppm) Sb stock
2.5mL (1000ppm) Se stock
0.5mL (1000ppm) Ti stock
0.5mL (1000ppm) Tl stock
0.5mL (1000ppm) V stock

10mL HNO_3
475.25mL reagent H_2O
total vol.=500mL

This sample serves as an initial calibration standard for the above analytes.

TRACE 3

0.5mL (10,000ppm) Al stock
0.5mL (10,000ppm) Ca stock
1.0mL (10,000ppm) Fe stock
0.5mL (10,000ppm) Mg stock
5.0mL (10,000ppm) Na stock

10mL HNO_3
482.5mL reagent H_2O
total vol.=500mL

This sample serves as an initial calibration standard for the above analytes.

TRACE 4

2.5mL (1000ppm) Sn stock
0.5mL (1000ppm) Zn stock

10mL HNO_3
487mL reagent H_2O
total vol.=500mL

This sample serves as an initial calibration standard for the above analytes.

TRACE 5

2.5mL (10,000ppm) K stock

10mL HNO_3
487.5mL reagent H_2O
total vol.=500mL

This sample serves as an initial calibration standard for the above analyte.

ICV

100mL 61E ICV
0.25mL (1000ppm) Ag stock
2.0mL (1000ppm) B stock
0.50mL (1000ppm) Be stock
0.25mL (1000ppm) Cd stock
0.25mL (1000ppm) Cr stock
0.25mL (1000ppm) Cu stock
0.90mL (10,000ppm)Fe stock
2.0mL (10,000ppm) K stock
0.45mL (10,000ppm) Na stock
2.0mL (1000ppm) Se stock
2.0mL (1000ppm) Sb stock
2.0mL (1000ppm) Sn stock

20mL HNO_3
867.15mL reagent H_2O
total vol.=1000mL

This sample serves as the quality control sample for the above analytes.
All stock solutions used must be from a source independent of the calibration standards.

CCV

The CCV solution must be made from the same stock solutions as the calibration standards.
CCV solutions can be made using the corresponding Trace Standards at a dilution of 1:5. In the instances where instability is not an issue, a combination of Trace Standards is acceptable.

ICSAB

25mL **CLPP-ICS-A
2.5mL **CLPP-ICS-B
0.50mL (1000ppm) As stock
0.25mL (1000ppm) B stock
0.25mL (1000ppm) Mo stock
0.25mL (1000ppm) Sb stock
0.25mL (1000ppm) Se stock
0.25mL (1000ppm) Sn stock
0.25mL (1000ppm) Ti stock

20mL HNO_3
950.5 mL reagent H_2O
total vol.=1000mL

****(Certified Vendor.)**

**CLPP-ICS-A	**CLPP-ICS-B
5000ppm Al, Ca, Mg	100ppm Cd, Pb, Ni, Ag, Zn
2000ppm Fe	50ppm Ba, Be, Cr, Co, Cu, Mn, V

Alternately, the TRACE SICAB may be created through a 1:4 dilution of the 61E SICAB.
ICSA- The ICSA is created through a 1:4 dilution of the 61E ICSA solution.

TRACE only-Yttrium/Lithium internal standard

Yttrium stock solution
0.39g Yttrium solid (Yttrium Nitrate Tetrahydrate, 99.999%, or Yttrium Oxide, 99.999%)
2mL HNO_3
98mL reagent H_2O

Lithium stock solution
0.25 g (99.999%)
2mL HNO_3
98mL reagent H_2O

(Note: Use of Yttrium oxide requires that the solution be gently heated to dissolve.)

Working solution
25mL Yttrium solution
5mL Lithium
20mL HNO_3
950mL reagent H_2O
total vol.=1000mL
This solution is not used to determine a specific concentration but a constant absorbance.

TRACE Profile solution
0.5 mL (1000ppm) As stock
2mL HNO_3
97.5 mL reagent H_2O
total vol.=100mL

In TRACE analysis this solution is used to generate a peak on the arsenic line in order to profile the instrument, the final solution is ≈ 5ppm.

TRACE Table 3

All values are in (ppb)

Element	TRACE1	TRACE2	TRACE3	TRACE4	TRACE5	CCV	ICV	ICSA	ICSAB	LFB
Ag	BLANK	1,000	---	---	---	500	500	---	250	500
Al	BLANK	---	10,000	---	---	5,000	2,000	62,500	62,500	10,500
As	BLANK	1,000	---	---	---	500	500	---	500	500
B	BLANK	5,000	---	---	---	2,500	2,000	---	250	500
Ba	BLANK	5,000	---	---	---	2,500	2,000	---	125	500
Be	BLANK	1,000	---	---	---	500	550	---	125	500
Ca	BLANK	---	10,000	---	---	5,000	5,000	62,500	62,500	10,500
Cd	BLANK	1,000	---	---	---	500	500	---	250	500
Co	BLANK	1,000	---	---	---	500	500	---	125	500
Cr	BLANK	1,000	---	---	---	500	450	---	125	500
Cu	BLANK	1,000	---	---	---	500	500	---	125	500
Fe	BLANK	---	20,000	---	---	10,000	10,000	25,000	2,500	2,500
K	BLANK	---	---	---	50,000	25,000	25,000	---	---	25,000
Mg	BLANK	---	10,000	---	---	5,000	5,000	62,500	62,500	10,500
Mn	BLANK	1,000	---	---	---	500	500	---	125	500
Mo	BLANK	1,000	---	---	---	500	500	---	250	500
Na	BLANK	---	100,000	---	---	50,000	50,000	---	---	10,500
Ni	BLANK	1,000	---	---	---	500	500	---	250	500
Pb	BLANK	1,000	---	---	---	500	500	---	250	500
Sb	BLANK	5,000	---	---	---	2,500	2,500	---	250	500
Se	BLANK	5,000	---	---	---	2,500	2,500	---	250	500
Sn	BLANK	---	---	5,000	---	2,500	2,500	---	250	500
Ti	BLANK	1,000	---	---	---	500	500	---	250	500
Tl	BLANK	1,000	---	---	---	500	500	---	250	500
V	BLANK	1,000	---	---	---	500	500	---	125	500
Zn	BLANK	---	---	1,000	---	500	500	---	250	500

Multipoint calibration is performed using the listed standards as is, @1:2 dilutions, and @1:4 dilutions with the exception of Trace 3, which is diluted 1:10 instead of 1:4. All standard dilutions must be properly recorded in the working standards logbook.

A low level standard is run for all elements of interest at or near specific project reporting limits when applicable.

TABLE 2
POTENTIAL INTERFERENCES
ANALYTE CONCENTRATION EQUIVALENTS ARISING FROM INTERFERENCES AT THE 100-mg/L LEVEL[a]

		Interferent[a,b]									
Analyte	Wavelength (nm)	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Tl	V
Aluminum	308.215	--	--	--	--	--	--	0.21	--	--	1.4
Antimony	206.833	0.47	--	2.9	--	0.08	--	--	--	0.25	0.45
Arsenic	193.696	1.3	--	0.44	--	--	--	--	--	--	1.1
Barium	455.403	--	--	--	--	--	--	--	--	--	--
Beryllium	313.042	--	--	--	--	--	--	--	--	0.04	0.05
Cadmium	226.502	--	--	--	--	0.03	--	--	0.02	--	--
Calcium	317.933	--	--	0.08	--	0.01	0.01	0.04	--	0.03	0.03
Chromium	267.716	--	--	--	--	0.003	--	0.04	--	--	0.04
Cobalt	228.616	--	--	0.03	--	0.005	--	--	0.03	0.15	--
Copper	324.754	--	--	--	--	0.003	--	--	--	0.05	0.02
Iron	259.940	--	--	--	--	--	--	0.12	--	--	--
Lead	220.353	0.17	--	--	--	--	--	--	--	--	--
Magnesium	279.079	--	0.02	0.11	--	0.13	--	0.25	--	0.07	0.12
Manganese	257.610	0.005	--	0.01	--	0.002	0.002	--	--	--	--
Molybdenum	202.030	0.05	--	--	--	0.03	--	--	--	--	--
Nickel	231.604	--	--	--	--	--	--	--	--	--	--
Selenium	196.026	0.23	--	--	--	0.09	--	--	--	--	--
Sodium	588.995	--	--	--	--	--	--	--	--	0.08	--
Thallium	190.864	0.30	--	--	--	--	--	--	--	--	--
Vanadium	292.402	--	--	0.05	--	0.005	--	--	--	0.02	--
Zinc	213.856	--	--	--	0.14	--	--	--	0.29	--	--

[a] Dashes indicate that no interference was observed even when interferents were introduced at the following levels:

Al -	1000 mg/L	Mg -	1000 mg/L
Ca -	1000 mg/L	Mn -	200 mg/L
Cr -	200 mg/L	Tl -	200 gm/L
Cu -	200 mg/L	V -	200 mg/L
Fe -	1000 mg/L		

[b] The figures recorded as analyte concentrations are not the actual observed concentrations; to obtain those figures, add the listed concentrations to the interferent figure.
[c] Interferences will be affected by background choice and other interferences that may be present. Additional interference corrections are required with an axial view instrument.

V. Quality Assurance:

All quality control data should be maintained and available for easy reference or inspection.

Calibration Solutions

The calibration solutions are made using the same or similar acid matrix as the samples to be analyzed.

High Standards Check (HSC)

The HSC is the highest level standard applied in a multi-point calibration for each analyte of interest. The HSC is run immediately after the calibration when required to meet specific project requirements. The HSC recovery must be within $\pm$ 5% of the true value for each analyte of interest.

Initial Calibration Verification (ICV)

The ICV must be made from an outside second source different from that of the calibration standards' stock solutions.

The ICV is used to verify initially the calibration standards or stock solutions. The ICV must be run following the calibration. The ICV recovery must be within $\pm$10% of the true value for each analyte of interest.

Continuing Calibration Verification (CCV)

The CCV must be run periodically (every 10 samples) and at the end of each analytical sequence. The CCV is made from the same source as the calibration standards.

All recoveries must be $\pm$10% of the true value. The CCV may be run one additional time if the specified recoveries are not met, however if the second analysis fails, corrective action must be taken and any samples analyzed after the previous valid CCV must be re-analyzed.

Calibration Blank

The calibration blank contains the same acid matrix as the calibration standards and run with the ICV. The calibration blank is also used as the Continuing Calibration Blank (CCB) solution. See note 1.

The results of the calibration blank are to agree within two standard deviations of the mean blank value. If not, repeat the analysis two more times and average the results. If the average is not within three standard deviations of the background mean, terminate the analysis, correct the problem; re-calibrate, and reanalyze the previous 10 samples.

Laboratory Reagent Blank (LRB)

The LRB is a reagent blank carried through the entire sample preparation process.

Employ a minimum of one laboratory reagent blank with each batch of 20 or fewer samples of the same matrix, to verify the absence of contamination. The LRB must be less than the reported detection limit for each analyte of interest.

Laboratory Fortified Blank (LFB)

A laboratory fortified blank (LFB) must be run with each sample batch. If the recovery falls outside the control limit of 80-120% *or established control limits, the problem is to be identified and resolved before continuing. *The more restrictive limits prevail. The LFB is spiked, from a source independent of both the standards and ICV, prior to digestion and brought through the entire process.

Interference Check Solutions (ICS)

The ICS are analyzed in order to validate inter-element and background corrections applied to the samples.

The interference check solutions are prepared by combining known concentrations of interfering elements that will provide an adequate test of the correction factors, the "A fraction". Fortify the ICSAB solutions with the elements of interest in the 1 mg/L range, known as the "B fraction". In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero.

Analyze the ICSA and the ICSAB at the beginning and end of an analytical run or twice during every 8-hour work shift, whichever is more frequent. Recoveries of elements of interest should be within ±20% of the true values in the ICSAB and less than 2 times the reporting limit in the ICSA.

Sample Duplicate

Analyze one duplicate sample for every 20 samples. A duplicate sample is a sample brought through the entire sample preparation and analytical process. A control limit of ±20% for RPD shall be used for sample values greater than 10 times the instrument detection limit.

Laboratory Fortified Matrix / Duplicate (LFM/LFMD)

The LFM/LFMD pair must be run with each batch of 20 or fewer samples of the same matrix.

The LFM/LFMDs are prepared from fresh sample aliquots, spiked in the same manner as the LFB and carried through the entire preparation process.

The matrix spike and matrix spike duplicate spike recovery should be within ±25% of the true value, or documented control limits. Recovery calculations are not made if the spike concentration is less than 25% of the sample concentrations.

Inter-Element Corrections (IECs)

IECs are determined by analyzing a solution that contains an individual interfering element and is free of all other contaminates.

The positive or negative effects on the elements of interest are corrected by the following:

Correction value = true value of interfering element / concentration of the element of interest

IECs must only be evaluated and applied by analyst trained in there application.

IEC determination must be verified annually (at least) and updated, if necessary.

Linearity (L)

Dilute and reanalyze samples that are >90% of the established linear calibration limit or use an alternate, less sensitive line for which quality control data is established.

Linearity for all analytes must be updated quarterly.

Method Detection Limit (MDL)

MDLs must be maintained for each analyte of interest and updated once every year.

The determination of MDLs must be made in accordance with the following:

Fortify reagent water at a concentration of 2 to 3 times the estimated instrument detection limit.

Take seven replicate aliquots of the fortified reagent water and process through the entire analytical method.

Perform all calculations defined in the method and report the concentration values in the appropriate units.

Calculate the MDL as follows:

MDL = (t) x (s)

where:

t = students' t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.143 for seven replicates].

S = standard deviation of the replicate analyses.

The final calculated MDL must be greater than 20% of the original analyte spike level.

Matrix Evaluation

It is recommended that whenever a new or unusual sample matrix is encountered, a series of tests be performed prior to reporting concentration data for analyte elements. These tests will ensure the analyst that neither positive nor negative interferences are operating on any of the analyte elements to distort the accuracy of the reported values. They are as follows:

Serial dilution: If the analyte concentration is sufficiently high (minimally, a factor of 10 above the instrumental detection limit after dilution), an analysis of a 1:5 dilution should agree within 10% of the original determination. If not, a chemical or physical interference effect should be suspected.

Post (digestion) Spike: An analyte spike added to a portion of a prepared sample, or its dilution, should be recovered to within 70% to 130% of the known value or the established control limits. The spike addition should produce a minimum level of 10 times and a maximum of 100 times the instrumental detection limit. If the spike is not recovered within the specified limits, a matrix effect should be suspected. The use of a standard-addition analysis procedure may be used to compensate for this effect.

CAUTION: The standard-addition technique does not detect coincident spectral overlap. If suspected, use of computerized compensation (IECs), an alternate wavelength, or comparison with an alternate method is recommended.

Method of Standard Additions:

The standard-addition technique involves adding known amounts of standard to one or more aliquots of the processed sample solution. This technique compensates for a sample constituent that enhances or depresses the analyte signal, thus producing a different slope from that of the calibration standards. It will not correct for additive interferences which cause a baseline shift. The simplest version of this technique is the single-addition method, in which two identical aliquots of the sample solution, each of volume V_X**,** are taken. To the first (labeled A) is added a small volume V_S of a standard analyte solution of concentration C_S. To the second (labeled B) is added the same volume V_s of the solvent. The analytical signals of A and B are measured and corrected for non-analyte signals. The unknown sample concentration C_X is calculated:

$$C_X = \frac{S_B * V_S * C_S}{(S_A - S_B) * V_X}$$

where S_A and S_B are the analytical signals (corrected for the blank) of solutions A and B, respectively. V_S and C_S should be chosen so that S_A is roughly twice S_B on the average. It is best if V_S is made much less than V_X, and thus C_S is much greater than C_X, to avoid excess dilution of the sample matrix. If a separation or concentration step is used, the additions are best made first and carried through the entire procedure. For the results of this technique to be valid, the following limitations must be taken into consideration:

The analytical curve must be linear, the correlation coefficient must be >0.995.

The chemical form of the analyte must respond the same way as the analyte in the sample.

The interference effect must be constant over the working range of concern.

The signal must be corrected for any additive interference.

The absorbance of each solution is determined and then plotted on the vertical axis of a graph, with the concentrations of the known standards plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on the right side, but in the opposite direction from the ordinate.

VI. Calculations:

Results are read in ug/L directly from the ICP. Take into account any dilutions preformed during the digestion process for total metals.

The recoveries of spikes and relative percent difference between duplicate determinations are to be calculated as follows:

$$RPD = |C_S - C_D| / ((C_S + C_D) / 2)$$

$$Rec = 100 * (C_M - C_S) / C_T$$

where RPD = relative percent difference, %
Rec = matrix spike recovery, %
C_S = unspiked sample concentration, mg/L
C_D = duplicate sample concentration, mg/mL
C_M = matrix spike concentration, mg/L
C_T = theoretical spike concentration, mg/L

Report recovery and RPD to the nearest 1 %.

VII. Reagents and Materials:

Thermo Jarrell Ash 61E Simultaneous ICAP:

Capable of analysis and background correction for multi-element analysis

Thermo Jarrell Ash TRACE 61E Simultaneous ICAP:

Capable of trace analysis and background correction for multi-element analysis

Argon gas supply:

High purity, liquid or high pressure cylinders

Concentrated hydrochloric acid:

Metals analysis grade

Hydrochloric acid, 1:1 dilution:

Add 500 mL concentrated hydrochloric acid to 400 mL reagent water and dilute to 1 liter

Concentrated nitric acid:

Metals analysis grade

Nitric acid, 1:1dilution:

Add 500 mL concentrated nitric acid to 400 mL reagent water and dilute to 1 liter

Standard stock solutions:

Purchased from commercial suppliers

Second source solutions:

Purchased from commercial suppliers

Mixed calibration standard solutions:

Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric. Add the appropriate types and volumes of acids to match sample matrix. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. Transfer the mixed standard solutions to PFE fluorocarbon or previously unused polyethylene or polypropylene bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentration can change on aging. Calibration standards must be initially verified using a quality control sample and monitored for stability.

Important: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of reagent water and warm the flask until the solution clears. Cool and dilute to 100 mL with reagent water. For this acid combination, the silver concentration should be limited to 2 mg/L. Silver under these conditions is stable in a tap-water matrix for 30 days. Higher concentrations of silver require additional hydrochloric acid.

Note 1: If the sample analysis solution has a different acid concentration from that given, but does not introduce a physical interference or affect the analytical result, the same calibration standards may be used.

VIII. Safety

Every sample should be considered a hazardous when performing the analysis. Standard laboratory safety guidelines must be adhered to. Gloves, eye protection, and lab coats must be worn during sample retrieval, analysis and disposal.

IX. Pollution Prevention

Any and all remaining unused sample must be returned to the 4°C storage, sealed tightly in the original container. Benches and surrounding surfaces must be cleaned and wiped dry with paper toweling.

X. Waste management

Analyzed sample and used disposable equipment must be collected and disposed of in a manner consistent with the Premier Laboratory Chemical Hygiene Plan.

XI. Method Performance

Performance data is not currently available.

SOP Revision History

Date	Previous Revision No.	New Revision No.	Description of Changes	Effective Date	Initiated by
8/6/09	3.1	3.2	Added revision history table	8/6/09	LM

Benchmark Analytics, Inc.

EPA 903.0 – Alpha-Emitting Radium Isotopes in Drinking Water
EPA 9315 – Alpha-Emitting Radium Isotopes

Document No. RA 002

Revision No. 20

February 16, 2009

Written By L.S.H. Date: 2-16-09

Routing: [signature] Date: 2-16-09

Reviewed By: [signature] Date: 2-16-09

Management Approval: [signature] Date: 2-16-09

Note: The date of management approval is the effective date of this SOP.

CHANGES

Attachment A was updated to include drinking water matrix.

TABLE OF CONTENT

REFERENCES

EPA Method 903.0, EPA Method 9315, SOP G-029 Labware washing procedures, SOP G-039 Definitions, SOP G009 Method validation, SOP G-032 Acronyms, SOP RA001 Gross Alpha and Gross Beta, SOP RA 006 Alpha and Beta Eclipse Software Settings and Calculations SOP G-033 Preparation of a final Report under NELAP, SOP G-016 Calibration and method validation, SOP IN-041 TCLP Extractions, and NELAC Standard latest issue as well as CHP, RSPM and QAPM.

Standard Methods for the Examination of water and Wastewater 20th edition Method 7500-Ra B., EPA-600/4-80-032, 40CFR141 on drinking water, SW 846 Revision 0, New Jersey DEP Private Well Testing Act (PWTA), Regulations Governing the Certification of Laboratories and Environmental Measurements N.J.A.C. 7:18; US EPA SOW for Radiochemistry; National Primary Drinking Water Regulations: Radionuclides, Final Rule 40 CFR Parts 9, 141, 142, Dec 7, 2000 p 76708-76753. Radioactive Decay Law http://www.life.rmit.edu.au/mrs/kpm/mr212/radecay.html

1.0 GENERAL

1.1 PRINCIPLE

1.1.1 This method covers the measurement of the total soluble alpha emitting radioisotopes of radium (radium-223, radium-224, and radium-226) in drinking water, surface water, or ground water.

1.2 DEFINITIONS

1.2.1 Batch = 20 samples.

1.2.2 Beta rate = 1.29 * gamma rate (for Cs-137).

1.2.3 Ci = Curie (One curie = 3.7x1010 disintegrations per second = 3.7x1010 becquerels = 2.22x1012 disintegrations per minute.)

1.2.4 Counting efficiency (efficiency factor) = counts per minute / disintegrations per minute or cpm/dpm.

1.2.5 MDA = minimum detectable activity. Details on the calculation of the MDA are in SOP RA006.

1.2.6 MeV = megaelectronvolt = 106 Volt.

1.2.7 Rem = is the special unit of any of the quantities expressed as dose equivalent. The dose equivalent in rems is equal to the absorbed dose in rads multiplied by the quality factor (1 rem = 0.01 Sievert).

1.2.8 RSPM = Radiation Safety Program Manual.

1.2.9 Source = in this SOP this word refers to the original material. It does not specifically refer to radioactive source material of U and Th.

1.3 QUANTITATION LIMITS

1.3.1 The minimum detection limit or minimum detectable activity (MDA) is defined as the concentration which can be counted with a precision of plus or minus 100 percent at the 95 percent confidence level. The National Primary Drinking Water Regulations require a minimum detection limit or MDA of 1 pCi/L.

1.4 METHOD SUMMARY

1.4.1 The radium in the drinking water, surface water, or ground water sample is collected by coprecipitation with barium and lead sulfate, and purified by reprecipitation from EDTA solution. Citric acid is added to the water sample to assure that complete interchange occurs before the first precipitation step. The final $BaSO_4$ precipitate (including radium-226, radium-224 and radium-223) is alpha counted to determine the total disintegration rate of the radium isotopes.

1.4.2 The sensitivity of the method is a function of sample size, reagent and instrument background, counting efficiency, and counting time.

1.5 INTERFERENCES

1.5.1 The presence of significant natural barium in the sample will result in a falsely high chemical yield. This will affect the results because the radium content is directly proportional the barium content.

1.5.2 Radium isotopes are separated from other alpha emitting radionuclides.

1.5.3 The alpha count of the separated radium must be corrected for its partially ingrown alpha emitting daughters.

1.5.4 Planchets must be stored in a desiccator when not being counted.

1.5.5 When radium 228 is present, significant amounts of radium 224 may interfere with an estimate of the amount of radium 226 present in the sample.

1.6 SAFETY

1.6.1 The analyst must have completed the radiation safety training program prior to handling radioactive material. The training must be documented.

1.6.2 Radioactive standards are to be stored in a properly labeled area.

1.6.3 Personal protective equipment for handling radionuclide standards includes gloves, safety glasses, laboratory coat, etc.

1.6.4 Preparation of radioactive standards must be carried out on a tray with plastic-backed adsorbent liner to adsorb any spilled radioactive liquid.

1.6.5 Due to the nature of the low intensity radiation and the low dose rate of the radionuclide standards, radiation monitoring is not necessary.

1.6.6 The analyst should take appropriate precautions when using acids.

1.6.7 The analyst should take appropriate precautions when using centrifuges, most models will have locking lids.

2.0 LABWARE WASHING PROCEDURES

2.1 Glassware should be acid washed to assure removal of any solids. This must be followed by deionized water rinses. For details check the labware washing SOP G029.

3.0 APPARATUS

3.1 Glassware: including but not limited to 1500 or 2000 ml beakers, glass stir rods, volumetric flasks

3.2 Centrifuge

3.3 40 ml or larger centrifuge tubes with caps

3.4 Small vacuum pump with tubing

3.5 Tray(s) for radioactive standard preparation that are to be constructed of stainless steel, plastic, or fiberglass and lined with absorbent paper to avoid contamination.

3.6 Adsorbing liners with plastic backing

3.7 Analytical balance to 0.1 mg precision

3.8 Glass desiccator

3.9 Vortex mixer

3.10 Electric hot plate

3.11 Stainless steel counting planchets

3.12 Gas-flow proportional counter – Canberra Tennelec S5-XLB

3.13 Water Bath, Precision Model 180 or equivalent.

4.0 REAGENTS AND STANDARDS

4.1 General Comments

4.1.1 All reagents used must be analytical grade or better, whenever they are commercially available.

4.1.2 Materials of substandard reactivity or deterioration should not be used.

4.1.3 All reagents and reagent solutions should be properly labeled for identity, titer,

strength or concentration, recommended storage, preparation and expiration dates, and any other relevant information.

4.1.4 Any expired reagent or reagent solution should be discarded or revalidated.

4.1.5 All reagents are prepared using volumetric flasks, unless otherwise specified.

4.2 Deionized water

4.3 Acetic acid, 17.4N: glacial CH_3COOH (conc.), specific gravity 1.05, 99.8%

4.4 Ammonium Sulfate, 200 mg/ml: Dissolve 200 grams $(NH_4)_2SO_4$ in a minimum of water and dilute to 1000 ml, or equivalent. This solution has 6 months stability at room temperature.

4.5 Barium carrier, 16 mg/ml: Dissolve 28.46g $BaCl_2 \times 2H_2O$ in water, add 5 ml 16N HNO_3, dilute to 1000 ml with water, or equivalent. This solution has 6 months stability at room temperature.

4.5.1 Standardization: (in triplicate)

4.5.2 Pipette 2.0 ml carrier solution into a centrifuge tube containing 15 ml water. Add 1 ml 18N H_2SO_4 with stirring and digest precipitate in a water bath for 10 minutes (heat, not necessarily to a boil).

4.5.3 Cool, centrifuge and decant the supernatant. The precipitate should not move from the centrifuge tube while decanting.

4.5.4 Wash the precipitate with 15 ml water (washing means add the 15 ml DI water, vortex, centrifuge, and decant).

4.5.5 Check pH for neutrality. If not neutral repeat washing. Transfer the precipitate to a tared stainless steel planchet with a minimum of water. Dry on a hotplate, store in desiccator and weigh as $BaSO_4$.

4.5.6 The weight should be 54.4 mg of $BaSO_4$, which represents 32 mg of Barium.

4.6 Citric acid, 1M: Dissolve 192g $C_6H_8O_7 \times H_2O$ in water and dilute to 1000 ml, or equivalent. This solution has 6 months stability at room temperature.

4.7 EDTA reagent, basic, (0.25M): Dissolve 20g NaOH in a beaker containing 750 ml water, heat and slowly add 93g disodium ethylendinitriloacetate dihydrate ($Na_2C_{10}H_{14}O_8N_2 \times 2H_2O$). Heat and stir until dissolved, filter through course filter paper and dilute to 1 liter, or an equivalent dilution. This solution has 6 months stability at room temperature.

4.8 Lead carrier, 15 mg/ml: Dissolve 24g $Pb(NO_3)_2$ in water, add 5 ml 16N HNO_3 and dilute to 1000 ml with water, or equivalent. This solution has 6 months stability at room temperature.

4.9 Sodium hydroxide, 6N: Dissolve 240g NaOH in 800 ml water and dilute to 1000 ml, or equivalent. This solution has 6 months stability at room temperature. Use an ice bath.

4.10 Sulfuric acid, 18N: Cautiously mix 1 volume 36N H_2SO_4 (conc.) with 1 volume of water. Use an ice bath. This solution has 6 months stability at room temperature.

4.11 Sulfuric acid, 0.1N: Mix 1 volume 18N H_2SO_4 with 179 volumes of water. This solution has 6 months stability at room temperature.

4.12 Radioactive solid source

4.12.1 For instrument calibration: Radioactive Sealed Source Calibration Standards. Details on the calibration procedure are in SOP RA001 and RA006.

4.12.1.1 The instrument is calibrated for counting efficiency and for alpha and beta plateaus according to instrument manufacturer instructions for gross

alpha using a sealed source of Th-230 or a similar alpha source element and for gross beta using a sealed source of Sr-90 or a similar beta source element.

4.12.1.2 A suggested supplier is Isotope Products Laboratory. The geometry for the solid standard must be the same as that of the prepared samples and QC samples. A suggested geometry is 45 mm on stainless steel backing with aluminized Mylar cover or electroplated onto the stainless steel planchet.

- Th-230 Cat. # EAB-230-PL at about 40,000 dpm total alpha activity.
- Sr-90 Cat. #EAB-090-PL at about 30,000 dpm activity for Sr-90 only, as Y-90 exists in equilibrium in the standard.

4.13 Radioactive Stock Solution: A suggested supplier is Isotope Products Laboratory. Ra-226 Cat # 7226 at approximately 0.1 uCi/ 5 ml stock.

4.13.1 For LCS Sample Preparation: Dilute the Ra-226 stock 1:100 in 1M nitric acid to make approximately 200 pCi/ml solution.

4.13.2 The standard will be revalidated every five years. Analyzing a known concentration of the secondary standard may revalidate the primary standard. The recovery must be within 10% of the known concentration.

5.0 SAMPLE COLLECTION, PRESERVATION, HOLDING TIMES & STORAGE

5.1 Drinking water samples must be collected from a free-flowing source.

5.2 Ground water or surface water samples must have been collected in a manner which addresses the considerations discussed in SW 846 Revision 0, chapter 9

5.3 All samples should be collected into 1-liter plastic containers.

5.4 The samples should be preserved at the time of collection by adding enough HNO_3 to the sample to bring it to pH about 2 (15 ml 1N HNO_3 or 1-2 ml of conc. nitric acid per liter of sample is usually sufficient). This step eliminates formation of insoluble material, which could contain radioactive material and falsely lower the result.

5.5 Samples collected without preservation should be brought to the laboratory within 5 days, then preserved and held in the original container for a minimum of 16 hours before transfer or analysis.

5.6 Samples collected with preservative can be analyzed without additional waiting.

5.7 The holding time is six months. Samples should not be stored in the same room as the counter. Samples are stored at room temperature.

6.0 CALIBRATION

6.1.1 The counting efficiency for radium alpha particles with barium sulfate carrier present is determined with a standard radium alpha activity and 32 mg (2 ml) of barium carrier as $BaSO_4$. Spiking distilled water sample and following the procedure for regular samples will accomplish this.

6.1.2 The efficiency shall be determined initially, and if there is a change in method or instrument.

6.1.3 To calculate the radium-alpha counting efficiency with self-adsorption, E:

$$E = C / (A * I * R)$$

Where:

C = sample net cpm (gross counts minus background divided by the counting

time in minutes).

A = dpm of radium-226 added to the sample (pCi * 2.22).

I = ingrowth factor for the elapsed time from Ra-$BaSO_4$ precipitation to mid-point of counting time.

R = fractional chemical yield

Note: This equation is for the efficiency and self-adsorption. This can be found in SM 20: 7500-Ra B.

7.0 SOLID SAMPLE PREPARATION

7.1 Please see SOP RA 001 section 9.0

8.0 SAMPLE PREPARATION

8.1 To 1000 ml of water sample, add 5 ml 1M Citric Acid ($C_6H_8O_7.H_2O$), 1.0 ml lead carrier, and 2.0 ml barium carrier, all in a 1500 ml beaker. Heat to boiling.

8.2 Cautiously, while boiling add 20 ml 18N H_2SO_4. Stir briskly to aid precipitation. Analyst should use extreme caution. Digest (heat) 5 to 10 minutes and let the mixed $BaSO_4$-$PbSO_4$ precipitate settle overnight.

8.2.1 Gently siphon the supernate with a vacuum, leaving the precipitate intact.

8.3 Transfer the precipitate to a 40 ml or larger centrifuge tube using a minimum amount of 0.1N H_2SO_4. Centrifuge and discard supernate.

8.4 Wash the precipitate with 0.1N H_2SO_4 (add solution, vortex tube to unsettle precipitate, centrifuge and discard washes). Repeat this process one more time.

8.5 Add 15 ml basic EDTA reagent to dissolve precipitate. Heat in a hot water bath and add a few drops 6N NaOH to make the solution neutral.

8.6 Add 1 ml $(NH4)_2SO_4$ (200 mg/ml) and stir. Add 17.4N CH_3COOH drop wise until precipitation begins. Add 2ml extra. Digest (heat) 5 to 10 minutes.

8.7 Centrifuge, discard the supernate, and record the time. This marks the separation of the $BaSO_4$ and the beginning of the radon ingrowth.

8.8 Wash the $BaSO_4$ precipitate with 15 ml water (vortex, centrifuge, and discard wash).

8.9 Transfer the precipitate to a tared stainless steel planchet using a minimum of water. Dry planchet on a hotplate. Drying should be rapid but not too vigorous to minimizing any loss of radon-222 that has already grown into precipitate.

8.10 Cool, weigh, and store in desiccator. Weigh and determine the barium recovery: 54.4 mg $BaSO_4$ = 32 mg Ba.

8.11 Count in a gas-flow proportional counter. If there is a possibility that radium-228 was present in the initial sample then the planchets must be held before counting. If the measured radium-228 result was less than or equal to 3.5 pCi/L the planchets should be held for a minimum of 3 days. If the measured radium 228 result is greater than 3.5 pCi/L the planchets should be held a minimum of 10 days before counting. If there is no radium 228 result the planchets must be held for a minimum of 10 days before counting.

9.0 CALCULATIONS

9.1 Computation

Calculate the radium-226 concentration, D, in picocuries per liter:

$$D\ pCi/L = C / (2.22 \times E \times V \times R \times I)$$

Where:

C = net count rate, cpm

E = counter efficiency, with self-adsorption, for radium-226 in $BaSO_4$

V = liters of sample used

R = fractional chemical yield

I = ingrowth correction factor (see section 8.11)

2.22 = conversion factor from dpm/pCi

The value of R is determined by the following equation:

R = (Barium Recovered) / 32 mg (theoretical value)

9.2 Reporting

9.2.1 The customer report must contain the calculated value for RA-226, the MDA and the counting error.

9.2.2 Error Reporting. Each result must be reported with the measurement of uncertainty, also called error reporting. The counting error must be established and reported at the 95 % confidence level. The ECLIPSE software calculates the error as uncertainty with all results. The documentation is in the Canberra Technical Reference Manual. Copies of the methods, calculations and sequence are found in SOP RA006.

9.2.3 MDA Reporting: The Eclipse software has a MDA calculator. Use the calculator to determine the counting time required to reach the MDA of 1 pCi/L for RA-226. The MDA calculator equations are described in detail in SOP RA006.

9.2.4 If a MDA is unable to be achieved, for example due to low sample volume, the sample should be reported with the appropriate data qualifier.

9.2.5 If reanalysis is not possible the sample should be reported with the appropriate data qualifier.

9.2.6 If the result is above 5 pCi/L the client will be notified and a recommendation will be made to have additional volume sent to the lab and subcontracted for testing by the emanation method. Use Attachment A for notifying the client.

9.2.7 The full sample ID must be used throughout the entire procedure. At no point during preparation or reporting is an abbreviated sample ID used.

10.0 Quality Assurance

10.1 Method Blank (MB)

10.1.1 Method Blank must be performed at a frequency of one per preparation batch. The batch is defined as 20 samples (excluding the method blank and LCS).

10.1.2 The results of this analysis shall be for quality control measures, used to assess the batch.

10.1.3 The result of the method blank must be below the MDA for Ra-226.

10.1.4 When the acceptance criteria for the method blank are not met the specified corrective action and contingencies must be followed; results must be reported with the appropriate data qualifying codes. Corrective action may include some or all of the following: check planchet holder for contamination, check for area contamination, and assure that instrument background is in control.

10.1.5 Occurrence of a method blank failure, as well as the actions taken, must be noted in the raw data.

10.1.6 The method blank must not be subtracted from the sample results.

10.1.7 The method blank must be prepared with similar aliquot size to that of the routine samples. If this is not possible, the method blank must be calculated in a way that compensates for sample results based upon differing aliquot size.

10.1.8 NOTE: The weekly background is applied to all analyzed samples and QC and does not depend on the method blank result associated with the analytical batch.

10.1.9 Management is notified when out-of-control or unacceptable data occurs.

10.2 Laboratory control samples (LCS)

10.2.1 Shall be performed at a frequency of one per preparation batch. The batch is defined as 20 samples (excluding the method blank and LCS).

10.2.2 The LCS must be of similar aliquot size to that of routine samples.

10.2.3 The results of this analysis shall be for quality control measures, used to assess the batch and must be within 26 % of the expected value for Alpha emitting radium isotopes. The LCS acceptance criteria will be re-evaluated at least once a year. QC charting of the LCS data will be done to facilitate this.

10.2.4 When the acceptance criteria for the LCS are not met the specified corrective action and contingencies must be followed, including but not limited to recounting the sample and assuring that the instrument calibration parameters are in control.

10.2.5 Occurrence of a LCS failure, as well as the actions taken, must be noted in the raw data.

10.2.6 A practical level for the LCS is at about 10 pCi/L for Ra-226, which is greater than five times the detection limit. Choose a comparable level of the samples if the samples exceed five times the detection limit.

10.2.7 Prepare a solution with approximately 10 pCi/L of Ra-226 and test as a sample. To 1000 ml DI water add 50 uL of the solution from section 4.13.1.

10.2.8 Management is notified when out-of-control or unacceptable data occurs.

10.3 Matrix spike

10.3.1 There is no requirement for a matrix spike when performing the precipitation test method for Ra-226.

10.4 Analytical Variability / Reproducibility--Replicate

10.4.1 Determine the chemical yield for barium. This factor is used to assess the sample result acceptance. The theoretical yield should be 54.4 mg adjusted for the standardization based on 32 mg Ba. The acceptable fractional chemical yield should be between 0.75 to 1.25. If this criterion is not met one or more of the following is done, reweigh the planchets, re-prep the sample, or prepare new carrier solutions. Matrix interference can also cause a recovery failure. Occurrence of a carrier recovery failure, as well as the actions taken, will be noted in the laboratory report. The acceptance criteria will be re-evaluated at least once a year.

10.4.2 The carrier shall be added to the sample after subsampling but before any chemical treatment.

10.4.3 When there is enough sample, a replicate must be performed once for every 10 samples to assess the quality of the run. Calculate the normalized absolute difference (NAD) between the sample and the laboratory duplicate. This factor is used to assess result acceptance and should be < or = 3. The results are recorded. Acceptance criteria will be re-evaluated once a year.

$$NAD = (S-D) / [(TPU_S)^2 + (TPU_D)^2]^{1/2} = \text{or} < 3$$

where,

S = sample result

D = duplicate result

TPU_S = 1s total propagated uncertainty of the sample

TPU_D = 1s total propagated uncertainty of the duplicate

10.4.4 If the criteria is not met, the specified corrective action and contingencies will be followed (nonhomogeneity should be considered as a cause for failed replicate). The RPD of the total solids may be used as an acceptance criterion to prove reproducibility. The acceptance criteria is < or = 10%. To Calculate the RPD: [((MS-MSD)*2)/(MS+MSD)]*100

10.4.5 Occurrence of a replicate failure, as well as the actions taken, must be noted in the raw data.

10.4.6 If samples are less than three times the detection limit, a duplicate LCS can be used to determine reproducibility within a batch.

10.4.7 When there is insufficient sample volume, a duplicate LCS can be used to determine reproducibility within a batch. Follow section 10.2 for preparation. The NAD is also used to assess result acceptance.

10.4.8 Management is notified when out-of-control or unacceptable data occurs.

10.5 Nonconformance

10.5.1 Root cause of nonconformance must be done. Check appropriate count times, dilutions, aliquot size, detector efficiency, and detector background. If the nonconformance is due to inadequate sample volume, elevated radioactivity levels, sample matrix interference such a high amount of suspended solids, etc., explain these factors in the report.

10.5.2 To address nonconformance of QC results consult the troubleshooting section of the instrument manual. It addresses the following problems: gas flow, plateau, background, efficiency and spillover, count timer incrementing and data reproducibility.

10.6 Demonstration of Capability

10.6.1 Must be done initially and again if there is a significant change in instrument type, personnel, or method.

10.6.2 Proficiency test samples

10.6.2.1 The laboratory will use the results as an evaluation of its ability to produce accurate data.

10.6.3 For the DOC, prepare 4 samples at approximately 10 pCi/L for Ra-226. The samples are carried through the sample preparation steps and counted.

10.6.4 To 1000 ml DI water add 50 uL of the solution from 4.14

10.6.5 It is also acceptable to use 4 or more sample batches and generate the DOC from the LCS data of those batches.

10.6.6 Calculate the Ra-226 activity in pCi/L.

10.6.7 The recovery must be at or below the following criteria:

10.6.7.1For Ra-226 +/- 26 % precision and +/- 25% RPD (relative percent

difference).

10.7 QC SAMPLE SUMMARY

10.7.1 The cover page for the data packet includes a QC checklist, which shows criteria for the QC in section 10.7.2. The reviewer of the data pack is responsible to check that all criteria are met, and that if a criterion is not met that the appropriate notation is made in the raw data. The reviewer should also review and QA the batch in the Omega LIMS. This cover page also has an analyst checklist, items that the analyst who ran the batch is responsible for.

10.7.2 For each batch of 20 or less samples there will be:

- 1 solid standard for alpha counting efficiency
- 1 solid standard for beta counting efficiency
- 1 instrument background
- 1 MB in DI water
- 1 sample duplicate or, if there is insufficient sample volume, 1 LCS DUP for every ten samples at approximately 10 Ci/L activity
- 1 LCS at approximately 10 pCi/L activity

10.8 System calibration

10.8.1 Initial instrument calibration

a. Calibration of the instrument is required when purchased, serviced, moved, and when the instrument's response has changed as determined by a performance check or when the instrument's response exceeds predetermined acceptance criteria for the instrument quality control. Calibration includes determination of plateaus, efficiencies and background. See SOP RA001 and RA 006 for details.

10.8.2 Continuing instrument calibration verification

a. To ensure the instrument is operating properly and the calibration has not changed, a daily counting efficiency check and background check is to be performed on a day of use basis. These parameters are charted on a monthly basis by the Eclipse software. For batches of samples that uninterruptedly count for more than a day a performance check can be performed at the beginning and end of the batch as long as the time interval is no greater than one week. A weekly background must be performed and these results subtracted from the sample CPM. See SOP RA001 and RA 006 for details.

10.9 QC Summary Table

QC Summary Table	Ra-226	Limit	reference
LCS	10 pCi/L	+ / - 26 %	At least 5 x MDA
Sample Duplicate		NAD < or = 3	
LCS DUP	10 pCi/L	+ / - 26 % NAD < or = 3	At least 5 x MDA
DOC study	10 pCi/L	+ / - 26 %, +/- 25 % RPD	At least 5 x MDA
carrier recovery Ba		60% to 125 %	

MDA specs		< 1 pCi/L	
Background		< 1 pCi/L	< MDA

10.10 Method Steps

Ra-226 EPA 903.0									
step	sample	add	do	why	Pb	Ba	Ra-226		Radon
8.1a	1L acidified	5 ml 1M citric acid	heat to boiling		add	add			
8.1b		1 ml Pb carrier							
8.1c		2 ml Ba carrier							
8.2		20 ml 18 N sulfuric acid	vigorous stir, heat 10 min. let BaSO4/PbSO4 settle over night	decant and discard supernate	ppt	ppt	ppt		
8.3	precipitate	0.1 N sulfuric acid	transfer to centrif. tube and spin	discard supernate	ppt	ppt	ppt		
8.4a	precipitate	0.1 N sulfuric acid	wash the ppt and spin	discard supernate	ppt	ppt	ppt		
8.4b	precipitate	0.1 N sulfuric acid	wash the ppt and spin	discard supernate	ppt	ppt	ppt		
8.5a	precipitate	15 ml basic EDTA	dissolve & heat	dissolve ppt	solution	solution	solution		
8.5b		6N NaOH	to complete dissolution	dissolve ppt	solution	solution	solution		
8.6a	solution	amm. sulfate	stir	Ba, U and Pb sulfate ppt form	ppt	ppt	ppt		
8.6b		17.4 N acetic acid	to precipitate, heat 10 minutes						
8.7			centrifuge	discard supernate, start radon ingrowth				record time	in ppt
8.8	precipitate	15 ml water	wash the ppt and spin	discard supernate	ppt	ppt	ppt		
8.9	precipitate		transfer to planchet with water	dry					
8.10			cool, weigh, store in desiccator	determine Ba recovery					
8.11			count for alpha						in ppt

10.11 Ingrowth Factor and Curve

10.11.1 The ingrowth factor is dependent on the Ra-222 remaining in the sample at the time of counting. With a half-life of 3.82 days the amount present after one half-life is based on this equation:

$$T_{1/2} = LN(2)/(3.82*24) = 0.00756051$$

10.11.2 The ingrowth factor for Ra-226 is then calculated by this equation:

$$\text{Ingrowth Factor} = 3*(1-EXP(-T_{1/2} * \text{hours from separation}))+1$$

The following table and graph in Appendix 1 are used to determine the ingrowth factor after 10 days from separation.

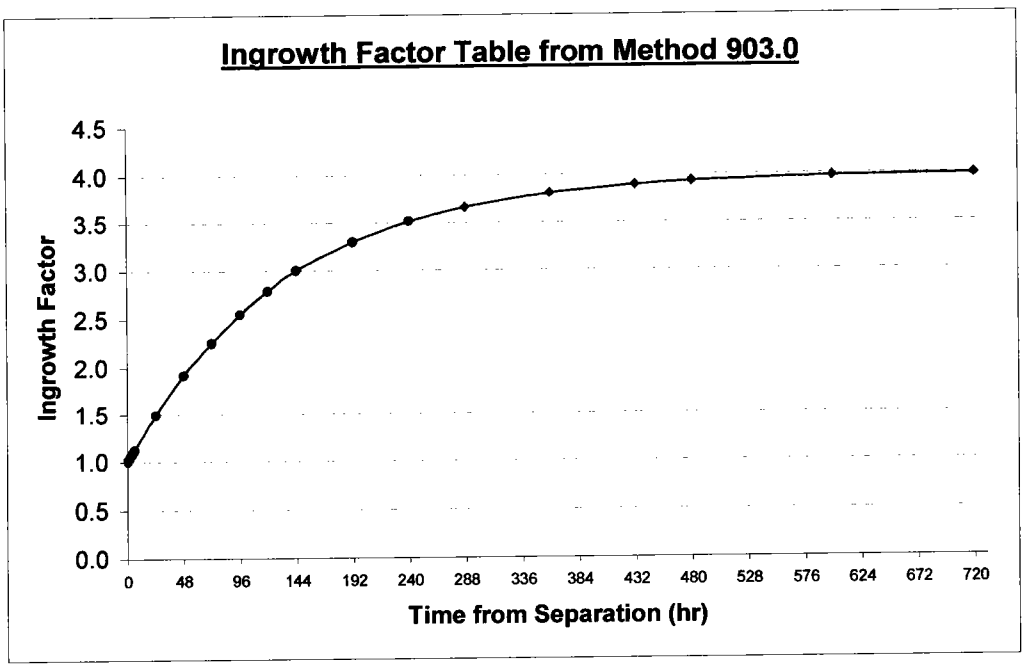
11.0 Pollution Prevention & Waste Management

11.1 See BENCHMARK ANALYTICS QAPP.

Appendix 1. Ingrowth Factor over Time

Time from Separation (hr)	Ingrowth Factor (903.0)	Ingrowth Factor (Calc.)	Days
0	1.00	1.00	
1	1.02	1.02	

2	1.04	1.05	
3	1.06	1.07	
4	1.08	1.09	
5	1.10	1.11	
6	1.12	1.13	
24	1.49	1.50	
48	1.91	1.91	
72	2.25	2.26	
96	2.54	2.55	
120	2.78	2.79	
144	2.99	2.99	
192	3.29	3.30	
240	3.51	3.51	
288		3.66	(12d)
360		3.80	(15d)
432		3.89	(18d)
480		3.92	(20d)
600		3.97	(25d)
720		3.99	(30d)



Attachment A.

BENCHMARK ANALYTICS, INC.
4777 SAUCON CREEK ROAD
CENTER VALLEY, PA. 18034

PHONE (610) 974-8100
FAX (610) 974-8104

Subject: Radium 226

To: _____

Date Your Sample Was Received:_____

Your Sample Description:_____

Our WorkOrder Number:_____

The radium 226 for the above sample was greater than 5 pCi/L. For a drinking water sample it is recommended that the sample be retested using the Emanation procedure, EPA method 903.1. If you would like us to subcontract that analysis please send additional sample volume. If you have any questions, please call at extension 20 or e-mail to c.medei@benchmarkanalyticslabs.com. Thank you.

Attachment B:

Benchmark Analytics Page_____

RA226 Worksheet: EPA 903.0

SOP RA 002 Revision _____

Prep Analyst: _____
Start Date & Time: _____
Ba Carrier Lot# : _____ **Exp.** _____
Ra226 Standard Lot# : _____ **Exp.** _____

Note: Counting may begin 3 days after ingrowth if Ra-228 is </= 3.5 pCi/L, 10 days after ingrowth if Ra-228 is > 3.5 pCi/L

3 days after ingrowth: _____
10 days after ingrowth: _____
Count Date: _____
BatchKey - Instrument: _____
Book #: _____
Omega Lims #: _____
Acetic Acid Lot# : _____ **Exp.** _____

Balance used: _____ **Start of Ingrowth:** _____

#	Sample ID	Volume ml	Planchet #	Initial wt. g	Final Wt. 1 g	Final Wt. 2 g	Delta wt. mg	Ba Yield T.V. =	Ra-228 </= 3.5 pCi/L
1	MB								
2	LCS								
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									

Notes:

_____
_____
_____

All Samples pH < 2 ? _____

Reviewed by: _____

Attachment C: **Page # ____**

Solution: Ammonium Sulfate, 200 mg/ml

SOP RA002 Instructions: Dissolve 200 grams $(NH_4)_2SO_4$ in a minimum of water and dilute to 1000 ml, or equivalent. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment D: **Page # ____**

Solution: Barium carrier, 16 mg/ml

SOP RA002 Instructions: Dissolve 28.46g $BaCl_2 \times 2H_2O$ in water, add 5 ml 16N HNO_3, dilute to 1000 ml with water, or equivalent. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment E: **Page # ____**

Solution: Citric acid, 1M

SOP RA002 Instructions: Dissolve 192g $C_6H_8O_7 \times H_2O$ in water and dilute to 1000 ml, or equivalent. This solution has 6 months stability at room temperature.

Solution Date Made / Lot #	Solution Exp. Date	Amount Made	Stock Reagent(s) Used	Stock Reagent Lot #(s)	Stock Reagent Exp. Date(s)	Balance Used	Date Solution Placed In Use	Date Solution Discarded	SOP Revision Followed	Initials

Attachment F: **Page # ____**

Solution: EDTA reagent, basic, (0.25M)

SOP RA002 Instructions: Dissolve 20g NaOH in a beaker containing 750 ml water, heat and slowly add 93g disodium ethylendinitriloacetate dihydrate ($Na_2C_{10}H_{14}O_8N_2 \times 2H_2O$). Heat and stir until dissolved, filter through course filter paper and dilute to 1 liter, or an equivalent dilution. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment G: **Page # ____**

Solution: Lead carrier, 15 mg/ml

SOP RA002 Instructions: Dissolve 24g $Pb(NO_3)_2$ in water, add 5 ml 16N HNO_3 and dilute to 1000 ml with water, or equivalent. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment H: **Page # ____**

Solution: Sodium hydroxide, 6N

SOP RA002 Instructions: Dissolve 240g NaOH in 800 ml water and dilute to 1000 ml, or equivalent. This solution has 6 months stability at room temperature. Use an ice bath.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment I: **Page # ____**

Solution: Sulfuric acid, 18N

SOP RA002 Instructions: Cautiously mix 1 volume 36N H_2SO_4 (conc.) with 1 volume of water. Use an ice bath. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment J: **Page # ____**

Solution: Sulfuric acid, 0.1N

SOP RA002 Instructions: Mix 1 volume 18N H_2SO_4 with 179 volumes of water. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment K:

Benchmark Analytics
Radiochemistry Data Package Review
Last Revision: 04-18-07

RADIUM 226

Date: 07/26/07 Instrument: Canberra Tennelec S5-XLB
Method: EPA 903.0 LIMS#: _____
SOP: RA002 Latest Revision

Instrument (circle one)	1	2	3	4	5
0-Mass Alpha Efficiency	27.40%	26.65%	28.28%	26.62%	27.54%
0-Mass Beta Efficiency	52.16%	54.02%	55.56%	52.71%	55.23%

CHECKLIST

Analyst	QC	Criteria
❑ Daily QC Done	❑ Daily Alpha	1) 35.8% 2) 35.8% 3) 38.3% 4) 36.4%
❑ Count Rate Report Printed	Efficiency	5) 38.5% at +/- 5%
❑ Sample Reports Printed	❑ Daily Beta	1) 46.0% 2) 45.2% 3) 46.0% 4) 43.7%
❑ Sample Manager Printed	Efficiency	5) 48.0% at +/- 5%
❑ All MDAs < 1 pCi/L	❑ Daily Background	Alpha < 1 CPM, Beta < 4 CPM
❑ Work Book Complete and	❑ Method Blank	< or = 1.00pCi/L
Copied	❑ LCS	+/- 26%
❑ Spike Inventoried	❑ Duplicate	NAD < or = 3 or RPD < or = 10%
❑ All QC recorded in Excel	❑ MDAs	< or = 1 pCi/L

STANDARDS USED

Solid	Source Ref. #	Half Life	Reference Date	Contained Radioactivity
Instruments #3 and #4				
Th-230	4979-S	75,400 years	04/01/2005	19.38 nCi / 43020 dpm
Sr-90	4979-S	28.5 years	04/01/2005	14.05 nCi / 31190 dpm
Instruments #1 and #2				
Th-230	4223-S	75,400 years	12/15/2002	19.56 nCi / 43420 dpm
Sr-90	4223-S	28.5 years	01/01/2003	13.38 nCi / 29700 dpm
Instruments #5				
Th-230	20002-S	75,400 years	07/01/2007	14.35 nCi / 31860 dpm
Sr-90	20002-S	28.5 years	07/01/2007	14.35 nCi / 31860 dpm

Preparation Analyst: _____ **Date:** _____

Instrument Analyst: _____ **Date:** _____

LIMS Entry By: _____ **Date:** _____

Reviewed and LIMS QA By: _____ **Date:** _____

Note: Reviewer is responsible for checking the entire data package and may choose to sign only the front cover sheet.

Benchmark Analytics, Inc.

EPA 904.0 Radium-228 in Drinking Water

EPA 9320 Radium-228

Document No. RA 003

Revision No. 20

January 11, 2010

Written By_____ Date: 2-9-10

Routing:_____ Date: 2-9-10

Reviewed By:_____ Date: 02-11-2010

Management Approval:_____ Date: 2-11-10

Note: The date of management approval is the effective date of this SOP.

CHANGES

Revision	Description	Date Issued
20	Section 5.2.16 updated to save supernatant.	1/11/10
19	Section 7.3.9 updated to include the RPD calculation. Units on Attachment D fixed to read mg/mL.	1/26/09

TABLE OF CONTENT

REFERENCES

EPA 904.0, EPA 9320, SW 846 Revision 0, SM#20: 7500-Ra D, SOP G-039 for definitions, SOP RA 001 Gross alpha and gross beta, SOPs G-032 for acronyms, SOP RA 006 for Calculations and G-016 for calibration and method validation, SOP G-033 Preparation of a final Report under NELAP, SOP IN-041 TCLP Extractions, National Primary Drinking Water Regulations: Radionuclides Final Rule 40 CFR Parts 9, 141, 142, Dec 7, 2000 PP 76708-76753; US EPA SOW for Radionuclides, and NELAC Standard latest issue as well as CHP, RSPM and QAPM.

****

1.0 General

1.1 Scope & Application

1.1.1 This method covers the measurement radium-228 in drinking water or ground water and, if desired the determination of radium-226 in the same sample. The National Primary Drinking Water Regulations state that if the alpha-screening test

reveals a gross alpha activity above 5 pCi/L. a radium-226 analysis must also be performed. If the level of radium-226 is above 3pCi/L, the sample must also be measured for radium-228.

1.1.2 This technique is devised so that beta activity from actinium-228, which is produced by decay of radium-228, can be determined and related to the radium-228 that is present in the sample.

1.2 Summary of Method

1.2.1 The radium in drinking water or ground water is collected by coprecipitation with barium and lead sulfate, and purified by reprecipitation from EDTA solution. Both radium-226 and radium-228 are collected in this manner. After a 36-hour ingrowth of actinium-228 from radium-228, the actinium-228 is carried on yttrium oxalate, purified and beta counted.

1.2.2 If radium-226 is also desired, the activity in the supernatant can be reserved for method 903.1 by coprecipitation on barium sulfate, dissolving in EDTA and storing for ingrowth in a sealed radon bubbler.

1.3 DEFINITIONS

1.3.1 Batch = refers to a preparation batch which is 20 samples or less not including QA samples and blanks.

1.3.2 Beta rate = 1.29 * gamma rate (for Cs-137).

1.3.3 Ci = Curie (One curie = 3.7x1010 disintegrations per second = 3.7x1010 becquerels = 2.22x1012 disintegrations per minute.)

1.3.4 Counting efficiency (efficiency factor) = counts per minute / disintegrations per minute or cpm/dpm.

1.3.5 MDA = minimum detectable activity. The calculation for the MDA is in SOP RA 006.

1.3.6 MeV = megaelectronvolt = 106 Volt.

1.3.7 Rem = is the special unit of any of the quantities expressed as dose equivalent. The dose equivalent in rems is equal to the absorbed dose in rads multiplied by the quality factor (1 rem = 0.01 Sievert).

1.3.8 RSPM = Radiation Safety Program Manual.

1.3.9 Source = in this SOP this word refers to the original material. It does not specifically refer to radioactive source material of U and Th.

1.3.10 Spillover = the number of erroneous counts in a counting channel (alpha or beta). See instrument manual for more detail.

1.4 Sample Handling, Preservation, Holding Time & Storage

1.4.1 It is recommended that samples be preserved at the time of collection by adding enough 1N HNO_3 to the sample to bring it to pH 2. If using 1N HNO_3 15 ml per liter of sample is usually sufficient. If using conc. HNO3, 2 ml per liter of sample is usually sufficient. If samples are collected with out preservation, they should be brought to the lab within 5 days, then preserved and held in the original container for a minimum of 16 hours before analysis or transfer of the sample.

1.4.2 The container of choice should be plastic over glass to prevent loss due to breakage during transport and handling.

1.4.3 Drinking water samples must be collected from a free-flowing source.

1.4.4 Ground water samples must have been collected in a manner which addresses

the considerations discussed in SW 846 Revision 0, chapter 9

1.4.5 The holding time is six months. Samples should not be stored in the same room as the counter. Samples are stored at room temperature.

1.5 Quantitation Limits

1.5.1 The minimum detection limit or minimum detectable activity (MDA) is defined as the concentration which can be counted with a precision of plus or minus 100 percent at the 95 percent confidence level. The National Primary Drinking Water Regulations require a MDA of 1 pCi/L. Refer to SOP RA006 for details on calculating the MDA.

1.6 Interferences

1.6.1 The presence of strontium-90 in the water sample gives a positive bias to the radium-228 activity measured.

1.6.2 Excess barium in the drinking water or ground water sample might result in a falsely high chemical yield.

1.6.3 Moisture absorbed by the sample residue is interference as it affects counting and self-absorption characteristics. Planchets must be stored in a desiccator when not being counted.

1.7 Safety

1.1.1 The analyst must have completed the radiation safety-training program prior to handling radioactive material. The training must be documented. Refer to the RSPM and the Radiation Safety Officer for details.

1.1.2 Radioactive standards are to be stored in a properly labeled area.

1.1.3 Radioactive standards and samples must be prepared in an area specifically designated for those purposes.

1.1.4 Personal protective equipment for handling radionuclide standards includes gloves, safety glasses and laboratory coat.

1.1.5 Preparation of radioactive standards must be carried out on a tray with adsorbent liner to absorb any spilled radioactive liquid.

1.1.6 Due to the nature of the low intensity radiation and the low dose rate of the radionuclide standards, radiation monitoring is not necessary.

1.7.1 Analyst should take appropriate precautions when using acids and alkalis.

1.7.2 Ammonium sulfide is toxic. Handle only in vented area.

1.7.3 The analyst should take appropriate precautions when using centrifuges, most models will have locking lids.

2.0 APPARATUS

2.1 Gas-flow proportional counting system Canberra Tennelec S5-XLB.

2.2 Electric hot plate

2.3 Centrifuge, Swinging Bucket recommended.

2.4 Metricel 47-mm Membrane Filters (GA-6, 0.45 μ-pore size) or equivalent

2.5 Glassware, including but not limited to beakers, graduated cylinders, volumetric flasks.

2.6 Stainless steel counting planchets 2 inch diameter with an 1/8" raised wall.

2.7 Analytical balance, minimum scale readability 0.1 mg.

2.8 Desiccator

2.9 Calibrated pipettes with disposable tips

2.10 Graduated disposable plastic pipettes 5, 10 and 25 ml.

2.11 Water Bath, Precision Model 180 or equivalent.

3.0 REAGENTS AND STANDARDS

3.1 General Comments

3.1.1 All reagents used must be analytical grade or better, whenever they are commercially available.

3.1.2 Materials of substandard reactivity or deterioration should not be used.

3.1.3 All reagents and reagent solutions should be properly labeled for identity, titer, strength or concentration, recommended storage, preparation and expiration dates, and any other relevant information.

3.1.4 Any expired reagent or reagent solution should be discarded or revalidated.

3.1.5 All reagents are prepared using volumetric flasks, unless otherwise specified.

3.2 Deionized (DI) water

3.3 Acetic Acid, 17.4 N: glacial acetic acid (conc.), specific gravity 1.05 g/ml, 99.8%

3.4 Ammonium hydroxide 15N: NH_4OH (conc.), specific gravity 0.90 g/ml, 56.6%

3.5 Ammonium Oxalate 5 %: dissolve 50 g $(NH_4)2C_2O_4 \times H_2O$ in water and dilute to 1000 ml, or equivalent. Stir on magnetic stirrer until dissolved. This takes at least 1 hour. This solution has 6 months stability at room temperature.

3.6 Ammonium sulfate 200 mg/ml: dissolve 200 g $(NH_4)_2SO_4$ in water and dilute to 1000 ml, or equivalent. This solution has 6 months stability at room temperature.

3.7 Ammonium sulfide 2 %: dilute 10 ml $(NH_4)_2S$ (20-24 %) to 100 ml with water, or equivalent. Prepare fresh on day of use at room temperature.

3.8 Barium Carrier 16 ml/ml standardized: dissolve 28.46 g $BaCl_2 \times 2\ H_2O$ in water, add 5 ml 16 N HNO_3 and dilute to 1000 ml with water, or equivalent. This solution has 6 months stability at room temperature. If precipitate is observed, prepare a fresh batch.

3.8.1 Standardization (in triplicate): pipette 2.0 ml carrier solution into a centrifuge tube containing 15 ml of water. Add 1 ml 18 N H_2SO_4 with stirring and digest precipitate in a water bath for 10 minutes. Cool, centrifuge and decant the supernatant. Wash precipitate with 15 ml water and centrifuge. Transfer the precipitate to a tared stainless steel planchet with a minimum of water. Dry on hotplate to constant weight, store in desiccator and weigh as $BaSO_4$.

3.8.2 When a fresh batch of this carrier is prepared it must be restandardized.

3.9 Citric acid 1M: dissolve 192 g $C_6H_8O_7 \times H_2O$ in water and dilute to 1000 ml, or equivalent. This solution has 6 months stability at room temperature.

3.10 EDTA reagent, basic 0.25 M: dissolve 20 g NaOH in a beaker containing 750 ml water, heat and add slowly 93 g disodium ethylenedinitroacetate dihydrate while stirring. After the salt is in solution filter through a coarse filter paper and dilute to 1 L, or an equivalent dilution. This solution has 6 months stability at room temperature.

3.11 Lead carrier 15 mg/ml: dissolve 23.97 g $Pb(NO_3)_2$ in water, add 5 ml 16 N HNO_3 and dilute to 1000 ml with water, or equivalent. This solution has 6 months stability at room temperature.

3.12 Lead carrier 1.5 mg/ml: dilute 10 ml lead carrier (15 mg/ml) to 100 ml with water, or

equivalent. This solution has 6 months stability at room temperature.

3.13 Methyl orange indicator 0.1 %: dissolve 1 g methyl orange indicator in 1000 ml water, or equivalent. Stir until completely dissolved. This solution has 6 months stability at room temperature.

3.14 Nitric acid 16 N: HNO_3 (conc.), specific gravity 1.42 g/ml, 70.4%

3.15 Nitric acid, 1 N: Mix 64 ml 16 M HNO_3 with DI water and dilute to 1000 ml, or use an equivalent dilution. This solution has 6 months stability at room temperature.

3.16 Nitric acid 6 N: Mix 3 volumes 16 N HNO_3 (conc.) with 5 volumes of water. This solution has 6 months stability at room temperature.

3.17 Sodium hydroxide 18 N: dissolve 720 g NaOH in water and dilute to 1000 ml, or equivalent. Use an ice bath. This solution has 6 months stability at room temperature.

3.18 Sodium hydroxide 10 N: dissolve 400 g NaOH in water and dilute to 1000 ml, or equivalent. Use an ice bath. This solution has 6 months stability at room temperature.

3.19 Strontium carrier 10 mg/ml: dissolve 24.16 g $Sr(NO_3)_2$ in water and dilute to 1 liter. This solution has 6 months stability at room temperature.

3.20 Sulfuric acid 18 N: cautiously mix 1 volume 36 N H_2SO_4 (conc.) with 1 volume of water. Add the acid to the water. Do not add the water to the acid!!! Use an ice bath. This solution has 6 months stability at room temperature.

3.21 Yttrium carrier 18 mg/ml: add 22.85 g Y_2O_3 to an Erlenmeyer flask containing 20 ml DI water. Heat to boiling and continue stirring on hot plate while adding 16N HNO_3 in small amounts. About 30 ml HNO_3 is necessary to dissolve the yttrium oxide. Add 70 ml 16N HNO_3. Transfer to 1L volumetric flask after dissolution and bring to mark with DI water. This solution has 6 months stability at room temperature.

3.22 Yttrium carrier 18 mg/ml: add 77.55 g $Y(NO_3)_3 \times 6 H_2O$ to DI water and acidify with conc. HNO_3, bring to 1000 mL final volume, or equivalent. This solution has 6 months stability at room temperature.

3.23 Yttrium carrier 9 mg/ml: dilute 50 ml yttrium carrier (18 mg/ml) to 100 ml with water, or equivalent. This solution has 6 months stability at room temperature.

3.24 Strontium-Yttrium mixed carrier 0.9 mg/ml Sr and 0.9 mg/ml Y:

3.24.1 Solution A: dilute 10.0 ml yttrium carrier (18 mg/ml) to 100 ml, or equivalent.

3.24.2 Solution B: Dissolve 0.4348 g $Sr(NO_3)_2$ in water and dilute to 100 ml, or equivalent.

3.24.3 Combine solutions A and B and label. This solution has 6 months stability at room temperature.

3.25 Radioactive solid source

3.25.1 For instrument calibration: Radioactive Sealed Source Calibration Standards. Details on the calibration procedure are in SOP RA001 and RA006.

a. The instrument is calibrated for counting efficiency and for alpha and beta plateaus according to instrument manufacturer instructions for gross alpha using a sealed source of Th-230 or a similar alpha source element and for gross beta using a sealed source of Sr-90 or a similar beta source element.

b. A suggested supplier is Isotope Products Laboratory. The geometry for the solid standard must be the same as that of the prepared samples and QC samples. A suggested geometry is 45 mm on stainless steel backing with aluminized Mylar cover or electroplated onto the stainless steel planchet.

- Th-230 Cat. # EAB-230-PL at about 40,000 dpm total alpha activity.
- Sr-90 Cat. #EAB-090-PL at about 30,000 dpm activity for Sr-90 only, as Y-90 exists in equilibrium in the standard.

3.26 Radioactive stock solutions:

a. Ra-228 Cat. # 7328 at approximately 0.1 uCi/5ml (Ra-228 only) stock.

b. Dilute the Ra-228 stock 1:100 in 1 M HNO_3 to make approximately 200 pCi/ml solution. This is used in all QC spiking for the batch.

c. The standard will be revalidated every five years. Analyzing a known concentration of the secondary standard may revalidate the primary standard. The recovery must be within 20% of the known concentration.

3.27 P-10 Counting Gas containing 10 % methane in 90% argon. The counting gas should contain no water vapor. The calibration plateau, background and efficiency must be verified whenever the gas is changed. Changes of gas cylinders must be recorded in the maintenance manuals.

4.0 SOLID SAMPLE PREPARATION

4.1 Please see SOP RA 001 section 9.0

5.0 PROCEDURE:

5.1 Calibration

5.1.1 Instrument calibration, counter efficiency, and background are described in SOP RA001 and RA 006.

5.1.2 Attenuation Curve

5.1.2.1 Prepare about 1 liter artificial hard water as in SM20:8010 to approximately 880 mg/L total solids, see RA001 section 4.13

5.1.2.2 Add the artificial hard water plus DI water to achieve the target final concentration of total solids in each aliquot covering a range of 0 to 150 mg.

5.1.2.3 To each aliquot add the same amount of the beta isotope described in RA001 section 4.14.3 b.

5.1.2.4 Process these similar to a routine sample as in RA001.

5.1.2.5 The self-adsorption calibration curve must be verified at least annually by preparing and counting standards at three different solids levels. The efficiency must be the expected efficiency plus/ minus 1.5 %. For example if the expected efficiency is 50%, the acceptable range is 48.5 % to 51.5%. If at least one of the standards is not acceptable the curve must be redone. Planchets prepared from an existing attenuation curve may be reused for this verification. Alternately, the calibration curve may be re-done annually by re-using the planchets from an existing calibration curve or preparing a new set.

5.2 Sample Preparation

Several steps in the procedure require monitoring of the time. Select one timepiece and use the same one throughout the procedure for consistent timing.

5.2.1 For each liter of drinking water or ground water add 5 ml 1 M $C_6H_8O_7 \times H_2O$ and few drops of methyl orange indicator. The solution should be red. It may take for example 1-2 ml for the method blank and 2-4 ml for samples and QC samples.

Note: see section 1.4.1 for sample preparation.

5.2.2 Add 10 ml lead carrier (15 mg/ml), 2.0 ml strontium carrier (10 mg/ml), 2.0 ml barium carrier (16 mg/ml), and 1.0 ml yttrium carrier (18mg/ml); stir well. Heat on hotplate to incipient boiling and maintain at this temperature for 30 minutes.

5.2.3 Add 15 N NH_4OH until a definite yellow color is obtained (about 2-6 ml), then add a few drops excess. Precipitate lead and barium sulfates by adding 18 N H_2SO_4 until the red color reappears (about 2-3 ml), then add 0.25 ml excess. Add 5 ml $(NH_4)_2SO_4$ (200 mg/ml) for each liter of sample. Stir frequently and keep at a temperature of about 90°C for 30 minutes.

5.2.4 Remove from hotplate, but keep in hood. Cool until no visible vapors, then filter with suction through a 47-mm Metricel membrane filter (GA-6, 0.45 µ pore size). Make a quantitative transfer of precipitate to the filter by rinsing last particles out of beaker with a strong jet of water.

5.2.5 Carefully place filter with precipitate in the bottom of a 250 ml beaker. Add about 10 ml of 16 N HNO_3 and heat gently until the filter dissolves completely. Transfer the precipitate into a polypropylene centrifuge tube with additional 16 N HNO_3. Use a washbottle with 16 N HNO_3. Be sure that all of the precipitate has been transferred to the centrifuge tube. Balance the centrifuge tubes before loading into the centrifuge. Use counterweights of sand and water, balance the tubes for all subsequent spinning steps. Centrifuge and remove the supernatant. Do not loose any precipitate. Be cautious while handling the nitric acid!!

5.2.6 Wash the precipitate with 15 ml 16 N HNO_3, centrifuge and remove the supernatant. Do not loose any precipitate.

5.2.7 Repeat step 5.2.6.

5.2.8 Add 25 ml basic EDTA reagent, heat in hot water bath, and stir well. Add a few drops 10 N NaOH if the precipitate does not readily dissolve. This step generates fumes and must be done in the hood.

5.2.9 Add 1 ml strontium-yttrium mixed carrier and stir thoroughly. Add a few drops 10 N NaOH if any precipitate forms.

5.2.10 Add 1 ml $(NH_4)_2SO_4$ (200 mg/ml) and stir thoroughly. Add 17.4 N CH_3COOH until barium sulfate precipitates (about 3-5 drops each), then add 2 ml excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernatant.

5.2.11 Add 20 ml basic EDTA reagent, heat in a hot water bath and stir until precipitate dissolves. Repeat steps 5.2.9 and 5.2.10. Note the time of the last barium sulfate precipitation; this is the beginning of the actinium-228 ingrowth time (start t3).

5.2.12 Dissolve the precipitate in 20 ml basic EDTA reagent as before, then add 1.0 ml yttrium carrier (9 mg/ml) and 1 ml lead carrier (1.5 mg/ml). If any precipitate forms, dissolve by adding a few drops of 10 N NaOH. Cap the polypropylene tube and age at least 36 hours. A longer waiting time is advantageous.

5.2.13 Add 0.3 ml $(NH_4)_2S$ and stir well. Work in the hood. Add 10 N NaOH drop wise with vigorous stirring until the black lead sulfide precipitates, then add 10 drops excess. Vortex intermittently on low speed for about 10 minutes. Centrifuge and decant supernatant into a clean tube.

5.2.14 Add 1 ml lead carrier (1.5 mg/ml), 0.1 ml $(NH_4)_2S$, and a few drops of 10 N NaOH. The black lead sulfide will reappear. Repeat precipitation of lead sulfide as before. Centrifuge and filter supernatant through Whatman #42 filter paper into a clean tube. Wash filter with a few ml water. Discard the residue.

5.2.15 Add 5 ml 18 N NaOH, stir well and digest in a hot water bath until the white fluffy

yttrium hydroxide coagulates. Centrifuge and decant supernatant into a beaker. Save for barium yield determination, step 5.2.20. Note the time of yttrium hydroxide precipitation; this is the end of the actinium-228 ingrowth time: end t3. It is also the beginning of actinium-228 decay time: start t1.

NOTE: Work rapidly from step 5.2.15 until step 5.2.19 to minimize the t1 value due to the short half-life of Ac-228 (6 hours!!!).

5.2.16 Dissolve the precipitate in 2 ml 6 N HNO_3. Heat and stir in a hot water bath about 5 minutes. Add 5 ml water and reprecipitate the white yttrium hydroxide with 3 ml 10 N NaOH. Heat and stir in a hot water bath until precipitate coagulates. Centrifuge the samples. The supernatant should be added to the supernate saved in step 5.2.15. Do not loose any precipitate.

5.2.17 Dissolve precipitate with 1 ml 1 N HNO_3 and heat in hot water bath for a few minutes. Dilute to 5 ml (use marking on centrifuge tube) and add 2 ml 5% $(NH_4)_2C_2O_4$ x H2O. Heat to coagulate (this is white and not fluffy), centrifuge and remove the supernatant. Do not loose any precipitate.

5.2.18 Add 10 ml DI water, 6 drops 1 N HNO3 and 6 drops 5 % $(NH_4)_2C_2O_4$ x H_2O. Heat and stir in a hot water bath for a few minutes. Centrifuge and remove the supernatant. Do not loose any precipitate.

5.2.19 To determine yttrium yield, transfer quantitatively to a tared stainless steel planchet with a minimum amount of water and use vortex to break loose. Dry on hotplate to a constant weight of the yttrium oxalate and count for beta activity.

5.2.20 To the supernatant in the beaker in step 5.2.15 add 4 ml 16 N HNO_3 and 2 ml $(NH_4)_2SO_4$ (200 mg/ml), stirring well after each addition. Add 17.4 N CH_3COOH until barium sulfate precipitates, then add 2 ml excess. Digest on a hot plate until precipitate settles. Allow volume to decrease to less than 40 ml. Transfer to a centrifuge tube using DI water. Centrifuge and discard supernatant.

5.2.21 Add 20 ml basic EDTA reagent, heat in a hot water bath, stir until precipitate dissolves. Add a few drops 10 N NaOH if precipitate does not readily dissolve.

5.2.22 Add 1 ml $(NH_4)_2SO_4$ (200 mg/ml) and stir thoroughly. Add 17.4 N CH_3COOH until barium sulfate precipitates, then add 2 ml excess. Digest in a hot water bath until precipitate settles. Centrifuge and discard supernatant.

5.2.23 Wash precipitate with 10 ml DI water. Centrifuge and discard supernatant.

5.2.24 Transfer precipitate to a tared steel planchet with a minimum amount of DI water using vortex to break the precipitate. Dry on hotplate to a constant weight and weigh for barium yield determination.

5.3 Sample Analysis

5.3.1 Determine the chemical yield for yttrium. The theoretical yield should be 22.5 mg yttrium oxalate based on 9 mg Y. The acceptable fractional chemical yield should be between 0.60 to 1.25. If this criterion is not met one or more of the following is done, reweigh the planchets, re-prep the sample, or prepare new carrier solutions. Matrix interference may also cause a carrier failure. Occurrence of a carrier recovery failure, as well as the actions taken, will be noted in the laboratory report.

5.3.2 Determine the chemical yield for barium. The theoretical yield should be 54.4 mg adjusted for the standardization in step 3.8.1 based on 32 mg Ba. The acceptable fractional chemical yield should be between 0.60 to 1.25. If this criterion is not met one or more of the following is done, reweigh the planchets, or prepare new carrier solutions. Occurrence of a carrier recovery failure, as well as the actions taken, will be noted in the laboratory report.

5.3.3 The carrier shall be added to the sample after subsampling but before any chemical treatment.

5.3.4 Measure the beta net count rate (ncpm in the Eclipse program)

5.3.5 The program will generate the counter efficiency based on the weight of yttrium oxalate entered.

5.3.6 The t1 end values are generated in the program.

6.0 Calculation

6.1 Background

The background of the system is measured and subtracted by the Eclipse software. This background is done on a weekly basis. The weekly background is applied to all analyzed samples and QC and does not depend on the method blank result associated with the analytical batch. No additional calculations need to be done. The method blank differs from this and is never subtracted.

6.2 Computation

Calculate the radium-228 concentration, D, in picocuries per liter as follows:

$$D\ (pCi/L) = C/(2.22 \times EVR) \times \lambda t2/(1-e^{-\lambda t2}) \times 1/(1-e^{-\lambda t3}) \times 1/(e^{-\lambda t1})$$

Where:

C = average net count rate, cpm

E = counter efficiency for beta activity

V = volume of sample aliquot in liters

R = fractional chemical yield of yttrium carrier (step 5.2.19) multiplied by the chemical yield of barium (step 5.2.24).

2.22 = conversion factor from disintegrations/minute to picocuries (dpm/pCi)

λ = the decay constant for actinium (0.001884 min^{-1})

t1 = the time interval (in minutes) between the first yttrium hydroxide precipitation in step 5.2.15 and the start of the counting time

t2 = the time interval of counting in minutes, and

t3 = the ingrowth time of actinium-228 in minutes measured from the last barium sulfate precipitation in step 5.2.11 to the first yttrium hydroxide precipitation in step 5.2.15.

Note:

$\lambda t2/(1-e^{-\lambda t2})$ is a factor to correct the average count rate to count rate at beginning of the counting time.

6.3 Reporting

6.3.1 The concentration of Radium 228 in pCi /L corrected to the time of sample collection must be reported. The counting error and MDA must also be reported. See SOP RA001 and RA006 for details.

$$A = A_0 e^{(-0.693t/(T1/2))} = A_0(1/2)^N$$

Where:

A = activity at time t

A_0 = initial activity at t=0

$T_{1/2}$ = half-life (in same units as t)

N = # half-lives = $t/T_{1/2}$

6.3.2 The customer report must contain the calculated value for RA-228, the MDA and the counting error.

6.3.3 Error Reporting. Each result must be reported with the measurement of uncertainty, also called error reporting. The counting error must be established and reported at the 95 % confidence level. The ECLIPSE software calculates the error as uncertainty with all results. The documentation is in the Canberra Technical Reference Manual. Copies of the methods, calculations and sequence are found in SOP RA006.

6.3.4 MDA Reporting: The Eclipse software has a MDA calculator. Use the calculator to determine the counting time required to reach the MDA of 1 pCi/L for RA-228. The MDA calculator equations are described in detail in SOP RA006.

6.3.5 If a MDA is unable to be achieved, for example due to low sample volume, the sample should be reported with the appropriate data qualifier.

6.3.6 If reanalysis is not possible the sample should be reported with the appropriate data qualifier.

6.3.7 The full sample ID must be used throughout the entire procedure. At no point during preparation or reporting is an abbreviated sample ID used.

7.0 QUALITY CONTROL

7.1 METHOD BLANK (MB)

7.1.1 The frequency of a method blank is one method blank per preparation batch. The batch is defined as 20 samples or less (excluding the method blank, and LCS).

7.1.2 Prepare a method blank by using 1000 ml of DI water and treat it the same as all of the samples. Add 2 ml of 16 N HNO_3. The method blank must be prepared with similar aliquot size to that of the routine samples. If this is not possible, the method blank must be calculated in a way that compensates for sample results based upon differing aliquot size.

7.1.3 The result of this analysis is recorded as a quality control measure to assess the batch.

7.1.4 The result of the blank must be below the MDA for Ra-228.

7.1.5 When the acceptance criterion for the method blank is not met the specified corrective action and contingencies shall be followed; results should be reported with the appropriate data qualifying codes. The corrective action may include some or all of the following:

- check planchet holder for contamination
- check for area contamination
- Assure that the instrument background is in control.

7.1.6 Note in the laboratory report if a method blank fails. The corrective actions must be recorded in the raw data.

7.1.7 Management is notified when out-of-control or unacceptable data occurs.

7.1.8 NOTE: The method blank may not be subtracted from the sample results.

7.2 LABORATORY CONTROL SAMPLES (LCS)

7.2.1 One LCS is prepared for each preparation batch. The batch is defined as 20 samples or less (excluding the method blank, and LCS).

7.2.2 The LCS must be of similar aliquot size to that of routine samples.

7.2.3 A practical level for the LCS is at about 10 pCi/L for Ra-228, which is greater than five times the detection limit. Choose a comparable level of the samples if the samples exceed five times the detection limit.

7.2.4 Prepare a solution with approximately 10 pCi/L of Ra-228 and test as a sample. To 1000 ml DI water add 50 uL of the solution from section 3.26 b.

7.2.5 The result of the LCS is recorded as a quality control measure to assess the batch and must be within 43 % of the expected value for Ra-228. The LCS acceptance criteria will be re-evaluated and adjusted (if necessary) at least once a year. QC charting of the LCS data will be done to facilitate this.

7.2.6 When the acceptance criterion for the LCS is not met, follow the specified corrective action and contingencies. The corrective actions may involve but are not limited to recounting the LCS and assure that the instrument calibration parameters are in control.

7.2.7 Occurrence of a LCS failure must be noted in the laboratory report. The corrective actions must be recorded in the raw data.

7.2.8 Management is notified when out-of-control or unacceptable data occurs.

7.3 REPRODUCIBILTY; Matrix Spike/Matrix Spike Duplicate (MS/MSD), Laboratory Fortified Blank/ Laboratory Fortified Blank Duplicate (LFB/LFBD)

7.3.1 One matrix spike and one matrix spike duplicate sample must be run for every ten samples to assess the quality of the run. The batch is defined as 20 samples or less (excluding the method blank, and LCS).

7.3.2 The matrix spike and the matrix spike duplicate are spiked after subsampling but before any chemical treatment.

7.3.3 A practical level for the MS/MSD is at about 20 pCi/L for Ra-228, which is greater than five times the detection limit. To 1000 ml of sample add 100 uL of the solution from section 3.26 b.

7.3.4 DI water LFB and LFBD may be used when there is not enough sample volume.

7.3.5 Prepare and read the samples along with the other QC samples and field samples.

7.3.6 The result of the MS/MSD or LFB/LFBD are recorded as a quality control measure to assess the batch and must be within 43 % of the expected value for Ra-228. The spike and spike duplicate acceptance criteria will be re-evaluated and adjusted (if necessary) at least once a year. QC charting of the spike and spike duplicate data will be done to facilitate this.

7.3.7 Calculate the normalized absolute difference (NAD) between the MS/MSD or LFB/LFBD. This factor is used to assess result acceptance and should be < or = 3. The results are recorded. Acceptance criteria will be re-evaluated once a year.

$$NAD = (S-D) / [(TPU_S)^2 + (TPU_D)^2]^{1/2} = \text{or} < 3$$

Where,

S = sample result

D = duplicate result

TPU_S = 1s total propagated uncertainty of the sample

TPU_D = 1s total propagated uncertainty of the duplicate

7.3.8 If the specified criteria are not met specified corrective action and contingencies must be followed.

7.3.9 If the duplicate data is not acceptable, determine the RPD of the weight for each of the carriers Ba and Y. If both MS/MSD or LFB/LFBD samples are out of range use a qualifier statement on the report. If one of the MS/MSD or LFB/LFBD samples is out of range, accept the batch. To Calculate the RPD: [((MS-MSD)*2)/(MS+MSD)]*100

7.3.10 Occurrence of a MS/MSD or LFB/LFBD failure, as well as the actions taken, must be noted in the laboratory report.

7.3.11 The analyst must make a note in the laboratory report if there is not enough sample to perform the duplicate analysis.

7.3.12 Management is notified when out-of-control or unacceptable data occurs.

7.4 NONCONFORMANCE

7.4.1 Root cause of nonconformance must be done. Check appropriate count times, dilutions, aliquot size, detector efficiency, and detector background. If the nonconformance is due to inadequate sample volume, elevated radioactivity levels, sample matrix interference such a high amount of suspended solids, etc., explain these factors in the report.

7.4.2 To address nonconformance of QC results consult the troubleshooting section of the instrument manual. It addresses the following problems: gas flow, plateau, background, efficiency and spillover, count timer incrementing and data reproducibility.

7.5 DEMONSTRATION OF CAPABILITY/MDA

7.5.1 Detection limits must be determined prior to sample analysis. They also must be established annually by each qualified analyst for each analyte.

7.5.2 It must be done initially and done again if there is a significant change in instrument type, personnel, or method.

7.5.3 For DOC, prepare 4 samples at approximately 10 pCi/L for Ra-228. Ra-228 is added to the 4 samples. The samples are carried through the sample preparation steps and counted on the simultaneous mode.

7.5.4 To 1000 ml DI water add 50 uL of the solution from section 3.26 b.

7.5.5 It is also acceptable to use 4 or more sample batches and generate the DOC from the LCS data of those batches.

7.5.6 Calculate the Ra-228 activity in pCi/L.

7.5.7 The recovery must be at or below the following criteria:

7.5.7.1 For Ra-228 +/- 43 % precision and +/- 25% RPD (relative percent difference).

7.5.8 Proficiency Sample Results

7.5.8.1 The laboratory will use the results of proficiency samples as an evaluation of the ability to produce accurate data.

8.0 QC SAMPLE SUMMARY

8.1 The cover page for the data packet includes a QC checklist, which shows criteria for the

QC in section 8.2. The reviewer of the data pack is responsible to check that all criteria are met, and that if a criterion is not met that the appropriate notation is made in the raw data. The reviewer should also review and QA the batch in the Omega LIMS. This cover page also has an analyst checklist, items that the analyst who ran the batch is responsible for.

8.2 For each batch of 20 or less samples there will be:

- 1 solid standard for alpha counting efficiency
- 1 solid standard for beta counting efficiency
- 1 instrument background
- 1 MB in DI water
- 1 MS and 1 MSD or 1 LFB and 1 LFBD for every ten samples at approximately 20 Ci/L activity
- 1 LCS at approximately 10 pCi/L activity

9.0 QC Summary Table (approximate values)

	Ra-228	Limit	Reference
LCS	10 pCi/L	+/-43 %	At least 5 x MDA
MS, MSD, LFB, LFBD	20 pCi/L	+/-43 %	> 5 x MDA
NAD		< / = 3	
DOC study	10 pCi/L	+/- 43 %, +/- 25 % RPD	At least 5 x MDA
carrier recovery Y		60 % to 125 %	SOP
carrier recovery Ba		60 % to 125 %	SOP
MDA specs		1 pCi/L	40 CFR 141,142
background		<1 pCi/L	< MDA

10.0 Pollution Prevention & Waste Management

10.1 See BENCHMARK ANALYTICS QAPP.

Appendix A. Method Steps

Ra-228 EPA 904.0										
step	sample	add	do	why	Y	Ra-226	Ra-228	Pb	Ba	Ac
8.1	1 L sample with HNO3 preservative		Check for preservation. If unpreserved, acidify to pH < 2 with HNO3							
8.2a	1L sample pH <2:	+ 5ml citric acid		complexing agent to keep in solution						
		methyl orange indicator	should be red	verify that acidic						
8.2b		+ 10 ml Pb carrier		for coprecip				added		
8.2c		+ 2 ml Sr carrier		Remove Sr-90						
8.2d		+ 2 ml Ba carrier		for coprecip					added	
8.2e		+ 1 ml Y carrier	stir, boil, 30 minutes	Remove Ac-228	added					
8.3a		NH4OH	to yellow color	pH change to alkaline						
8.3b		sulfuric acid	pH somewhat acidic	ppt of PbSO4, BaSO4, Ra sulfates						
8.3c		ammonium sulfate	stir, keep at 90 C for about 30 minutes	ppt of PbSO4, BaSO4, Ra sulfates						
8.4			filter, transfer all particles	keep precipitate - discard supernate which contains Y-SO4 & Sr-SO4	removed	in ppt	in ppt	in ppt	in ppt	
8.5	precipitate	nitric acid	dissolve filter, place in centrifuge	discard supernate						

	wash		tube, spin								
8.6	precipitate wash	nitric acid	wash and spin	discard supernate							
8.7	precipitate wash	nitric acid	wash and spin	discard supernate							
8.8	dissolve ppt	basic EDTA	heat & stir, add more NaOH	dissolve ppt as EDTA complex							
8.9a		+ 1 ml Sr-Y carrier	stir	Remove Sr & Ac	added						
8.9b			add more NAOH	to keep from precipitating							
8.10a		+ 1 ml NH4sulfate	stir	to make Ba & Pb & Ra - sulfates							
8.10b		+ acetic acid	until BaSO4 precipitates	make more acidic to break the EDTA complex and form precipitates							
8.10c			digest in hot water bath until ppt settles	spin - discard supernate which contains Sr-Y sulfates	removed	in ppt	in ppt	in ppt	in ppt		
8.11a	dissolve ppt: will be done 3 times as shown below	basic EDTA	heat & stir	dissolve ppt as EDTA complex							
8.11b		+ 1 ml Sr-Y carrier	stir	Remove Sr & Ac	added						
8.11c			add more NAOH	to keep from precipitating							
8.11d		+ 1 ml NH4sulfate	stir	to make Ba & Pb & Ra - sulfates							
8.11e		+ acetic acid	until BaSO4 precipitates	make more acidic to break the EDTA complex and form precipitates							
8.11f			digest in hot water bath until ppt settles	spin - discard supernate which contains Sr-Y sulfates	removed	in ppt	in ppt	in ppt	in ppt		
8.11g	dissolve ppt	basic EDTA	heat & stir	dissolve ppt as EDTA complex							
8.11h		+ 1 ml Sr-Y carrier	stir	why	added						
8.11l			add more NAOH	to keep from precipitating							
8.11j		+ 1 ml NH4sulfate	stir	to make Ba & Pb & Ra - sulfates							
8.11k		+ acetic acid	until BaSO4 precipitates	make more acidic to break the EDTA complex and form precipitates		in ppt	in ppt	in ppt	in ppt		
8.11l				note beginning of actinium ingrowth time							ingrowth start T3
8.11m			digest in hot water bath until ppt settles	spin - discard supernate which contains Sr-Y sulfates	removed						
8.12a	dissolve ppt	basic EDTA	heat & stir	dissolve ppt as EDTA complex							
8.12b		+ 1.0 ml Y carrier		this is the Y carrier for internal standard step	Y internal std. addition						
8.12c		+ 1.0 ml Pb carrier	keep from precipitating with more NaOH	cap and age at least 36 hours				added			
	Ra-228 EPA 904.0 cont.										
step	sample	add	do	why	Y	Ra-226	Ra-228	Pb	Ba	Ac	
8.13a		+ amm. sulfide	stir	add sulfide for PbS		solution		solution			
8.13b		+ NaOH	dropwise until PbS forms, then access	ppt forms at more alkaline pH from EDTA complex							
8.13c	*Stir intermittently*		spin - decant supernate into clean tube	discard PbS ppt - keep supernate which contains Y, not Pb				removed			
8.14a	supernate	+ 1 ml Pb carrier						added			
8.14b		+ amm.sulfide									
8.14c		+ NaOH	until PbS forms, stir 10 minutes and spin	remove Pb		solution		solution			
8.14b			filter thru paper, wash w. water	discard PbS ppt - keep supernate which contains Y, not Pb				removed			
8.15a	supernate	+ 5ml NaOH	stir &digest in hot water bath until Y(OH)3 coagulates		in ppt						
8.15b			spin - save ppt & supernate	note end of actinium ingrowth time and start of decay time							ingrowth end T3 & decay start T1
8.15c	supernate		decant supernate into clean tube - save for Ba step 8.20						ppt		
8.16a	precipitate	+ HNO3	dissolve ppt, heat and stir								
8.16b		+ water									
8.16c		+ NaOH	reprecipitate Y(OH)3								

8.16d			heat and stir until coagulates							
8.16e			spin, discard supernate							
8.17a	precipitate	+ HNO3	dissolve ppt, heat and stir							
8.17b			+ 2 ml amm. oxalate							
8.17c			heat to coagulate and stir							
8.17d			spin	discard supernate	in ppt					
8.18a	precipitate	+ 10 ml water								
8.18b		drops HNO3	heat in water bath few minutes							
8.18c			dilute to 5 ml							
8.18d			add amm.oxalate							
8.18e			heat to coagulate and stir							
8.18f			spin	discard supernate						
8.19a	precipitate		transfer to SS planchet quantitatively							
8.19b			dry to constant weight	weigh for Y yield as Y(OH)3	yield					
8.19c			count in beta counter							end decay T1
8.20a	supernate from 8.15c	+4 ml HNO3	stir						ppt	
8.20b		+ amm.sulfate	stir							
8.20c		acetic acid	until BaSO4 precipitates							
8.20d		add more, heat until ppt settles	spin	discard supernate					ppt	
8.21a	precipitate	+ 20ml EDTA	to dissolve ppt							
8.21b		few drops NaOH	to dissolve ppt						solution	
8.22a	solution	+ 1ml amm.sulfate								
8.22b		+ acetic acid	until BaSO4 precipitates							
8.22c		add more, heat until ppt settles	spin	discard supernate					ppt	
8.23a	precipitate	wash with water	spin	discard supernate					ppt	
8.24a	precipitate		transfer to SS planchet quantitatively							
8.24b			dry to constant weight	weigh for Ba yield					yield	

Attachment A

Benchmark Analytics

Page____

RA228 Worksheet: EPA 904.0

SOP RA 003, Revision___

Prep Analyst: _____ **All samples pH<2?** _____

Start Date & Time: _____ **t3 start:** _____ **Count Date:** _____

Yttrium Carrier Lot#: Exp. _____ **t3 end / t1 start :** _____ **LIMS Run #:** _____

Barium Carrier Lot#: Exp. _____ **Ammonium Sulfide Lot#:** Exp. _____ **Batch\Key - Instrument:** _____

Ra228 Standard Lot#: Exp. _____ **Balance used:** _____ **Book#:** _____

#	Sample ID	Date Collected	Vol. ml	Y/B #	Y Init. Wt. g	Y Final Wt.1 g	Y Final Wt.2 g	Delta Wt. mg	Y Yield T.V.=22.5	B Init. Wt. g	B Final Wt.1 g	B Final Wt.2 g	Delta Wt. mg	Ba Yield T.V.=
1	MB													
2	LCS	2/15/2003												
3														
4														
5														
6														
7														
8														
9														
10														
11														
12														
13														
14														
15														
16														
17														
18														
19														
20														
21														
22														
23														
24														

Nitric Acid Lot#: Exp. _____ 47 mm, 0.45 um filter lot: _____

Ammonium Hydroxide Lot#: Exp. _____ Reviewed by: _____

Acetic Acid Lot#: Exp. _____ Whatman 42 filter lot: _____

Attachment B: **Page # ____**

Solution: Ammonium Oxalate 5 %

SOP RA003 Instructions: Dissolve 50 g $(NH_4)2C_2O_4 \times H_2O$ in water and dilute to 1000 ml, or equivalent. Stir on magnetic stirrer until dissolved. This takes at least 1 hour. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment C: **Page # ____**

Solution: Ammonium sulfate 200 mg/ml

SOP RA003 Instructions: dissolve 200 g $(NH_4)_2SO_4$ in water and dilute to 1000 ml, or equivalent. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment D: **Page # ____**

Solution: Barium Carrier 16 mg/ml standardized

SOP RA003 Instructions: dissolve 28.46 g $BaCl_2$ x 2 H_2O in water, add 5 ml 16 N HNO_3 and dilute to 1000 ml with water, or equivalent. This solution has 6 months stability at room temperature. If precipitate is observed, prepare a fresh batch.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment E: **Page # ____**

Solution: Citric acid 1M

SOP RA003 Instructions: dissolve 192 g $C_6H_8O_7 \times H_2O$ in water and dilute to 1000 ml, or equivalent. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment F: **Page # ____**

Solution: EDTA reagent, basic 0.25 M

SOP RA003 Instructions: dissolve 20 g NaOH in a beaker containing 750 ml water, heat and add slowly 93 g disodium ethylenedinitroacetate dihydrate while stirring. After the salt is in solution filter through a coarse filter paper and dilute to 1 L, or an equivalent dilution. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment G: **Page # ____**

Solution: Lead carrier 15 mg/ml

SOP RA003 Instructions: dissolve 23.97 g $Pb(NO_3)_2$ in water, add 5 ml 16 N HNO_3 and dilute to 1000 ml with water, or equivalent. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment H: **Page # ____**

Solution: Lead carrier 1.5 mg/ml

SOP RA003 Instructions: dilute 10 ml lead carrier (15 mg/ml) to 100 ml with water, or equivalent. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment I: **Page # _____**

Solution: Methyl orange indicator 0.1 %

SOP RA003 Instructions: dissolve 1 g methyl orange indicator in 1000 ml water, or equivalent. Stir until completely dissolved. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment J: **Page # ____**

Solution: Nitric acid 6 N

SOP RA003 Instructions: Mix 3 volumes 16 N HNO_3 (conc.) with 5 volumes of water. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment K: **Page # ____**

Solution: Sodium hydroxide 18 N

SOP RA003 Instructions: dissolve 720 g NaOH in water and dilute to 1000 ml, or equivalent. Use an ice bath. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment L:

Page # ____

Solution: Sodium hydroxide 10 N

SOP RA003 Instructions: dissolve 400 g NaOH in water and dilute to 1000 ml, or equivalent. Use an ice bath. This solution has 6 months stability at room temperature.

Solution Date Made / Lot #	Solution Exp. Date	Amount Made	Stock Reagent(s) Used	Stock Reagent Lot #(s)	Stock Reagent Exp. Date(s)	Balance Used	Date Solution Placed In Use	Date Solution Discarded	SOP Revision Followed	Initials

Attachment M: **Page # ____**

Solution: Strontium carrier 10 mg/ml

SOP RA003 Instructions: dissolve 24.16 g $Sr(NO_3)_2$ in water and dilute to 1 liter. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment N: **Page # ____**

Solution: Sulfuric acid 18 N

SOP RA003 Instructions: cautiously mix 1 volume 36 N H_2SO_4 (conc.) with 1 volume of water. Add the acid to the water. Do not add the water to the acid!!! Use an ice bath. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment O: **Page # ____**

Solution: Yttrium carrier 18 mg/ml

SOP RA003 Instructions: add 22.85 g Y_2O_3 to an Erlenmeyer flask containing 20 ml DI water. Heat to boiling and continue stirring on hot plate while adding 16N HNO_3 in small amounts. About 30 ml HNO_3 is necessary to dissolve the yttrium oxide. Add 70 ml 16N HNO_3. Transfer to 1L volumetric flask after dissolution and bring to mark with DI water. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment P: **Page # ____**

Solution: Yttrium carrier 18 mg/ml

SOP RA003 Instructions: add 77.55 g $Y(NO_3)_3 \times 6\ H_2O$ to DI water and acidify with conc. HNO_3, bring to 1000 mL final volume, or equivalent. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment Q: **Page # ____**

Solution: Yttrium carrier 9 mg/ml

SOP RA003 Instructions: dilute 50 ml yttrium carrier (18 mg/ml) to 100 ml with water, or equivalent. This solution has 6 months stability at room temperature.

Solution Date Made / Lot #	Solution Exp. Date	Amount Made	Stock Reagent(s) Used	Stock Reagent Lot #(s)	Stock Reagent Exp. Date(s)	Balance Used	Date Solution Placed In Use	Date Solution Discarded	SOP Revision Followed	Initials

Attachment R: **Page # ____**

Solution: Strontium-Yttrium mixed carrier 0.9 mg/ml Sr and 0.9 mg/ml Y

SOP RA003 Instructions: Solution A: dilute 10.0 ml yttrium carrier (18 mg/ml) to 100 ml, or equivalent. Solution B: Dissolve 0.4348 g $Sr(NO_3)_2$ in water and dilute to 100 ml, or equivalent. Combine solutions A and B and label. This solution has 6 months stability at room temperature.

Solution Date Made / Lot #	Solution Exp. Date	Amount Made	Stock Reagent(s) Used	Stock Reagent Lot #(s)	Stock Reagent Exp. Date(s)	Balance Used	Date Solution Placed In Use	Date Solution Discarded	SOP Revision Followed	Initials

Attachment S: **Page # ____**

Solution: Nitric acid, 1 N

SOP RA003 Instructions: Mix 64 ml 16 M HNO_3 with DI water and dilute to 1000 ml, or use an equivalent dilution. This solution has 6 months stability at room temperature.

Initials										
SOP Revision Followed										
Date Solution Discarded										
Date Solution Placed In Use										
Balance Used										
Stock Reagent Exp. Date(s)										
Stock Reagent Lot #(s)										
Stock Reagent(s) Used										
Amount Made										
Solution Exp. Date										
Solution Date Made / Lot #										

Attachment T:

Benchmark Analytics
Radiochemistry Data Package Review
Last Revision: 04-18-07

RADIUM 228

Date:	07/26/07		Instrument:	Canberra Tennelec S5-XLB	
Method:	EPA 904.0		LIMS# :	_____	
SOP:	RA003 Latest Revision				
Instrument (circle one)	1	2	3	4	5
0-Mass Alpha Efficiency	27.40%	26.65%	28.28%	26.62%	27.54%
0-Mass Beta Efficiency	54.59%	53.33%	53.57%	52.09%	55.23%

CHECKLIST

Analyst	QC	Criteria
☐ Daily QC Done	☐ Daily Alpha Efficiency	1) 35.8% 2) 35.8% 3) 38.3% 4) 36.4% 5) 38.5% at +/- 5%
☐ Count Rate Report Printed		
☐ Sample Report Printed	☐ Daily Beta Efficiency	1) 46.0% 2) 45.2% 3) 46.0% 4) 43.7% 5) 48.0% at +/- 5%
☐ Sample Manager Report Printed	☐ Daily Background	Alpha < 1 CPM, Beta < 4 CPM
☐ All Beta MDAs < 1 pCi/L	☐ Method Blank	< or = 1 pCi/L
☐ Work Book Completed and Copied	☐ LCS	+/- 43%
	☐ Duplicate	NAD < or = 3 or RPD < or = 10%
☐ Spike Inventoried	☐ MDAs	< or = 1 pCi/L
☐ All QC in Excel		

STANDARDS USED

Solid	Source Ref. #	Half Life	Reference Date	Contained Radioactivity
Instruments #3 and #4				
Th-230	4979-S	75,400 years	04/01/2005	19.38 nCi / 43020 dpm
Sr-90	4979-S	28.5 years	04/01/2005	14.05 nCi / 31190 dpm
Instruments #1 and #2				
Th-230	4223-S	75,400 years	12/15/2002	19.56 nCi / 43420 dpm
Sr-90	4223-S	28.5 years	01/01/2003	13.38 nCi / 29700 dpm
Instruments #5				
Th-230	20002-S	75,400 years	07/01/2007	14.35 nCi / 31860 dpm
Sr-90	20002-S	28.5 years	07/01/2007	14.35 nCi / 31860 dpm

Preparation Analyst: _____ **Date:** _____

Instrument Analyst: _____ **Date:** _____

LIMS Entry By: _____ **Date:** _____

Reviewed and LIMS QA By: _____ **Date:** _____

Note: Reviewer is responsible for checking the entire data package and may choose to sign only the front cover sheet.

Benchmark Analytics, Inc. Document Training Sheet

Document Number: RA 003

Revision Number: 20

Document Title: Ra-228

Please enter the names, and dates of people who read and understood the above described document revision. Have each person sign after their name to make this an official record of training and their understanding that they are now required to use this document. Please return this form to the quality assurance department.

Date	Name (printed)	Signature
2-9-10	Dominic Gehrer	
02-11-2010	Jason R Ackerman	
2-11-10	Chris Medel	
02-15-10	Tabbi Barnes	
02-15-10	Brigitte Hagman	

QUALITY ASSURANCE PROJECT PLAN (QAPP) –ENG ADDENDUM

CRRA STEWARDSHIP PROGRAM

CRRA- Shelton Landfill
EPA ID No. CTD000604546
866 River Road
Shelton, Connecticut

March 12, 2010

Prepared For:

Connecticut Resources Recovery Authority
100 Constitution Plaza
Hartford, Connecticut 06106

Prepared By:

HRP Associates, Inc
197 Scott Swamp Road
Farmington, Connecticut

TABLE OF CONTENTS

CRRA Corporate Stewardship QAPP
Shelton Landfill

SECTION **PAGE**

1. Title and Approval Page

CRRA STEWARDSHIP PROGRAM QUALITY ASSURANCE PROJECT PLAN (QAPP)
SHELTON LANDFILL, RIVER ROAD
SHELTON, CONNECTICUT

Stewardship Permit Number: DEP/HWM/CS-126-005

Prepared By: HRP Associates, Inc.
197 Scott Swamp Road
Farmington, Connecticut 06032

Preparer: _____
Signature

_____
Print Name/Date

Project Manager: _____
Signature

_____
Print Name/Date

Project QA Officer: _____
Signature

_____
Print Name/Date

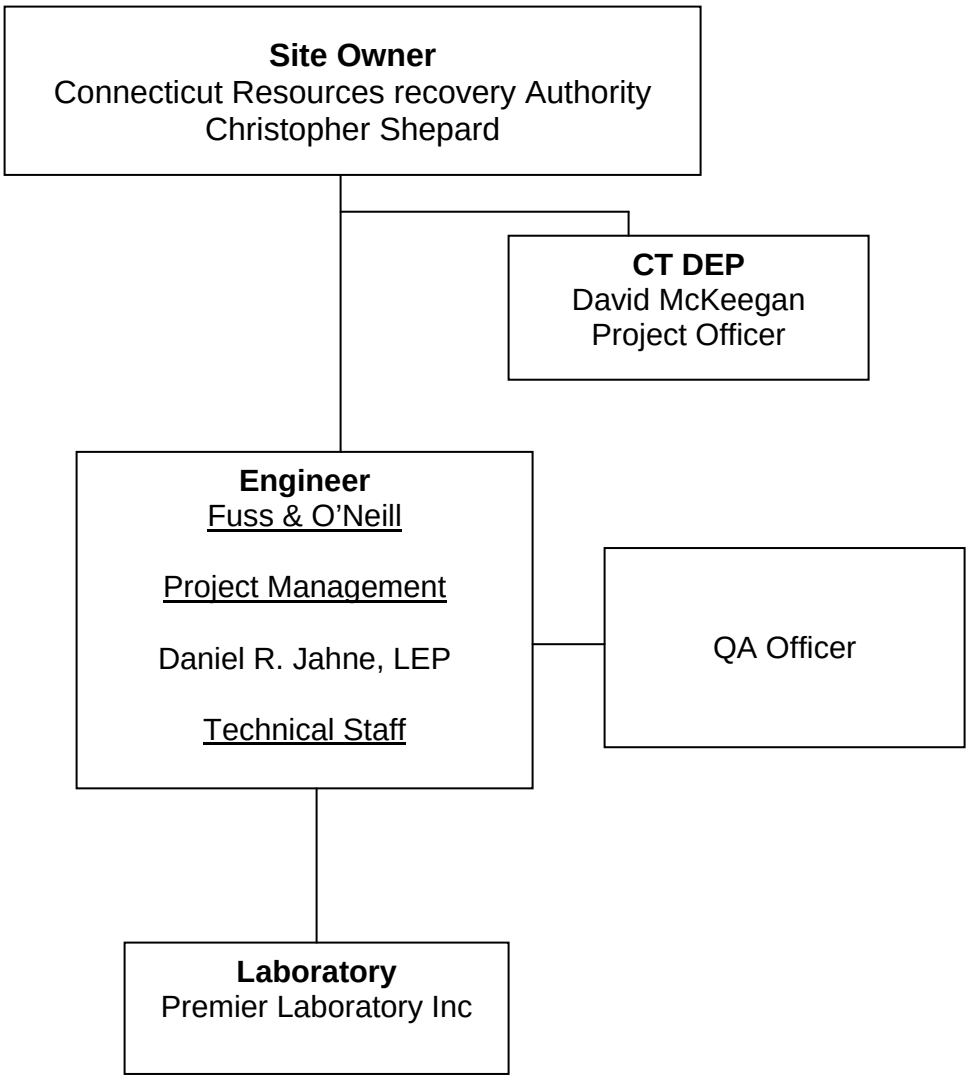
CRRA Representative: _____
Signature

Christopher R. Shepard, P.E.
Print Name/Date

CT DEP: _____
Signature

_____
Print Name/Date

2. Project Organization and Responsibility



A form with individual contact telephone and email address information will be included with each site specific QAPP.

3. Problem Definition

(Refer to Generic QAPP-GEN)

4. Project Description

(Refer to Generic QAPP-GEN)

5. Sampling Design and Site Figures

(Refer to Generic QAPP-GEN)

6. Sampling and Analytical Methods Requirements

(Refer to Generic QAPP-GEN and site-specific QAPP-LAB addendum)

7. Method and SOP Reference Tables

(Refer to Generic QAPP-GEN and site-specific QAPP-LAB addendum)

8. Field Equipment Calibration and Corrective Action
(Refer to Generic QAPP-GEN)

9. Laboratory Equipment Calibration and Corrective Action

(Refer to site-specific QAPP-LAB addendum)

10. Sample Handling and Custody Requirements

(Refer to site-specific QAPP-LAB addendum)

11. Analytical Sensitivity and Project Criteria

(Refer to Generic QAPP-GEN and site-specific QAPP-LAB addendum)

12. Field Quality Control Requirements

(Refer to Generic QAPP-GEN)

13. Laboratory Quality Control Requirements

(Refer to site-specific QAPP-LAB addendum)

14. Data Management and Documentation

(Refer to Generic QAPP-GEN)

15. Assessment and Response Actions

(Refer to Generic QAPP-GEN)

16. Project Report

(Refer to Generic QAPP-GEN)

17. Field Data Evaluation

(Refer to Generic QAPP-GEN)

18. Laboratory Data Evaluation

(Refer to Generic QAPP-GEN)

19. Data Usability and Project Evaluation

(Refer to Generic QAPP-GEN)

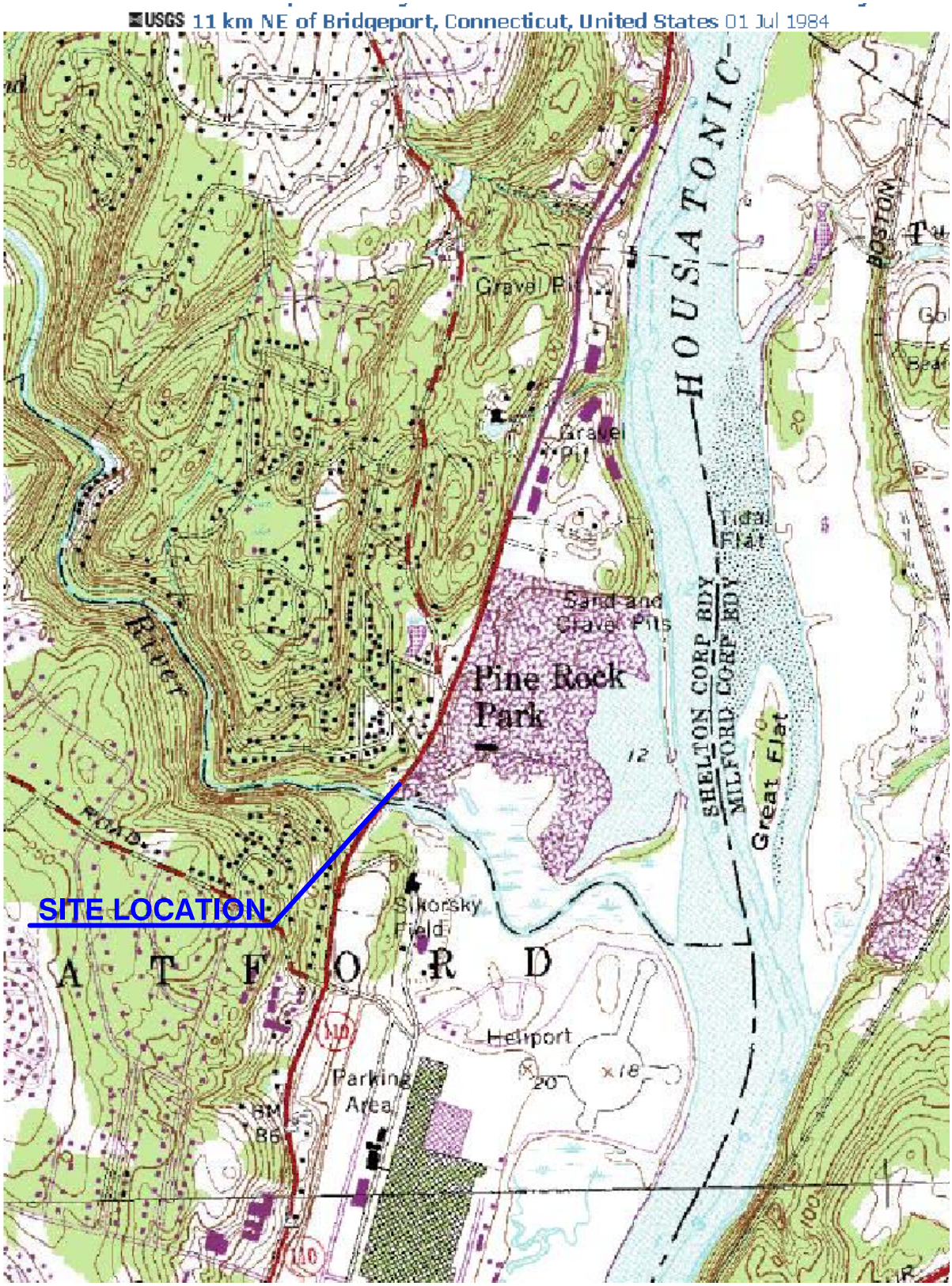
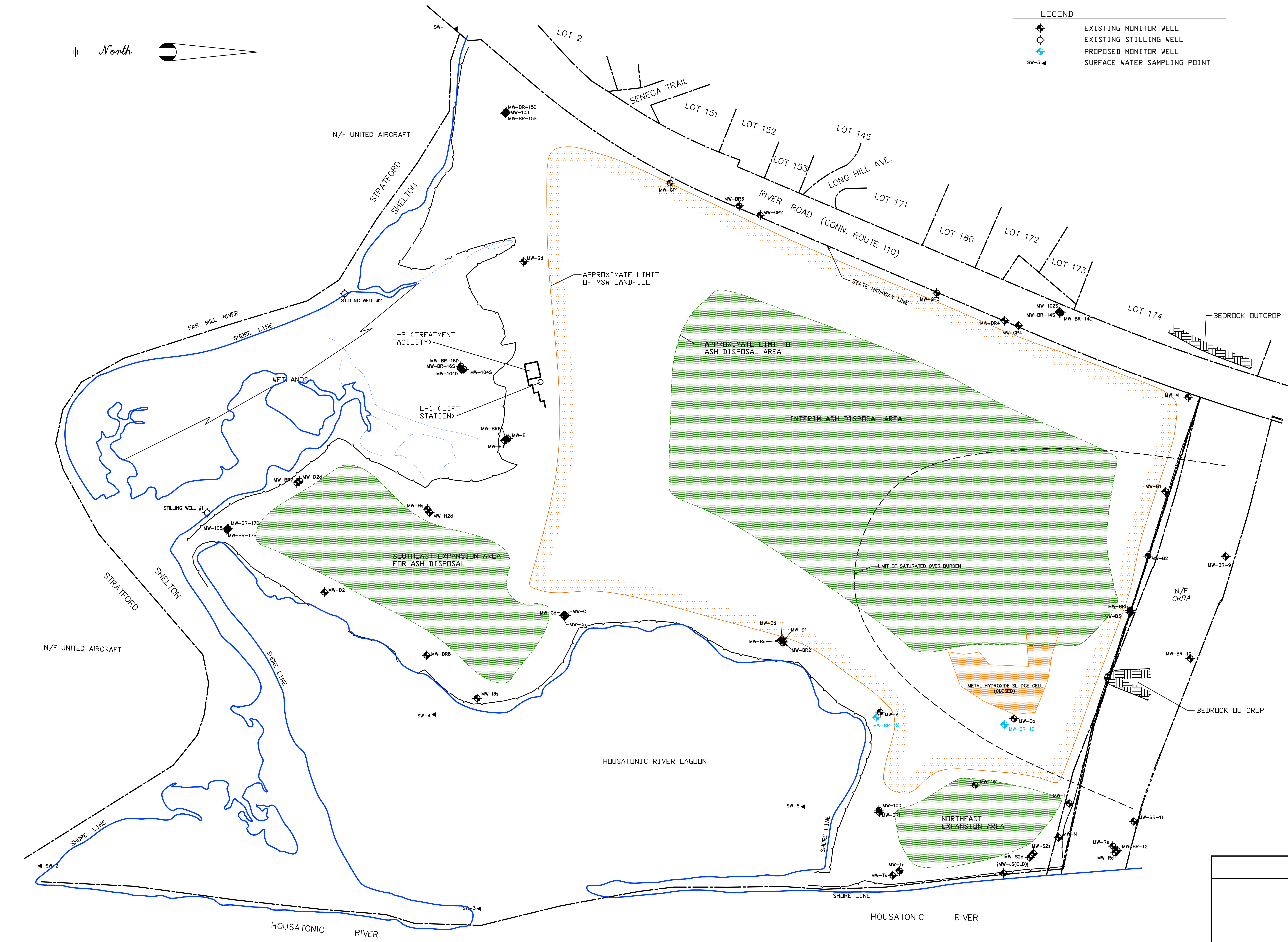


Image courtesy of the U.S. Geological Survey

North

FIGURE 1
SITE LOCATION
CRRA SHELTON LANDFILL
RIVER ROAD
SHELTON, CT
HRP# CRR0149.GW

J:\C\CRRAU - CT RESOURCES RECOVERY AUTHORITY\RIVER RD, SHELTON\CRR0149GW\CAD\FIGURE 1 - SITE LOCATION.dwg, Layout1, 3/12/2010 3:04:03 PM, Adobe



REVISIONS

NO.	DATE	DESCRIPTION
1	3-02-10	ADDED MW-BR-18 & 19

SITE PLAN

CRRA SHELTON LANDFILL

RIVER ROAD (ROUTE 110)
SHELTON, CONNECTICUT

HRP Associates, Inc.
Environmental/Civil Engineering & Hydrogeology
Creating the Right Solutions Together
Connecticut, New York, South Carolina, Florida, Indiana
197 Scott Swamp Road
Farmington, Connecticut 06032
Ph:(860)674-9570 Fax:(860)674-9624
www.hrpassociates.com

GTS DESIGNED	BPW APPROVED	1" = 120'± SCALE
BOB DRAWN	2/23/10 DATE	FIG. 2 SHEET NO.
GTS CHECKED	CRR0149.GW PROJECT NO.	

J:\C\CRRAU - CT RESOURCES RECOVERY AUTHORITY\RIVER RD, SHELTON\CRR0149GW\CAD\FIGURE 2 - SITE PLAN - REV 3-02-10.dwg, Layout1, 3/12/2010 4:03:35 PM, DWG To PDF.pc3, Plot stamp

CRRA STEWARDSHIP PROGRAM

QUALITY ASSURANCE PROJECT PLAN
(QAPP)

FOR

WALLINGFORD LANDFILL
(Permit #DEP/HWM/CS-148-004)
PENT ROAD
WALLINGFORD, CT

HRP #CRR0148.GW

PREPARED FOR: **Connecticut Resourcess Recovery Authority**
100 Constitution Plaza, 6th Floor
Hartford, CT 06103-1722
c/o Mr. Christopher R. Shepard, P.E.

ISSUED ON: **March 12, 2010**

TABLE OF CONTENTS

CRRA Corporate Stewardship QAPP
Wallingford Landfill

SECTION **PAGE**

FIGURES

APPENDICES

Title and Approval Page

CRRA STEWARDSHIP PROGRAM QUALITY ASSURANCE PROJECT PLAN (QAPP)
WALLINGFORD LANDFILL, PENT ROAD
WALLINGFORD, CONNECTICUT

Stewardship Permit Number: DEP/HWM/CS-148-004

Prepared By: HRP Associates, Inc.
197 Scott Swamp Road
Farmington, Connecticut 06032

Date: March 15, 2010

Preparer: Zoe A. Belcher
Signature

for Joanna L. Wozniak
Print Name/Date

Project Manager: Zoe A. Belcher
Signature

Zoé A. Belcher, LG, LEP
Print Name/Date

Project QA Officer: _____
Signature

Tom Sicilia
Print Name/Date

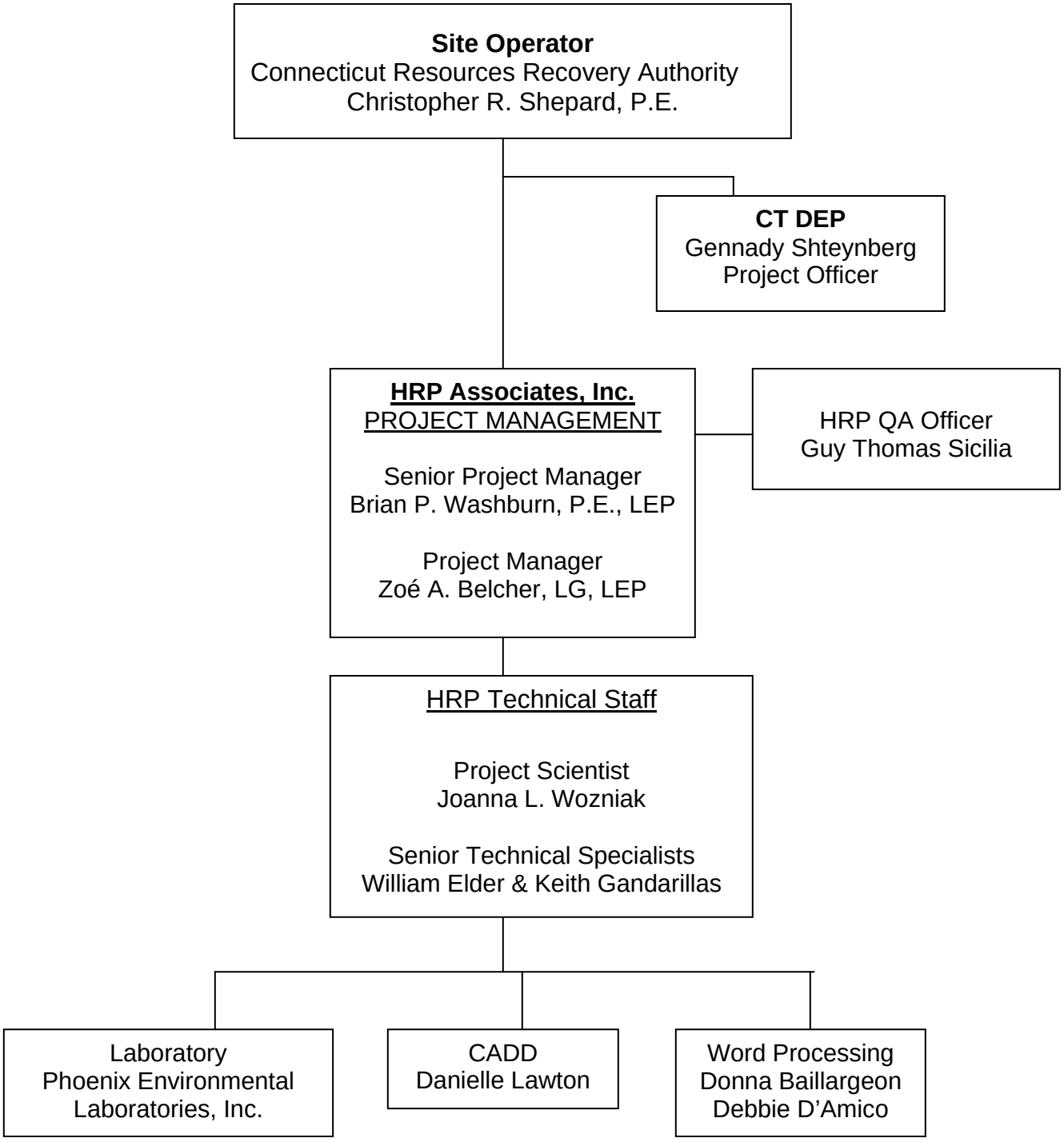
CRRA Representative: _____
Signature

_____
Print Name/Date

CT DEP: _____
Signature

_____
Print Name/Date

2. Project Organization and Responsibility



3. Problem Definition

The Wallingford Landfill is located along the Quinnipiac River, approximately 1.0 mile north of the Wallingford/North Haven town line (Figure1). The site is bounded on the north by the Wallingford Sewage Treatment Plant and the Town of Wallingford Recycling and Leaf Composting Area, on the east by South Cherry Street and Pent Road, on the south by the Former Barberino Property, which is now vacant land that is owned by Connecticut Resources Recovery Authority (CRRA), and on the west by the Quinnipiac River (Figure 2). Cytec Industries (formerly American Cyanamid) is located to the south of the former Barberino property. Industrial land use occurs on the east side of South Cherry Street and Pent Road.

Topography on the landfill property ranges from 20 feet above mean sea level (amsl), on the west portion of the site, along the Quinnipiac River to approximately 120 feet amsl at the peak of the landfill (Figure 2). From this point, the land slopes down to the east to an elevation of approximately 40 feet amsl along Pent Road.

The Town of Wallingford began operation of the 82-acre landfill in the early 1950s, which it opertad prior to September 4, 1988. Since that time, (CRRA) has leased the landfill property from the Town of Wallingford consistent with the start-up operations of the Wallingford Waste-to-Energy Facility, converting municipal solid waste to ash residue. From September 1988 to November 1995, ash residue as well as solid waste residue was placed at the landfill. Since 2000, there have been no daily activities at the landfill except for the operation by the Town of a resident drop off area and bulky waste transfer station at the front of the landfill. Wallingford Landfill is now closed and is no longer accepting waste. Pursuant to the lease between CRRA and the Town, CRRA is responsible for the post-closure maintenance and monitoring of the Landfill. The final area of the Landfill was closed in 2002 and Connectictu Department of Environmental Protection (CTDEP) certification of closure was received in February 2005.

The 82-acre Wallingford Landfill is divided into the following five parts: Emergency Bypass/Non-Processibles Area, Ash Residue Area, Former Bulky Waste Area, MSW Area, and Metal Hydroxide Sludge Cell Area.

In 2001, CRRA purchased the Former Barberino Property adding it to the Landfill parcel, to gain monitor of the southern edge of the leachate plume. Prior to CRRA's purchase, the Former Barberino Property was developed with a trailer park and residential dwellings which were served by an on-site domestic well and septic system. The trailer park was developed on-site between 1951 and 1957. All structures on the 45-acre lot have been demolished and the Site is currently vacant. The Former Barberino Property is therefore part of the "Site," as defined in the Stewardship Permit that has been issued to CRRA by CTDEP, but it is specifically excluded from the definition of "Facility" because no hazardous waste or solid waste treatment, storage or disposal activities have ever been conducted on the Former Barberino Property.

The site is underlain by two overburden aquifers (the upper aquifer and the lower aquifer) separated by a thick varved clay layer. Groundwater flow from the upper aquifer is towards the Quinnipiac River, while flow in the lower aquifer is towards a pumping industrial well lo-

cated along the southern boundary of the Former Barberino Property. This well is actively operated by Cytec Industries.

The groundwater beneath the Site is mapped by the CTDEP (1993) as "GC". Groundwater classified as "GC" has been authorized to receive a discharge with approval from CTDEP in accordance with all regulatory requirements. Groundwater in this area is not suitable for human consumption and can be used for assimilation of the authorized discharges (CTDEP, 2002).

The groundwater to the north and south of the Site is mapped by the CTDEP (1993) as "GB." Such groundwater may not be suitable for human consumption without treatment due to waste discharges, spills, leaks of chemicals, or land use impacts (CTDEP, 2002).

The Quinnipiac River flows in a southerly direction along the western side of the Site. The unnamed stream flows in a southwesterly direction off of the former Barberino Property and is a tributary to the Quinnipiac River.

The closest surface water body, the Quinnipiac River, is mapped by the CTDEP (1993) as "C/B" (Figure 5). Such inland surface waters are known or presumed to not be suitable for the following designated uses: recreational use, fish and wildlife habitat, agricultural and industrial supply, and other legitimate uses (CTDEP, 2002).

The unnamed tributary is mapped by the CTDEP (1993) as "A." Inland surface waters classified by the CTDEP as "A" are those known or presumed to meet Class "A" Water Quality Criteria that support the following designated uses: potential drinking water supply; fish and wildlife habitat; recreational use; agricultural, industrial supply and other legitimate uses, including navigation (CTDEP, 2002).

4. Project Description

A total of twenty-one monitoring groundwater monitoring wells are included in the groundwater monitoring system. Located within the upper aquifer, these wells range from approximately 10 to 70 feet deep. Thirteen of the monitoring wells are located on the Wallingford Landfill property, while 8 monitoring wells are located on the Former Barberino Property.

Monitoring well completion details are summarized in Table 1. The locations of the wells are presented on Figure 2.

TABLE 1
Summary of Monitoring Well Construction

Well Number	Dedicated Sampling Apparatus	Ground Elevation (feet)	Top of Steel Elevation (feet)	Measured Well Depth[b] (feet)	Well Bottom Elevation (feet)	Date of Installation
MW-1A	Tubing	58.50	62.37	26.77	35.60	09/01/81
MW-2A	Tubing	59.50	61.13	32.05	29.08	11/01/88
MW-3	Tubing	22.60	23.59	11.90	11.69	09/01/81
MW-4R	Tubing	42.10	43.87	22.17	21.70	07/01/92
MW-5	Tubing	25.80	27.48	9.95	17.53	09/01/81
MW-9	Tubing	43.90	46.01	33.15	12.86	05/01/86
MW-10	Tubing	36.20	36.82	40.75	-3.93	05/01/86
MW-10A	Tubing	37.00	37.23	20.40	16.83	05/01/86
MW-11	Bladder Pump	49.80	51.12	72.55	-21.43	11/01/88
MW-13	Tubing	61.00	65.68	37.45	28.23	12/01/88
MW-100	Bladder Pump	51.70	53.90	40.62	13.28	11/01/83
MW-101R	Bladder Pump	54.50	55.84	40.37	15.47	07/01/92
MW-200	Tubing	29.10	30.64	14.45	16.19	12/01/88
CEE-3	Tubing	N/A	31.46	13.88	17.58	11/11/92
CEE-4	Tubing	N/A	30.37	14.54	15.83	03/26/93
CEE-5	Tubing	N/A	37.82	14.13	23.69	03/25/93
CEE-6	Tubing	N/A	34.95	14.02	20.93	03/29/93
CEE-7	Tubing	N/A	30.88	14.87	16.01	03/26/93
CEE-8	Tubing	N/A	29.05	14.80	14.25	03/29/93
CEE-9	Tubing	N/A	27.99	14.52	13.47	03/26/93
CEE-10	Tubing	N/A	32.15	14.82	17.33	03/29/93

[a] Historical depth to bottom of well casing [b] As measured from top of steel casing in October 2009
Wells designated "CEE-__" are located on the former Barberino property. All other wells are located on the Wallingford Landfill property.
N/A = Not Available

A synoptic groundwater measurement will be completed on the first day of each semi-annual monitoring event to determine the groundwater elevations at all sampled monitoring wells prior to any purging and sampling activities. At each monitoring well, the depth to groundwater and the depth to the bottom of the will be measured with either an electronic water level indicator or a steel tape accurate to within 0.01 feet. All measurements will be made relative to the surveyed data point at each well, i.e., the top of the PVC casing (Table 1).

The water level measuring device will be decontaminated between monitoring wells to ensure that cross-contamination does not occur. The decontamination will consist of rinsing the measuring device with deionized water.

The following sample collection procedures will be followed during each sampling event:

- A "Monitoring Well Field Data Sheet" which summarizes well elevation data, well condition, purge data, observed water yield and quality comments, sampling data, and results of measured field parameters will be completed for each well sampled (Appendix A).

- Measure depth to water, depth to bottom, depth of sample using decontaminated equipment referenced to top of PVC (or casing) and record on the data sheet.

- Provide an in-line meter (or equivalent methodology which mitigates exposure to the atmosphere) to concurrently measure pH, temperature, specific conductivity, dissolved oxygen (DO), and redox potential (RP), as applicable, during purging. Also, provide a device to measure turbidity. A minimum of four readings of each parameter shall be taken and recorded during purging.

- Perform purging using dedicated bladder pump equipment [at three of the sampled wells] or a peristaltic pump with dedicated tubing [at eighteen of the sampled wells] at low flow rates, not taking the first reading until at least one pump volume plus one discharge tubing volume have passed. The purged groundwater may be discharged to the ground. Sampling personnel are to monitor the drawdown in the wells and ensure that the drawdown is maintained at less than or equal to 0.3 feet during the entire purging and sampling process. If drawdown cannot be maintained at the lowest achievable flow rate, it should be noted as such on the Monitoring Well Field Data Sheets. Wells shall be purged at a rate of less than or equal to 300 ml/minute. Field parameter readings shall be recorded at a minimum of 5 minute intervals, until turbidity is stabilized such that three consecutive reading are within 10% of each other for readings >5 NTU, or readings are within 2 NTU of each other for readings <5 NTU. Per US EPA Region I Standard Operating Procedure GW-0001 – "Low Stress (Low Flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells" (January 19, 2010-Revision 3), if the turbidity has not stabilized after 4 hours of purging, collect samples and provide full explanation of attempt to achieve stabilization. Provide a summary of periodic readings and time of reading for all parameters.

- Sample collection should proceed from high parameter volatility to low parameter volatility at a low flow rate. Samples for volatile parameters should be transferred slowly to the sample container to eliminate creation of air bubbles. Samples are to be collected in proper containers and properly preserved in the field, as summarized in Section 6.

- No filtering of samples is to occur, <u>except</u> where analysis of dissolved metals is specified, i.e. surface water samples. Where analysis of dissolved metals is specified, sam-

ple filtration is to be performed in the field during sample collection with an in-line 0.45-micron filter.

- All observations relating to the well sampling, well conditions and any deviations from the sampling plan are to be recorded on the Monitoring Well Field Data Sheet.

4a. Project Timeline

Activities (list products)	Dates	
	Activity Start	**Activity End**
Sampling (groundwater & surface water)	Semi-annual to occur first week of April and October each year	Approximately two to three working days after activity start date
Reporting to CTDEP	Immediately following sampling	Within sixty calendar days following the last day of sampling

5. Sampling Design and Site Figures

In order to fulfill the requirements of the Stewardship Permit, CRRA will sample groundwater and surface water at the site to monitor the leachate plume at the site. In order to achieve this, CRRA will sample on-site wells near each area of concern on a semi-annual basis. The sampling regime is described in the table below. Each well location is presented on Figure 2.

Table 3
Well-Specific Monitoring Parameters

Notes: S= Analyzed semi-annually in April and October A= Analyzed annually in April	Wallingford Landfill													Former Barberino Property							
	MW-1A	MW-2A	MW-3	MW-4R	MW-5	MW-9	MW-10	MW-10A	MW-11	MW-13	MW-100	MW-101R	MW-200	CEE-3	CEE-4	CEE-5	CEE-6	CEE-7	CEE-8	CEE-9	CEE-10
Field Parameters																					
Depth to Water	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Water Elevation (msl)	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
pH	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Temperature	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Specific Conductivity	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Dissolved Oxygen	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Redox Potential	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Turbidity	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Leachate Indicator Parameters																					
Alkalinity, Total	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Total Dissolved Solids (TDS)	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Hardness	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Biochemical Oxygen Demand (BOD)	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Chemical Oxygen Demand (COD)	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Chloride	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Nitrate	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Ammonia (N)	-	-	S	S	S	-	-	S	-	-	S	S	-	-	-	-	-	-	-	-	-
Cyanide, Total	-	-	-	-	-	-	-	-	S	-	S	S	-	-	-	-	-	-	-	S	S
Sulfate, Total	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Total Suspended Solids (TSS)	S	S	S	S	S	S	S	S	S	S	S	S	A	S	S	S	S	S	S	S	S
Metals, Total																					
Arsenic	S	S	S	S	S	S	S	S	S	S	S	S	-	S	S	S	S	S	S	S	S
Chromium, Total	S	S	S	S	S	S	S	S	S	S	S	S	-	S	S	S	S	S	S	S	S
Copper	S	S	S	S	S	S	S	S	S	S	S	S	-	S	S	S	S	S	S	S	S
Iron	S	S	S	S	S	S	S	S	S	S	S	S	-	S	S	S	S	S	S	S	S
Lead	S	S	S	S	S	S	S	S	S	S	S	S	-	S	S	S	S	S	S	S	S
Managanese	S	S	S	S	S	S	S	S	S	S	S	S	-	S	S	S	S	S	S	S	S
Nickel	S	S	S	S	S	S	S	S	S	S	S	S	-	S	S	S	S	S	S	S	S
Potassium	S	S	S	S	S	S	S	S	S	S	S	S	-	S	S	S	S	S	S	S	S
Sodium	S	S	S	S	S	S	S	S	S	S	S	S	-	S	S	S	S	S	S	S	S
Zinc	S	S	S	S	S	S	S	S	S	S	S	S	-	S	S	S	S	S	S	S	S
Dioxins/Furans																					
Method 1613B	-	-	A	-	-	-	-	-	-	-	-	-	A	-	-	-	-	-	-	-	-

Notes: S= Analyzed semi-annually in April and October	Annual Surface Water Sampling Wallingford, CT									
	SW-1	SW-2	SW-3	SW-4	SW-5	SW-6	SW-9	SW-10	SW-11	SW-12
Field Parameters										
pH	S	S	S	S	S	S	S	S	S	S
Temperature	S	S	S	S	S	S	S	S	S	S
Turbidity	S	S	S	S	S	S	S	S	S	S
Redox Potential	S	S	S	S	S	S	S	S	S	S
Dissolved Oxygen	S	S	S	S	S	S	S	S	S	S
Specific Conductivity	S	S	S	S	S	S	S	S	S	S
Leachate Indicator Parameters										
Alkalinity	S	S	S	S	S	S	S	S	S	S
COD	S	S	S	S	S	S	S	S	S	S
Hardness	S	S	S	S	S	S	S	S	S	S
Sulfate	S	S	S	S	S	S	S	S	S	S
Total Dissolved Solids - TDS	S	S	S	S	S	S	S	S	S	S
Total Suspended Solids -TSS	S	S	S	S	S	S	S	S	S	S
Ammonia as N	S	S	S	S	S	S	S	S	S	S
Dissolved Metals										
Aluminum	S	S	S	S	S	S	S	S	S	S
Arsenic	S	S	S	S	S	S	S	S	S	S
Barium	S	S	S	S	S	S	S	S	S	S
Beryllium	S	S	S	S	S	S	S	S	S	S
Cadmium	S	S	S	S	S	S	S	S	S	S
Chromium, Total	S	S	S	S	S	S	S	S	S	S
Copper	S	S	S	S	S	S	S	S	S	S
Iron	S	S	S	S	S	S	S	S	S	S
Lead	S	S	S	S	S	S	S	S	S	S
Magnesium	S	S	S	S	S	S	S	S	S	S
Manganese	S	S	S	S	S	S	S	S	S	S
Mercury	S	S	S	S	S	S	S	S	S	S
Nickel	S	S	S	S	S	S	S	S	S	S
Potassium	S	S	S	S	S	S	S	S	S	S
Sodium	S	S	S	S	S	S	S	S	S	S
Selenium	S	S	S	S	S	S	S	S	S	S
Silver	S	S	S	S	S	S	S	S	S	S
Thallium	S	S	S	S	S	S	S	S	S	S
Vanadium	S	S	S	S	S	S	S	S	S	S
Zinc	S	S	S	S	S	S	S	S	S	S

6. Sampling and Analytical Methods Requirements

The following tables summarize sampling and analytical protocols that may be utilized during the semi-annual monitoring program.

Groundwater				Containers per Sample			Preservation Requirements			
Parameter	Matrix	Number of Samples (including Field QC)	Analytical Method*	No.	Size	Type	Temp.	Light Sensitive	Chemical	Maximum Holding Time
Total Dissolved Solids	Water	41 Groundwater 20 Surface Water 4 Duplicates	SM2540C	1	100 ml	plastic	Cool to 4 ± 2º C	No	None	7 days
Total Suspended Solids	Water	41 Groundwater 20 Surface Water 4 Duplicates	SM2540D	1	100 ml	plastic	Cool to 4 ± 2º C	No	None	7 days
Alkalinity	Water	41 Groundwater 20 Surface Water 4 Duplicates	SM2320B	1	100 ml	plastic	Cool to 4 ± 2º C	No	None	14 days
Hardness	Water	41 Groundwater 20 Surface Water 4 Duplicates	EPA 200.7	1	100 ml	plastic	Cool to 4 ± 2º C	No	HNO3 pH <2	6 months
Biochemical Oxygen Demand (BOD)	Water	41 Groundwater 2 Duplicate	SM5210B	1	500 mL	plastic	Cool to 4 ± 2º C	No	None	24 Hours
Chemical Oxygen Demand (COD)	Water	41 Groundwater 20 Surface Water 4 Duplicates	SM5220D	1	50 ml	plastic	Cool to 4 ± 2º C	No	H2SO4 pH<2	28 Days
Chloride	Water	41 Groundwater 2 Duplicate	EPA 300.0	1	120 mL	Plastic	Cool to 4 ± 2º C	No	None	28 Days
Nitrate	Water	41 Groundwater 2 Duplicate	EPA 300.0	1	50 mL	plastic	Cool to 4 ± 2º C	No	None	48 Hours
Ammonia as N	Water	12 Groundwater 20 Surface Water 4 Duplicates	Method 4500-NH3 B. and G.; Method 4500-Norg B	1	250 mL	plastic	Cool to 4 ± 2º C	No	H2SO4 pH<2	28 Days
Sulfate	Water	41 Groundwater 20 Surface Water 4 Duplicates	EPA 300.0	1	50 mL	Plastic	Cool to 4 ± 2º C	No	None	28 Days
Cyanide	Water	10 Groundwater	EPA 335.4-9010	1	100 ml	Plastic	Cool to 4 ± 2º C	No	NaOH	28 days
Metals (Total)	Water	41 Groundwater 2 Duplicate	EPA 6010-200.7	1	250 mL	Plastic	Cool to 4 ± 2º C	No	HNO3 pH <2	6 Months
Metals (Dissolved)	Water	20 Surface Water 2 Duplicate	EPA 6010-200.7	1	250 mL	plastic	Cool to 4 ± 2º C	No	Field filter with 0.45 um filter, then HNO3 pH <2	6 Months
Mercury (Dissolved)	Water	20 Surface Water 2 Duplicate	EPA 245.1	1	250 mL	plastic	Cool to 4 ± 2º C	No	Field filter with 0.45 um filter, then HNO3 pH <2	28 Days
Polychlorinated Dibenzo-p-Dioxins and Poly-chlorinated Dibenzofurans	Water	2 Groundwater	1613B	2	1 L	Amber glass bottle with Teflon lined cap	Cool to 4 ± 2º C	Yes	None	1 Year

* Analytical Methods in accordance with CT DEP Reasonable Confidence Protocol (where applicable).

7. Method and SOP Reference Tables

The following table presents all of the analytical methods, Phoenix Laboratory Standard Operating Procedures (SOPs), sample preparation methods, and Phoenix's sample preparation SOPs for all of the parameters listed. A copy of each of the laboratory SOPs referenced below is included in Appendix B.

Analytical Method Reference					Laboratory SOP Reference					
SOP Ref.	**Analytical Method**	**Document Title**	**Revision Number**	**Date**	**SOP Ref.**	**Document Title**	**Date**	**Revision Number**	**SOP Reference Number**	**Author's Name**
1A	SW-846 Method 6010B	"Recommended Reasonable Confidence Protocols Quality Assurance and Quality Control Requirements Determination of Trace Metals By SW-846 Method 6010 Inductively Coupled Plasma-Atomic Emission Spectrometry"	2.0	July 2006	1B	"Determination of Trace Elements by Inductive Coupled Argon Plasma (ICP Spectroscopy (AR-COS)"	5/6/09	1	505	
2A	SW-846 Method 300.0	"Determination Of Inorganic Anions by Ion Chromatography"	2.1	August 1993	2B	"Ion Chromatography for the Analysis of Anions"	1/11/10	2	301.300.0	
3A	Method 4500-NH3 B. and G.; Method 4500-Norg B.; Methods for QuikChem Automated Ion Analyzer	"Standard Methods for the Examination of Water and Wastewater; Method 4500-Norg B., C.; Methods for QuikChem Automated Ion Analyzer"	20	1997	3B	"Ammonia/TKN Phenate Method"	4/30/09	8	304.4500NH3 G	
4A	SW-846 Method 335.4	"Determination of Total Cyanide by Semi-Automated Colorimetry"	1.0	August 1993	4B	"Total, Amenable, and Free Cyanide"	1/20/10	6	309.335.4	
5A	SW-846 Method 9010	"Total and Amenable Cyanide: Distillation"	3.0	November 2004	5B	"Total, Amenable, and Free Cyanide"	1/20/10	6	309.335.4	

Analytical Method Reference					Laboratory SOP Reference					
SOP Ref.	**Analytical Method**	**Document Title**	**Revision Number**	**Date**	**SOP Ref.**	**Document Title**	**Date**	**Revision Number**	**SOP Reference Number**	**Author's Name**
6A	Method 200.7	“Determination of Metals and Trace Elements in Water and Wastes by Inductively Coupled Plasma-Atomic Emission Spectrometry”	4.4	1994	1B, 6B	“Determination of Trace Elements by Inductive Coupled Argon Plasma (ICP Spectroscopy (AR-COS)” and “Hardness Determination by Calcula-tion”	5/6/09, 12/20/07	1, 2	505, 225.2340B	
7A	SM2540C	“Total Dissolved Solids Dried at 180^{o}C”		1997	7B	“Total Dissolved Solids”	11/10/09	3	323.2540C	
8A	SM2540D	“Total Suspended Solids Dried at 103–105°C”		1997	8B	“Total Suspended Solids (TSS) dried at 103°-105°C”	1/15/10	4	324.2540D	
9A	SM2320B	“Titration Method”		1997	9B	“Total Alkalinity”	6/11/07	6	305.2320B	
10A	SM5210B	“5-Day BOD Test”		1999	10B	“Biological Oxygen Demand (BOD and cBOD)	12/28/09	4	306.5210B	
11A	SM5220D	“Chemical Oxygen Demand (COD)”		1997	11B	“Chemical Oxygen Demand (COD)”	7/5/07	3	311.5220D	
12A	EPA 1613B	“Tetra- through Octa-Chlorinated Dioxins and Furans by Iso-tope Dilution HRGC/HRMS”	B	October 1994	12B	“Preparation and Analysis of Samples for the Determination of Dioxins and Furans by USEPA Method 1613B”	9/28/09	13	S-MN-H-OOZ-Rev. B	SAC
13A	EPA 245.1	"Recommended Reasonable Confidence Protocols Quality Assurance and Quality Control Requirements Determination of Mercury By SW-846 Methods 7470/7471 Cold Vapor Atomic Absorption Spectroscopy"	2.0	July 2006	13B	“Determination of Mercury by Automatic Cold Vapor Atomic Absorption:	10/15/09	5	503.HG	

HRP has incorporated the appropriate ASTM standards as our Standard Field Investigation and Sampling Operation Procedures. A copy of each ASTM standard is maintained at HRP and updated as newer versions are issued. All HRP personnel have reviewed these standards and are aware of where they are housed at HRP.

SOP Ref.	Document Title	Date
1.0	D4750-87R01 Test Method for Determining Subsurface Liquid Levels in a Borehole or Monitoring Well (Observation Well)	1987 (Reapproved 2001)
2.0	D5088-02 Practices for Decontamination of Field Equipment Used at Waste Sites	2002 (Reapproved 2008)
3.0	D5978-96R05 Guide for Maintenance and Rehabilitation of Ground-Water Monitoring Wells	1996 (Reapproved 2005)
4.0	D6089-97R03E01 Guide for Documenting a Ground-Water Sampling Event	1997 (Reapproved 2003)
5.0	D6452-99R05 Guide for Purging Methods for Wells Used for Ground-Water Quality Investigations	1999 (Reapproved 2005)
6.0	D6517-00R05 Guide for Field Preservation of Ground-Water Samples	2000 (Reapproved 2005)
7.0	D6564-00R05 Guide for Field Filtration of Ground-Water Samples	2000 (Reapproved 2005)
8.0	D6634-01R06 Guide for the Selection of Purging and Sampling Devices for Ground-Water Monitoring Wells	2001 (Reapproved 2006)
9.0	D6771-02 Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations	2002
10.0	D6911-03 Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis	2003
11.0	D7069-04 Guide for Field Quality Assurance in a Ground-water Sampling Event	2004
12.0	D0888-05 Test Methods for Dissolved Oxygen in Water	2005
13.0	D1067-06 Test Methods for Acidity or Alkalinity of Water	2006

SOP Ref.	Document Title	Date
14.0	D1125-95R05 Test Methods for Electrical Conductivity and Resistivity of Water	1995 (Reapproved 2005)
15.0	D1293-99R05 Test Methods for pH of Water	1999 (Reapproved 2005)
16.0	D1498-07 Test Method for Oxidation-Reduction Potential of Water	2007 (Revised 2008)
17.0	D4453-02R06 Practice for Handling of Ultra-Pure Water Samples	2002 (Reapproved 2006)
18.0	D4840-99R04 Guide for Sample Chain-of-Custody Procedures	1999 (Reapproved 2004)
19.0	D6764-02R07 Guide for Collection of Water Temperature, Dissolved-Oxygen Concentrations, Specific Electrical Conductance, and pH Data from Open Channels	2002 (Reapproved 2007)
20.0	D4448-01R07 Guide for Sampling Ground-Water Monitoring Wells	2001 (Reapproved 2007)
21.0	D5358-93R03 Practice for Sampling with a Dipper or Pond Sampler	1993 (Reapproved 2003)
22.0	F1779-97R03 Practice for Reporting Visual Observations of Oil on Water	1997 (Revised 2008)
23.0	D7353-07 Practice for Sampling of Liquids in Waste Management Activities Using a Peristaltic Pump	2007
24.0	U.S. Environmental Rental Corp. YSI 6000 Series Calibration with the 650 MDS	Reviewed 2008
25.0	D6759-07 Practice for Sampling Liquids Using Grab and Discrete Depth Samplers	2007
26.0	US EPA Region I Standard Operating Procedure GW-0001 – “Low Stress (Low Flow) Purging and Sampling Procedure for the Collection of Groundwater Samples from Monitoring Wells”	1996 (Revised January 2010)

8. Field Equipment Calibration and Corrective Action

Instrument	Activity	Frequency	Acceptance Criteria	Corrective Action
pH meter	Calibration	Daily	N/A Compare to historical data when applicable	Recalibrate
Specific Conductance Meter	Calibration	Daily	N/A Compare to historical data when applicable	Recalibrate
ORP Meter	Calibration	Daily	–400 mV to 800 mV	Recalibrate
DO Meter	Calibration	Daily	Between 0 and 4 mg/l unless historically shown to be above 4 mg/l. Should not be negative.	Recalibrate Change Membrane
YSI 600 Series**	Calibration	Between Each Rental Checked Daily	Appendix C	Appendix C Cease use and Contact Rental Company to Recalibrate or Replace
Turbidity Meter**	Calibration	Between Each Rental Checked Daily	Appendix C Should NEVER be negative	Appendix C Cease use and Contact Rental Company to Recalibrate or Replace

** Rental Equipment
N/A – Not Applicable

9. Laboratory Equipment Calibration and Corrective Action

Copies of all of Phoenix's SOPs have been provided in Appendix B.

Instrument	Activity	Frequency	Acceptance Criteria	Corrective Action	SOP Ref.
ICP	Calibration	Daily or at the end of run	0.9975 correla-tion coefficient	Recalibrate	SOP#505
AA	Calibration	Daily	As above	Recalibrate	SOP#501
Hg Analyzer	Calibration	Daily	As above	Recalibrate	SOP#503
Lachat	Calibration	Daily	As above	Recalibrate	SOP#302
CF	Calibration	Daily	As above	Recalibrate	SOP#301

Acronym List:
AA: Atomic Absorption
CF: Calibration Factor
ICP: Inductively Coupled Plasma

10. Sample Handling and Custody Requirements

All samples will be collected in the appropriate containers and preserved according to the analytical method guidelines. Samples containers will be clearly labeled with the company name, job number, date, time, sampler's initial and sample identification (i.e., location, depth, etc.). Samples will be stored in coolers with ice until arrival at the laboratory. Holding times for various parameters are specified in the most recent promulgated method for the requisite analytical parameter. Questions on holding times will be directed to the analytical laboratory.

All samples will be tracked via a chain-of-custody (COC, Appendix A). The chain of custody will include job number, date, time, sample identification (i.e., location, depth, etc.), and parameters to be analyzed. Each individual handling the sample must sign the COC. The original COC will remain with the sample through out the duration of the sampling event and will be kept in the permanent project file. Copies of the COC will be distributed to the working project file, laboratory manager, and the data package. When required, the contract laboratory will follow the CTDEP's Final Reasonable Confidence Protocols (RCP), approved on August 21, 2006; therefore the RCP worksheet will accompany the COC (Appendix A).

At the laboratory, the samples are set up on the counter in the sample receiving area and checked against chain of custody. If all bottles agree with the chain of custody, the chain of custody is signed and the samples are logged into the laboratory LIMS system. Phoenix sample numbers are assigned and printed out on waterproof labels. The labels are then affixed to the corresponding sample bottles. The samples are brought to the walk-in cooler where they are stored at 4 degrees C in numerical order. The chain of custody is then scanned into the LIMS system for permanent record. The physical copy of the chain of custody is then checked against what has been logged in the LIMS system as a double check.

11. Analytical Sensitivity and Project Criteria

Analyte	Matrix	Units	Reporting Limit	MDL	Precision	Accuracy	CT RSR SWPC
Metals - Aqueous							
Aluminum	Aqueous	mg/l	0.010	0.004	20%	75-125%	NE
Arsenic	Aqueous	mg/l	0.004	0.004	20%	75-125%	0.004
Barium	Aqueous	mg/l	0.02	0.002	20%	75-125%	NE
Beryllium	Aqueous	mg/l	0.001	0.0002	20%	75-125%	0.004
Cadmium	Aqueous	mg/l	0.001	0.0003	20%	75-125%	0.006
Chromium, total	Aqueous	mg/l	0.001	0.0005	20%	75-125%	0.110
Copper	Aqueous	mg/l	0.001	0.0006	20%	75-125%	0.048
Iron	Aqueous	mg/l	0.002	0.0007	20%	75-125%	NE
Lead	Aqueous	mg/l	0.002	0.001	20%	75-125%	0.013
Magnesium	Aqueous	mg/l	0.010	0.0009	20%	75-125%	NE
Manganese	Aqueous	mg/l	0.001	0.0002	20%	75-125%	NE
Mercury	Aqueous	mg/l	0.0002	.00012	20%	75-125%	0.0004
Nickel	Aqueous	mg/l	0.001	0.001	20%	75-125%	0.880
Potassium	Aqueous	mg/l	0.10	0.009	20%	75-125%	NE
Sodium	Aqueous	mg/l	0.10	0.003	20%	75-125%	NE
Selenium	Aqueous	mg/l	0.010	0.005	20%	75-125%	0.050
Silver	Aqueous	mg/l	0.001	0.0004	20%	75-125%	0.012
Thallium	Aqueous	mg/l	0.002	0.002	20%	75-125%	0.063
Vanadium	Aqueous	mg/l	0.002	0.0002	20%	75-125%	NE
Zinc	Aqueous	mg/l	0.002	0.001	20%	75-125%	0.123
Additional Methods							
Sulfide	Aqueous	mg/L	3.0	0.9	20%	75-125%	NE
Cyanide	Aqueous	mg/l	0.010	0.005	20%	75-125%	0.052
Chloride	Aqueous	mg/L	3.0	0.9	20%	85-115%	NE
TDS	Aqueous	mg/l	10	4..3	20%	NA	NE
BOD	Aqueous	mg/l	2.0	2.0	20%	70-130%	NE
COD	Aqueous	mg/l	10	8.3	20%	75-125%	NE
Nitrate	Aqueous	mg/l	0.05	0.016	20%	75-125%	NE
Ammonia	Aqueous	mg/l	0.02	0.018	20%	75-125%	NE
TSS	Aqueous	mg/l	5.0	2.5	20%	NA	NE
Hardness	Aqueous	mg/L as CaCO3	0.10	NA	NA	NA	NE
Alkalinity	Aqueous	mg/l	20	1.0	20%	75-125%	NE

Analyte	Matrix	Units	Reporting Limit	MDL	Precision	Accuracy	CT RSR SWPC
2,3,7,8-TCDF	Aqueous	pg/L	10	3.78	20%	67-158%	NE
2,3,7,8-TCDD	Aqueous	pg/L	10	3.00	20%	75-158%	NE
1,2,3,7,8-PeCDF	Aqueous	pg/L	50	1.93	20%	70-142%	NE
2,3,4,7,8-PeCDF	Aqueous	pg/L	50	25	20%	80-134%	NE
1,2,3,7,8-PeCDD	Aqueous	pg/L	50	1.19	20%	68-160%	NE
1,2,3,4,7,8-HxCDF	Aqueous	pg/L	50	5.42	20%	70-164%	NE
1,2,3,6,7,8,-HXCDF	Aqueous	pg/L	50	4.96	20%	76-134%	NE
2,3,4,6,7,8-HxCDF	Aqueous	pg/L	50	3.25	20%	64-162%	NE
1,2,3,7,8,9-HxCDF	Aqueous	pg/L	50	2.45	20%	72-134%	NE
1,2,3,4,7,8- HcCDD	Aqueous	pg/L	50	2.94	20%	84-130%	NE
1,2,3,6,7,8,-HXCDD	Aqueous	pg/L	50	4.81	20%	78-130%	NE
1,2,3,7,8,9-HxCDD	Aqueous	pg/L	50	5.94	20%	70-156%	NE
1,2,3,4,6,7,8-HpCDF	Aqueous	pg/L	50	6.79	20%	70-140%	NE
1,2,3,4,7,8,9-HpCDF	Aqueous	pg/L	50	3.6	20%	82-122%	NE
1,2,3,4,6,7,8-HpCDD	Aqueous	pg/L	50	4.8	20%	78-138%	NE
OCDF	Aqueous	pg/L	100	50	20%	78-144%	NE
OCDD	Aqueous	pg/L	100	19.63	20%	63-170%	NE
Total TCDF	Aqueous	pg/L	10	NA	20%	NA	NE
Total TCDD	Aqueous	pg/L	10	NA	20%	NA	NE
Total PeCDF	Aqueous	pg/L	50	NA	20%	NA	NE
Total PeCDD	Aqueous	pg/L	50	NA	20%	NA	NE
Total HxCDF	Aqueous	pg/L	50	NA	20%	NA	NE
Total HxCDD	Aqueous	pg/L	50	NA	20%	NA	NE
Total HpCDF	Aqueous	pg/L	50	NA	20%	NA	NE
Total HpCDD	Aqueous	pg/L	50	NA	20%	NA	NE

NA = Not Applicable NE = Not Established

12. Field Quality Control Requirements

QC Sample	Frequency	Acceptance Criteria	Corrective Action
Duplicate	Duplicate of MW-3 and SW-1 (if insufficient water level in SW-1, duplicate from SW-5)	RPD is < 30% of original sample	Flag in data report

13. Laboratory Quality Control Requirements

Phoenix Laboratory

QC Sample	Frequency	Acceptance Criteria	Corrective Action
ICP-metals: ICV	Daily	90-110% recovery	Recalibrate
ICP-metals CCV	Every 10 samples	90-110% recovery	Recalibrate/Reanalyze affected samples
ICP-metals LCS	Every batch of 20 samples	80-120% recovery	Redigest/Reanalyze batch
ICP-metals MS/MSD	Every batch of 20 samples	75-125% recovery	Narrate nonconformance
Hg- ICV	Daily	90-110% recovery	Recalibrate
Hg- CCV	Every 10 samples	80-120% recovery	Recalibrate/Reanalyze affected samples
Hg- LCS	Every batch of 20 samples	80-120% recovery	Redigest/Reanalyze batch
Hg- MS/MSD	Every batch of 20 samples	75-125% recovery	Narrate nonconformance
Cyanide ICV	Daily	90-110% recovery	Recalibrate
Cyanide CCV	Every 10 samples	90-110% recovery	Recalibrate/Reanalyze affected samples
Cyanide LCS	Every batch of 20 samples	80-120% recovery	Redistill/reanalyze batch
Cyanide MS	Every batch of 20 samples	75-125% recovery	Narrate nonconformance
Other Lachat parameters: NH3- ICV	Daily	90-110% recovery	Recalibrate
NH3-CCV	Every 10 samples	90-110% recovery	Recalibrate/Reanalyze affected samples
NH3-LCS	Every batch of 20 samples	80-120% recovery	Redistill/reanalyze batch
NH3- MS	Every batch of 20 samples	75-125% recovery	Narrate nonconformance
Ion Chromatography ICV	Daily	90-110% recovery	Recalibrate
Ion Chromatography CCV	Every 10 samples	90-110% recovery	Recalibrate/Reanalyze affected samples
Ion Chromatography LCV	Every batch of 20 samples	80-120% recovery	Reanalyze affected samples
Ion Chromatography MS	Every batch of 20 samples	75-125% recovery	Narrate nonconformance

QC Sample	Frequency	Acceptance Criteria	Corrective Action
Other Wet Chemistry ICV	Daily	90-110% recovery	Recalibrate
Other Wet Chemistry CCV	Every 10 samples	90-110% recovery	Recalibrate/Reanalyze affected samples
Other Wet Chemistry LCS	Every batch of 20 samples	80-120% recovery	Reanalyze affected samples
Other Wet Chemistry MS	Every batch of 20 samples, except for TSS, TDS	75-125% recovery	Narrate nonconformance

14. Data Management and Documentation

Field Data

Low-flow groundwater sampling data will be recorded on Monitoring Well Data Sheets (Appendix A). All other field data will be recorded in a permanently bound waterproof notebook. All notes will include the date, sampling location, weather conditions, any measurements taken, and any problems encountered in the field. Monitoring Well Data Sheets will be scanned and archived in the project file. The sampling labels and the chains-of-custody will be clearly written and consistent with one another.

Laboratory Data

The following deliverables will be provided by the laboratory:

1. Client's Name
2. Project Number
3. Laboratory Sample ID
4. Client Sample ID
5. Collection Date
6. Sample Matrix
7. Analyses
8. Analytical Results/Data Results Sheets
9. Reporting Limits
10. Reporting Units
11. Dilution Factor
12. Date Analyzed
13. Method Blank Results
14. Surrogate Recoveries and Acceptance Limits
15. Matrix Spike/Matrix Spike Duplicate Results and Acceptance Limits
16. Spike/ Duplicate Results and Acceptance Limits
17. Laboratory Control Sample Results and Acceptance Limits
18. Project Narrative which contains all observations and deviations

Types of information the laboratory will provide include:

1. Analytical Summary Sheets
2. QC Summary Sheets

The following will be maintained by the laboratory:

- All raw data including chromatograms
- Copies of Instrument Logbooks
- Copies of internal chains-of-custody
- PE sample results
- ICP Serial Dilution Results

- ICP Interference Check Sample Results

The laboratory will provide analytical reports in a hard-copy form and electronic data deliverables (Excel format).

Project Files

Working files will be stored via hard copy and electronically with the Project Staff during the operation of the Scope of Work. Subsequent to the completion of the project and issuance of all final documents, all pertinent information will be stored electronically in HRP's archive files for future reference.

15. Assessment and Response Actions

All field personnel will be provided with a copy of the QAPP to review prior to commencement of field activities. Subsequent to the review and prior to beginning any site work, the Project Manager will review the QAPP with field personnel. At the conclusion of each field day, field personnel will provide a verbal report to the Senior Technical Staff member, Project Manager, and/or Project QA Officer. Any deviations from the QAPP will be documented. If significant, the client and/or CTDEP Project Manager will be contacted.

Following completion of field activities, the Project QA Officer will perform a final review of the scope of sampling activities and sample handling practices to ensure that the activities are consistent with the QAPP. Any previously unidentified discrepancies will be reported to the Project Manager for review. All discrepancies and deviations from the QAPP will be documented in the final report.

16. Project Report

HRP

The reporting process will be conducted on a semi-annual basis following each sampling event.

Each report will include the following items:

- Brief discussion of the event,
- Tabulated data summary of analytical results, field parameters, and ground water elevations,
- Groundwater contour maps,
- Monitoring data sheets,
- UOD calculations, and
- RCP laboratory reports.

The October report will serve as the semi-annual and annual report. In addition to the information listed above, the October will have the following additional information:

- Background discussion of the Wallingford Landfill/Former Barberino property,
- Overview of the sampling results for the current year,
- Updated parameter trend graphs incorporating the current year's data,
- Data Quality Assessment and Data Usability Evaluation completed in accordance with *Laboratory Quality Assurance and Quality Control Data Quality Assessment and Data Usability Evaluation Guidance Document* (CTDEP, May 2009),
- Evaluation of test results with respect to the SWPC,
- Any proposed changes to the monitoring program that can be supported by site data, and
- General conclusions/recommendations.

In an effort to reduce paper usage, CRRA will no longer submit paper copies of the lab reports. CRRA will maintain the paper copies at its office; however, a hard copy of the RCP documentation and an electronic copy (CD) of the laboratory reports will be submitted with the report. Per the Stewardship Permit, surface and groundwater reports will be submitted within 60 days of the sampling event.

Laboratory

The laboratory will provide HRP with an electronic copy of the analytical results.

17. Field Data Evaluation

All field screening and sampling procedures will be reviewed with the field personnel. An HRP geologist will oversee all field screening and sampling events. All personnel that perform field screening and sampling activities have been trained in the use of the SOPs to be utilized pursuant to the QAPP. Field personnel will be given a copy of this QAPP to read prior to performing any field screening and sampling activities or will be directed by the Project Manager and/or Senior Project Technician as to what screening and sampling procedures are to be employed. The Project Manager and/or Senior Project Technician will speak to the field sampling team on a daily basis to verify that the screening and sampling procedures specified in the QAPP are being followed. These managerial controls will verify that the field screening and sampling procedures contained in this QAPP are utilized. The project manager will be responsible to verify that the field screening and sampling procedures are appropriate to meet the objective of the proposed investigations.

18. Laboratory Data Evaluation

The laboratory will perform internal validation procedures as per their SOPs. The contract laboratory will follow the CTDEP's Final Reasonable Confidence Protocols, approved on August 21, 2006.

An HRP QA Manager will review the laboratory data deliverables received from the Connecticut certified laboratory. The following tasks will be performed:

A Summary of Technical Usability

HRP will identify and document the following:

- Laboratory and laboratory project number
- Number of samples and sample field identifications (IDs) submitted to the laboratory by comparing the laboratory narrative to the chain-of-custody
- The laboratory sample IDs
- List parameters analyzed by comparing the laboratory narrative to the chain-of-custody

B Technical Issues Affecting Accuracy

HRP will review, document, and comment on:

- Whether CT RCP protocols were met
- Sample holding times compared to acceptable holding times
- Sample minimum detection limits are below applicable RSR criteria
- Laboratory control sample recoveries compared to acceptable laboratory control sample recoveries as established by the method standard operating procedures of the laboratory internal procedures
- Matrix spike recoveries compared to acceptable matrix spike recoveries as established by the method standard operating procedures of the laboratory internal procedures

C Technical Issues Affecting Precision and Representativeness

The relative percent differences (RPD) will be calculated between samples and sample duplicates and between matrix spikes and matrix spike duplicates. The acceptable RPD for water is an RPD<30% (see Section 13).

D Technical Issues Affecting Sensitivity

HRP will review and comment on any contaminants identified in the following in the Method Blanks.

HRP will review the laboratory report's minimum detection limits (MDLs).

E Summary of Completeness, Documentation, and Chain-of-Custody Issues

HRP will review the deliverable package for the following components:

- Laboratory Narrative
- RCP Forms
- Data Results Sheets
- Method Blank Results
- Surrogate Recoveries and Acceptance Limits
- Matrix Spike/Matrix Spike Duplicate Results and Acceptance Limits
- Laboratory Control Sample Results and Acceptance Limits
- Project Narrative which contains all observations and deviations

If any sample or QC issues are documented in the narrative that are not included as part of the data package deliverables, the laboratory will be contacted, copies of the relevant information obtained, and a discussion of any limitations on the use of the data will be presented in the validation section of the final report. If the data deliverables package is incomplete, the laboratory will be contacted and requested to provide the missing documentation.

The laboratory will perform internal validation procedures as per their SOPs.

19. Data Usability and Project Evaluation

Present Field Duplicate Results

All field duplicate results will be presented in tables throughout the corresponding reports. Relative Percent Difference (RPD) will be calculated for select compounds on all sample/duplicate pairs using the formula below:

$$RPD = 100 \times \frac{|difference|}{Average}$$

Any RPD greater than or equal to 30% will be noted, and the affect on the data usability noted.

Representativeness

Site figures, maps, and/or groundwater contouring will be used to ensure that samples are collected in the appropriate locations to be representative of the objectives of the site activities. Site figures and/or maps will be prepared and included in the final report. Groundwater contour maps will be used to determine if wells have been placed appropriately to identify impact from a release. HRP will review all data and flag any unexpected and/or anomalous results in the corresponding reports. HRP will consult field personnel and as for clarification on any anomalous data. Field personnel will also be asked to provide any missing data. All findings will be presented in the final report.

Comparability

In order to insure comparability from location to location and event to event, HRP will follow the same sampling procedures and request the same laboratory protocols throughout the project. HRP will also review field notes and laboratory data to ensure the QAPP has been adhered too. HRP will consult with the field technician or laboratory personel if any missing anomalous data is encountered. Deviation in the field duplicates will be compared to the criteria specified in the QAPP. If necessary, the laboratory will be asked to reanalyze samples to varify results.

Groundwater results will be compared to the Surface Water Protection Criteria of the Connecticut Remediation Standard Regulations (RSR).

Where possible, HRP will present data in table and graph format. If historical data is available, such as multiple groundwater monitoring events, it will be discussed in reports to evaluate the contaminant trends.

Sensitivity

HRP will compare all groundwater laboratory minimum reporting limits to the RSRs to verify that they are below the standards. If reporting limits are found above the standard, the laboratory will be contacted to rerun the sample at a reporting limit below the standard. If it is not possible to achieve reporting limits below the RSR criteria the analyte will be flagged in the report.

Usability Summary

Data will be reviewed in accordance with the *Laboratory Quality Assurance and Quality Control Data Quality Assessment and Data Usability Evaluation Guidance Document* (CT DEP, May 2009) in order to identify deviations from RCP QA/QC performance criteria and their potential impact on the project objectives. Any deviations will be discussed in a Data Usability Evaluation (DUE) section of the corresponding report.

FIGURES

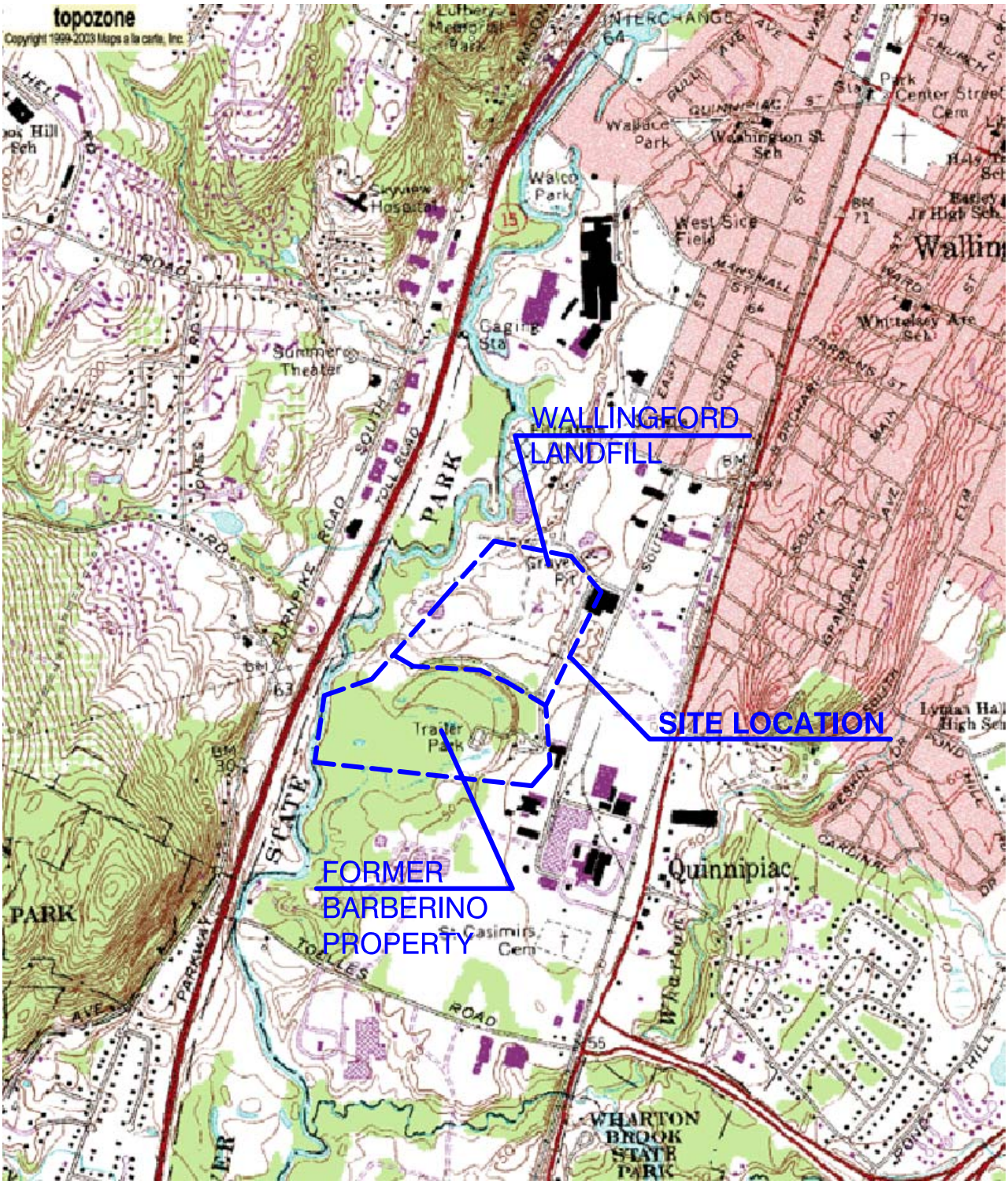


FIGURE 1
SITE LOCATION
WALLINGFORD LANDFILL AND
FORMER BARBERINO PROPERTY
PENT ROAD
WALLINGFORD, CONNECTICUT
HRP# CRR0148.GW

J:\C\CRRAD - CT RESOURCES RECOVERY AUTHORITY\WALLINGFORD LANDFILL\CRR0148GW\CAD\SITE LOCATION.dwg, Layout1, 2/12/2010 7:10:05 AM
Adobe PDF

LEGEND

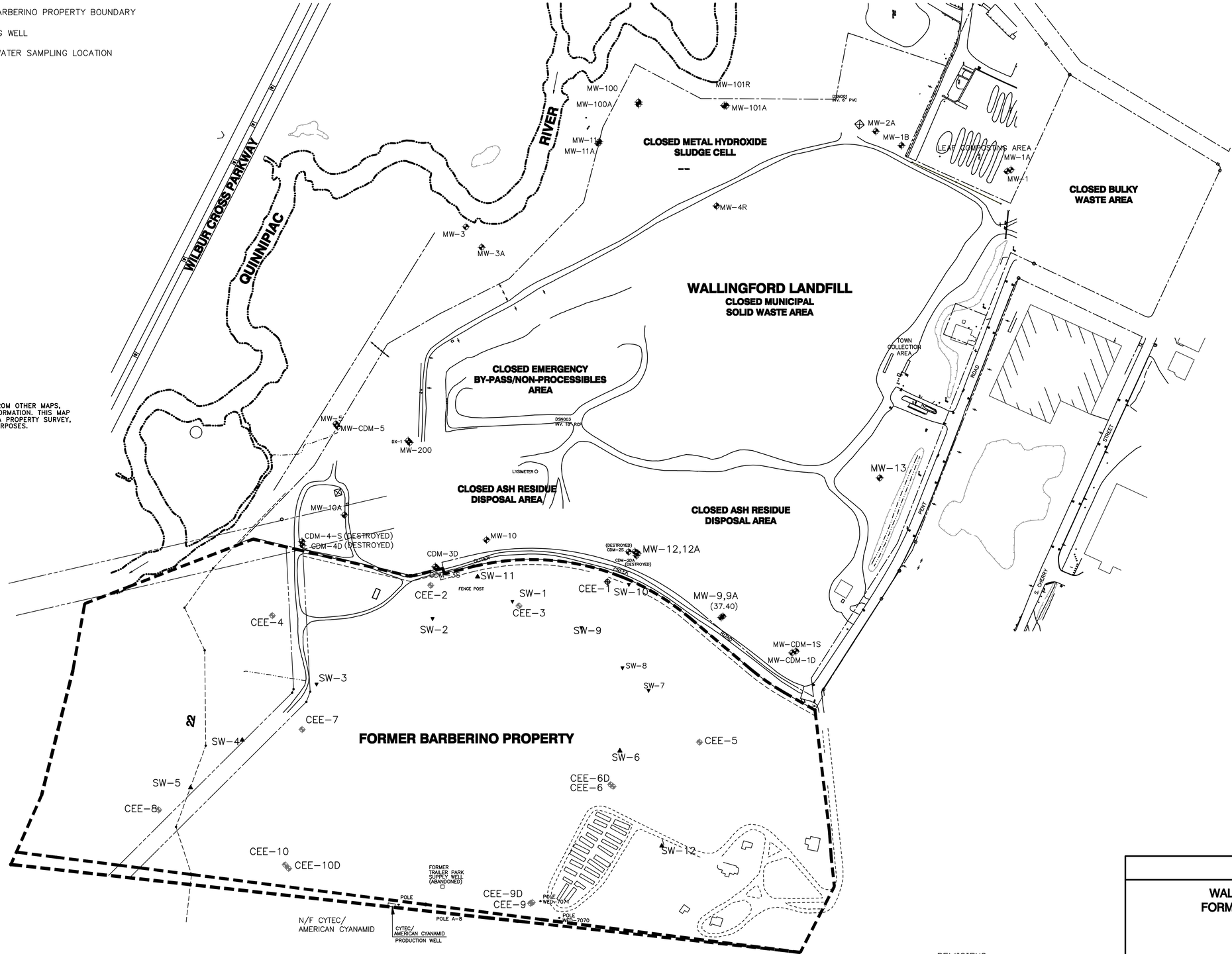
—·—·— WALLINGFORD LANDFILL PROPERTY BOUNDARY

▬▬▬ FORMER BARBERINO PROPERTY BOUNDARY

⊕ MONITORING WELL

▼ SURFACE WATER SAMPLING LOCATION

NOTE:
THIS MAP HAS BEEN COMPILED FROM OTHER MAPS, DEEDS, AND/OR SOURCES OF INFORMATION. THIS MAP SHOULD NOT BE CONSTRUED AS A PROPERTY SURVEY, NOR USED FOR CONSTRUCTION PURPOSES.



REVISIONS

NO.	DATE	DESCRIPTION

SITE PLAN

WALLINGFORD LANDFILL AND FORMER BARBERINO PROPERTY

PENT ROAD WALLINGFORD, CT

HRP Associates, Inc.
Environmental/Civil Engineering & Hydrogeology
Creating the Right Solutions Together
Connecticut, New York, South Carolina, Florida, Indiana
197 Scott Swamp Road
Farmington, Connecticut 06032
Ph:(860)674-9570 Fax:(860)674-9624
www.hrpassociates.com

JLW DESIGNED	ZAB APPROVED	1" = 150' SCALE	
DML DRAWN	2/12/10 DATE		FIG. 2
JLW CHECKED	CRR0148.GW PROJECT NO.		SHEET NO.

J:\C\CRRAU - CT RESOURCES RECOVERY AUTHORITY\WALLINGFORD LANDFILL\CRR0148GW\CAD\SITE PLAN - GW BASE MAP.dwg, HRP, 2/12/2010 7:19:28 AM, DWG To PDF.pc3

APPENDIX A

HRP FORMS

HRP Associates, Inc.
197 Scott Swamp Rd.
Farmington, CT 06033
(860) 674-9570

Monitor Well Data Sheet

Page ____ of ____

Well ID: MW-1

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	71.00

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:	Special Well
Good	No		

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH	YSI 650 MDS Serial #
Temp.	
Sp. Cond.	
ORP	
DO	
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft):				Time:				
Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Bladder				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
2 Amber	1 L	As Is

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is
1 plastic	125 mL	As Is specimen cup

HRP Associates, Inc.
197 Scott Swamp Rd.
Farmington, CT 06033
(860) 674-9570

Monitor Well Data Sheet

Page ____ of ____

Well ID: MW-1A

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	26.77

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Peristaltic Pump				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

HRP Associates, Inc.
197 Scott Swamp Rd.
Farmington, CT 06033
(860) 674-9570

Monitor Well Data Sheet

Page ____ of ____

Well ID: MW-1B

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	30.60

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft):				Time:				
Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Peristaltic Pump				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Well ID: MW-2A

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	32.05

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft):				Time:				
Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^oC)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Peristaltic Pump				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Well ID: MW-3

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	11.90

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	Special Well DUPE MW-3

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Peristaltic Pump				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
2 Amber	1 L	As Is

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is
1 plastic	125 mL	As Is specimen cup

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Well ID: MW-3A

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	165.00

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Bladder				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Well ID: MW-4R

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	22.17

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Peristaltic Pump				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Well ID: MW-5

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	9.95

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Peristaltic Pump				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Well ID: MW-9

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	33.15

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Peristaltic Pump				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Well ID: MW-9A

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	161.30

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Bladder				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Well ID: MW-10

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	40.75

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Peristaltic Pump				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Well ID: MW-10A

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	20.40

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Peristaltic Pump				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Well ID: MW-11

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	72.55

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Bladder				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Well ID: MW-11A

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	186.00

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Bladder				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Well ID: MW-12

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	17.15

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Peristaltic Pump				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Monitor Well Data Sheet

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Well ID: MW-12A

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	150.40

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Bladder				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Monitor Well Data Sheet

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Well ID: MW-13

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	37.45

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Peristaltic Pump				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Monitor Well Data Sheet

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Well ID: MW-100

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	40.62

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Bladder				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Monitor Well Data Sheet

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Well ID: MW-100A

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	136.00

Measurement Point: 2" PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Bladder				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Monitor Well Data Sheet

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Well ID: MW-101A

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	142.00

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:	
Good	No	Special Well	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH	YSI 650 MDS Serial #
Temp.	
Sp. Cond.	
ORP	
DO	
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft):				Time:				
Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Bladder				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
2 amber	1 L	As Is

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is
1 plastic	125 mL	As Is specimen cup

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Monitor Well Data Sheet

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Well ID: MW-101R

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	40.37

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:
Good	No	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH Temp. Sp. Cond. ORP DO	YSI 650 MDS Serial #
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft): **Time:**

Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Bladder				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
1 plastic	125 mL	As Is specimen cup

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is

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Monitor Well Data Sheet

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Well ID: MW-200

Site Background Information

Site Location:	CRRA - Wallingford Landfill	**Sampling Dates:**	
Job Number:	CRR0147.GW	**Field Team Leader:**	
Weather:		**Team Personnel:**	KG, BE

Ground Water Elevation Data

Date	Time	Sampler Name	Equipment Model		Depth to Water (ft)		Depth to Bottom (ft)	
			Solinst-101		uncorrected		uncorrected	
			corr. factor		corrected		corrected	14.45

Measurement Point: 2 " PVC SP

Well Condition (circle one)

General Condition	Visible Well ID	Well Cap Present	Well Plumbness	Lock
Good	Yes	Yes	Good	Yes

Concrete Collar	Ponded Water	Comments:	
Good	No	Special Well	

Well Purging Data

Date	Time						Sampler Initials	Instrument Calibration Date
	Equipment Set-up		Purging		Sample Collection			
	Start	Finish	Start	Finish	Start	Finish		

Instrument Mfg & Model	
pH	YSI 650 MDS Serial #
Temp.	
Sp. Cond.	
ORP	
DO	
Turbidity	HF Scientific DRT-15CE Serial #

Initial Water Depth (ft):				Time:				
Time	Water Depth (ft)	Flow Rate (ml/min)	pH (s.u.)	Temp (^{o}C)	Sp Con (uS)	ORP (mV)	DO (mg/l)	Turbidity (ntu)
Req. Limits for Last 3 Readings			+/- 0.1	3%	3%	+/- 10 mv	10%	10%

Pump Mfg & Model	Color	Odor	Purge Vol (ml)	Sample Depth (ft.)
Peristaltic Pump				

Sample Containers

Type & No.	Volume	Preservative
3 vials	3X40 mL	HCL
2 Vials	2X40 mL	As Is
1 plastic	250 mL	HNO3
1 plastic	1 L	As Is
2 Amber	1 L	As Is

Type & No.	Volume	Preservative
1 Plastic	250 mL	NAOH
1 Plastic	250 mL	Filter HNO3
1 Amber	250 mL	H_2SO_4
1 Amber	1 L	H_2SO_5
1 Amber	500 mL	As Is
1 plastic	125 mL	As Is specimen cup

CHAIN OF CUSTODY RECORD

PHOENIX Environmental Laboratories, Inc.

587 East Middle Turnpike, P.O. Box 370, Manchester, CT 06040
Email: info@phoenixlabs.com Fax (860) 645-0823
Client Services (860) 645-8726

Temp Pg of

Data Delivery:
☐ Fax #: _____
☐ Email: _____

Customer: HRP Associates
Address: Farmington Business Center, 197 Scott Swamp Rd
Farmington, CT 06032

Project: CRRA: Wallingford/Former Barberino
Report to: Zoe Belcher
Invoice to: Zoe Belcher

Project P.O:
Phone #: 860-674-9570
Fax #: 860-674-9624

Client Sample - Information - Identification

Sampler's Signature _____ Date: _____

Matrix Code:
DW=drinking water **WW**=wastewater **S**=soil/solid **O**=oil
GW=groundwater **SL**=sludge **A**=air **X**=other

Analysis Request

Phoenix Sample #	Customer Sample Identification	Sample Matrix	Date Sampled	Time Sampled												Soil VOA Vials [ ] methanol [ ] Sod Bisulfa	GL Soil container ( ) oz	GL Soil container ( ) oz	40 ml VOA Vial [ ] As is [ ] HCl	GL Amber 1000ml [ ] As is [ ] H2SO4	PL As is [ ] 250ml [ ] 500ml [ ] 1000ml	PL H2SO4 [ ] 250ml [ ] 500ml	PL HNO3 250ml	PL NaOH 250ml	Bacteria Bottle
					x	x	x	x	x	x	x	x	x	x	x											

Relinquished by:	Accepted by:	Date:	Time:

Comments, Special Requirements or Regulations:

Turnaround:
☐ 1 Day*
☐ 2 Days*
☐ 3 Days*
☐ Standard
☐ Other

* **SURCHARGE APPLIES**

CT/RI
☒ RCP Cert
☐ GW Protect
☐ GA Mobility
☐ GB Mobility
☐ SW Protection
☐ Res. Vol.
☐ Ind. Vol.
☐ Res. Criteria
☐ Other

MA
☐ MCP Certification
☐ GW-1
☐ GW-2
☐ GW-3
☐ S-1
☐ S-2
☐ S-3
☐ MWRA eSMART
☐ Other

State where samples were collected: _____

Data Format
☐ Excel
☐ PDF
☐ GIS/Key
☐ EQuIS
☐ Other _____

Data Package
☐ ASP-A
☐ NJ Reduced Deliv. *
☐ NJ Hazsite EDD
☐ Phoenix Std Report
☐ Other

APPENDIX B

PHOENIX OPERATING PROCEDURES (SOPS)

SOP No.: **505**

Title: Determination of Trace Elements by Inductive Coupled Argon Plasma (ICP) Spectroscopy (ARCOS)

Scope: This procedure describes the determination of dissolved and total recoverable elements in ground water, drinking water and waste water by ICP. This procedure is also applicable to total recoverable elements in sediment, sludges, biological tissue and solid waste samples. This procedure is the general ICP procedure, which covers the requirements of the SW-846 6010 and EPA 200.7 as approved in 40 CFR part 136 and 40 CFR part 141.

1.0 Summary

This procedure describes the simultaneous analyses of metals on the following elements (Al, Sb, As, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Fe, Pb, Li, Mg, Mn, Mo, Ni, P, K, Se, Ag, Au, Zr, Na, S, Sr, Tl, V, and Zn) by ICP. All samples are digested prior to analysis, with the exception of drinking water samples with turbidity of less than 1 NTU.

2.0 Sample Collection, Preservation and Storage

- Samples can be collected in plastic, teflon or glass. They must be preserved with HNO_3 to a pH < 2. They must be stored at 4°C until the time of analysis.
- Samples have a holding time of 6 months.
- Digestions holding time is 180 days.

3.0 Interferences

3.1 Spectral interferences are minimized by the optimization of background points and the use of inter-element correction factors.

3.2 Physical interferences are associated with viscous samples and can be minimized by diluting the sample.

3.3 Memory interferences result when analytes from the previous sample contribute to a signal in the new sample.

3.4 An internal standard measured to increase the reproducibility of measurements of high concentrations or help correcting for samples with varying viscosities.

4.0 Equipment and Supplies

- 100 mL Volumetric Flasks
- 100 mL Graduated Cylinders
- 250 mL Beakers
- 1000, 500, and 250 mL Plastic Storage Bottles
- 20.0 L Nalgene Carboy
- 10 and 50 mL Polystyrene Disposable Beakers
- Pipettes and Pipette Tips
- 10.0 mL Oxford
- 1 mL Eppendorf
- 0.1 mL Eppendorf
- Pump Tubing (Cole-Palmer and Glass Expansion)
- Argon Gas (Liquid)

5.0 Instrumentation

- SPECTRO Model ARCOS CCD ICP-EOP with pneumatic nebulizer, Laboratory computer and printer: and Cetac ASX-520 Autosampler.
- Sample induction system consists of four major components: Modified Lichte Nebulizer, cyclonic spray chamber and torch.
- Fiber Optics use as optical transfer devices.

6.0 Reagents and Standards

- Argon Gas
- Deionized water, ASTM Type or equivalent
- Concentrated Hydrochloric Aicd. Trace Metals Grade.
- Concentrated Nitric Acid. Trace Metals Grade.
- 2.5% Nitric Acid (HNO_3) - used in standards preparations.
    - Preparation: Prepare fresh daily. Fill 1000 mL volumetric flask half-full with DI water, add 25 mL concentrated HNO_3, dilute to 1000 mL with Di water. Use this solution in the preparation of all standards and dilutions of all samples.
- Standards – Metal Plasma Grade Standards
- Calibration Verification (CV), Laboratory Control Sample (LCS), and Interference check sample (ICS) standards are currently supplied by Inorganic Ventures and Environmental Express.

GENERAL PRECAUTIONS:

- Avoid contamination of Stock Standards. Always pour out a small volume of standard stock solution into a new beaker before taking an aliquot.
- Never insert a pipet directly into the bottle.

7.0 Definitions

- Laboratory Control Sample (LCS) – A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.
- Preparation Blank (Prep Blank) – An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents, or glassware.
- Calibration Standard – A solution prepared from the dilution of stock standard solutions. The Calibration solutions are used to calibrate instrument response with respect to analyte concentration.
- Matrix Spike (MS) – An aliquot of environmental sample to which a known quantity of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

8.0 Procedure

8.1 Preparation of Calibration Standards

- BLANK (2.5% HNO_3) – 25 mL of trace metal grade nitric acid diluted to 1000 mL DI water.
- CLP 1 + 3 – 5 mL of CLP-CAL-1 and 5 mL of CLP-CAL-3 diluted to 500 mL with 2.5% HNO_3
- CRQL – 0.5 mL of CLP-AES-CRQL diluted to 500 mL of 2.5% HNO_3
- ICSA – 10 ml of 2007ICS-4 diluted to 1000 mL 2.5% HNO_3.
- IPC 2 + 3 – 10 mL of WW-IPC-2 and 10 mL of WW-IPC-3 diluted to 1000 mL with 2.5% HNO_3.
    - A 1:10 dilution of the IPC standard is also ran during instrument calibration.

All Standards are prepared and transferred to storage bottles and labeled.

8.2 QC Sample Preparation

Calibration Verification:

- QCP 1 + 2 – 5 mL of QCP-QCS-1 and 5 mL of QCP-QCS-2 diluted to 500 mL with 2.5% HNO_3
- CRDL – 0.5 mL of ICRDL-100 diluted to 500 ml with 2.5% HNO_3
- ICSA – 10 mL of 2007ICS-4 diluted to 1000 mL with 2.5% HNO_3
- ICSAB – 10 mL of 2007ICS-4 and 10 mL of CLPP-ICS-B diluted to 1000 mL with 2.5% HNO_3
- IPC 2 + 3 – 10 mL of WW-IPC-2 and 10 mL of WW-IPC-3 diluted to 1000 mL with 2.5% HNO_3

All Standards are prepared and transferred to storage bottles and labeled.

Interference Check Standards: Cr, Mn, Ti, Zn (10.0 ppm) are prepared with 1.0 mL of a 1000 ppm stock standard from Environmental Express and diluted to 100 mL with 2.5% HNO_3 A 1.0 ppm standard of As is prepared with 0.1 mL of 1000 ppm stock from Environmental Express and diluted to 100 mL with 2.5% HNO_3 Other interfering check standards are Ca 200.0 ppm, Al 50.0 ppm, Fe 200.0 ppm, and Na 500.0 ppm.

Spiked Sample Analysis: Inorganic Ventures QCP-QCS-1 & 2.

The spike is added before the digestion. Take 0.5 mL of each spiking solution and add to the sample. The final volume is 50 mLs. When performing a post-digestion spike, take 0.08 mL of each QCP-QCS-1 and QCP-QCS-2 and bring up to 8.0 grams of sample. For soil matrix post digestion spike take 0.16 mL of each QCP-QCS-1 and QCP-QCS-2 and dilute to 8.0 grams of sample.

8.3 Tuning and Calibration of the ICP.

8.3.1 Torch Maitenance - Open the Torch box and visually inspect the glass, and RF load coils for cleanliness and any oxidation. Check all connections – Drain hose, nebulizer cap, Argon lines, and cooling water.

8.3.2 Peristaltic Pump - Install new pump tubing if the old one shows signs of flattening or stretching and connect to the nebulizer with capillary tubing. Pump DI water and adjust pressure on tension arms to obtain a smooth flow.

8.4 Start-Up

8.4.1 Turn the main switch on the unit to "ON". Switch on the computer allowing the operating system to boot up.

8.4.2 Start the unit software "Smart Analyzer Vision" after the operating system has been completely booted. Allow they unit to stabilize for at least 60 minutes after switching it on. Also make sure that the operating temperature (15°C) has been reached

8.4.3 On the Smart Analyzer Vision software select the Analysis view. Flush the sample introduction system with argon for approximately 2 minutes by clicking the "flush" button. The following conditions should be set:

Coolant: 13.4 L/min
Auxiliary: 0.70 L/min – 1.0 L/min
Nebulizer: 0.9 L/min

8.4.4 To ignite the plasma click on the "plasma" button.

8.4.4.1 The sample introduction system is automatically flushed with argon again at this point. In the status line "Plasma is starting" should be displayed. It takes about 2 minutes for the plasma to ignite.

8.4.5 Start the peristaltic pump by clicking the "pump" button

8.4.5.1 Allow rinse water (5% HNO3) to run through the system for 30 minutes to allow the unit to heat up and stabilize the components.

8.4.5.2 After the nitric rinse: rinse the unit with 1:1 HCL to rinse out metals like Fe, Cu, and Zn that the nitric doesn't completely rinse out.

8.5 Optimization

8.5.1 Make sure the optical system is "ICAlized". The system needs to be "ICALized":

- After a software message (wavelength drift).
- After switching on the unit and temperature stabilization.
- In the event of changes concerning the sample induction system (torch or nebulizer changed).
- Before setting up a new method.
- Before carrying out high-precision measurements.

8.5.2 To perform an "ICALization"

8.5.2.1 After the plasma has been ignited and the system flushed and rinsed select the function "ICALization" in the "System" menu. Follow the instructions displayed by the software.

8.6 Measuring the Samples:

8.6.1 Perform the calibration using:

8.6.1.1 Blank: 2.5% HNO3, CLP 1 + 3, CRQL, ICSA, IPC and IPC 1:10.

8.6.1.2 After completing the calibration a regression sheet is printed. The correlation coefficient should be no less than 0.996 for each element.

8.6.1.3 To control the quality of results measure:

- Calibration verification standard. (IPC 1+2) ± 10%
- Laboratory control standard (QCP 1+2) ± 15%
- Interference check standard (ICSAB) ± 20%
- Calibration Blank
- CRDL
- ICSA

8.6.2 Fill the autosampler trays with samples.

8.6.2.1 Sequence Generator

8.6.2.1.1 In the Phoenix LIMS program open the QA/QC Batching, ICP Sequence. Once the sequence page is open select the instrument you are running and press "new", click yes for the prompt to build a new sequence.

8.6.2.1.1.1 At this point you can manually type in the sample number you are running and select the matrix.

8.6.2.1.1.2 You can add a whole batch by clicking "Add Batch". Type in the whole batch (ex. TMD-SM-XXXXXX). Click add batch to sequence.

8.6.2.1.1.3 Once all the samples/batches have been added to the sequence click on "build sequence" click ok. Go to the software and paste into the tray position.

8.6.2.2 Analyze prep blank, blank spike, sample duplicate, sample spike and samples. Analyze calibration verification standard and calibration blank every 10 samples to ensure the calibration is still consistent.

8.7 Switching off the Instrument.

8.7.1 Flush the sample introduction system for approximately 10 minutes with the rinse solution. This is to eliminate the potential for crystallization within the sample introduction system.

8.7.2 Select the anaylsis view. Switch off the plasma by clicking the "Plasma" button.

8.7.3 Exit the software.

8.7.4 Shut down the computer.

8.7.5 Switch of the exhaust and the coolant water.

8.7.6 Release the pressure clamps on the peristaltic pump and release the pump tubing.

8.7.7 To switch off the unit completely turn the main switch to "Off".

9.0 Maintenance

9.1 Daily Checks

9.1.1 Clean OPI. Using DI water and a Q-Tip clean the face of the OPI.

9.1.2 Change Torch.

9.1.3 Check Elbow. Make sure the elbow has no water or condensation in it. Change the elbow if any water droplets are present.

9.1.4 Change peristaltic pump tubing.

9.1.5 Check all tubing and feed hoses. Change anything that is kinked, flattened, or stretched.

9.1.6 Make sure you have enough rinse water in the carboy.

9.1.7 Check discharge container: if more than ¾ full empty and replace.

9.1.8 Change all QC and Calibration standards.

9.1.9 Check peaks on all elements you are calibrating. Au, Zr, and S need to be checked also.

9.1.10 Check Sc counts during calibration and check the spray chamber to verify nebulizer flow. A drastic drop in Sc count could be a partially clogged nebulizer. Clean or replace the nebulizer if you suspect it to be clogged.

9.2 Weekly Checks

9.2.1 Inspect torches. Remove all torches that apper to have deposits or residue in aerosol tube. Torches with excessively pitted ends of the tube should also be removed.

9.2.2 Clean torches by soaking them in Aqua Regia (mix 1 part concentrated nitric acid and 3 parts concentrated hydrochloric acid.) After allowing the torches to soak to remove residue thoroughly rinse all torches with DI water and bake in oven at 120°F. This is primarily to dry the torches. Once they are dry shutoff the oven and allow to cool, once cool cover the ends of the torch with Parafilm.

9.2.3 Clean elbows by running a small brush with soap through it and rinsing with hot tap water followed by a DI water rinse. Bake the elbows at 120°F allow to cool and cover the ends with Parafilm.

9.2.4 The spray chamber needs to be cleaned and rinsed. They spray chamber does not need to be dried. High levels of sodium can be rinsed out faster with DI water than with the normal rinse operation.

9.2.5 Chiller water levels should be checked weekly to ensure proper OPU cooling.

9.3 Monthly Checks

9.3.1 Inspect window for spotting or debris. Sudden drops in low intensity lines should warrant this check. Sb, Se, Pb, and As are pretty good indicators.

9.3.2 All introduction tubing should also be changed. Torch tubing should be checked and replaced if it becomes too easy to remove from the torch. Nebulizer tubing should also be changed if its stretched from over pressurization.

9.3.3 Filter media should be cleaned or replaced.

10.0 Trouble Shooting and Corrective Action

10.1 Problem: Stable plasma won't start.
Action: Check system for leaks.

10.2 Problem: Generator cannot be started.
Action: Check power supply (fuses, circuit breaker).

10.3 Problem: ARGON lamp is lit.
Action: Increase argon admission pressure, or replace argon supply if empty.

10.4 Problem: WATER lamp is lit.
Action: Check for and remove blockages (dirt, lime buildup) to the system.

10.5 Problem: Melting of the torch tubes.
Action: Re-adjust torch, remove and clean blockages in the aerosol tube, search for and repair leaks, increase auxiliary gas flow rate, check that exhaust is turned on.

10.6 Problem: Plasma does not ignite.
Action: Re-adjust torch, flush the system with argon by pressing <+> and <-> key wrong argon quality (purity >99.996%).

10.7 Problem: Plasma trembles or pulsates.
Action: Clean and dry torch the aerosol tube, increase power slightly, clean nebulizer.

10.8 Problem: Nebulizer gas flow too low.
Action: Clean nebulizer.

10.9 Problem: Sparking-over at the coil.
Action: Dry coil with tissue paper, clean any dirt, adjust torch (must not touch coil).

10.10 Problem: CV fails for an element.
Action: The instrument may need to be re-calibrated.

10.11 Problem: ICSA or ICSAB fails for an element.
Action: Check background points for that element.

**** SEE ATTACHED CHART FOR MORE TROUBLESHOOTING.**

11.0 Quality Control

11.1 At least once per year the following are performed:

11.1.1 Method Detection Limits (MDL) are established for each element per the guidelines established in 40 CFR part 136 appendix B.

11.1.2 Accuracy and Precision studies are evaluated for each element.

11.1.3 The linear range of the calibration curves are evaluated by analyzing the highest standard (should be within 5% of true value).

11.2 To evaluate the instrument calibration, the following are analyzed:

11.2.1 The calibration verification (CV) standard is the mid level standard it is analyzed after calibration and every 10 samples (acceptance criteria is ± 10%)

11.2.2 The laboratory control sample is a second source standard that is analyzed prior to the samples to verify the validity of the calibration standards (acceptance criteria is ± 15%)

11.2.3 The interference check standard is analyzed to verify the instrument background corrections and the interelement correction factors (acceptance criteria is ± 20%)

11.3 To evaluate the sample preparation, the following are analyzed:

11.3.1 The preparation blank is analyzed to determine any possible contamination. If analytes are found above the reporting level, the analyst requests a re-digestion of that batch of samples.

11.3.2 The prep blank ICP spike is used to evaluate the efficiency of the sample prepartation (acceptance criteria is ± 15%).

11.3.3 The matrix spike evaluates both sample matrix affect and efficiency of sample preparation. If recovery falls outside of ± 25%, the analyst narrate. A post spike is performed with every batch.

12.0 Safety

12.1 The toxcitity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.

12.2 Always wear safety glasses for eye protection as well as a lab coat.

12.3 Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures.

13.0 Pollution Prevention

13.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.

13.2 Standards should be purchased in volumes consistent with laboratory use to minimize the volume of expired standards to be diposed.

14.0 Waste Management

14.1 It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hood and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.0 Method Performance

15.1 This method was validated through internal QA/QC monitoring, including annual method detection limit studies, precision and accuracy studies, initial and continuing calibration verifications, blank analysis, laboratory control samples and matrix spikes and duplicates.

15.2 See section 11 Quality Control in this SOP for acceptance limits.

16.0 Corrective Action for Out-of-Control or Unacceptable Data

16.1 Should the calibration curve have a correlation coefficient of <0.9975, remake and reanalyze curve before processing samples.

16.2 Should the preparation blank, LCS, or inhouse standards fail accetance criteria, redigest and reanalyze batch.

16.3 Should the matrix spike or sample duplicate analysis fail acceptance criteria. A non-conformance report must be generated or the sample QC must be reanalyzed.

17.0 References

17.1 "Methods for Chemical Analysis of Water and Wastes", Environmental Protection Agency, Environmental Monitoring Systems Laboratory – Cincinnati (EMSL-CL), EPA-600/4-79-020, Revised March 1983 (Method 200.7 version 4.4).

17.2 "Test Methods for Evaluating Solid Waste (SW-846), Third Edition, EPA Office of Solid Waste, Final Update III December 1996 (Method 6010).

17.3 SPECTRO Analytical Instruments Operator's Manual.

Fault	Cause	Remedy
Generator does not start	Power Supply	Check instrument power supply (fuses, main switch)
Error Message: Argon Pressure too low	Argon supply interrupted	
Error Message: Insufficient OPI cooling flow	Cooling agent supply interrupted.	• Check to ensure system (tubing etc) is not blocked (dirt, lime, deposits) • Check flow amount.
	Cooling agent supply pressure too low.	Increase inlet pressure (approximately 4 bar/60 psi)
Error Message: Unit door not closed.	Door not properly closed	Check closing mechanism
Error Message: Plamsa exhaust error	Exhaust capacity too low	Check the unit filter for soiling or check the exhaust capacity.
Error Message: Current error on start	Error during start routine	Repeat start procedure

Plasma Torch melts	Torch incorrectly adjusted within the load coil.	Check whether the torch is positioned correctly.
	Aerosol tube blocked	Clean the torch.
	Leak in the argon connection to the torch.	Search for the leak with soapy solution (Snoop) and seal.
	Insufficient auxiliary gas flow setting.	Increase the auxiliary gas flow.
	Leak in the nebulizer system.	Search for leak with soapy solution (Snoop) and seal.
Plasma cannot be ignited	No Tesla discharge	Ignition cable not connected correctly
		Check the insulation for correct installation
	Torch not correctly centered within the load coil	Check the load coil setting
	Oxygen in sample introduction system	Flush the sample introduction system with argon
	Wrong argon quality	Argon with a quality of 4.6 or better is required (purity = 99.996%)
Plasma asymmetrical	Argon flush out of the OPI/SPI too high	Reduce the flow rate

	Plasma chamber extraction set too high	Reduce extraction
Plasma flickers or pulsates	Humidity or deposits in the aerosol tube of the torch.	Clean and dry the torch or replace it.
	Aerosol pulsates	• Clean the nebulizer • Replace the pump tube.
Plasma too bright	Power set too high	Decrease power
	Oxygen in sample introduction system.	Check for leaks and seal
Plasma extinguishes when nebulizer gas flow is switched on	Sample introduction tube not connected to the nebulizer.	Connect the tube and check fitting
	Oxygen in sample introduction system	Flush the system with argon before plasma ignition
	Leak in the sample introduction system	Find the leak and seal
No channel visible in the plasma	Nebulizer gas flow setting too low	Optimize the nebulizer gas flow
	Nebulizer blocked	Clean the nebulizer
	Leak in spray chamber outlet	Find the leak and seal
Error Message: Waste container level indicator	Waste container is full	Remove the cover of container and properly dispose of the content

Sparking-over at the load coil	Humidity	Turn off generator and dry the load coil with tissue paper (if humidity is visible)
	Dirt on the load coil	Switch off the generator and clean the load coil using a toothbrush.
Error Message: A new ICALization is required	Control peak drift detection	ICALize
Error Message: ICALization failed	Incorrect sample or incorrect flush time	Use the correct sample. Check the measurement parameters. Repeat the ICALization
	In the current method, no ICAL reference spectrum is defined	Select an ICAL reference spectrum for the method under method development
Error Message: ICAL reference does not fit to current transformation data.	A method with other ICAL basic parameters was loaded	ICALize the new method with the correct nebulizer type.
Error Message: Network Connection No communication between the PC and the unit.	IP address incorrect or used for a different purpose	Enter the correct IP address (online help). Only qualified IT staff should enter the address.

SOP No.: 324.2540D

Title: Total Suspended Solids (TSS) dried at 103°-105°C

Scope: This method covers the determination of suspended solids in drinking, surface, saline waters, and domestic and industrial wastes. The practical range of the determination is 5.0-2000mg/L. Samples containing more than 2000mg/L suspended solids require sample dilution prior to analysis.

I. Summary of Method

A. A well-mixed sample is filtered through a pre-weighed glass fiber filter. The filter is retained and dried to a constant weight at 104°C. The increase in filter weight represents the total suspended solids (TSS).
B. If total dissolved solids (TDS) is being determined on the sample, the filtrate may be retained for TDS analysis.

II. Interferences

A. Exclude large floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Because excessive residue on the filter may form a water-trapping crust, limit sample to that yielding no more than 200mg residue.
B. For samples with high TDS, thoroughly wash filter to insure no TDS will be measured as part of the TSS.

III. Sample Collection, Preservation and Storage

A. Samples for solids analysis are unpreserved and stored at 4°C prior to analysis.
B. Samples are analyzed as soon as possible, but not after a holding time of 7 days after sample collection.

IV. Equipment and Supplies

A. Glass fiber filters, Whatman 934-AH or equivalent.
B. Gooch crucibles of same size as filters, with adapter.
C. Filter flasks, 250ml or 500ml volume.
D. Drying oven, 104°C +/-1°C.
E. Desiccator. Change desiccant every month, or when desiccant changes color.
F. Graduated cylinder, 100mL.

G. Analytical balance, capable of weighing to 0.1mg. Calibration checked before use using Class "S" weights: 50g, 10g, 1g.

V. Reagents and Standards

A. Laboratory deionized water.
B. Laboratory Control Sample; purchased. Ultra Solids Check #QCI-711 or equivalent.

VI. Definitions

A. Laboratory Control Sample (LCS)- A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.
B. Preparation Blank (Prep Blank)- An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents or glassware.
C. Sample Replicates (Rep)- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of the sample and duplicate indicate precision associated with laboratory procedures.

VII. Procedure

A. Preparation of gooch crucibles.
1. Clean and rinse well enough crucibles to complete a full batch of twenty samples, allowing one crucible for each sample, plus one for a LCS, one for a blank, and two crucibles for sample replicates. Be sure crucibles are marked for identification purposes.
2. Attach filter flasks to the filter set-ups. Place the rubber adapter to the top of the flask.
3. Insert a glass fiber filter disc into a clean gooch crucible, grid side down. Place the crucible to the adapter. With vacuum applied, wash the disc with 30mL DI water to insure a snug fit, and to rinse loose fibers from filter. Discard filtrate. Place crucibles in oven at 104°C for one hour.
4. Move crucibles to desiccator to cool for 1 hour. Handle crucibles using forceps. Oils from the skin can effect final results.

B. Batch Creation
1. Open Phoenix Laboratories Lims and click on QA/QC Batching,TSS/TDS/TS Batching.
2. Click on "New Batch" and use the pull-down menu to select TSS analysis. This will bring up all samples in the batching program that need to be run.
3. Create a batch of 20 samples or fewer by clicking on the box in the "Select" column.

4. Using the pull-down menus at the bottom of the window, choose a QC sample. If the batch contains more than 11 samples, choose a sample for the second rep. Click "OK"; this will bring up a TSS Batch Worksheet.
5. Using forceps to handle each gooch crucible, record the Dish ID # in the appropriate column. Then record the initial weight of each crucible in the"Tare Weight" column of the spreadsheet electronically. (Please note: it is important to use forceps when handling the crucibles, as oils from skin can affect final results).

C. Preparation of samples.

1. Allow samples to come to room temperature before analysis.

D. Preparation of filter set-up.

1. Attach filter flasks to the filter set-ups. Place the rubber adapter to the top of the flask.
2. The flask will contain the sample filtrate. Mark it as waste unless TDS is to be performed in conjunction with TSS. Be sure to use clean, DI rinsed filter flasks for TDS determination.

E. Filtration of samples.

1. Place a pre-weighed gooch crucible on the adaptor, shake sample vigorously and rapidly measure 100mL into a graduated cylinder.
2. Pour the sample into the filter set-up. Rinse the graduated cylinder with three successive 20mL portions of DI water, and pour washings into the filter set-up. Allow complete drainage between washings.
3. Continue suction for 3 minutes after filtration is complete.
4. If more than 10 minutes is needed to complete filtration, decrease sample volume.
5. If a representative sample aliquot is not possible by decanting, due to floating material, use a pipet submerged to the center of the sample container to extract a homogeneous representative sample aliquot. Exclude from analysis sand or other heavy materials that settle to the bottom of the sample container after vigorous shaking.
6. Place gooch crucibles with samples particulates trapped on the filter into the drying oven at 104°C. Reserve sample filtrate if TDS is to be determined.
7. Record on the TSS Batch worksheet: sample volume used, oven temperature, time and date samples were put into the oven.

F. Final Analysis of TSS.

1. After one hour in the oven at 104C, transfer the crucibles to a desiccator.
2. Cool in desiccator for 1 hour and determine the first weight. Record weight electronically under the appropriate batch number.
3. Return crucibles to the 104C oven for 1 hour.
4. Cool in desiccator for 1 hour and determine the second weight. Record the weight electronically.

5. Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% previous weight or less than 0.5mg, whichever is less.
6. Print out each completed batch number and file in the TSS logbook.

VIII. Calculations

A. The TSS value is calculated using the following equation:

$$TSS\ (mg/L) = \frac{(A - B) \times 1000}{SV}$$

Where: TSS = total suspended solids (mg/L)
A = average of final weights within constant weight criteria (g)
B = initial weight of gooch crucible (g)
SV = sample volume (L)

B. Calculating RPD:
The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$RPD, \% = \frac{(R1 - R2) \times 100}{(R1+R2)/2}$$

where: R1 = TSS value achieved for sample, mg/L
R2 = TSS value achieved for sample replicate, mg/L

C. Calculating the LCS:
The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the LCS sample, and then apply it to the following calculation:

$$\%\ Recovery, \% = \frac{(RL) \times 100}{(LTV)}$$

where: RL = achieved value for LCS sample, mg/L
LTV = true value of LCS, mg/L

IX. Quality Control

A. A reagent blank is analyzed with every batch of 20 or fewer samples. If the blank has a positive TSS value, the sample results are acceptable only if the blank is no more than 10% of the sample result. If the blank has a negative result of less than –5.0 mg/L, the sample results are acceptable only if the absolute value of the blank is no more than 10% of the sample result.
B. A Laboratory Control Standard (LCS) will be analyzed with every batch of 20 or fewer samples. The LCS must be recovered between 85-115%.
C. Sample replicates are analyzed every 10 of fewer samples. The RPD must be ≤20%, else repeat sample and duplicate analysis to prove matrix effect.
D. Oven temperatures are recorded daily to insure stable oven temperatures. The drying oven must maintain temperature within 103°-105°C.
E. The calibration of the analytical balance is checked daily using Class "S" weights: 50.0000g, 10.0000g, and 1.0000g. The balance is calibrated annually barring any problems throughout the year.

X. Safety

A. The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.
B. Always wear safety glasses for eye protection as well as lab coats and gloves.
C. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

XI. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.
B. Reagents and chemicals should be purchased and/or prepared in volumes consistant with laboratory use to minimize the volume of disposal.

XII. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

XIII. Method Performance

A. This method was validated through internal QA/QC monitoring, including annual method detection limit studies, precision and accuracy studies, proficiency test samples, blank analysis, laboratory control samples and sample replicates.

B. See section IX Quality Control in this SOP for acceptable limits.

XIV. Corrective Action for Out-of-Control or Unacceptable Data

A. Should the preparation blank or LCS fail the acceptance criteria given in Section IX, reanalyze batch.

B. Should the sample replicate analysis fail acceptance criteria, reanalyze the sample and replicate should sample volume permit. If sample volume is limited, replicate another sample in that batch.

XV. References

A. Standard Methods for the Examination of Waste and Wastewater, 18th edition. Method No. 2540D.

SOP No.: 301.300.0

Title: Ion Chromatography for the Analysis of Anions

Scope: This method covers the determination of Bromide, Chloride, Fluoride, Nitrate as N, Nitrite as N, O-phosphate as P, and Sulfate, using the Dionex 120 Ion Chromatograph. This method is applicable to drinking water, surface water, mixed domestic and industrial wastewater, groundwater, reagent water, and leachate (when no acetic acid is used).

I. Summary of Method:

A. A small volume of sample, 25 uL, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

B. The first two columns, the guard column and the analytical column are packed with low-capacity, strongly basic anion exchanger. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The suppressor column reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample to their corresponding acids. The separated anions in their acid forms are measured using a conductivity detector. Anions are identified based on their retention times compared to a known standard. Quantitation is accomplished by measuring the peak height and area as compared to a calibration curve.

C. Interferences:

1. Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems associated with retention times.
2. The water dip or negative peak that elutes near, and can interfere with, the fluoride peak can usually be eliminated by using the eluent for sample dilution and standard preparation.
3. Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms. For this reason, all glassware used in ion chromatography is dedicated as such. And disposable processing apparatus is used whenever possible. Prepare fresh any reagent that is causing interference.
4. Samples and reagent solutions that contain particles larger than 0.20 um require filtration to prevent damage to instrument columns and flow systems.
5. Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

6. The acetate anion elutes early during the chromatographic run. The retention times of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetic acid is used for pH adjustment.

II. Reagents and Apparatus

A. Balance. Analytical, capable of accurately weighing to the nearest 0.0001 g.
B. Ion chromatograph. Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gases and detectors.
C. Anion guard column. Ion Pac AG4A-SC Product No. 43175.
D. Anion analytical column. Dionex AS4A-SC Product No. 43174.
E. Anion suppressor device. Dionex ASRS-II Product No. 46081.
F. Detector. Conductivity cell: approximately 1.25 uL internal volume. Dionex DX-120.
G. Data Chromatography Software. Dionex PeakNet Software.
H. Reagent water (de-ionized water). Water should contain particles no larger than 0.20um.
I. Eluent solution: sodium bicarbonate (CAS RN 144-55-8) 1.7 mM; sodium carbonate (CAS RN 497-19-8) 1.8 mM. Dissolve 0.2856 g sodium bicarbonate (NaHCO3) and 0.3816 g sodium carbonate (Na2CO3) in reagent water and dilute to 2 L.
J. Stock standard solutions. 1000 mg/L (1 mg/mL): Stock standard solutions are purchased as certified solutions from Ricca. Product No.: Fluoride-3173, Chloride-1955, Nitrite-5445, Bromide-1180, Nitrate-5307, o-Phosphate-5839, and Sulfate-8112.
K. Standard solutions. Prepare as directed by Table 1.

III. Procedure

A. Calibration and Standardization. Perform Instrument Calibration when calibration checks fail, or at least once every quarter. For each analyte of interest, prepare calibration standards at five concentration levels and a blank by adding accurately measured volumes of one or more stock standards to a volumetric flask and diluting to volume with eluent.
   1. Pour prepared standards in order of increasing concentration into disposable sample cups and load into cartridges.
   2. Prepare sequence by entering the Browser screen and opening the "Default Sequence" file of the current month's folder. The first sample will be straight eluent "Standard F", which is recorded under the sample name (see Figure 1). Continue with "Standard E" as the second sample, and so on for all 6 standard levels. The "type" of sample in the sequence screen should read "Standard" and the "Status" is set at "single" (see Figure 1).
   3. The 6 standards in the sequence are followed by a LCS (Laboratory Control Standard), CALCHK (continuing calibration check), LFB (Laboratory Fortified Blank), and a BLANK (unfortified eluent).

4. The final line of the sequence lets the computer know to stop sampling and to shut down. Type "END" in the "name" field and enter "EPA 300_0 STOP" in the "Program" field (see Figure 1).
5. After the sequence is prepared, save it under the current month's folder as the current date, preceded by "CAL", i.e. CAL112102.
6. Go to "My Panels" and select "System #1". Next, start the eluent pumping by selecting the "Pump", "SRS", and "Eluent Pressure" boxes located on the left hand side of the screen. Once the flow rate, pressure, and conductivity stabilize, the sequence is ready to run.
7. Run the sequence by going to "Batch' from the main pull-down menu. Select "Start", then "Add", and lastly the file you just created, i.e. CAL112102. Click "Ready Check" and then "Start" once the "Ready Check Successful" message appears.
8. After the standards have run, view the calibration curve from the "Browser" screen. Double-click on any of the 6 calibration standards and select the "Calibration" tab at the bottom of the screen. This screen displays the number of points in each calibration curve and also the Correlation Coefficient for each analyte. The Correlation Coefficient should be at least 99.75%.

Sequence: TEST
Operator: george
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Printed: 11/21/2002 1:38:07 PM

Title:
Datasource: DIONEX2K_local
Location: DIONEX2K_1\sequence\November 2002
Timebase: DIONEX2K_1
#Samples: 11
Created: 11/21/2002 1:37:28 PM by george
Last Update: 11/21/2002 1:37:29 PM by george

No.	Name	Dil. Factor	Pos.	Program	Status	Type	Inj. Vol.	Method	Inj. Date/Time
1	Standard F	1.0000	201	EPA 300_0	Single	Standard	25.0	EPA 300_0	
2	Standard E	1.0000	202	EPA 300_0	Single	Standard	25.0	EPA 300_0	
3	Standard D	1.0000	203	EPA 300_0	Single	Standard	25.0	EPA 300_0	
4	Standard C	1.0000	204	EPA 300_0	Single	Standard	25.0	EPA 300_0	
5	Standard B	1.0000	205	EPA 300_0	Single	Standard	25.0	EPA 300_0	
6	Standard A	1.0000	206	EPA 300_0	Single	Standard	25.0	EPA 300_0	
7	LCS # 1	1.0000	1	EPA 300_0	Single	Unknown	25.0	EPA 300_0	
8	CALCHK	1.0000	2	EPA 300_0	Single	Unknown	25.0	EPA 300_0	
9	LFB	1.0000	3	EPA 300_0	Single	Unknown	25.0	EPA 300_0	
10	BLANK	1.0000	4	EPA 300_0	Single	Unknown	25.0	EPA 300_0	
11	END	1.0000	5	EPA 300_0 STOP	Single	Unknown	25.0	EPA 300_0	

Figure 1.

B. Analyzing sample sets.

1. Enter the "Browser" screen and follow the format laid out in section III.A.2 for building a sequence. Sample ID in the "Name" column, dilution (if any) in the

second, and "single" in the fifth, and "Unknown" in the sixth column (see Figure 2).

2. When building a sequence, include the following at the appropriate frequency:
   *Blank (unfortified eluent) at the beginning and end of every sample set, and once every 10 samples. The blank must be BDL (Below Detection Level) throughout the run.
   *LCS (laboratory Control Standard) at the beginning and end of every sample set, and once every 20 samples. The LCS must recover 90-110% of the true value. The LCS is purchased through ERA and contains all method anions at a mid-range level. Consult the Standards Prep Logbook for specific directions on LCS preparation. ERA Product No.: Fluoride-050, Chloride-047, Nitrite-053, Bromide-046, Nitrate-051, o-Phosphate-060, and Sulfate-062.
   *LFB (Laboratory Fortified Blank) at the beginning of every sample set and once every 20 samples. The LFB must be recovered 90-110%.
   *CALCHK (Continuing Calibration Check) which is a mid-range calibration standard, at the beginning and end of every sample set and once every 10 samples. The CCC must be recovered 90-110%.
   *Rep (Sample matrix Replicate), which is a sample run in duplicate must be analyzed at a frequency of once every 20 samples in a sample set. The replicate must have a RPD (Relative Percent Difference) of no more than 20%.
   *LFM (Laboratory Fortified Matrix Spike) which is a sample to which known quantities of the method analyses are added in the laboratory. The LFM is analyzed at a frequency of once every 20 samples in a sample set. The LFM must be recovered 80-120%.
3. The last line of the sequence is used to end the run and shut down the instrument. Type "END" in the "name" field and "EPA 300_0 STOP" in the program field.
4. After the sequence has been prepared, save it as the current date under the current month's folder (i.e. \November 2002\112102), and start the Batch as outlined in sections III.A.6. and 7.
5. Sample "Data Sheet" reports will print out one for each sample. Report only data which passes all QC criteria outlined in section III.B.2., and which fall within the limitations of the calibration curve.
6. If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.
7. If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

Sequence: 111202 — Page 1 of 4
Operator: george — Printed: 11/22/2002 8:44:27 AM

Title:
Datasource: DIONEX2K_local
Location: DIONEX2K_1\sequence\November 2002
Timebase: DIONEX2K_1 — Created: 11/11/2002 3:11:11 PM by george
#Samples: 77 — (Modified, not saved)

No.	Name	Dil. Factor	Pos.	Program	Status	Type	Inj. Vol.	Method
1	Standard F	1.0000	201	EPA 300_0	Finished	Standard	25.0	EPA 300_0
2	Standard E	1.0000	202	EPA 300_0	Finished	Standard	25.0	EPA 300_0
3	Standard D	1.0000	203	EPA 300_0	Finished	Standard	25.0	EPA 300_0
4	Standard C	1.0000	204	EPA 300_0	Finished	Standard	25.0	EPA 300_0
5	Standard B	1.0000	205	EPA 300_0	Finished	Standard	25.0	EPA 300_0
6	Standard A	1.0000	206	EPA 300_0	Finished	Standard	25.0	EPA 300_0
7	LCS # 1	1.0000	1	EPA 300_0	Single	Unknown	25.0	EPA 300_0
8	CALCHK	1.0000	2	EPA 300_0	Single	Unknown	25.0	EPA 300_0
9	LFB	1.0000	3	EPA 300_0	Single	Unknown	25.0	EPA 300_0
10	BLANK	1.0000	4	EPA 300_0	Single	Unknown	25.0	EPA 300_0
11	AE48449	1.0000	5	EPA 300_0	Single	Unknown	25.0	EPA 300_0
12	AE48456	1.0000	6	EPA 300_0	Single	Unknown	25.0	EPA 300_0
13	AE48470	1.0000	7	EPA 300_0	Single	Unknown	25.0	EPA 300_0
14	AE48470	5.0000	8	EPA 300_0	Single	Unknown	25.0	EPA 300_0
15	AE48471	1.0000	9	EPA 300_0	Single	Unknown	25.0	EPA 300_0
16	AE48471	5.0000	10	EPA 300_0	Single	Unknown	25.0	EPA 300_0
17	AE47633	5.0000	11	EPA 300_0	Single	Unknown	25.0	EPA 300_0
18	AE47634	5.0000	12	EPA 300_0	Single	Unknown	25.0	EPA 300_0
19	AE47636	25.0000	13	EPA 300_0	Single	Unknown	25.0	EPA 300_0
20	AE47637	5.0000	14	EPA 300_0	Single	Unknown	25.0	EPA 300_0
21	CALCHK	1.0000	15	EPA 300_0	Single	Unknown	25.0	EPA 300_0
22	BLANK	1.0000	16	EPA 300_0	Single	Unknown	25.0	EPA 300_0

Figure 2.

IV. Calculations

A. Calculating RPD:

The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$RPD, \% = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

where: R1 = value achieved for sample, mg/L
R2 = value achieved for sample replicate, mg/L

B. Calculating the LFM spike recovery:

The sample spike is a test if the sample matrix is suitable for accurate testing. To calculate the % recovery, first calculate both the sample and the spiked sample. Then apply the two results to the following calculation:

$$\% \text{ Recovery, } \% = \frac{(SR - R)}{STV} \times 100$$

where: SR = value of sample with added spike, mg/L
R = value of sample, mg/L
STV = true value of spike added to sample, mg/L

C. Calculating the LCS:
The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the value of the LCS sample, and then apply it to the following calculation:

$$\% \text{ Recovery, } \% = \frac{(RL)}{(LTV)} \times 100$$

where: RL = calculated value for LCS sample, mg/L
LTV = true value of LCS, mg/L

D. Converting NO_2 as NO_2 to NO_2 as N:
Since all nitrite results must be reported as nitrogen, convert results from the calibration curve, which are expressed as NO_2 as NO_2, to NO_2 as N by multiplying the result by 0.300.

E. Converting NO_3 as NO_3 to NO_3 as N:
Since all nitrate results must be reported as nitrogen, convert results from the calibration curve, which are expressed as NO_3 as NO_3, to NO_3 as N by multiplying the result by 0.226.

F. Converting PO_4 as PO_4 to PO_4 as P:
Since all o-phosphate results must be reported as phosphorus, convert results from the calibration curve, which are expressed as PO_4 as PO_4, to PO_4 as P by multiplying the result by 0.326.

V. Quality Control

A. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and the daily analysis of laboratory reagent blanks, fortified blanks and other laboratory solutions as a continuing check on performance.

B. Linear Calibration Range (LCR) is verified every quarter or whenever a significant change in instrument response is observed or expected. The verification of linearity must use a minimum of a blank and three standards. If any verification data exceeds the initial values by 10%, linearity must be re-established.

C. MDLs are determined annually, when a new operator begins work or whenever there is a significant change in the background or instrument response. To determine MDL values, take seven replicate aliquots of low concentration (estimated 3-7 times expected DL) standard and process through the entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

MDL = (t) x (S)
t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]; and S = standard deviation of the replicate analyses.

VI. Safety

A. The toxicity and carcinogenicity of the reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.
B. Always wear safety glasses for eye protection as well as gloves and lab coats.
C. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

VII. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.
B. Standards should be purchased in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

VIII. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

IX. Method Performance

A. This method was validated through internal QA/QC monitoring, including annual method detection limit studies, precision and accuracy studies, initial and continuing calibration verifications, blank analysis, laboratory control samples and matrix spikes and duplicates.
B. See section III.B. Procedure in this SOP for acceptable limits.

X. Corrective Action for Out-of-Control or Unacceptable Data

A. See the Procedure section of this SOP for specific limits.
B. Should the calibration curve have a correlation coefficient of <0.9975, remake and reanalyze curve before processing samples.

C. Should the preparation blank, LCS or inhouse standard fail acceptance criteria, reanalyze batch.

D. Should the matrix spike or sample duplicate analysis fail acceptance criteria, a non-conformance report must be generated or the sample QC must be reanalyzed.

XI. References:

A. United States Environmental Protection Agency, Environmental Monitoring Systems Laboratory Cincinnati, OH 45268. Office of Research and Development Revised August 1993. EPA Method 300.0 Determination of Inorganic Anions by Ion Chromatography Revision 2.1 John D. Pfaff.

SOP No: 302

Title: Lachat QuikChem 8000 & 8500 Operation and Maintenance

Scope: This method covers the operation and maintenance of the Lachat QuikChem 8000 & 8500 Auto-analyzers. This SOP is a supplement to the methods run on the instrument. Refer to the specific analyte SOP for information on proper analysis. References to this SOP will be found in methods for nitrate and nitrite, chloride, phenol, cyanide, ammonia and TKN.

1 Summary of Method

1.1. Both the Lachat QuikChem 8000 & 8500 are composed of a XYZ Autosampler, a multi-channel peristaltic reagent pump, a multi-channel system unit, a system controller, and a printer. The basic principle of the instrument is to introduce standards and samples onto the manifold (via the XYZ autosampler and pump) where they react in the proper proportions and timing with the reagents to form a color change. The color change is quantified at the detector head by a change in absorbance at a specified wavelength. The changes in absorbance of the standards are plotted against the concentrations of the standards, and a linear regression is applied. Samples undergoing the same treatment will generate a color change that is compared to the linear regression, and the value of the analyte in the sample is determined. Samples containing color or turbidity may interfere with colorimetric analysis, and must be filtered or diluted prior to analysis.

2 Reagents and Apparatus

2.1. Reagents will vary between chemistries, each defined as the following:

2.1.1. Carrier. The Carrier is a non-interfering liquid that carries the sample through the manifold. It also rinses the manifold between samples.

2.1.2. Buffer. The buffer, not necessary for all chemistries, adjusts the pH on the manifold so that the chemistry occurs at the proper pH.

2.1.3. Color Reagents. Since all Lachat QuikChem chemistries are colorimetric analyses, the color reagents work to react with the

sample and buffer to produce a color whose intensity is directly related to the concentration of the target analyte. Often, there is more than one color reagent in a procedure. Multiple reagents may react with each other, then the sample to produce color.

2.1.4. Standards are prepared per requirements of the specific methods, and are used to calibrate the instrument. The instrument requires calibration each day of use.

2.1.5. Lachat QuikChem 8000 or 8500 System.

2.1.6. Helium is often required by methods to degas reagents. Phenol, Cyanide, Ammonia and TKN require degassing of reagents before analysis.

2.1.7. Disposable 13x100 culture tubes.

3 Set up

3.1. Make all necessary reagents and calibration standards and record in Logbook.

3.2. Attach manifold to instrument with plastic tubing into the flow fit valve. Finger tighten tubing to avoid possible blockage from crimped tubing.

3.2.1. Position 1 and 4 contains the sample loop.

3.2.2. Position 2 is for carrier tubing

3.2.3. Position 3 is for tubing going to the appropriate manifold

3.2.4. Position 5 is for the waste tubing and waste connection after detector should always be connected.

3.3. Insert the light filter upright into the detector head.

3.4. Connect the pump tubes with cartridges that press the tubing over the pump rollers.

3.5. Put reagent lines into proper reagents. The manifold will fill with reagents and establish a steady baseline.

Caution: Air will cause baseline to jump. All air should be excluded from the system. If you see air spikes in the system, check connections and make sure all reagents are flowing properly.

4 Procedure

4.1. Open instrument to initial page. Click on initials and analyte icon. A template will appear with previously stored standards.

4.2. Highlight (left click) and append (right click) rows corresponding to the number of samples.

4.3. Highlight all samples added. To number samples, scroll down to columns and right click.

4.4. Change to Calibration Standard. Change limit accordingly.

4.5. Set sample position (usually S9)

4.6. Left click on sample type, down arrow, and check standard. You should be on "Run Properties" section of page.

4.7. Set values for check standard with window of +/- 10% of calibration standard.

4.8. Left click on cup number and change check standard to S9 (cup in the top row of autosampler). After Calibration standard is set, left click on CalStd sample number column. Scroll down to "Define DMQ set" and set number of samples between cal standard check (usually 10). Undo check mark on "after end of run" and press O.K. This will insert the Calibration standard after 10 samples.

4.9. Go to toolbar and click RUN.

4.10. Scroll down and click export worksheet. This will print out a worksheet that contains all information in the run.

4.11. If a sample needs to be diluted, refer to the MDF (Manual Dilution Factor) on worksheet. To activate the field, check the box to left of column and insert dilution factor. This information is used when final report is made.

Note: Calibration of instrument is done automatically with the criteria set. If it does not meet the minimum correlation coefficient of 0.9975, the instrument stops and correct actions are taken before recalibration. The same is done for check standards. Criteria is set at +/- 10 % of the particular standard used.

4.12. After analyte is run, go to "Tools" on the toolbar. Click on custom report then follow each page and click on type is appropriate material hitting apply each time then close. (This is the icon on the toolbar that looks like a cheese wheel).

4.13. Click on printer icon and print page.

4.14. At end of run, place the lines in DI water and pump for at least 5 minutes. Remove lines from water and pump for an additional 5 minutes.

4.15. Dismantle manifold, making sure all pieces are properly attached.

5 Calculations

5.1. The instrument calculates calibration data, calibration checks, and dilution factors automatically. The analyst is required to calculate all sample replicate RPD values, sample spike recovery, LCS recovery, and soil sample concentrations.

5.2. Calculating RPD: The RPD is the Relative Percent Difference, and is a measure of the consistency of the sample replicate for the sample test. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation.

$$RPD\ \% = \frac{(R1 - R2)}{(R1 + R2)/2} \times 100$$

R1= value achieved for sample, mg/L
R2= value achieved for sample replicate, mg/L

5.3. Calculating the sample spike recovery:

The sample spike is a test if the sample matrix is suitable for accurate testing. To calculate the % recovery, first calculate both the sample and the spiked sample. Then apply the two results to the following calculation:

$$\%\ Recovery\ \% = \frac{(SR - R)}{STV} \times 100$$

Where: SR = value of sample with added spike, mg/L
R = value of sample, mg/L
STV = true value of spike added to sample, mg/L

5.4. Calculating the LCS:

The LCS is the Laboratory Control Sample and is a test of the accuracy and calibration of the test. To calculate the % recovery of the LCS, calculate the value of the LCS sample and apply it to the following calculation:

$$\% \text{ Recovery, } \% = \frac{(RL)}{(LTV)} \times 100$$

where: RL = value for LCS sample, mg/L
LTV = true value of LCS, mg/L

5.5. Soil samples are generally analyzed as waters, diluting the weight of water into the weight of liquid. The dilution factor is based on 1 g soil = 1 mL water. This dilution factor can be included as a sample dilution in the Sample ID screen.

6 Quality Control

6.1. Quality Control guidelines are specified in SOP's written for specific analytes.

6.2. Record all Lachat runs in daily maintenance logbook. Include date, analyst, chemistry that was run, baseline, gain, as well as any alterations or repairs performed on the instrument.

7 References

7.1. QuikChem Series 8000 Automated Ion Analyzer Training Manual, Lachat Instruments, Milwaukee, WI. May 1992.

7.2 QuikChem Series QC8500 Automated Ion Analyzer Training Manual. Lachat Instruments, Milwaukee, WI. 2004.

SOP Number: 304.4500NH3 G

Title: Ammonia/TKN Phenate Method

Scope: This method covers the determination of ammonia, organic nitrogen, and Kjeldahl nitrogen in drinking, surface and saline waters, domestic and industrial wastes, soils and leachates. The working range for water samples is 0.02-10.0mg/L, and 2.0-400mg/kg for solids. Higher concentrations may be determined by sample dilutions.

I. Summary of Method

A. The sample is buffered at a pH of 9.5 with borate buffer in order to decrease hydrolysis of cyanides and organic nitrogen compounds, and then distilled into a sulfuric acid solution. The ammonia ion in the sulfuric acid solution is then determined by colorimetric analysis. This method is based on the Berthelot reaction. Ammonia reacts with alkaline phenol, then with sodium hypochlorite to form indophenol blue. Sodium nitroprusside (nitroferricyanide) is added to enhance sensitivity. The absorbance of the reaction produced is measured at 630nm, and is directly proportional to the original ammonia concentration.

B. The determination of organic nitrogen (ORGN) is based on the ammonia (NH3) and TKN results of a sample. ORGN conc. = TKN conc. – NH3 conc. Using this relationship, it is also possible to determine the concentration of TKN, when the ORGN and NH3 are known.

II. Interferences

A. When present, residual chlorine must be removed by pretreatment of the sample with sodium thiosulfate before distillation. During sample development calcium and magnesium ions may precipitate if present in sufficient concentrations. EDTA is added to the sample in-line in order to prevent this problem. Distillate turbidity may interfere and can be removed by manual filtration.

III. Sample Collection, Preservation and Storage

A. Samples can be collected in plastic or glass. They must be stored at 4°C until time of analysis.

B. Samples must be H_2SO_4 preserved to pH 1.5-2 and analyzed within 28 days of collection.

IV. Equipment and Supplies

A. Kjeldahl tubes.

B. Snap Cap, 70mL with 50mL lines.

C. Graduated cylinders, 50 mL.

D. Lachat QuickChem 8000 autoanalyzer with XYZ autosampler.

E. Digestion heating block with temperature control.

F. Reflux condenser distillation unit with temperature control.

V. Reagents and Standards

(NOTE: Use only reagent grade chemicals for standards and reagents)

A. Ammonia Stock Solution (1.0 ml=1000mg NH3-N): Dissolve 3.819g reagent grade ammonium chloride (NH4CL), that has been oven dried and desiccated, in DI water and bring to volume in a 1 liter volumetric flask.

B. Intermediate Ammonia Standard (1.0 ml=20 mg NH3-N): Dilute 20.0mL ammonia stock solution in 1-liter volumetric flask. Bring up to volume with DI water.

C. Ammonia Spiking Solution (1.0 ml=100 mg NH3-N): Dilute 100mL ammonia stock solution in 1-liter volumetric flask. Bring up to volume with DI water.

D. Ammonia Working Standards:

Std. ID	mL of Inter. Std.	Dilute to	Concentration
1	100	200mL	10.0 mg/L
2	50	250mL	4.00 mg/L
3	40	500mL	1.60 mg/L
4	5	250mL	0.40 mg/L
5	1.0	200mL	0.10 mg/L
6	0.4	200mL	0.04 mg/L
7	0.5	500mL	0.02 mg/L
8	0	250mL	0.00 mg/L

Note: All working standards are to be diluted and taken to volume with DI water. Working standard C is the calibration check standard.

E. Sodium hydroxide solution, 6 N: While stirring in a cold water bath, dissolve 240g Sodium Hydroxide (NaOH) in 1 liter of DI water.

F. Sodium hydroxide solution, 0.2 N: In a 1-liter volumetric, dissolve 8g of Sodium Hydroxide (NaOH) in 800mLs of DI water. Dilute to volume and mix.

G. Borate buffer: Add 44mls of 0.2 N NaOH solution to 500 ml of DI water. Add sodium tetraborate (2.5g anhydrous $Na_2B_4O_7$ or 4.75g $Na_2B_4O_7 * 10H_2O$) and dilute to 1 liter.

H. Sulfuric Acid Solution, 1.0N, to about 800mL DI water, add 28mL concentrated H_2SO_4,then bring to a final volume of 1L with DI. Invert 3 times.

I. Sulfuric acid solution, 0.02N: To about 800mL DI water, add 20mL 1.0N H_2SO_4 (see N above). Dilute to 1L with DI water.

J. Phenolphthalein Indicator Solution: Dissolve 5.0g phenolphthalein in 500mL 95% ethyl or isopropyl alcohol and dilute to 1L with DI water.

K. Sodium Phenolate: In a 1 liter volumetric flask, dissolve 88ml of 88% liquefied phenol or 83g crystalline phenol in approximately 600ml of DI water. While stirring, slowly add 32g sodium hydroxide. Allow to cool, then dilute to volume and mix. **CAUTION: WEAR GLOVES! Phenol causes severe burns and is rapidly absorbed through skin!**

L. Sodium Hypochlorite: In a 500-ml volumetric flask, dilute 250ml "Regular Strength" bleach (5.25% NaOCl) to volume with DI water. (NOTE: DO NOT use "Industrial Strength" or "Ultra Strength" Bleach as they contain higher concentrations of NaOCl.)

M. Buffer Solution: In a 1-liter volumetric flask, dissolve 50.0g disodium ethylenediamine tetraacetate (Na_2EDTA) and 5.5g sodium hydroxide in about 900mls DI water. Dilute to volume and mix.

N. Sodium Nitroprusside: In a 1-liter volumetric flask, dissolve 3.50g sodium nitroprusside (sodium nitroferricyanide) and dilute to volume with DI water.
CAUTION: WEAR GLOVES! Health Hazard -- Affects the Central Nervous System.

O. Carrier: DI water.

P. TKN Digestion Reagent: Dissolve 134g K_2SO_4 and 7.3g $CuSO_4$ in 500mL DI water. Slowly add 134mL concentrated H_2SO_4. Bring to a final volume of 1L with DI water.

Q. TKN Sodium Hydroxide-thiosulfate reagent: Slowly dissolve 500g NaOH and 25g $Na_2S_2O_3*5H_2O$ in water and dilute to 1 liter with DI water. **Prepare this reagent in a cooling waterbath, as it is exothermic.**

VI. Definitions

A. Laboratory Control Sample (LCS)- A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.

B. Preparation Blank (Prep Blank)- An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents or glassware.

C. Calibration standard- A solution prepared from the dilution of stock standard solutions. The calibration solutions are used to calibrate instrument response with respect to analyte concentration.

D. Matrix Spike (MS)- An aliquot of environmental sample to which a known quantity of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

VII. Procedure

A. Samples are preserved with H_2SO_4 to pH of <2 at time of sampling, and stored at 4°C until time of analysis. Samples to be determined for ammonia or TKN have a holding time of 28 days from time of collection.

B. Ammonia distillation:

1. Rinse Kjeldahl tubes with DI water. Measure 50mL of aqueous sample (or 0.01g of soil diluted to 50mL DI water) into a Kjeldahl tube containing boiling stones. Add 5mL borate buffer, 2-3 drops of phenolphthalein, and enough 6N NaOH to turn the sample light pink. If too much 6N NaOH was added, add 0.02N H_2SO_4 drop-wise until sample is light pink. Phenolphthalein is light pink at a pH of 9.5; this is the pH at which the distillation should occur. Add 1.0mL of Ammonia Spiking Solution to all matrix and blank spike tubes (T.V.= 2.0mg/L). Label the tubes with sample ID number and sample volume using a permanent marker. Record information on the Ammonia - TKN batch sheet.
2. Place Kjeldahl tubes containing prepared sample onto the distillation heating block, and attach reflux unit. Turn on condenser water.
3. Label clean snap cap tubes with appropriate sample ID number and sample dilution information, and add 10mL 0.02N H_2SO_4 to each tube. Place the snap cap under the

condenser, and raise it so that the tip of the condenser is below the surface of the sulfuric acid, but not touching the bottom.

4. Turn on the block and set upper temperature limit to 300°C.
5. Some sample matrices require the addition of an anti-foaming reagent. If a sample begins to bubble and climb up the sides of the tube, add a few drops of antifoam. If a sample is suspected or expected to foam, antifoam may be added as part of sample pretreatment.
6. After 40mL has been distilled, remove snap caps from under the condensers, and bring up to 50mL with DI water. Refrigerate at 4°C until time of color development on Lachat.
7. If sample requires TKN or organic nitrogen determination, save the remainder of sample in the Kjeldahl tube for digestion.

C. Organic Nitrogen/TKN digestion:

1. If samples require NH3 & TKN (or ORGN only), perform ammonia distillation procedure as described in III.B. above, discard distillate, and allow the remainder of the sample in the Kjeldahl tube to cool. If only TKN is requested, place 50mL sample in a clean Kjeldahl tube containing boiling stones.
2. Move to TKN digestion heating block, carefully add 10mL TKN digestion reagent to Kjeldahl tube. Add 1.0mL of Ammonia Spike Solution to all matrix and blank spike tubes (T.V. = 2.0mg/L). Do not attach reflux unit. Turn on block and set upper limit temperature to 400°C. Boil under a ventilation hood until copious white fumes are observed. Continue to digest for another 30 minutes after copious fumes are observed and after the temperature is at least 380°C.
3. Allow samples to cool up to 2 minutes, and dilute with 50mL DI water (NOTE: If samples are allowed to cool longer than 2 minutes, the residue has a tendancy of sticking to the bottom of the tube even with vortexing). Vortex to mix. Make sure that boiling chips are free from the dried slurry in the bottom of the tubes and that the acid residue is dissolved into the water!
4. Move to distillation heating block.
5. Tilt tube away from personnel, towards the back of the hood, and carefully add 10mL sodium hydroxide-thiosulfate reagent to form an alkaline layer at tube bottom. Connect tube to distillation apparatus and swirl tube to insure complete mixing. Do not swirl the tube until the reflux unit is attached. The pH of the solution should exceed 11.0.
6. Label clean snap cap tubes with appropriate sample ID number and sample dilution information, and add 10mL 0.02N H_2SO_4 to each tube. Place the snap cap under the condenser, and raise it so that the tip of the condenser is below the surface of the sulfuric acid, but not touching the bottom.
7. Turn on condenser water. Turn on the block. Make sure the sample ID numbers on the Kjeldahl tubes match the ID numbers on the other end of the condenser.
8. Some sample matrices require the addition of an anti-foaming reagent. If a sample begins to bubble and climb up the sides of the tube, add a few drops of antifoam. If a sample is suspected or expected to foam, antifoam may be added as part of sample pretreatment.
9. After 40mL has been distilled, remove snap caps from under the condensers, and bring up to 50mL with DI water. Refrigerate at 4°C until time of color development on Lachat.

D. Development Procedure on Lachat Autoanalyzer:

1. Refer to SOP #302, Lachat operation, for a more detailed description of instrument use.
2. Turn on power to all modules except pump. Turn on heating unit, set on 65°C, and allow to warm to temperature.

2. Attach ammonia manifold. Be sure to use the 650cm heater block. Refer to manifold diagram if necessary.
3. Load background and generate a sample tray. Be sure to include all sample dilutions and quality control samples (blank, prep blank, LCS, replicates, spikes, check standards, blank spikes) for each form of nitrogen (ammonia, TKN).
4. Use helium to degas all Lachat reagents except for sodium phenolate reagent and sodium nitroprusside.
5. Place feed lines into proper reagent containers. Check that the correct waste container is in place. The sample waste stream is acid waste, and the end waste stream is alkaline/phenol waste.
6. Hook pump tubing onto pump tube cassettes, and push into place onto pump. Start pump. Wait while all reagents flow through lines to establish a steady baseline.
9. Place calibration standards in the tray marked S1-S8 in order of descending concentration.
10. Start calibration and samples. The calibration curve correlation coefficient must be 0.9975 or better. If the calibration fails, the standards may have to be remade.
11. Print out calibration statistics and attach it to the last page of the report. Once the run is complete, staple a copy of the lachat run to all associated batch sheets and results sheets. Leave the completed report on the Wet Chemistry supervisor's desk for review.

VIII. Calculations

A. Calculating RPD:
The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$\text{RPD, \%} = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

where: R1 = value achieved for sample, mg/L
R2 = value achieved for sample replicate, mg/L

B. Calculating the sample spike recovery:
The sample spike is a test if the sample matrix is suitable for accurate testing. To calculate the % recovery, first calculate both the sample and the spiked sample. Then apply the two results to the following calculation:

$$\text{\% Recovery, \%} = \frac{(SR - R)}{STV} \times 100$$

where: SR = value of sample with added spike, mg/L
R = value of sample, mg/L
STV = true value of spike added to sample, mg/L

C. Calculating the LCS:
The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the value of the LCS sample, and then apply it to the following calculation:

$$\% \text{ Recovery, } \% = \frac{(RL)}{(LTV)} \times 100$$

where: RL = value for LCS sample, mg/L
LTV = true value of LCS, mg/L

IX. Quality Control

A. Prep Blank must be analyzed every batch of 20 or fewer samples. This is a DI water aliquot treated like a sample, undergoing all treatments the samples undergo. The prep blank must yield undetectable amounts of ammonia.
B. Laboratory Control Standards must be analyzed every batch of 20 or fewer samples. It must be recovered 85-115%. A failing LCS for a batch of samples requires re-analysis of the batch.
C. Blank spike must be analyzed every batch of 20 or fewer samples. This is a DI water aliquot fortified by the lab with a known quantity of ammonia. The blank spike must be recovered 75-125%.
D. Continuing calibration checks must be analyzed every 10 samples, as is written into the software of the Lachat QuickChem 8000. They must pass within 90-100%. The calibration check for ammonia is the 1.6mg/L standard (Std 3) from the calibration curve.
E. Sample replicates must be done every batch of 20 or fewer samples. They must have a RPD of no more than 20%.
F. Sample spikes must be done every batch of 20 or fewer samples. A known amount of ammonia is added to a sample to test the sample matrix. The spike need be recovered 75-125%.
G. MDL studies are performed annually or when a different analyst is performing the analysis. Seven replicates of a 0.10 mg/L standard are distilled and analyzed for ammonia. Seven replicates of a 0.50 mg/L standard are distilled and analyzed for TKN.
H. Sample preparations are documented in the Standards Prep Logbook.
I. Reagent preparations are documented in the Reagent Prep Logbook.
J. Lachat use and maintenance is documented in the Lachat Maintenance Logbook.

X. Safety

A. The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.
B. Always wear safety glasses for eye protection as well as lab coats.
C. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

XI. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.
B. Standards should be purchased in volumes consistant with laboratory use to minimize the volume of expired standards to be disposed.

XII. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

XIII. Method Performance

A. This method was validated through internal QA/QC monitoring, including annual method detection limit studies, precision and accuracy studies, initial and continuing calibration verifications, blank analysis, laboratory control samples and matrix spikes and duplicates.
B. See section IX Quality Control in this SOP for acceptable limits.

XIV. Corrective Action for Out-of-Control or Unacceptable Data

A. Should the calibration curve have a correlation coefficient of <0.9975, remake and reanalyze curve before processing samples.
B. Should the preparation blank, LCS or inhouse standard fail acceptance criteria, redistill/redigest and reanalyze batch.
C. Should the matrix spike or sample duplicate analysis fail acceptance criteria, a non-conformance report must be generated or the sample QC must be reanalyzed.

XV. References

A. Method 4500-NH3 B. and G., Standard Methods for the Examination of Water and Wastewater, 20th edition.
B. Method 4500-Norg B., Standard Methods for the Examination of Water and Wastewater, 20th edition.
C. Methods for QuikChem Automated Ion Analyzer, Lachat Instruments, Method 10-107-06-1-C, August 1993.

SOP Number: 305.2320B

Title: Total Alkalinity

Scope: This method covers the determination of alkalinity in drinking, surface, and saline waters, domestic and industrial wastes. Samples with an alkalinity of less than 20mg $CaCO_3$/L need to be titrated by low-level method included in this SOP. Samples with an alkalinity greater than 300 mg $CaCO_3$/L need to be diluted prior to titration.

I. Summary of Method

A. The Alkalinity of a sample represents the acid-neutralizing capacity of a sample. Strong acid is added to the sample until it reaches a designated pH. The amount of acid added is a function of the alkalinity of the sample.

B. Interferences.

1. Dissolved gases may be lost or gained during sample storage, and can add to or reduce the alkalinity of a sample. Minimize this interference by titrating promptly, by avoiding vigorous shaking, and by keeping the sample at a constant temperature.
2. Color may obscure the endpoint during titration. Note the presence of sample color interference in logbook. Sample dilution may be required to remove or diminish this interference.

II. Reagents and Apparatus

A. Buret capable of reading at 0.1mL increments.

B. pH meter.

C. Sulfuric Acid Solution, 0.10N. Dilute 2.8mL reagent grade conc. H_2SO_4 to 1 liter with DI water.

D. Sulfuric Acid Titrant, 0.02N. Dilute 200mL Sulfuric Acid Solution to 1 liter with DI water.

E. Sodium Carbonate Solution, 0.05N. Weigh 0.50g oven-dried and desiccated reagent grade Na_2CO_3 into a 200mL volumetric flask containing 100mL DI water. Dilute to mark with DI water. Prepare fresh weekly.

F. Methyl purple indicator solution. Purchased through vendor already prepared.

G. Phenolphthalein indicator solution. Dissolve 5.0g phenolphthalein into 500mL 95% isopropyl alcohol. Dilute to 1 Liter with DI water.

III. Procedure

A. Standardization of the titrant.

1. Pipet 10.0 mL Sodium carbonate solution into a rinsed 125mL Erlenmeyer flask. Add 40 mL DI water to bring the final volume to 50mL.
2. Add 5 drops Methyl purple indicator to Erlenmeyer flask.
3. Titrate with 0.02N H2SO4 titrant to a purple endpoint.

4. Record the volume of titrant used.
5. Repeat procedure using only DI water (50mL). One drop of titrant should be required to reach the endpoint on this blank DI water sample.
6. Calculate the normality of the titrant.

B. Sample Analysis.

NOTE: If Carbonate, Bicarbonate or Hydroxide Alkalinity is needed, follow steps 1 thru 10. If only Total Alkalinity is needed, omit steps 2-4.

1. Pipet 50.0mL sample into a rinsed 125mL Erlenmeyer flask.
2. Add 2-3 drops Phenolphthalein indicator to Erlenmeyer flask.
3. Titrate with 0.02N H_2SO_4 titrant to a clear endpoint.
4. Record the volume of titrant required to reach endpoint (P).
5. Add 5 drops Methyl purple indicator to Erlenmeyer flask.
6. Titrate with 0.02N H_2SO_4 titrant to a purple endpoint.
7. Record the TOTAL volume of titrant (from steps 1-6) required to reach endpoint (T).
8. If more than 10mL 0.02N H_2SO_4 titrant is required, dilute sample and rerun the titration.
9. If less than 1.0mL titrant is required to reach the endpoint, and the client is requesting an MDL of less than 20mg $CaCO_3$/L, then proceed to the III.C..
10. Calculate the alkalinity of the sample (use Table 1 below for Carbonate, Bicarbonate or Hydroxide Alkalinity relationships).

Table 1. Alkalinity Relationships

Result of Titration	Hydroxide Alkalinity as $CaCO_3$	Carbonate Alkalinity as $CaCO_3$	Bicarbonate Concentration as $CaCO_3$
$P = 0$	0	0	T
$P < \frac{1}{2}T$	0	2P	T − 2P
$P = \frac{1}{2}T$	0	2P	0
$P > \frac{1}{2}T$	2P − T	2(T − P)	0
$P = T$	T	0	0

*Key: P = phenolphthalein alkalinity; T = total alkalinity.

C. Low-level Alkalinity Determination.

1. Pipet 100 to 200mL sample into a rinsed 250mL Erlenmeyer flask.
2. With a calibrated pH meter, measure the pH of the sample. Record this value in logbook.
3. Add 0.02N H_2SO_4 titrant slowly to the sample, while stirring and measuring the pH.
4. Titrate to a pH of 4.5 ± 0.2. Record the volume of titrant required to reach this pH, and record the exact pH.
5. Carefully add enough 0.02N H_2SO_4 titrant to bring the pH down exactly 0.3 pH units. Record this volume.
6. Calculate the low-level alkalinity of the sample.

D. ASTM-Hydroxide Alkalinity

1. Crush sample until it is powder-like.
2. To 0.5g of sample, add 200mL of DI water and spin for 1 hour.
3. Take 2mL of this solution and bring it to 50mL with DI water (a 10,000x dilution)
4. Add 2-3 drops of phenothelien, turning the sample pink.
5. Use 0.02N H2SO4 titrant and turn the sample clear.
6. Add 2-3 drops of methyl purple, turning the sample green.
7. Titrate the sample until the sample turns purple.
8. Calculations:

$$N=\frac{2.5 \times 10}{53 \times mL \text{ of titrant}} \qquad \text{Alkalinity} = mgCaCO3 = \frac{mL \text{ titrant} \times N \times 50{,}000}{mL \text{ sample}}$$

IV. Calculations

A. Calculating the Normality of the titrant.

$$N = \frac{(A * B)}{53 * C}$$

Where: N = Normality of the titrant
A = grams of Na_2CO_3 weighed into 1L DI water (2.5g)
B = mL $NaCO_3$ solution used (15mL)
C = mL 0.02N H_2SO_4 titrant required to reach endpoint.

B. Calculating the alkalinity of the sample.

$$\text{Alk. (mg } CaCO_3/L) = \frac{(A * N * 50000)}{V}$$

Where: A = Volume of titrant required to reach endpoint. (mL)
N = Normality of the titrant (N)
V = Volume of sample used in titration (mL)

C. Calculating the low-level alkalinity of the sample.

$$\text{Alk. (mg } CaCO_3/L) = \frac{(2B - C) * N * 50000}{V}$$

Where: B = Volume of titrant required to reach first recorded pH (mL)
C = Volume of titrant required to reach second recorded pH (mL)
N = Normality of titrant (N)
V = Volume of sample used in titration (mL)

D. Calculating RPD.

The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$\text{RPD, \%} = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

Where: R1 = value achieved for sample, mg/L
R2 = value achieved for sample replicate, mg/L

E. Calculating the LCS:

The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the LCS sample, and then apply it to the following calculation:

$$\text{\% Recovery, \%} = \frac{(RL)}{(LTV)} \times 100$$

Where: RL = achieved value for LCS sample, mg/L
LTV = true value of LCS, mg/L

V. Quality Control

A. All reagents and standards are to be labeled with the following information: date prepared, date expires, preparer's initials, analyte, contents, and concentration of contents. Record preparation of all reagents in the reagent prep logbook.

B. A sample prep blank of dilution water must be analyzed with each batch of twenty or fewer samples, as well as at the end of every run. Prep blanks must be determined to be BDL (below detectable level).

C. A bought standard (LCS) is run with each batch of twenty or fewer samples. The acceptable recovery of a LCS is 85-115%.

D. Sample replicates are analyzed every 10 of fewer samples. The RPD must be $\leq$20%, else repeat sample and duplicate analysis to prove matrix effect.

E. The normality of the titrant should be determined daily. Record procedure in sample logbook.

F. Each lot of Methyl purple indicator must be shown to change color at the proper pH range.

VI. References

A. Standard Methods for the Examination of Waste and Wastewater, 19th edition. Method No. 2320B, Revised 1995.

B. EPA Methods for Chemical Analysis of Water and Wastes, Method 310.1, Revised 1983.

Effective Date: 12/28/09
Version Number: 4
Initiated By: _____
Approved By: _____

SOP No.: 306.5210B

Title: Biological Oxygen Demand (BOD and cBOD)

Scope: The Biological Oxygen Demand is used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. Application of this test to organic waste discharges allows calculation of the effect of discharges on the oxygen resources of the receiving water.

While BOD is a measure of the oxygen demands of the *biochemical degradation* of a sample, the measurement also includes and oxygen demands of the *oxidation of reduced forms of nitrogen*. By adding a nitrification inhibitor to the sample, the nitrogenous demand is eliminated, and the result is carbonaceous demand (CBOD).

Extended incubation times are a variation on the methodology, and are defined in the name of the test (i.e. BOD-5 is incubated for the standard 5 days, while BOD-20 is incubated for and extended 20 days).

I. Summary of Method

A. The sample is diluted with oxygen-saturated buffered water, sealed in an airtight container, and incubated in the dark at 20.0° C for 5 or 20 days. Reduction of dissolved oxygen (DO) concentrations in the diluted sample during the incubation time yields a measure of the BOD.

B. Because proper analysis of BOD requires successful bacterial growth, conditions must remain suitable. This includes maintaining proper pH during incubation, and elimination of toxins in the sample and sample containers. The pH of the sample is tested before sample dilution and a buffer is added to the dilution water to ensure proper pH throughout the incubation period. Residual chlorine in the sample is tested and eliminated, if necessary, before sample dilution. 300ml sample bottles are rinsed with de-ionized water before use to eliminated any residues from previous use or cleaning. Some samples may contain toxins beyond the scope of this method, which kill or slow the growth of bacteria during incubation. Such samples may require special study and treatment.

II. Sample Collection, Preservation and Holding Times

A. Samples are to be collected in plastic containers with no preservative. A minimum of 500 mls must be collected for analysis.

B. The holding time for BOD and cBOD samples is 24 hours from time of collection. In the case of a composite, the holding time is 24 hours from the end of composite sampling.
C. Store sample at 4°C until just before time of analysis. Warm to 20°C at time of analysis.

III. Apparatus and Materials

A. *BOD Magic* Software and auto-sampler.
B. Incubators capable of maintaining an even temperature at 20.0 +/- 0.50°C.
C. Incubation bottles (300mL volume) and a complement of caps and plastic cups to ensure an airtight seal. Rinse thoroughly and drain before use.
D. Large clean Nalgene carboy, with spigot at bottom.
E. Glass wand with porous end capable of diffusing the air pumped through it.
F. Air pump.
G. PH sensitive paper with accurate range 6.5 – 7.5 pH units.

IV. Reagents and Standards

A. HACH nutrient buffer pillows.
B. Polyseed seed inoculum.
C. 1N H_2SO_4: Slowly add 28mL conc. sulfuric acid to de-ionized water. Dilute to 1 L. Use caution when handling concentrated acid!
D. 1N NaOH: Dissolve 40g sodium hydroxide in de-ionized water. Dilute to 1L.
E. Potassium Iodide starch paper (KI starch paper).
F. Sodium sulfite solution: Dissolve 0.1575g Na_2SO_4 in 100mL de-ionized water. Prepare fresh daily.
G. HACH nitrification inhibitor: 2% 2-chloro-6-(trichloromethyl) pyridine. Use caution when handling.
H. Glucose-glutamic acid solution: Dissolve 150mg each of oven-dried reagent-grade glucose (dextrose) and glutamic acid to de-ionized water and dilute to 1L. Prepare fresh immediately before use. As an alternative, dilute to 100 ml and pipet 0.60 ml aliquots into each BOD bottle, stopper and freeze.
I. Laboratory Control Sample (LCS) True value = 120mg/L BOD (use 10 mls): Dissolve 150 mg reagent-grade potassium hydrogen phthalate (KHP), which has been oven-dried and desiccated, into 1000mL DI water in a volumetric flask. Store in refrigerator and prepare fresh every month. Prepare fresh upon appearance of biological growth.

V. Definitions

A. Laboratory Control Sample (LCS)- A purchased or prepared standard of a known concentration that is from a different source than the primary standard. The LCS is used to determine laboratory performance.

B. Preparation Blank (Prep Blank)- An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents or glassware.

C. Matrix Spike (MS)- An aliquot of environmental sample to which a known quantity of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

D. cBOD or Carbonaceous BOD- A biochemical oxygen demand that has been nitrogen inhibited by using a chemical.

VI. Procedure

A. Preparation of buffer water: Fill a large carboy with de-ionized water to the 18L mark, and begin aeration by placing aerating wands into the carboy, and starting the air pump. Air bubble should be seen spraying through the water. Continue aeration of the water for at least two hours. This should also allow the water to come to 20° C.

After aeration is complete, remove the aerating wands, and add one HACH nutrient buffer pillow for every 3L of water (6 pillows for 18L of water). Mix by capping the carboy and gently shaking the carboy.

B. Preparation of seed inoculum: In a clean 500mL Erlenmeyer flask, add the contents of one seed pill (discarding the plastic coat), and 500mL prepared buffer water. Stir on stir-plate for at least 30 minutes. Not all samples will require seed inoculum.

C. Sample pre-treatment:

1. Residual chlorine: Dip chlorine sensitive KI starch paper into an aliquot of sample. A blue color on the paper indicates the presence of chlorine. If chlorine is detected, add sodium sulfite solution drop-wise to a 200mL aliquot of sample until the lead acetate paper comes out clear. Do not re-use paper strips. Discard unused portion of treated sample, do not return it to refrigerator. Record any sample treatment in logbook. It should be noted that the addition of sodium sulfite may effect the BOD result. A treated blank should be analyzed when sample treatment is required.
2. pH: Dip pH paper into sample aliquot. If the pH is not in the range of 6.5-7.5, it must be adjusted prior to sample dilution. If the pH is <6.5, add 1N NaOH to the sample aliquot until it is in the proper range. If the pH is >7.5, add 1N H_2SO_4 to the sample aliquot until it is in the proper range. Make sample pH adjustments using calibrated pH meter. Discard unused portion of treated sample. Do not return treated sample to refrigerator.
3. Sample temperature adjustment: Bring samples to 20° C before making sample dilutions.
4. For samples supersaturated with DO (have an initial DO >9 mg/L), reduce DO to saturation at 20°C by shaking vigorously in partially filled BOD bottle before adding seed or dilution water.

5. Samples requiring CBOD analysis: Add two injections of HACH nitrification inhibitor to the BOD bottle for each dilution. When analyzing for CBOD, a CBOD blank and a CBOD GGA must also be analyzed once per batch.

D. Setting up *BOD Magic*:

1. Load the program onto the screen by selecting the program icon from the windows program manager. Once it is loaded, select *RUN*, and *CREATE A NEW WORKSHEET*.
2. Enter your initials as operator ID, and BOD-5 or BOD-20 as a description. Click on *OK*. An empty worksheet will appear. BOD-5 and BOD-20 require separate worksheets, as they require different incubation times. BOD-5 and CBOD-5 may be incorporated onto one worksheet so long as the CBOD is denoted such as part of its Phoenix ID #.
3. To make the worksheet, select *BUILD A SAMPLE LIST*. This will bring you to a screen that will allow you to select from the backlog of previous samples, organized by client names. Always start a worksheet with the proper QC requirements: Blank (buffer water); Blank check (buffer water); Seeded blank (buffer water with 2mL seed); Treated blank (buffer water with sodium sulfite solution---to be run only if a sample in the batch required treatment for chlorine); GGA (2% Glucose, glutamic acid solution); and a LCS (Laboratory Control Check). After those, select the samples to be run from the list on the right side of the screen. The required dilutions and seed requirements will appear on the display, all you will need to add is the Phoenix ID # for each sample. Compile your sample set on the left by clicking the *ADD* button as you pull samples up on the right. Add a sample spike and replicate every 10 samples. Close the sample set with another LCS and blank check. When the sample set is ready, click on *EXPAND* to create the worksheet.

E. Setting up the racks:

1. Each sample rack has a unique ID number, represented both numerically and as a bar code. Each rack has 24 positions, the first position being at the far left and in the back row when the rack is in position on the auto-sampler. The blank will be in this first position. The second position will hold the blank check and is at the position at the far left, second from the back. The third position is at the far left, third from the back. The fourth is far left, front row. The fifth position is at the second row from the left, in the back row. The numbering continues like this throughout the rack. These numbers match the positions on the worksheet: 1-24. The 25th will be on the next rack at the first position.
2. Using a Sharpie marker, or any permanent marker, label each sample bottle in the trays to be used with the rack ID# and the numerical position of that bottle on the rack. This will make it easier to follow the screen when preparing sample dilutions, as well as ensure that sample bottles make it back to the right position on the right rack for final DO analysis.

In the event of limited incubator space, it may be necessary to remove the samples form the rack and use the incubator doors.

3. Using the worksheet as your guide, make sample dilutions as shown on the worksheet, paying attention to seed requirements. Add 2mL of seed to BOD bottle when seed is required. Note that multiple sample dilutions are required.
4. To make dilutions, add the required amount of sample (such that will yield a DO depletion of more than 2 mg/L and a residual DO of at least 1.0 mg/L) and bring up to 300mL using a siphon hose from the carboy containing the prepared buffer water. The siphon will transfer the water without agitation.
5. In determining the appropriate dilutions to be made for a sample, there are three tools: appearance, COD (Chemical Oxygen Demand), and historical data. A minimum of three different dilutions must be prepared for samples whose BOD is unknown. Samples which are clear, have no odor, and do not foam or bubble when shaken are typically low in BOD. Dilutions of 150mL, 60mL, and 20mL are appropriate for these samples. Samples which have a septic odor, or that foam when shaken, typically have a higher BOD value. Dilutions of 1mL, 3mL, and 10mL are appropriate for these samples. While there is no ratio between the COD and the BOD of a sample, the two are empirically related. If the COD is high, the BOD will likely be high. Finally, if the sample is a routine sample, whose BOD is expected to be the same as it has historically been, then fewer sample dilutions can be run.

F. Calibration of DO meter:

1. Allow the DO probe to warm up for at least 1 hour before use.
2. Use the manual control option in the software to move the DO probe to the first position in the rack (the blank). To do this, select *MANUAL CONTROL*, and enter a cup location of 1. Send it there by clicking on *SEND*.
3. With the DO probe sitting in the blank, and the DO meter on the *EXTERNAL CONTROL* setting, allow the DO and temperature readings to stabilize.
4. Read the temperature readings from the display, and refer to the chart on the incubator to get the oxygen saturation at that temperature. That is the target reading for calibration. Type that number in as such on the MANUAL CONTROL screen.
5. Keep the DO probe sitting in the blank and switch settings on the DO meter to *CALIBRATE* and confirm calibration on meter. Once it beeps, change the setting back to *EXTERNAL CONTROL*.
6. Keep the DO probe sitting in the blank and select *GET VALUES* on the *MANUAL CONTROL* screen. The display on the top half of the screen will show the detected DO of the blank, what percent of the target DO that it represents. Any fluctuation in these values suggests a problem with the

membrane on the DO probe, and should be addressed before continuing. Once satisfied with the calibration, move the probe back to the wash station by typing "W" in the cup location box and clicking on *SEND*. Close *MANUAL CONTROL* dialog on the screen.

7. Check calibration against Winkler titration.

G. Measurement of initial DO:

1. Select the *START* icon when the first rack is ready to be analyzed for initial DO. The sample bottles should all be sitting straight in their positions, with no bottles tilted or in misalignment. The sample bottles should be filled to the top with diluted sample or buffer water. The rinse station should be receiving a slow stream of water to rinse probe between readings.
2. After START is selected, the computer will ask what rack number is positioned on the auto-sampler. Either enter the number here or use the bar-code reader to identify the sample rack ID. The latter is most preferable since it will remove any chance of inadvertent transposition of numbers. This is the rack number the computer will identify with this sample set alone. The rack ID numbers can not be shared by another sample set during the 5 or 20 day incubation period.
3. The DO probe will move from position 1 to 24 taking initial DO values, recording them on the worksheet, and rinsing in the wash in between samples. When it is finished with the first rack, it will ask what the rack ID number is for the second rack. Enter a number or use the bar-code reader. The DO probe will move from positions 1 to 24 taking initial DO values and recording them for positions 25-48 on the worksheet. This will continue until all of the samples on the worksheet have initial DO readings.
4. After all of the initial readings have been made, print the worksheet by clicking on the printer icon.
5. The information will save automatically, just click on *CLOSE* to leave the worksheet.
6. As the racks come off the auto-sampler, cap them tightly with the airtight caps leaving no air bubbles in the bottles. The bottles should have a water seal, meaning that the well on top of the bottle should retain some water so that no air can escape or creep into the bottle. The bottle should then be capped with a plastic seal so that the water seal does not evaporate.
7. The racks of samples are incubated in the dark at 20 C for 5 days +/-4 hours.

H. Measurement of final DO:

1. After the 5-day incubation (or 20-day incubation) has passed within 4 hours, a final measurement must be taken.
2. Allow the DO meter to warm up for at least 30 minutes.
3. Remove the plastic seals and bottle caps from the BOD samples to be read back. Place the first rack of the sample set on the auto-sampler.

4. Start the *BOD Magic* software by clicking on the *BOD Magic* icon. Once you see the main screen, select *RUN*.
5. Select the sample set that requires final analysis from the list of pending sample sets shown on the screen.
6. Follow the directions from section III.F. to calibrate the DO meter. Use the blank in the first position on the first rack to calibrate the instrument.
7. Once the instrument is calibrated, the DO probe is in the rinse station, and the MANUAL CONTROL screen is closed, click on the *START* icon to begin analysis of the final DO.
8. The DO probe will read the final DO values and record them in the final DO column of the worksheet. As the instrument collects data, it will automatically calculate the BOD for each sample dilution. The instrument will not average data or select appropriate data points (see section IV).
9. Note the change in DO values in the blank check sample. It should not be greater than 0.20 mg/L.
10. When one rack is completed, remove it and load the next one. Be sure all BOD bottles are seated right in the racks and that none are tilted or in misalignment. Be sure all plastic seals and bottle caps are removed from bottles before loaded onto the auto-sampler.
11. When all of the samples in the sample set have been analyzed, print a copy of the worksheet by clicking on the printer icon. Attach the copy of the initial readings from 5 (or 20) days ago behind the final readings and file in a 3-ring book.

VII. Calculations

A. Calculating BOD result:

1. The calculation for a seeded sample is:

$$\text{BOD5, mg/L} = \frac{(D1 - D2) - (B1 - B2)}{P}$$

The calculation for an unseeded sample is:

$$\text{BOD5, mg/L} = \frac{(D1 - D2)}{P}$$

Where: D1 = DO of diluted sample immediately after preparation, mg/L
D2 = DO of diluted sample after 5 d incubation at 20C, mg/L
P = decimal volumetric fraction of sample used
B1 = DO of seed control before incubation, mg/L
B2 = DO of seed control after incubation, mg/L

2. When calculating the BOD of a sample, look at the series of dilutions made for that one sample. Disregard any results for dilutions that do not

meet all of the following criteria: the final DO value must be at least 1 mg/L, the DO depletion must be at least 2 mg/L, there is no evidence of toxicity in higher sample concentrations and no obvious anomaly. Average the final BOD results of the remaining sample dilutions to yield the final result.

B. Calculating RPD:
The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$RPD, \% = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

where: R1 = BOD value achieved for sample, mg/L
R2 = BOD value achieved for sample replicate, mg/L

C. Calculating the sample spike recovery:
The sample spike is a test if the sample matrix is suitable for accurate testing. To calculate the % recovery, first calculate both the sample and the spiked sample. Then apply the two results to the following calculation:

$$\% \text{ Recovery}, \% = \frac{(SR - R)}{STV} \times 100$$

where: SR = BOD value of sample with added spike, mg/L
R = BOD value of sample, mg/L
STV = true value of spike added to sample, mg/L

D. Calculating the LCS:
The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the BOD of the LCS sample, and then apply it to the following calculation:

$$\% \text{ Recovery}, \% = \frac{(RL)}{(LTV)} \times 100$$

where: RL = BOD value for LCS sample, mg/L
LTV = true value of LCS, mg/L

VIII. Quality Control

A. Blank check samples must be analyzed at a frequency of once every 20 samples or once every batch, which ever is fewer. Blank check samples must result in a DO depletion of less than 0.2 mg/L after 5 days of incubation.

B. Blank check samples that represent the treatment of the samples must be included in all batches of samples that required sample treatment. Use the treated blank in the calculation of BOD of treated samples. When CBOD is analyzed, also add nitrification inhibitor to a CBOD blank.

C. Sample replicates must be analyzed at a frequency of once every 10 samples or once every batch of 10 or fewer samples. Calculated RPD must be </= 20%.

D. Sample spikes must be analyzed at a frequency of once every 10 samples or once every batch of 10 or fewer samples. Calculated % recovery for spikes must be within inhouse limits (approx. 60-150%).

E. Laboratory control standards must be analyzed at a frequency of twice every batch of 20 or fewer samples. Sample sets should include a LCS at the beginning and end of every worksheet. Calculated % recovery for LCS must be within inhouse limits (approx. 70-125%).

F. Glucose-glutamic acid sample is included to establish control limits over an extended period of time. GGA solution should be analyzed at a frequency of once every batch of 20 or fewer samples. When cBOD samples are analyzed, a cGGA should be analyzed in each batch. (cGGA= nitrification inhibitor is added to GGA sample). Calculated GGA result should be 198 +/- 30.5 mg/L.

G. Incubators require daily monitoring of internal temperature, and must be shown to be capable of maintaining an internal temperature of 20.0 +/- 0.50^{0}C.

IX. Safety

A. The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.

B. Always wear safety glasses for eye protection as well as lab coats and gloves.

C. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

X. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.

B. Reagents and chemicals should be purchased and/or prepared in volumes consistent with laboratory use to minimize the volume of disposal.

XI. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

XII. Method Performance

A. This method was validated through internal QA/QC monitoring, including annual proficiency sample analysis, blank analysis, laboratory control samples and matrix spikes and duplicates.
B. See section VIII Quality Control in this SOP for acceptable limits.

XIII. Corrective Action for Out-of-Control or Unacceptable Data

A. Should the GGA and LCS be out of acceptance limits, results cannot be reported. Determine problem and re-read the final dissolved oxygen values. Because samples are beyond holding time, reanalysis is not valid.
B. Should the matrix spike or sample duplicate analysis fail acceptance criteria, investigate possible explanation. Because samples are beyond holding time, reanalysis is not valid.
C. Should a sample deplete all the oxygen or not enough oxygen, a greater than or less than value must be reported. Because samples are beyond holding time, reanalysis is not valid.

XIV. References

A. Standard Methods for the Examination of Water and Wastewater, 19th ed., 1995.

SOP Number: 309.335.4

Title: Total, Amenable, and Free Cyanide

Scope: This method covers the determination of Total, Amenable and Free Cyanide in drinking waters, wastewaters, ground waters, surface waters, as well as soils and solid wastes. The applicable range is from 0.005-1.0 mg/L. Samples containing greater than 1.0 mg/L Cyanide need to be diluted prior to colorimetric analysis.

I. Summary of Method

A. The cyanide, as hydrocyanic acid (HCN), is released from cyanide complexes by means of a midi-reflux distillation operation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined by colorimetric analysis. In the colorimetric measurement, the cyanide is converted to cyanogen chloride $CNCl_2$ by reaction with Chloramine-T, which subsequently reacts with pyridine/barbituric acid to produce a red colored complex. The intensity of the color developed, as determined by its absorbance at 570nm, is quantified and compared to a calibration curve.

II. Interferences

A. While distillation removes most sample matrix interference, the presence of sulfides, nitrate, nitrite, and oxidizing agents such as chlorine can interfere with proper analysis. Samples are tested and treated for these interferences before distillation.

III. Sample Collection, Preservation and Holding Time

A. Aqueous samples may be collected in plastic or glass containers and preserved with NaOH to a pH of >12. If necessary, dechlorinate samples upon receipt.
B. Soils are to be collected in 2 oz. or larger soil jars.
C. Samples must be stored at 4°C until time of analysis.
D. Samples must be analyzed within 14 days of collection.

IV. Equipment and Supplies

A. DI water. Ion pure system.
B. Lachat QuickChem 8500. Flow injection system with auto-sampler, pump, photometric detector, and related software.

C. Ultra Scientific midi distillation setup with custom cyanide glassware.
D. Condenser water
E. Vacuum pump
F. Graduated cylinders, 50 mL.
G. Volumetric flasks, assorted sizes
H. Pipetters and pipets, assorted sizes
I. Pipet bulb
J. Analytical Balance

V. Reagents and Standards

A. Potassium iodide-starch paper.
B. Nitrate/nitrite sensitive test strips.
C. Sodium hydroxide solution, 0.25N. Dissolve 20g reagent grade NaOH in 2 L of DI water.
D. Sulfamic acid. Reagent grade.
E. Lead acetate test paper.
F. Lead carbonate. Reagent grade.
G. Sulfuric acid, 18N. Slowly add 500mL reagent grade H_2SO_4 to 500mL DI water. EXOTHERMIC REACTION---USE CAUTION.
H. Magnesium Chloride Solution. Weigh 510 g of reagent grade $MgCl_2*6H_2O$ into a volumetric flask and dilute to mark with DI water.
I. Chloramine-T solution. Dissolve 1.0 g of reagent grade chloramine-T in 250mL DI water. Prepare fresh daily.
J. Calcium Hypochlorite. Reagent grade. Dissolve 2.0 g into 100 mls of DI water.
K. Sodium Thiosulfate Pentahydrate. Reagent grade. Dissolve 2.0 g into 100 mls of DI water.
L. Potassium phosphate monobasic buffer. Dissolve 97 g Potassium phosphate monobasic (KH_2PO_4) in a 1-L volumetric flask containing 800mL of DI water, dilute to mark. Refrigerate this solution.
M. Pyridine-barbituric acid (PBA) solution. Place 15 g of reagent grade barbituric acid in a 1-L volumetric flask. Wash the sides of the flask with ~100mL DI water. UNDER A VENTILLATION HOOD, add 75mL reagent grade pyridine and mix. Add 15mL reagent grade conc. HCl and mix on a stirrer, adding sufficient DI water to bring flask to volume.
N. Cyanide Stock Solution, 1000 mg/L. Dissolve 4.4 g KOH in 1 L DI water and carefully add exactly 2.51g reagent grade KCN. KCN IS HIGHLY TOXIC---AVOID CONTACT OR INHALATION. Store in refrigerator and prepare fresh after 6 months. As an alternative, purchase. Ricca 1000ppm CN- standard.
O. Cyanide Calibration Standards. Refer to Standards preparatory logbook for directions on preparing the calibration standards ranging in concentration from 0.005 mg/L to 1.0 mg/L. Store in refrigerator and prepare fresh after 1 week.

VI. Definitions

A. Laboratory Control Sample (LCS)- A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.

B. Preparation Blank (Prep Blank)- An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents or glassware.

C. Calibration standard- A solution prepared from the dilution of stock standard solutions. The calibration solutions are used to calibrate instrument response with respect to analyte concentration.

D. Matrix Spike (MS)- An aliquot of environmental sample to which a known quantity of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

VII. Procedure

A. Aqueous samples are preserved with NaOH at time of sampling, as cyanide is not stable at neutral and acidic pH. If samples cannot be analyzed immediately, store at 4^{o} C until time of analysis. Analyze within 14 days of sampling.

B. Treat samples for possible interferences:

1. Sulfides adversely affect the procedure by producing hydrogen sulfide during distillation. If a drop of the sample on lead acetate test paper indicates the presence of sulfide, treat an aliquot of the sample with powdered lead carbonate. Maintain the pH of the sample aliquot at >12. Repeat until the drop of sample on lead acetate paper yields no color change. Yellow cadmium sulfide precipitates if the sample contains sulfide. After the sulfide has all been neutralized, filter the sample through dry filter paper into a dry beaker, and from the filtrate measure the sample aliquot to be distilled. Avoid a large excess of lead carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material.
2. Nitrates and nitrites may result in erroneously high measurements of cyanide. During the distillation, nitrate and nitrite will form nitrous acid that will react with some organic compounds to form oximes. These oximes will decompose under test conditions to generate HCN. The interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.
3. Chlorine and other oxidizing agents decompose the free and weakly bound forms of cyanide. Adding 2 drops of 2% sodium thiosulfate pentahydrate (as described in III D.2) will decompose any chlorine.
4. Color and turbidity can interfere in the analysis of free cyanide. A sample color blank is run on the lachat to eliminate this interference.

C. Pretreatment of Amenable Cyanide sample: This portion of the method is applicable to the determination of cyanides amenable to chlorination. After part of the sample is chlorinated to decompose cyanides, both the chlorinated and the untreated sample are subjected to distillation. The difference between the CN- concentrations found in the two samples is expressed as cyanides amenable to chlorination.

1. Place 50 ml of sample into a 100 ml beaker with spin bar.
2. Begin spinning sample.
3. Slowly add Calcium Hypochlorite solution dropwise to sample, checking with Potassium Iodide paper for presence of chlorine.
4. Allow chlorinated sample to spin for an hour, maintaining a pH of >12 by checking the pH and chlorine every 15 minutes.
5. After an hour, add Sodium Thiosulfate Pentahydrate dropwise to the sample to neutralize the Calcium Hypochlorite. When the Potassium Iodide indicator paper turns clear, the sample has been neutralized.
6. The sample is now ready to be run on the midi-distillation unit.

D. Distillation of samples

1. Each sample set of twenty samples includes a prep blank, a blank spike, a LCS, two replicates and two sample spikes.
2. Place 50mL of aqueous sample or approximately 1.0g soil or solid sample diluted with 50mL DI water into the midi distillation boiling-flask. Add 2 drops of sodium thiosulfate pentrahydrate to decompose any chlorine. Add 3-4 Teflon boiling chips, and place into the heating block in the back of the unit.
3. Place 50mL of 0.25N NaOH solution into the midi distillation base traps, and place into the positions in the front of the unit.
4. Attach the inlet tube, cold-fingers, and absorber to close the system.
5. Turn on the condensing water to 60gph.
6. Start a slow stream of air entering the boiling flash by turning on the vacuum (equipped with an acid trap) and adjust to maintain a bubble rate of 3 bubbles per second in each reflux flask. Allow to flow for 3 minutes.
7. Add 2g sulfamic acid down the inlet tube if NO_3 and/or NO_2 are present.
8. Slowly add 5mL of 18N H_2SO_4 through the inlet tube above the reflux flask and let the flask contents mix for 3 minutes. Pipet 2mL $MgCl_2$ solution into the inlet tube. Repeat this procedure for each sample being run. Rinse the inlet tube with a small volume of DI water to ensure accurate measurement into the reflux flask.
9. Turn the unit on by depressing the red rocker switch on each manifold. Light will glow. The heater is preset to 125° C
10. Set timing knob to 110 minutes. It may be necessary to adjust the vacuum knobs during heating to maintain the proper bubble rate. Monitor the distillation frequently to ensure proper bubble rate.

11. Timer will automatically shut off the heating unit, but continue to reflux for an additional 15 minutes.
12. Shut off vacuum source and disconnect tubing between reflux flask and absorber flask.
13. Using a pipet bulb, force air into the top of the absorber to expel any remnant solution out of the absorber frit. Do this at least 3 times. Transfer the 50mL absorber liquid to a 50mL Nalgene container, marked with sample identification. Refrigerate distilled sample until time of colorimetric analysis.
14. Discard the sample left in the reflux flask into the acid waste drum.
15. Clean all glassware thoroughly between distillation runs.

E. Colorimetric Analysis

1. Refer to SOP #302 on use of the Lachat QuickChem 8500 for general information on the operation of the instrument. This method includes information unique to the cyanide chemistry.
2. Attach manifold for Cyanide chemistry. Be sure to include backpressure loop and heater.
3. Load background.
4. Create a worksheet for the samples to be analyzed, including all QC requirements. Check standards will be included automatically after 10 samples. They must pass within 90-110% of true value, otherwise the system recognizes the error and stops automatically.
5. Degas NaOH carrier and set the heater to 60°C. Start reagents flowing.
6. Start standards and samples.
7. Review calibration. If the correlation coefficient is at least 0.9975 and the RPD values are at 10% or less, the calibration passes. It may be necessary to remake standards.
8. NOTE: This step is only necessary if Free Cyanide has been run. After samples have been analyzed and all dilutions have been run, take the PBA color reagent line out of the bottle and place it in DI to run color blanks for Free Cyanide. Rerun all samples requiring Free Cyanide and subtract out the color blanks to get the corrected results.
9. Ensure all QC criteria have been met and print out calibration statistics. Leave run on Wet Chemistry supervisor's desk for review.
10. Run DI water through the manifold to wash out any chemicals that might dry, encrust the tubing and cause blockages the next time. Allow the pump to run a few minutes after the water, to dry the tubing after rinsing.

VIII. Calculations

A. Amenable CN- mg/L= Total CN- results (mg/L) – Treated sample CN- results (mg/L).

B. Calculating RPD:
The RPD is the relative percent difference. and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$RPD, \% = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

where: R1 = value achieved for sample, mg/L
R2 = value achieved for sample replicate, mg/L

C. Calculating the sample spike recovery:
The sample spike is a test if the sample matrix is suitable for accurate testing. To calculate the % recovery, first calculate both the sample and the spiked sample. Then apply the two results to the following calculation:

$$\% \text{ Recovery}, \% = \frac{(SR - R)}{STV} \times 100$$

where: SR = value of sample with added spike, mg/L
R = value of sample, mg/L
STV = true value of spike added to sample, mg/L

D. Calculating the LCS:
The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the value of the LCS sample, and then apply it to the following calculation:

$$\% \text{ Recovery}, \% = \frac{(RL)}{(LTV)} \times 100$$

where: RL = value for LCS sample, mg/L
LTV = true value of LCS, mg/L

E. Calculating Soils results:
Take Lachat result in $\frac{mg}{L}$ x $\frac{50mL \text{ final volume}}{\text{grams of sample used}}$ / decimal percent solids

IX. Quality Control

A. Prep Blank must be analyzed every batch of 20 or fewer samples. This is a DI water aliquot treated like a sample, undergoing all treatments the samples undergo. The prep blank must yield undetectable amounts of cyanide.

B. Laboratory Control Standards must be analyzed every batch of 20 or fewer samples. This second source standard comes from ERA or Ultra and has a certified value. It must be recovered 85-115%. A failing LCS for a batch of samples requires re-analysis of the batch.

C. Blank spike must be analyzed every batch of 20 or fewer samples. This is a DI water aliquot fortified by the lab with a known quantity of cyanide. The blank spike must be recovered 90-110% or re-analyze batch.

D. Continuing calibration checks must be analyzed every 10 samples, as is written into the software of the Lachat QuickChem 8500. They must pass within 90-100%. The calibration check for cyanides is the C standard from the calibration curve.

E. Sample replicates must be done every batch of 20 or fewer samples. They must have a RPD of no more than 20%.

F. Sample spikes must be done every batch of 20 or fewer samples. A known amount of cyanide is added to a sample to test the sample matrix. The spike need be recovered 75-125%. If the spike recovery is outside of these windows, narrate non-conformance.

G. MDL studies are performed annually or when a different analyst is performing the analysis. Seven replicates of a 0.025 mg/L standard are distilled and analyzed.

H. Sample preparations are documented in the Cyanide Standards Prep Logbook.

I. Reagent preparations are documented in the Cyanide Reagent Prep Logbook.

J. Lachat use and maintenance is documented in the Lachat Maintenance Logbook.

X. Safety

A. KCN is highly toxic. Avoid contact or inhalation.

B. The toxicity and carcinogenicity of other reagents used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.

C. Always wear safety glasses for eye protection as well as lab coats.

D. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

XI. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.

B. Standards should be purchased in volumes consistant with laboratory use to minimize the volume of expired standards to be disposed.

C. This method is a "midi" form, from sample distillation to development on the Lachat, which greatly reduces the waste generated.

XII. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

B. All standards and sample waste must added to the NaOH/Cyanide waste stream.

XIII. Method Performance

A. This method was validated through internal QA/QC monitoring, including annual method detection limit studies, precision and accuracy studies, initial and continuing calibration verifications, blank analysis, laboratory control samples and matrix spikes and duplicates, as well as aqueous and soil matrix proficiency samples and internal blinds.

B. See section IX Quality Control in this SOP for acceptable limits.

XIV. Corrective Action for Out-of-Control or Unacceptable Data

A. See the Quality Control section of this SOP for specific limits.

B. Should the calibration curve have a correlation coefficient of <0.9975, remake and reanalyze curve before processing samples.

C. Should the preparation blank, LCS or inhouse standard fail acceptance criteria, redistill and reanalyze batch.

D. Should the matrix spike or sample duplicate analysis fail acceptance criteria, a non-conformance report must be generated or the sample QC must be reanalyzed.

XV. References

A. Method 335.4 Determination of Total Cyanide by Semi-automated Colorimerty, EPA Methods for Chemical Analysis of Water and Wastewater, Revised August 1993.

B. Method 4500-CN, Standard Methods for the Examination of Water and Wastewater, 19th edition, Revised 1995.

C. Test Methods for Evaluating Solid Wastes, EPA SW846, Method 9010/9012 Total and Amenable Cyanide.

SOP No.: 311.5220D

Title: Chemical Oxygen Demand (COD)

Scope: This method covers the determination of chemical oxygen demand ranging from 10-1000ppm in domestic and industrial waste, ground waters, and surface waters. Samples containing more than 1000ppm COD require initial dilution prior to analysis.

I. Summary of Method

A. The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. For samples from a specific source, COD can be related empirically to BOD, TOC, or organic matter. Once that correlation has been established, COD values can be used in monitoring a source.

B. Samples, blanks and standards in sealed tubes are heated in a block digester in the presence of excess potassium dichromate at 150°C. After two hours, the tubes are removed to cool and the dichromate reduction is measured spectrophotometrically at 620nm, and compared to a calibration curve.

C. Chlorides are quantitatively oxidized by dichromate and represent a positive interference. Mercuric sulfate is added to the digestion tubes to complex excess chlorides, or the sample can be diluted to reduce the chloride concentration to inconsequential levels.

D. Samples are preserved with sulfuric acid to a pH <2 in glass bottles if possible. Use plastic only of it is known that no organic contaminants are present in the containers. Properly preserved samples may be analyzed up to 28 days after sampling. Unpreserved samples can be filtered through carbon free filters and then acidifed to be analyzed for dissolved COD if necessary.

II. Definitions

A. Laboratory Control Sample (LCS)- A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.

B. Preparation Blank (Prep Blank)- An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents or glassware.

C. Matix Spike (MS)- An environmental sample to which known quantities of the method analyte is added in the laboratory. The MS is analyzed exactly like a sample and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

III. Reagent and Apparatus

A. HACH COD digestion vials, or equivalent, high range.
B. Block digester 150°C, with 120-minute timer.
C. Class "A" pipets.
D. Eppendorf pipettor and pipet tips (2mL).
E. Volumetric flasks, 25mL, 50mL and 100mL.
F. Pall 0.45 um carbon-free syringe filters, P/N 4614, if dissolved COD is requested. (NOTE: USING A FILTER THAT IS NOT CARBON-FREE WILL CAUSE A FALSE POSITIVE RESULT.)
G. Spectrophotometer, 620nm.
H. 5000ppm COD stock solution: Dissolve 425mg reagent-grade potassium hydrogen phthalate (KHP), which has been oven-dried and desiccated, into 100mL DI water. 1.00mL=5000ug COD. Store in refrigerator and prepare fresh every 3 months, or when a new calibration is required. Prepare fresh upon appearance of biological growth.
I. Calibration Standards: Prepare standards ranging from 10-1000ppm. Refer to section IV.E..

IV. Procedure

A. Turn block digester on and allow it to warm to 150°C. Turn on spectrophotometer and allow it to warm up for at least 30 minutes.
B. Set COD vials in a test tube rack and label with appropriate sample numbers, standards, blanks, etc. A preparation blank (DI water), a Laboratory Control Standard, and 100ppm and 500ppm calibration standards must be included for every batch of 20 or fewer samples. A sample spike and sample replicated must be included for every 20 or fewer samples.
C. Pipet 2.0 mL of sample into HACH digestion vial using an Eppendorf pipet and fresh pipet tips. Shake well. If the sample turns the solution in the vial green, a sample dilution is required. Use only class "A" volumetric flasks when preparing dilutions.
D. Prepare sample spikes by pipetting 0.5mL stock solution to a 25mL volumetric flask and bring to volume with sample to be spiked. Pipet 2.0 mL of spiked sample into digestion vial. Shake well.
E. Prepare sample replicates by pipetting 2.0mL of sample to be replicated into digestion vial. Shake well.
F. Prepare LCS and calibration standards as samples, pipetting 2.0mL into digestion vial. Shake well.
G. Prepare preparation blank by pipetting 2.0 mL of laboratory DI water into digestion vial.
H. Place all vials into pre-heated block digester and turn the timer to 120 minutes. The block digester will turn off automatically after 120 minutes.
After digestion, remove vials from block and place in a rack to cool. Allow turbidity to settle. DO NOT SHAKE VIALS AFTER DIGESTION. If there is floating material in vial, centrifudge before reading on spectrophotometer.

I. Vials can be placed directly into spectrophotometer (in lieu of decanting into sample cell), covered to keep out all ambient light. Read at 620nm against digested blank.

J. The records in the COD logbook include: absorbance of samples and QC, dilutions made, final result, analyst initials, date (including year), calibration curve reference ID, calibration curve calculation (y=mx+b, where y=,x=,m=, and b=), calibration standard reference ID's, spike source, spike true value, LCS source, LCS true value, and the Lot number of HACH digestion vials.

V. Calculations

A. Calculating RPD:
The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$\text{RPD, \%} = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

where: R1 = COD value achieved for sample, mg/L
R2 = COD value achieved for sample replicate, mg/L

B. Calculating the sample spike recovery:
The sample spike is a test if the sample matrix is suitable for accurate testing. To calculate the % recovery, first calculate both the sample and the spiked sample. Then apply the two results to the following calculation:

$$\text{\% Recovery, \%} = \frac{(SR - R)}{STV} \times 100$$

where: SR = COD value of sample with added spike, mg/L
R = COD value of sample, mg/L
STV = true value of spike added to sample, mg/L

C. Calculating the LCS:
The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the COD of the LCS sample, and then apply it to the following calculation:

$$\text{\% Recovery, \%} = \frac{(RL)}{(LTV)} \times 100$$

where: RL = COD value for LCS sample, mg/L

LTV = true value of LCS, mg/L

D. Calculate the calibration standards (100ppm and 500ppm) as the LCS is calculated.

E. The calculation of the COD is determined using an 8 point linear regression. Refer to the Standards Prep Logbook for the most current calibration curve. Using COD stock solution (II.G), and following the guidelines in the Standards Prep Logbook, prepare the following standard solutions: 1000ppm, 500ppm, 250ppm, 200ppm, 100ppm, 50ppm, 25ppm, and 10ppm. First, blank out the spectrophotometer, set at 620nm, using a prep blank. Next, use 2mL of each standard, and analyze them as samples, recording the absorbance at 620nm. Plot the absorbances against the corresponding concentrations using a graphing calculator or computer program. Follow with a linear regression, and use the equation to calculate sample concentrations:

$Y = (MX + B) * DF$, where: Y = COD (mg/L)
M = slope of the linear regression
X = absorbance at 620nm
B = y-intercept of linear regression
DF = dilution factor, if any

Note that M and B values will differ with each calibration.

VI. Quality Control

A. All reagents and standards are labeled with the following: concentration, analyte, initials, date prepared, and date expires. All chemicals are used on a first in first out system. All reagent and standard preparations are logged in reagent prep logbook or standards prep logbook.

B. Sample spike recovery must be between 75-125%.

C. Sample replicate RPD must be <20%.

D. Laboratory Control Standard (LCS) recovery must be between 85-115%.

E. Standards from the calibration curve must be within 5%. If not, a new calibration curve is generated.

F. A new calibration curve is generated with every new Lot number of COD digestion vials or when new stock solution is made.

VII. Safety

A. The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.

B. Always wear safety glasses for eye protection as well as lab coats.

C. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures.

VIII. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.
B. Standards should be prepared in volumes consistant with laboratory use to minimize the volume of expired standards to be disposed.

IX. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

X. References

A. Methods of Chemical Analysis of Water and Wastes, EPA 600, 1983.
B. HACH Water Analysis Handbook, 2nd ed., 1992.
C. Standard Methods for the Examination of Water and Wastewater, Method 5220D, 19th ed., 1995.

SOP No.: 323.2540 C

Title: Total Dissolved Solids (TDS)

Scope: This method covers the determination of dissolved solids in drinking, surface, saline waters, and domestic and industrial wastes. The TDS value of a sample is a measure of the total minerals in the sample. The practical range of the determination is 5.0-2000mg/L. Samples containing more than 2000mg/L dissolved solids require sample dilution prior to analysis.

I. Summary of Method

A. A well-mixed sample is filtered through a glass fiber filter, and the filtrate is evaporated to dryness in a pre-weighed beaker and dried to a constant weight at 180°C. The increase in beaker weight represents the total dissolved solids (TDS).

B. If total suspended solids (TSS) is being determined on the sample, the solids retained on the glass-fiber filter of a pre-weighed gooch crucible may be utilized for TSS.

II. Interferences

A. Highly mineralized waters with high calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation and rapid weighing. Samples high in bicarbonate require prolonged drying to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200mg residue.

III. Sample Collection, Preservation and Storage

A. Samples are to be unpreserved and stored at 4°C prior to analysis.

B. Samples are analyzed as soon as possible, but not after a holding time of 7 days from time of sampling.

IV. Equipment and Supplies

A. Glass fiber filters, Whatman 934-AH or equivalent.

B. Gooch crucibles of same size as filters, with adapter.

C. Filter flasks, 250ml or 500ml volume.

D. Beakers, 150mL capacity.

E. Drying oven, 180°C +/-2C.

F. Desiccator. Change desiccant every month, or when desiccant changes color.

G. Graduated cylinder, 100mL.

H. Analytical balance, capable of weighing to 0.1mg. Calibration checked before use using Class "S" weights: 50g, 10g, 1g.

V. Reagents and Standards

A. Laboratory deionized water.
B. Laboratory Control Sample; purchased. Ultra Solids Check #QCI-711 or equivalent.

VI. Definitions

A. Laboratory Control Sample (LCS)- A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.
B. Preparation Blank (Prep Blank)- An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents or glassware.
C. Sample Replicates (Rep)- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of the sample and duplicate indicate precision associated with laboratory procedures.

VII. Procedure

A. Preparation of evaporating dishes.
1. Clean and rinse enough beakers to complete a full batch of twenty samples, allowing one beaker for each sample, plus one for a LCS, one for a blank, and two beakers for sample replicates. Be sure beakers are marked for identification purposes.
2. Place beakers in oven at 180°C for one hour.
3. Move beakers to the designated desiccator and cool for 3 hours.

B. Batch Creation
1. Open Phoenix Laboratories Lims and click on QA/QC Batching, TSS/TDS/TS Batching.
2. Click on "New Batch" and use the pull-down menu to select TDS analysis. This will bring up all samples in the batching program that need to be run.
3. Create a batch of 20 samples or fewer by clicking on the box in the "Select" column.
4. Using the pull-down menus at the bottom of the window, choose a QC sample. Choose a second rep whenever there are 11 or more samples in a batch. Click "OK"; this will bring up a TDS Batch Worksheet.
5. Record the ID # for each beaker in the appropriate space. Then electronically record the initial weights for each beaker into the space in the "Tare Weight" column. Handle beakers with forceps as oils from skin can affect final results.

C. Preparation of samples.
1. Allow samples to come to room temperature before analysis.

D. Preparation of filter set-up.
1. Attach clean, DI water rinsed 250 mL filter flasks to the filter set-ups. Place the rubber gooch crucible adapter to the top of the flask.

2. Insert a glass fiber filter disc into a clean gooch crucible, grid side down. Place the crucible to the adapter. With vacuum applied, wash the disc with 30mL DI water to insure a snug fit, and to rinse loose fibers from filter. Discard filtrate. If TSS is to be performed in conjunction with TDS, use the prepared and pre-weighed gooch crucibles.

E. Filtration of samples.

1. After the filter has been rinsed with DI water, shake sample vigorously and rapidly measure 100mL into a graduated cylinder.
2. Pour the sample into the filter set-up. Rinse the graduated cylinder with three successive 10mL portions of DI water, and pour washings into the filter set-up. Allow complete drainage between washings.
3. Continue suction for 30 seconds after filtration is complete.
4. If more than 10 minutes is required to complete filtration, decrease sample volume.
5. If a representative sample aliquot is not possible by decanting, due to floating material, use a pipet submerged to the center of the sample container to extract a homogeneous representative sample aliquot. Exclude from analysis sand or other heavy materials that settle to the bottom of the sample container after vigorous shaking.
6. Place beakers with filtrate into the 180°C drying oven. Reserve gooch crucibles if TSS is to be determined.
7. Record in the TDS spreadsheet: sample volume used, oven temperature, date, analyst initals, and time samples were put into the oven.

F. Final Analysis of TDS

1. After all sample has evaporated and beakers have dried, transfer from the 180°C oven to the designated dessicator.
2. Cool in desiccator to room temperature and determine the first weight. Record this weight, date, time, & oven temperature into the spreadsheet.
3. Return beakers to the 180°C oven for 1 hour.
4. Cool in desiccator and determine the second weight. Record this weight, date, time, & oven temperature into the spreadsheet.
5. Repeat the cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% previous weight or less than 1.0mg, whichever is less.
6. Transfer data from the speadsheet(s) into Labworks. Check the results in Labworks to ensure the transfer was accurate and correct.
7. Print out data from each completed TDS batch number and file in the TDS logbook.

VIII. Calculations

A. The TDS value is calculated using the following equation:

$$\text{TDS (mg/L)} = \frac{(A - B) \times 1000}{SV}$$

Where: TDS = total dissolved solids (mg/L)

A = average of final beaker weights within constant weight criteria (g)
B = initial weight of beaker (g)
SV = sample volume (L)

B. Calculating RPD:
The RPD is the relative percent difference, and is a measure of the consistency of the sample replicate for the sample set. First, calculate the results for both the sample and the sample replicate. Then apply the two results to the following calculation:

$$\text{RPD, \%} = \frac{(R1 - R2)}{(R1+R2)/2} \times 100$$

where: R1 = TDS value achieved for sample, mg/L
R2 = TDS value achieved for sample replicate, mg/L

C. Calculating the LCS:
The LCS is the laboratory control standard and is a test of the accuracy of the calibration and the test overall. To calculate the % recovery of the LCS, calculate the LCS sample, and then apply it to the following calculation:

$$\text{\% Recovery, \%} = \frac{(RL)}{(LTV)} \times 100$$

where: RL = achieved value for LCS sample, mg/L
LTV = true value of LCS, mg/L

IX. Quality Control

A. A reagent blank is analyzed with every batch of 20 or fewer samples. If the blank has a positive TDS value, the sample results are acceptable only if the blank is no more than 10% of the sample result. If the blank has a negative result of less than –10mg/L, the sample results are acceptable only if the absolute value of the blank is no more than 10% of the sample result.

B. A Laboratory Control Standard (LCS) will be analyzed with every batch of 20 or fewer samples. The LCS must be recovered between 85-115%.

C. Sample replicates are analyzed every 10 of fewer samples. The RPD must be ≤20%, else repeat sample and duplicate analysis to prove matrix effect.

D. Oven temperatures are recorded daily to insure stable oven temperatures. The 180°C oven must maintain temperature within 178°-182°C. The drying oven must maintain temperature within 103°-105°C.

E. The calibration of the analytical balance is checked daily using Class "S" weights: 50.0000g, 10.0000g, and 1.0000g. The balance is calibrated annually barring any problems throughout the year.

X. Safety

A. The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.
B. Always wear safety glasses for eye protection as well as lab coats and gloves.
C. Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

XI. Pollution Prevention

A. Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.
B. Reagents and chemicals should be purchased and/or prepared in volumes consistant with laboratory use to minimize the volume of disposal.

XII. Waste Management

A. It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

XIII. Method Performance

A. This method was validated through internal QA/QC monitoring, including annual method detection limit studies, precision and accuracy studies, proficiency test samples, blank analysis, laboratory control samples and sample replicates.
B. See section IX Quality Control in this SOP for acceptable limits.

XIV. Corrective Action for Out-of-Control or Unacceptable Data

A. Should the preparation blank or LCS fail the acceptance criteria given in Section IX, reanalyze batch.
B. Should the sample replicate analysis fail acceptance criteria, reanalyze the sample and replicate should sample volume permit. If sample volume is limited, replicate another sample in that batch.

XVI. References

A. Standard Methods for the Examination of Waste and Wastewater, 18th edition. Method No. 2540C.

Effective Date: 12/20/07
Version Number: 2
Initiated By: _____
Approved By: _____

SOP Number: 225.2340B

Title: Hardness Determination by Calculation

Scope: This method is applicable to drinking, surface, and ground waters, and industrial and domestic wastes. This method is applicable to all samples in the range of 5.0 mg/L to saturated solutions. This method is for Total Hardness and Calcium Hardness.

I. Summary of Method

A. The preferred method for determining total hardness is to compute it from the results of separate determinations of calcium and magnesium.
B. Calcium hardness is determined using only the calcium result.
C. Refer to metals digestion and ICP analysis methods for specific information about interferences and method summaries.

II. Reagents and Apparatus

A. Calcium and magnesium data from ICP.

III. Procedure

A. Calculate the hardness of the sample.
B. Record the calcium, magnesium and resulting hardness concentrations in the logbook.

IV. Calculations

A. Calculate the hardness of the sample.

$$\text{Total Hardness (mg CaCO3/L)} = 2.497\,(C) + 4.118\,(M)$$

Where: C = Calcium concentration in sample, mg/L
M = Magnesium concentration in sample, mg/L

B. Calculate the calcium hardness by omitting the Magnesium information from the calculation.

$$\text{Calcium Hardness (mg CaCO3/L)} = 2.497\,(Ca)$$

V. Quality Control

A. Quality control criteria outlined in the procedures for Metals Prep and Metals Determination by ICP must be followed for hardness by Calculation.

VI. References

A. Standard Methods for the Examination of Waste and Wastewater, 19th edition. Method No. 2340B. Revised 1995.

SOP Number: 503.Hg

Title: Determination of Mercury by Automated Cold Vapor Atomic Absorption.

1.0 Scope and Application

This procedure describes the determination of mercury (total, dissolved, or TCLP) in ground water, wastewater, wastes, soils, and solids by automated cold vapor.

2.0 Summary of Method

2.1 All samples and quality control standards are digested prior to analysis. The digested sample is analyzed using an automated mercury system. Stannous chloride (SnCl) is added to the reaction vessel to reduce all mercury to elemental mercury. The mercury vapor is then purged into the absorbance cell with argon gas. The absorbance is measured at 253.7 nm and compared against calibration standards.

2.2 The typical detection limit for this method is 0.0002 mg/L.

3.0 Sample Collection, Preservation and Storage

3.1 Aqueous samples must be acidified to a pH of <2 with HNO_3 and stored in plastic or glass containers. The maximum holding time is 28 days.

3.2 Nonaqueous samples must be refrigerated and analyzed as soon as possible.

4.0 Interferences

4.1 Potassium permanganate is added to eliminate possible interference from sulfide.

4.2 Seawaters, brines, and industrial effluents high in chlorides require additional permanganate (as much as 25 ml) because, during the oxidation step, chlorides are converted to free chlorine, which also absorbs radiation of 253.7 nm.

5.0 Equipment and Supplies

5.1 Mercury analyzer, PSA Merlin with Avalon software

5.2 Argon gas

5.3 50 ml plastic vials, disposable

5.4 Transfer pipets, disposable

5.5 Volumetric pipets, assorted

5.6 Eppendorf micropipettors

5.7 Volumetric flasks, 1000 ml

6.0 Reagents and Standards

6.1 Deionized water.

6.2 Nitric Acid, conc., trace metals grade.

6.3 Nitric Acid Solution, 1%: Add 800 ml of deionized water to a 1 liter flask. Slowly add 10 ml of conc. HNO_3 and bring to volume with deionized water.

6.4 Hydrochloric Acid, conc., trace metals grade.

6.5 Hydrochloric Acid Solution, 10%: Add 800 ml of deionized water to a 1 liter flask. Under a hood, slowly add 100 ml of concentrated HCl (trace metals grade) and bring to volume with deionized water. Invert to mix.

6.6 SnCl solution: In a one liter flask, dissolve 20 grams of SnCl in 10% HCl. Bring to volume with the 10% HCl solution.

6.7 Mercury Stock Solution: 1000 ppb, purchased.

6.8 Mercury standards: Use 0.00 ppb, 0.2 ppb, 1.0 ppb, 2.0 ppb, 4.0 ppb and 5.0 ppb for curve. Prepare dilutions of the Mercury stock into 1% HNO_3 and bring to a final volume of 110 mls.

7.0 Definitions

7.1 Laboratory Control Sample (LCS)- A purchased standard of a known concentration that is from a different source than the calibration standards. The LCS is used to determine laboratory performance.

7.2 Preparation Blank (Prep Blank)- An aliquot of reagent water that is treated exactly as a sample. The prep blank is used to determine if method analytes are present in the lab environment, reagents or glassware.

7.3 Continuing Calibration Blank (CCB)- An aliquot of acidified DI water that has not undergone the digestion (prep) process. This blank is used to determine is there is carryover from CCV or high concentration samples.

7.4 Calibration standard (CCV, CRA)- A solution prepared from the dilution of stock standard solutions. The calibration solutions are used to calibrate instrument response with respect to analyte concentration.

7.5 Matrix Spike (MS)- An aliquot of environmental sample to which a known quantity of the method analytes are added in the laboratory. The MS is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results.

8.0 Procedure

8.1 Instrument Set up

8.1.1 Turn power switches on at back of units.

8.1.2 Turn argon switch to the up or open position.

8.1.3 Turn the switch on the back of the detector to "ref", and adjust the left screw until it reads 1100. Allow to warm up.

8.1.4 Turn the switch to the "ratio" position and adjust the right screw until it reads 1800. Allow to stabilize.

8.1.5 Plug cable from lamp into the back of the detector.

8.1.6 Tighten down the pressure fingers on the pump tubes that go to the stannous chloride and deionized water lines.

8.1.7 Reach over the back of this module, and turn the pump switch on. Make sure that the SnCl and water are pumping through.

8.2 Computer Program Set up & Instrument Operation

8.2.1 Turn computer on, and double click on the Avalon icon to open software. This also moves autosampler to the ready position.

8.2.2 Put standards in the following positions in the autosampler tray: #1 blank, #2 0.2 ppb std., #3 1.0 ppb std., #4 2.0 ppb std., #5 4.0 ppb std. and #6 5.0 ppb standard. Use large size gray cups and fill ¾ full.

8.2.3 Go to FILE, and open using NEW.

8.2.4 Go to CALIBRATE, NEW CURVE, ANALYZE. This starts analyzing the calibration curve. If you need to auto zero the baseline, press the escape key, and start this sequence over.

8.2.5 When the curve is complete, make sure that the correlation coefficient is acceptable (>0.9975), and go to FILE, PRINT, to print the curve statistics.

8.2.6 Take standards out of the autosampler tray, and start loading samples, starting with the following sequence: ICV (Ultra), Blank (ICB), Low level standard (CRA) and Prep blank. Note: When pouring out soil matrix samples into 50 ml plastic vials, start with a 1:2 dilution.

8.2.7 Go to PROGRAM, EDITOR. Change TYPE from *calibrate* to *sample.* One by one, type in sample numbers and ADD to run. Be sure to enter sample weights (found in Hg prep logbook) and dilution factor for each soil sample. Change units accordingly.

8.2.8 After every 10 samples, put up a sample duplicate and matrix spike. Then program it to read a CCV and CCB.

8.2.9 To reset autosampler to start at position 1, go to OPTIONS, and INSTRUMENT SET UP and click OK.

8.2.10 To start run, go to PROGRAM, RUN. Type in the tray position you would like to run to start at if different from position 1.

8.3 Instrument Shut Down

8.3.1 Place SnCl line in deionized water to rinse out.

8.3.2 Go to FILE, save data as text file using date, and EXIT.

8.3.3 Turn pump switch off when lines are rinsed.

8.3.4 Release pressure fingers from pump tubing.

8.3.5 Close Argon valve to the off or down position.

8.3.6 Turn off power switches on the backs of the units.

8.3.7 Unplug lamp cable.

8.3.8 Log off computer and shut down.

9.0 Quality Control

9.1 An initial calibration curve containing five standards must be analyzed daily, prior to sample analysis. The correlation coefficient must be >0.9975.

9.2 An Initial Calibration Verification (ICV) must be analyzed daily, immediately after calibration. It must be from a separate source and yield a recovery of 85-115%. We use an ULTRA standard for this requirement to check laboratory accuracy.

9.3 An Initial Calibration Blank (ICB) must be run following the ICV, to check sensitivity and evaluate contamination problems. This blank contains nitric acid but is not digested.

9.4 A CRA or CRDL (contract required AA or detection limit) standard of 0.20 ppb must be run at the beginning of the run to verify recovery.

9.5 A CCV or check standard must be analyzed after every ten samples and at the end of each run. It should be the same source as the calibration standards, and fall mid-range in the curve. The recovery must be 80-120%.

9.6 A blank (CCB) must be analyzed every ten samples, immediately following the CCV. It must be less than the reporting limit.

9.7 Preparation blanks must be analyzed for every matrix (WM, SM, TCLP etc.) and for each batch of 20 or fewer samples. They must be less than the reporting limit.

9.8 A Laboratory Control Sample (blank spike) must be digested with every batch of 20 or fewer samples. It must be matrix matched, a separate source from the calibration standards and yield an 80-120% recovery.

9.9 A sample matrix spike must be performed at a frequency of one per batch of 20 samples. It must be digested, and yield a 75-125% recovery for all matrices.

9.10 A sample duplicate must also be digested in every batch of 20 or fewer samples. The relative percent difference (RPD) must be +/- 20% for aqueous samples, and +/- 35% for soil matrices.

9.11 Method detection limit (MDL) studies must be performed annually.

10.0 Safety

10.1 The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. A reference file of material data handling sheets are available to all personnel involved in the chemical analysis.

10.2 Always wear safety glasses for eye protection as well as lab coats.

10.3 Refer to Phoenix SOP #805: Hazardous Chemical and Laboratory Safety Procedures

11.0 Pollution Prevention

11.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation.

11.2 Standards should be purchased in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

12.0 Waste Management

12.2 It is the laboratories responsibility to comply with all Federal, State and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

13.0 Method Performance

13.1 This method was validated through internal QA/QC monitoring, including annual method detection limit studies, precision and accuracy studies, initial and continuing calibration verifications, blank analysis, laboratory control samples and matrix spikes and duplicates.

13.2 See section 9 Quality Control in this SOP for acceptable limits.

14.0 Corrective Action for Out-of-Control or Unacceptable Data

14.1 Should the calibration curve have a correlation coefficient of <0.9975, remake and reanalyze curve before processing samples.

14.2 Should the preparation blank, LCS or in-house standard fail acceptance criteria, redigest and reanalyze batch.

14.3 Should the matrix spike or sample duplicate analysis fail acceptance criteria, a non-conformance report must be generated or the sample QC must be reanalyzed.

15.0 References

15.1 Methods for Chemical Analysis of Water and Wastes, EPA-600, December 1982, Method 245.1

15.2 Test Methods for Evaluating Solid Waste (SW-846), Third Edition, EPA Office of Solid Waste, Methods 7470/7471

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STANDARD OPERATING PROCEDURE

Preparation and Analysis of Samples for the Determination of Dioxins and Furans by USEPA Method 1613B

SOP NUMBER:	S-MN-H-002-Rev.13
EFFECTIVE DATE:	28 September 2009
SUPERSEDES:	S-MN-H-002-Rev. 12

APPROVAL

Laboratory General Manager — Date: 23 SEP 2009

Laboratory Quality Manager — Date: 28 Sep 2009

ANNUAL REVIEW

SIGNATURES BELOW INDICATE NO CHANGES HAVE BEEN MADE SINCE APPROVAL. SOP IS VALID FOR ONE YEAR FROM DATE OF LAST SIGNATURE.

Signature	Title	Date

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Table of Contents

1. PURPOSE

1.1 To describe the standard operating procedure for the preparation, analysis, processing and reporting of samples for the determination of dioxins and furans using USEPA Method 1613B.

1.2 If earlier versions of this method are requested (Method 1613, Method 1613A), this standard operating procedure is followed with applicable modifications from the referenced method.

2. SCOPE AND APPLICATION

2.1 Stable isotopically labeled analogs of 15 of the PCDDs and PCDFs are added to each sample. Samples containing coarse solids are prepared for extraction by grinding or homogenization. Water samples are extracted in separatory funnels or by solid phase extraction (SPE) followed by microwave assisted extraction (MAE). Soils and other finely divided solids are extracted using Soxhlet extraction apparatus or by MAE. Drinking water samples are analyzed using the current version of SOP S-MN-H-003.

2.2 After extraction, $^{37}Cl_4$-labeled 2,3,7,8-TCDD is added to each extract to measure the efficiency of the cleanup process. Sample cleanup procedures vary, including back extraction with acid and/or base, alumina, silica gel, and/or activated carbon chromatography.

2.3 Samples are spiked with two labeled recovery standards that are used to determine the portion of the analytes and internal standards that survived the extraction and enrichment processes. The extracts are then analyzed using high resolution gas chromatography/high resolution mass spectrometry to determine the concentration of PCDDs and PCDFs present in the samples.

2.4 This procedure is limited to the analysis of the dioxin and furan compounds listed in Attachment IV.

2.5 The accuracy of the method can be affected by matrix interferences, especially for non-isotope dilution analytes.

2.6 This method is also applicable with blood serum samples.

3. SUMMARY OF METHOD

3.1 Method 1613B was written primarily for use on water, sludge, and pulp samples. The approach outlined below has been determined to apply to soil, fly ash, tissue, waste materials, and food and feed product. This method can be expected to apply to most other matrices as well.

4. INTERFERENCES

4.1 Most samples analyzed for PCDD/PCDF content contain other organic compounds that interfere with or contaminate the mass spectrometric instrumental system. Therefore, after initial extraction, extracts are taken through the clean up steps outlined in the "Extract Enrichment/Clean Up" section of this procedure. Exceptions to performing the optional clean up steps of acid/base and carbon column cleanup steps are made with consultation of the laboratory manager and are usually limited to water matrices. The acid clean-up procedure is used to remove lipids in tissue samples and is required for this matrix.

4.2 Some contaminants (particularly chlorinated biphenyl ethers) cause matrix interferences when co-extracted from the sample and vary considerably from source to source. These biphenyl ethers rearrange in the mass spectrometry source to form dibenzofurans.

4.3 Some samples contain levels of interfering compounds which overload the analyte clean up columns. If column overload occurs, consult the laboratory manager for alternate procedures.

4.4 Rigorous glassware cleaning techniques must be used and method blank data must be monitored to evaluate the effectiveness of the glassware cleaning techniques.

4.5 HPLC grade solvents must be used for extractions. Solvents having new lot numbers must be screened for contamination prior to use by analyzing a solvent blank by the applicable analytical methods.

4.6 Raw data from all blanks, samples, and spikes are evaluated for interferences. Determine if the source of interferences is in the preparation and/or cleanup of the samples and take corrective action to eliminate the problem.

4.7 If chromatographic interferences are present (specifically, matrix components that interfere with the determination of PCDDs or PCDFs), the area from the least affected signal of the pair is used along with the theoretical ratio to determine the area of the second ion. These values are then used to calculate the estimated maximum concentration that is then reported as the estimated maximum possible concentration (EMPC).

4.8 Some interferences are reduced by analysis of a dilution of the extract.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical is regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) must be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advised.

5.3 MSDS sheets are located electronically on Groupwise and must be consulted prior to handling samples and standards. For assistance in locating the MSDS, see a supervisor or the front desk.

5.4 The 2,3,7,8-TCDD isomer has been found to be acnegenic, carcinogenic, and teratogenic in laboratory animal studies. Therefore, only highly trained personnel thoroughly familiar with handling and cautionary procedures and who understand the risks associated with this procedure handles all PCDDs and PCDFs.

5.5 Neat PCDDs and PCDFs require the use of respirators and are not to be handled in the laboratory.

5.6 Protective equipment must be worn when working with standards or samples under this procedure. This includes safety glasses, laboratory coat, and throwaway plastic gloves. Plastic sleeves, aprons, and other protective equipment are also readily available if needed. All steps of this procedure must be performed in a properly operating fume hood except those noted.

5.7 All personnel performing any part of this procedure must be properly trained in removing contaminated materials and properly disposing of them. This includes an awareness of personal hygiene as it pertains to the laboratory, personal actions as they affect coworkers, etc.

5.8 All samples analyzed by the Minnesota laboratory are held until analytical results have been reported. Samples containing PCDD/PCDFs above the allowable levels are labeled, segregated, and disposed of by personnel trained in handling toxic waste. Similarly grossly contaminated waste items including pipette tips and other laboratory equipment are segregated, collected in lined waste containers, properly labeled, and disposed of in accordance with hazardous waste regulations.

5.9 Laboratory staff wipe down a representative area of specified fume hoods at least annually using pre-sterilized gauze and hexane. These wipes are analyzed according to this method to ensure that good laboratory practices are observed at all times. The results of the wipes are archived for reference.

5.10 Additionally, personnel responsible for handling, analyzing and disposing blood samples are required to undergo blood borne pathogen training and protocols as deemed necessary by the Safety Officer.

6. DEFINITIONS

Definitions are located in the glossary of the Pace Analytical Services Quality Manual.

7. SAMPLE COLLECTION, PRESERVATION AND HANDLING

7.1 Sample size - One liter of water samples containing less than or equal to 1% solids must be extracted. Aqueous or solid samples containing greater than 1% solids must be considered as solids and sufficient volume extracted to provide a dry weight of 10 grams (except for tissue samples and other samples noted to be reported on an as received basis). One gram aliquots are typically extracted for waste samples and samples suspected to contain high analyte levels. 100 milligram aliquots are typically used for oil based samples. Sample amounts extracted for food samples containing fat are typically based on the lipid content of the sample. Non-fat foods and all feeds are based on the raw sample weight. The amounts typically needed for testing are provided in Attachment III.

7.2 Sample preservation and handling

7.2.1 Collect samples in glass containers following conventional sampling practices.

7.2.2 Maintain samples above freezing but below 6 °C under darkness from the time of collection until extraction. If solid samples will not be extracted within 30 days of sample collection, the samples must be stored frozen at < -10 °C. For Ohio VAP projects, the solid samples must be frozen upon receipt at the laboratory.

7.2.3 Samples must be checked to determine if residual chlorine is present in aqueous samples from chlorinated sources. If residual chlorine is present add 80 mg thiosulfate per one liter of water. Record that this check was performed and lot number of thiosulfate, if added, on extraction paperwork.

7.2.4 Sample pH must be confirmed. If sample pH is greater than 9, adjust the pH to 7-9 pH units with sulfuric acid prior to extraction. Record how much acid is added to the sample and the lot number of acid on the extraction paperwork.

7.2.3 Tissue samples are stored frozen at <-20°C under darkness.

7.2.4 All sample extracts are stored in the extract freezer at approximately -10°C until analysis.

7.3 Holding Times

7.3.1 Samples must be extracted within one year of sample collection and the extract analyzed within 40 days of extraction. Drinking water samples are extracted within 90 days of collection. Holding times between collection and extraction or extraction and analysis of up to one year do not invalidate the results.

7.4 Criteria for Acceptance/Rejection of Samples

7.4.1 Samples are to be rejected if information allowing determination of the applicable test and client information cannot be obtained.

7.4.2 If sample integrity has been compromised, the client must be contacted for instructions and permission to proceed with analysis. The client's comments and instructions are documented as part of routine laboratory policy.

8. EQUIPMENT AND SUPPLIES

8.1 Sample bottles - 1 Liter glass amber bottles for liquids which contain less than 1% solids; 500 mL wide mouth (or smaller) glass amber bottles for solids and sludges. All bottles are purchased pre-cleaned from the vendor. If glass amber bottles are not available, samples must be protected from the light. All bottles must have Teflon lined caps. It is optional to substitute laboratory cleaned bottles for pre-cleaned bottles. Bottles must be detergent washed, then solvent rinsed and baked at 450oC for one hour minimum.

8.2 8 dram open top glass vials

8.3 2 dram vials with Teflon-lined screw caps

8.4 Reacti vial - 2 mL borosilicate glass

8.5 1 Liter graduated cylinder

8.6 Balances - 0.01g and 0.0001g

8.7 Warring Explosion-proof Blender (or equivalent)

8.8 Stainless steel meat grinder - 3-5 mm hole

8.9 Drying Oven

8.10 Soxhlet extraction apparatus

8.11 Thimble, 33 x 90 mm to fit Soxhlet

8.12 Heating mantle

8.13 Beakers, 50, 100, 250, 500, 2000 mL

8.14 Stainless steel spatulas

8.15 Assorted syringes and/or Eppendorf digital pipettes

8.16 Filtration apparatus

8.17 Separatory funnel, 250, 500 and 2000 mL with Teflon stop cocks

8.18 Glass chromatographic column - 300mm x 12mm

8.19 Glass wool pre-extracted with methylene chloride dried, and stored in a clean air tight plastic bag

8.20 Silanized glass wool pre-extracted with methylene chloride

8.21 Glass funnel, 125-250 mL

8.22 Glass fiber filter paper (Whatman GF/D or equivalent)

8.23 Drying column, 15-20 mm chromatograph column, also used for macro-silica and acid washing

8.24 Centrifuge apparatus - capable of rotating 500 mL centrifuge bottles or 15 mL tubes at 5000 rpm minimum

8.25 Disposable Pasteur pipettes

8.26 Disposable serological 10 mL pipettes

8.27 40 mL vials with caps

8.28 60 mL vials with caps and septa

8.29 500 mL Kuderna Danish (KD) concentrator apparatus

8.30 Teflon boiling chips – pre-rinsed with methylene chloride

8.31 Water bath, ultrasonic

8.32 Desiccator

8.33 Nitrogen evaporation system with variable flow rate

8.34 Volumetric flasks - 5 mL, 10 mL, 15 mL, 20 mL, 25 mL and 100 mL

8.35 Teflon tape

8.36 High Resolution Mass Spectrometer (HRMS, AutoSpec or equivalent) system equipped with a gas chromatograph (GC Hewlett-Packard HP5890II, Agilent 6890 or equivalent)

8.37 DB-5MS capillary column (60m, 0.25mm ID, 0.25µ), or equivalent

8.38 DB-225 capillary column (30m, 0.25mm ID, 0.25µ)

8.39 Silica gel, 100-200 mesh. Baked in an oven at 400 °C for four hours and stored in an oven at over 100 °C.

8.39.1 Acidic Silica gel, (30% w/w)- Thoroughly mix 44.0g of concentrated sulfuric acid with 100.0 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw-cap.

8.39.2 Basic Silica gel, thoroughly mix 30 g of 1N sodium hydroxide with 100 g of activated silica gel in a clean container. Break up aggregates with a stirring rod until a uniform mixture is obtained. Store in a bottle with a fluoropolymer-lined screw cap

8.40 Neutral alumina.

8.41 Celite – Supelco, reagent grade.

8.42 100-400 mesh carbon/Celite mixture.

8.43 Low volume autosampler vials with crimp caps

8.44 Sodium hydroxide - reagent grade. Dissolve 40 g NaOH in 1L reagent water.

8.45 Potassium Phosphate, Monobasic, Prepare a 0.5 M solution (68.05 g KH_2PO_4 in 1L reagent water).

8.46 Sulfuric acid - reagent grade (sp gravity 1.84)

8.47 Sodium chloride - reagent grade. Prepare a 5% (w/v) solution in reagent water.

8.48 Anhydrous sodium sulfate - Rinse with methylene chloride (20 mL/g) and bake at 400°C for 1 hour minimum. Store baked anhydrous sodium sulfate in oven until use. Cool prior to use.

8.49 Solvents - Acetone, toluene, hexane, benzene, nonane, methanol and methylene chloride. All solvents must be distilled in glass and pesticide grade.

8.50 White quartz sand 60/70 mesh

8.51 Diatomeous earth

8.52 Reference matrices

8.52.1 Reagent water

8.52.2 Playground sand or similar material that is free of target compounds; prepared by extraction with methylene chloride and/or baking at 450°C for 4 hours.

8.52.3 Fish tissue, pre-tested to be analyte free or diluted corn oil.

8.52.4 Filter paper - Gelman type A or equivalent

8.52.5 Mineral oil

8.52.6 Sodium sulfate (for non-fat food and feed)

8.52.7 Tuna, packed in water

8.53 Individual standards prepared as described in Section 9.

8.54 CEM MARS 5 microwave assisted extraction system (or equivalent)

8.55 Supelco Visiprep vacuum SPE system

8.56 Nu phase C-18 SPE filters

8.57 Silver nitrate

8.58 Extraction Sheets (See Attachment I for an example)

9. REAGENTS AND STANDARDS

9.1 Standards and working solutions are prepared from or compared to certified standards or purchased as certified premixed standards. All standards are valid for 1 year from date opened (or prepared). All standards are stored in glass bottles. The temperature at which solutions are stored is not critical and does not impact their validity. Solutions prepared in nonane or other more volatile solvents are typically stored at -18°C ± 2°C to minimize solvent loss during storage. Re-verification of standards is performed by comparison to a valid native analyte solution. The final concentrations determined for any solution being re-verified must be within 20% of the expected concentrations for that solution.

9.2 The preparation of standards and working solutions is thoroughly documented in the appropriate standards notebook. Such documentation allows the traceability of each solution to a certified, purchased solution.

9.3 Primary Stock Solution of Internal Standards (AI2-#)

Note: Identification AI2-# - # denotes the next sequential number assigned to AI2 standard from the HRMS Standard Preparation Logbook.

Compound	Conc. (µg/mL)
2,3,7,8-TCDD-$^{13}C_{12}$	1.0
2,3,7,8-TCDF-$^{13}C_{12}$	1.0
1,2,3,7,8-PeCDD-$^{13}C_{12}$	1.0
1,2,3,7,8-PeCDF-$^{13}C_{12}$	1.0
2,3,4,7,8-PeCDF-$^{13}C_{12}$	1.0
1,2,3,4,7,8-HxCDD-$^{13}C_{12}$	1.0
1,2,3,6,7,8-HxCDD-$^{13}C_{12}$	1.0
1,2,3,4,7,8-HxCDF-$^{13}C_{12}$	1.0
1,2,3,6,7,8-HxCDF-$^{13}C_{12}$	1.0
1,2,3,7,8,9-HxCDF-$^{13}C_{12}$	1.0
2,3,4,6,7,8-HxCDF-$^{13}C_{12}$	1.0
1,2,3,4,6,7,8-HpCDD-$^{13}C_{12}$	1.0
1,2,3,4,6,7,8-HpCDF-$^{13}C_{12}$	1.0
1,2,3,4,7,8,9-HpCDF-$^{13}C_{12}$	1.0
OCDD-$^{13}C_{12}$	2.0

A stock solution containing labeled PCDDs and PCDFs at concentrations of 1.0 ng/uL (2.0ng/uL for OCDD-$^{13}C_{12}$) is available from Cambridge Isotope Laboratories (CIL). This solution is diluted 10X total to prepare the B12 secondary solution described below. Similar solutions are also available from Wellington Laboratories.

9.4 Preparation of Internal Standard Spiking Solution (BI2-#)

9.4.1 Sonicate the primary stock solution for five minutes and allow it to reach room temperature before using.

9.4.2 Dilute 1 mL of the stock internal standard solution to 10 mL with tridecane to prepare the 100 ng/mL (200 ng/mL OCDD-$^{13}C_{12}$) solution.

9.4.3 Sonicate for five minutes and transfer into clean, labeled vials. Identification includes: ID#, (BI2-#), log #, vial numbers, preparation date and preparer's initials.

9.4.4 Note: Identification BI2-# - # denotes the next sequential number assigned to BI2 standard from the HRMS Standard Preparation Logbook.

9.4.5 Seal with Teflon tape, mark the meniscus (now and after each use) and store in the standards refrigerator above freezing but below 6°C.

9.4.6 A low level food spiking solution is prepared by diluting this solution 5x with tridecane. This solution is used for food samples in conjunction with a 10 uL final extract volume and the low level calibration solutions.

9.4.7 Record all standard preparation information in HRMS Standard Preparation Logbook.

9.4.8 If not laboratory prepared, the internal spiking solution is purchsed as a prepared mix from Wellington Laboratories or equivalent.

9.4.9 Prior to extraction, 20 µL of this solution (BI2-#) is added to each sample.

9.5 Preparation of Primary Native Standard Spiking Solution (AN1-#)

Compound	Concentration (µg/mL)
2,3,7,8-TCDF	0.40
2,3,7,8-TCDD	0.40
1,2,3,7,8-PeCDD	2.0
1,2,3,7,8-PeCDF	2.0
2,3,4,7,8-PeCDF	2.0
1,2,3,4,7,8-HxCDD	2.0
1,2,3,6,7,8-HxCDD	2.0
1,2,3,7,8,9-HxCDD	2.0
1,2,3,4,7,8-HxCDF	2.0
1,2,3,6,7,8-HxCDF	2.0
1,2,3,7,8,9-HxCDF	2.0
2,3,4,6,7,8-HxCDF	2.0
1,2,3,4,6,7,8-HpCDD	2.0
1,2,3,4,6,7,8-HpCDF	2.0
1,2,3,4,7,8,9-HpCDF	2.0
OCDF	4.0
OCDD	4.0

9.5.1 This is a purchased solution in nonane (Wellington or CIL).

NOTE: One vendor source and standards prepared from the source are used for the ICAL. The other vendor source and standards diluted from it are used as an independent validation of all standards purchased.

9.6 Preparation of Native Spiking Solution (BN1-#)

9.6.1 Sonicate primary standard (AN1-#) for five minutes and allow it to reach room temperature before using.

9.6.2 Add 1.0 mL of AN1-# to a pre-rinsed 20 mL volumetric flask and bring to volume with tridecane to prepare this 20-200 ng/mL solution.

9.6.3 Sonicate for five minutes after preparation and transfer into 2 dram vials. Identification must include: Native Spiking Solution ID# (BN1-#), log #, preparation date, expiration date and preparer's initials.

9.6.4 Note: Identification BN1-# - # denotes the next sequential number assigned to BN1 standard from the HRMS Standard Preparation Logbook.

9.6.5 Seal vials with Teflon tape, mark the meniscus (now and after each use), and store in the standards refrigerator above freezing but below 6°C until ready to use.

9.6.6 A low-level food spiking solution is prepared by diluting this solution 5x with tridecane. This solution is used for food samples in conjunction with a 10-uL-extract volume and this low-level calibration solution.

9.6.7 Record all standard preparation information in HRMS Standard Preparation Logbook.

9.7 Preparation of Cleanup Standard Primary Stock (ACl4-#)

Compound	If Concentration is µg/mL	Amt Added (µL)	Final Conc. (µg/mL)
$^{37}Cl_4$ 2,3,7,8-TCDD	50	200	1.0

9.7.1 The 50 µg/mL solution is purchased in nonane (Cambridge or equivalent). Sonicate the solution for five minutes, allow the solution to reach room temperature and add 200 µL of the solution to a pre-rinsed 10 mL volumetric flask and bring to volume with tridecane to prepare this 1 ug/mL solution.

9.7.2 Transfer the standard to a 2 dram vial with color coded tape. Identification includes: $^{37}Cl_4$ Cleanup Standard: Primary Stock ID# (ACl4-#), log #, preparation date, expiration date and preparer's initials.

9.7.3 Note: Identification ACl4-# - # denotes the next sequential number assigned to ACl4 standard from the HRMS Standard Preparation Logbook.

9.7.4 Seal vials with Teflon tape, mark the meniscus (now and after each use), and store in the standards refrigerator above freezing but below 6°C.

9.7.5 Record all standards preparation information in HRMS Standard Preparation Logbook.

9.8 Preparation of $^{37}Cl_4$ Cleanup Standard Secondary Stock (BCl4-#)

9.8.1 Sonicate the Cleanup Standard Primary Stock (CSPS) for five minutes and allow it to reach room temperature.

9.8.2 Using an Eppendorf pipette, add 1 mL of CSPS (ACl4-#) into a pre-rinsed 25 mL volumetric flask. Bring to volume with tridecane to prepare this 40 ng/mL solution.

9.8.3 Sonicate for five minutes, transfer to 2 dram vials. Identification includes: ID# (BCl4-#), log #, vial numbers, preparation date, expiration date and preparer's initials.

9.8.4 NOTE: Identification BCl4-# - # denotes the next sequential number assigned to BCl4 standard from the HRMS Standard Preparation Logbook.

9.8.5 Seal vials with Teflon tape, mark the meniscus (now and after each use), and store in standards refrigerator above freezing but below 6°C.

9.8.6 A low-level food spiking solution is prepared by diluting this solution 5x with tridecane. This solution is used for food samples in conjunction with a 10-µL final extract volume and the low-level calibration solutions.

9.8.7 Record all standard preparation information in HRMS Standard Preparation Logbook.

9.9 Preparation of $^{37}Cl_4$ Cleanup Standard Spiking Solution (CCl4-#)

9.9.1 Sonicate the compound (BCl4-#) for five minutes and allow it to reach room temperature.

9.9.2 Using an Eppendorf pipette, add 2 mL of BCl4-# into a pre-rinsed 100 mL volumetric flask and bring to volume with toluene to prepare this 800 pg/mL. For food samples, it is appropriate to substitute the diluted food native standard solution for BC14-#.

9.9.3 Sonicate for five minutes and transfer to pre-rinsed 6 dram vials. Identification must include ID# (CCl4-#), log #, vial number, preparation date, expiration date and preparer's initials.

9.9.4 NOTE: Identification CCl4-# - # denotes the next sequential number assigned to CCl4 standard from the HRMS Standard Preparation Logbook.

9.9.5 Seal vials tightly with Teflon tape, mark the meniscus (now and after each use), and store in standards refrigerator above freezing but below 6°C.

9.9.6 Record all standard preparation information in HRMS Standard Preparation Logbook.

9.9.7 250 µL of this solution is added to each sample between extraction and enrichment.

9.10 Preparation of $^{13}C_{12}$ Recovery Standard Primary Stock (AR2-#)

Compound	Conc. (µg/mL)
1,2,3,4-TCDD-$^{13}C_{12}$	2.0
1,2,3,7,8,9-HxCDD-$^{13}C_{12}$	2.0

9.10.1 This solution is purchased at a concentration of 2.0 µg/mL (Wellington or CIL).

9.11 Preparation of $^{13}C_{12}$ Recovery Standard Spiking Solution (CR3-#)

9.11.1 Sonicate the $^{13}C_{12}$ Primary Recovery Standard for five minutes and allow it to reach room temperature before using.

9.11.2 Using an Eppendorf pipette, add 1 mL of AR2-# into a pre-rinsed 10 mL volumetric flask. Bring to volume with tridecane to prepare this 200 ng/mL solution.

9.11.3 Sonicate for five minutes, transfer to 2 dram vials labeled with tape. Identification must include: ID# (CR3-#), log #, vial numbers, preparation date, expiration date and preparer's initials.

9.11.4 NOTE: Identification CR3-# - # denotes the next sequential number assigned to CR3 standard from the HRMS Standard Preparation Logbook.

9.11.5 Seal vials with Teflon tape, mark the meniscus (now and after each use), and store in standards refrigerator above freezing but below 6°C.

9.11.6 Record all standard preparation information in HRMS Standard Preparation Logbook.

9.11.7 10 µL of this solution is added to each sample during the final concentration of the extract.

9.11.8 A low-level food spiking solution is prepared by diluting this solution 5x with tridecane. This solution is used for food samples in conjunction with a 10 uL final extract volume and the low level calibration solutions.

9.11.9 This solution is otherwise be purchased as a prepared mix from Wellington Laboratories or equivalent.

9.12 Initial Calibration Solutions

9.12.1 Calibration solutions are purchased from Wellington Laboratories (or equivalent) at the listed concentrations.

PCDD/PCDF	CS1 (ng/mL)	CS2 (ng/mL)	CS3 (ng/mL)	CS4 (ng/mL)	CS5 (ng/mL)
2,3,7,8-TCDD	0.5	2	10	40	200
2,3,7,8-TCDF	0.5	2	10	40	200
1,2,3,7,8-PeCDD	2.5	10	50	200	1000
1,2,3,7,8-PeCDF	2.5	10	50	200	1000
2,3,4,7,8-PeCDF	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDD	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDD	2.5	10	50	200	1000
1,2,3,4,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,6,7,8-HxCDF	2.5	10	50	200	1000
1,2,3,7,8,9-HxCDF	2.5	10	50	200	1000
2,3,4,7,8,9-HxCDF	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDD	2.5	10	50	200	1000
1,2,3,4,6,7,8-HpCDF	2.5	10	50	200	1000
1,2,3,4,7,8,9-HpCDF	2.5	10	50	200	1000
OCDD	5.0	20	100	400	2000
OCDF	5.0	20	100	400	2000
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100

$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	2	10	40	200
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

9.12.5 The CS-3 is also available with the window defining and column resolution isomers in the same solution (See Quality Control Section 12).

9.13 Food and feed analyses allow lower calibration and spiking levels. The initial calibration standard sequence is prepared by diluting each of the 5 calibration solutions 2.5x with nonane. Similarly, the internal standard, recovery standard, clean-up and native spiking solutions are diluted 5x with tridecane, as described above. (Since extracts are taken to 10 uL final volume rather than 20 uL, the amount of standard material added is reduced 5x to provide the same concentration in the extract as the 2.5x dilution of the calibration standards.) The ICAL solution concentrations are then 40% of the concentrations listed in the above table.

9.14 To bring the calibration range to a lower level, two low level calibration standards are analyzed in addition to the 5 point calibration curve. The lowest standard is prepared to contain the tetra and penta chlorinated isomers at 0.1 pg/µL, hexa and hepta chlorinated isomers at 0.2 pg/µL and octa chlorinated isomers at 0.5 pg/µL. The second solution contains the native isomers at double those levels. In both cases, the labeled compounds are present at 40 pg/µL, except labeled OCDD that is present at 80 pg/µL and the clean-up standard that is present at 4 pg/µL.

10. CALIBRATION

10.1 Initial Calibration

10.1.1 Prior to analyzing samples, the instrument is calibrated by analyzing a series of five standard solutions, one of which is at or below the reporting limit. This initial calibration (ICAL) is performed when the continuing calibration solution is replaced by one from a different lot or when the continuing calibration does not pass the method specified criteria (levels outside limits are flagged in Avalon). With the exception of the low-level food standards that require 3:1 signal to noise, the PCDD/PCDF signals must demonstrate an intensity of at least 10:1 signal to noise. All ion ratios must be within 15% of the theoretical value (values outside limits are flagged in Avalon).

10.1.2 Additional standards are analyzed to demonstrate chromatographic resolution and stability of the ICAL. These consist of the continuing calibration solution (VER) described above, and a solution containing the isomers required to demonstrate the chromatographic resolution of the 2,3,7,8-TCDD (25% valley) and the presence of the first and last eluting isomers of each congener class (Wellington 5TDWD or equivalent). A solution (Wellington EPA1613-CS3WT) is available and incorporates all of the above components into a single solution.

10.2 Calibration Standards Acceptance Criteria

10.2.1 Standards must meet the following requirements before analyzing samples.

10.2.1.1 Ratios must be within 15% of theoretical values. See Attachment V.

10.2.1.2 Percent relative standard deviation for each isomer in the initial calibration must be <35%.

10.2.1.2.1 Calculate response factors (RF) using the equation below

Equation 1.

$$Rf = \frac{Aa \times Qs}{As \times Qa}$$

where:

Rf = Response factor
Aa = Sum of integrated areas for analyte
Qs = Quantity of labeled standard
As = Sum of integrated areas for labeled standard
Qa = Quantity of analyte

10.2.1.2.2 Using the RFs from the initial calibration, calculate the percent relative standard deviation (%RSD) for each congener using Equation 2.

Equation 2

$$\%RSD = \frac{SD}{\overline{X}} x100$$

where:

RSD = Relative standard deviation.
SD = Standard deviation of average RFs for a compound
$\overline{X}$ = Mean of 5 initial RFs for a congener.

The standard deviation is calculated following Equation 3.

Equation 3

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_i - \overline{RF}\right)^2}{n-1}}$$

where:

$\mathbf{RF_i}$ = Each individual response factor
$\overline{RF}$ = Mean of the Response Factor
n = The total number of values

10.2.1.3 Response factors for continuing calibration standards must be within the limits in Attachment II.

10.2.1.4 Percent valley between 2,3,7,8-TCDD and any other peak in the column performance check must be <25%, relative to the height of 2,3,7,8-TCDD.

10.2.1.5 All peaks for a given PCDD/PCDF level of chlorination must elute within the time window(s) set up for that particular class.

10.2.1.6 Native compounds must elute within ±2 seconds of the expected elution time relative to the elution times of the corresponding internal standards.

10.2.2 Sample analysis cannot begin until initial calibration criteria can be met.

11 PROCEDURE

11.1 Glassware Cleaning

11.1.1 Separate glassware (macro silica and acid columns, Soxhlet apparatus) must be reserved for tissue and food samples since even very low levels of contamination potentially cause problems in providing usable results. Care must also be taken that this glassware is not contaminated by cleaning/soaking with glassware/solvents/brushes/etc. that have been exposed to elevated analyte levels.

11.1.2 Prior to use, glassware is cleaned using the following steps:

11.1.2.1 Wash with soap and water (water rinse).

11.1.2.2 Soak in Chemsolve (or equivalent) for one hour (water rinse).

NOTE: Chemsolve is changed on a weekly basis at minimum, or after washing of samples found to contain vary high analyte levels.

11.1.2.3 Rinse with tap water.

11.1.2.4 Rinse with 1:1 nitric acid and then a DI rinse

11.1.2.5 Rinse with Acetone.

11.1.2.6 Air Dry.

11.1.2.7 Prior to use, rinse with hexane and the solvent to be used for extraction just prior to glassware use.

NOTE: The brushes must be replaced on a weekly basis at minimum, or after glassware used for samples containing very high analyte levels, in order to minimize the chances for contamination during the cleaning process.

11.1.3 Occasionally, a more vigorous cleaning is required. If so, soak for several minutes to several hours in Chromerge after completing steps 11.1.2.1 through 11.1.2.4. Repeat steps 11.1.2.1 through 11.1.2.6 after the Chromerge step.

11.1.4 Microwave extraction cells receive a modified cleaning. The cells are washed with soap and water, soaked in the Chemsolve bath, and rinsed with water and acetone.

11.1.5 Soxhlet\Dean Stark Glassware Pre-extraction

11.1.5.1 Place 30-40 mL of toluene in the clean Soxhlet extractor and 200-250 mL in the flask along with approximately 5-8 Teflon boiling chips.

11.1.5.2 Pre-extract the glassware by heating the flask until the toluene is boiling. When properly adjusted, 1-2 drops of toluene fall per second from the condenser tip into the receiver. Extract the apparatus for 3-4 hours minimum (typically overnight).

11.1.5.3 After pre-extraction, disassemble the apparatus. Refill the apparatus with 200-250 mLs fresh extraction solvent.

11.1.6 Extraction Vessel Pre-Extraction (MARS)

11.1.6.1 Pre-rinse the system with acetone and twice with hexane.

11.1.6.2 Place 50 mL of hexane:toluene 80:20 in the clean MARS cell

11.1.6.3 Pre-extract the apparatus using the "Blank" program for extraction.

11.2 Preparation Prior to Sample Extraction

NOTE: Drinking water samples are prepared according to the current version of SOP S-MN-H-003.

11.2.1 Aqueous samples containing one percent solids (or less) are extracted in separatory funnels or by SPE/MAE.

11.2.2 In samples expected or known to contain high levels of the PCDDs and /or PCDFs, the smallest sample size representative of the entire sample is used, and the extract must be diluted, if necessary.

11.2.3 Determination of Percent Solids

11.2.3.1 Weigh 5-10 g of sample to three significant figures into a tarred weighing vessel. Fatty food samples are reported based on the lipid weight of the sample. Non-fatty food and all feed samples are reported based on the total weight of the sample extracted.

11.2.3.2 Dry overnight (minimum of 12 hours) at 110 ± 5°C and cool in a desiccator. Reweigh.

11.2.3.3 Calculate the percent solids with the following equation.

Equation 4

$$\% \text{ Solids} = \frac{\text{Wt dried sample (g)} \times 100}{\text{Wt wet sample (g)}}$$

11.2.3.4 Data are recorded electronically and printed out as needed.

11.2.4 Percent Lipids Determination – 1613B requires lipid content determination for tissue samples. Please see SOP S-MN-H-004 for this procedure.

11.2.5 Grinding, Homogenization, and Blending

11.2.5.1 Prior to spiking, samples with particle size greater than 1 mm are subjected to grinding, homogenization, or blending. The method of reducing particle size to less than 1 mm is matrix dependent.

11.2.5.2 In general, hard particles can be reduced by grinding with a metal bar. Softer particles can be reduced by grinding in a Wiley mill or meat grinder, by homogenization, or by blending.

11.2.5.3 The grinding, homogenization, or blending procedures must be carried out in a glove box or fume hood to prevent particles from contaminating the work environment.

11.2.5.4 Tissue samples, certain papers and pulps, slurries and amorphous solids can be ground in a Wiley mill or heavy duty meat grinder. In some cases, reducing the temperature of the sample to freezing or to dry ice or liquid nitrogen temperatures can aid in the grinding process.

11.2.6 Quality Control Samples

11.2.6.1 For each batch (up to 10 samples) to be extracted in the same twenty four hour shift, place two aliquots of the reference matrix into clean apparatus (See extraction sections for reference matrix type). One reference matrix serves as the method blank and the other is a laboratory control sample (LCS) Include one additional aliquot of reference matrix if larger batches (up to 20) are analyzed.

11.2.6.2 Method Blank: Spike 20 uL using a calibrated pipettor of the internal standard spiking solution into one reference matrix.

Note: When setting up method blanks, the glassware used must be varied randomly amongst the sets used for sample extraction.

11.2.6.3 LCS/LCSD: Using a calibrated pipettor, spike 20 µL of internal standard spiking solution and 10 µL of the native spiking solution into the remaining reference matrix(ces).

11.2.6.4 Matrix spikes/ matrix spike duplicates/ sample duplicates are spiked as described in 11.2.6.3. Sample material is used instead of blank matrix for matrix spikes and sample duplicates. If matrix spikes are prepared with an extraction batch, only one laboratory spike is required.

11.3 Aqueous Samples (<1% Solids)

11.3.1 Preparation

11.3.1.1 In the following extraction procedure, extraction steps involving aliquots of methylene chloride vary from the specified amount of methylene chloride solvent as described in Standard Method 1613B.

11.3.1.2 Weigh the sample in the bottle to ±1 g on a top loading balance. Record this weight. A typical sample aliquot for water samples is 1L.

11.3.1.3 Spike 20 µL of the internal standard spiking into the sample bottle. Cap the bottle and mix by carefully shaking for 2 minutes. Allow to equilibrate for 1-2 hours with occasional shaking.

11.3.1.4 Prepare batch QC as described above, using 1 liter of water for each QC sample. Sample material is used for matrix spikes and sample duplicates.

11.3.1.5 Samples with visible particulate are filtered or centrifuged prior to extraction. However, the results are reported based on the total sample weight extracted and are considered as a water matrix.

11.3.2 Sample Extraction by Separatory Funnel

11.3.2.1 Quantitatively transfer sample into a separatory funnel with three 35 mL rinses of MeCl2. Weigh the empty sample container for use in determination of the amount of sample extracted.

11.3.2.2 Extract by shaking the separatory funnel, venting any back pressure for a minimum of 2 minutes.

11.3.2.3 If an emulsion layer forms, allow it to dissipate, or use mechanical or chemical (salt, heat ,etc.) means to break the emulsion. Once the emulsion is broken, continue the extraction.

11.3.2.4 After the extraction allow the layers to separate.

11.3.2.5 Remove the methylene chloride layer. Repeat the extraction two times with fresh aliquots of methylene chloride, combining the three solvent portions.

11.3.2.6 Transfer the methylene chloride through a 10 cm plug of sodium sulfate and glass wool to a pre-extracted Kuderna Danish concentrator. Set aside for addition of filter and particulate extract (if applicable) or concentrate to approximately 1 mL using KD and N-evap apparatus and proceed with sample cleanup.

11.3.2.7 Concentrate to approximately 10 mL. Remove and allow to cool for 5 minutes.

11.3.2.8 Rinse Snyder column down into the flask with three 2 mL portions of hexane.

11.3.2.9 If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes, combine with the filtrate in a 500 mL separatory funnel or a 40 mL vial. Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel. Proceed to sample cleanup.

11.3.2.10 If acid washes are not required, transfer the extract through a drying column containing a 10 cm plug of glass wool and sodium sulfate, and combine with the filtrate portion of the extract (if applicable). Rinse the flask with hexane (3 x 30 mL) and add to the drying column. Concentrate to 1 mL using KD and N-evap apparatus and proceed with sample cleanup.

11.3.3 Aqueous Samples (<1% Solids) Extraction by SPE/MAE

11.3.3.1 Condition a Nu phase C-18 filter by sequential elution of 15 mL toluene, 15 mL acetone, 15 mL methanol and two times 50 mL DI water. Do not allow the disk to go dry from the point of methanol addition until the end of the extraction.

11.3.3.2 Quantitatively transfer the sample onto the preconditioned C-18 filter, rinsing three times with 35 mL aliquots of DI water.

11.3.3.3 Elute the sample through the filter stopping while the filter is still damp.

11.3.3.4 Remove the filter and place in a MAE cell. Use sodium sulfate to dry the disk.

11.3.3.5 Extract following the procedure described for Soil/Solid samples.

11.3.3.6 Process the extract through the sample cleanup procedures.

11.4 Solid Matrix Samples (Soil, Sediment, Ash, Filters, Multiphase, etc.)

11.4.1 Preparation

11.4.1.1 In the following extraction procedure, extraction steps involving aliquots of methylene chloride vary from the specified amount of methylene chloride solvent as described in Standard Method 1613B.

11.4.1.2 Use 10 grams of sand as the reference matrix for solid samples. For filters, also include a filter of similar type as used for sample filtration.

11.4.1.3 Weigh a 10 gram aliquot (dry weight) of the homogenized sample. If the sample material is wet, dry it by mixing with extracted anhydrous sodium sulfate until free flowing. If the sample is extracted using Soxhlet Dean-Stark apparatus (with toluene), do not add sodium sulfate. In certain cases, i.e., sludge or waste matrices, a smaller amount of sample is utilized to provide more workable extracts.

11.4.1.4 Spike the sample and QC aliquots as described above. Allow the spiked sample to equilibrate 1-2 hours with occasional shaking.

11.4.1.5 If the sample flows easily, assemble a Buchner funnel and a vacuum adapter on top of a clean 1 L Erlenmeyer flask. Apply a vacuum to the flask and pour the aliquot through a glass fiber filter in the Buchner funnel, swirling the sample remaining in the bottle to suspend any particulate. Rinse the bottle 3 times with 60 mL of reagent water pouring each aliquot through the filter. For multiphase samples, re-combine any non-aqueous filtrate with the solid portion of the sample.

11.4.1.6 If the sample cannot be filtered, use a centrifuge to separate the sample, decanting the liquid fraction. With this procedure, the correct sample amount is first transferred into a different container for centrifuging. After centrifuging, the entire solid portion is mixed with sodium sulfate and transferred to a Soxhlet extraction thimble, as described for solid sample preparation and aqueous portion preparation. For multiphase samples, re-combine any non-aqueous filtrate with the solid portion of the sample.

11.4.1.7 If filtered or centrifuged, rinse any particulate off the sides of the Buchner funnel or sample container with small quantities of methylene chloride and add to the Soxhlet apparatus for the sample. For MAE use toluene for the rinse solvent.

11.4.2 Solid Samples by Soxhlet Extraction

11.4.2.1 Place the prepared sample in the thimble into the Soxhlet extractor. The use of Dean-Stark attachments allow the substitution of the sodium sulfate drying step.

11.4.2.2 Add 300 mL of toluene and reflux for a minimum of 16 hours. Cycle at a rate of three cycles per hour. If applicable, drain the water from the receiver as needed.

11.4.2.3 Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. The extract can otherwise be quantitatively transferred to a K-D flask and concentrated on a steam bath.

11.4.2.4 Concentrate to approximately 10 mL. Remove and allow cooling for 5 minutes.

11.4.2.5 Rinse Snyder column down into the flask with three 2 mL portions of hexane.

11.4.2.6 If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes, combine with the filtrate extract in a 500 mL separatory funnel (or a 40 mL vial for the micro wash). Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel or vial. Proceed to acid washes.

11.4.2.7 If acid washes are not required, transfer the extract through a drying column containing a 10 cm plug of glass wool and sodium sulfate, and combine with the filtrate portion of the extract (if applicable). Rinse the flask with hexane (3 x 30 mL) and add to the drying column. Concentrate to 1 mL using KD and N-evap apparatus and proceed with extract clean up.

11.4.3 Soil/Solid Samples by Microwave Extraction

11.4.3.1 Add 50 mL of toluene:hexane (1:1) to the extraction cell, insert the Teflon plug and the cap. Seal the screw on cap tightly.

11.4.3.2 Insert the cells into the microwave and run using the "Dioxin Soil" program.

11.4.3.3 Carefully open each cell containing the extracted sample and collect (decant or pipet) the solvent extract.

11.4.3.4 Rinse the cell and sample material twice with 10 mL of hexane, combining the hexane with the original solvent extract.

11.4.3.5 Concentrate the extract to approximately 2-3 mL and proceed to sample enrichment.

11.4.3.6 If, based on the appearance (cloudy or emulsive) or color (not clear) of the extract, the extract requires acid washes, transfer the extract to a 500 mL separatory funnel or a 40 mL vial. Rinse the flask and KD with hexane (3 x 30 mL) and add to the separatory funnel. Proceed to extract clean up.

11.4.3.7 If acid washes are not required, transfer the extract through a drying column containing a 10 cm plug of glass wool and sodium sulfate, and combine with the filtrate portion of the extract (if applicable). Rinse the flask with hexane (3 x 30 mL) and add to the drying column. Concentrate to 1 mL using KD and N-evap apparatus and proceed with extract clean up.

11.5 Milk and Milk Product Samples

11.5.1 Accurately measure a 100 mL aliquot of milk and transfer to a 2 liter separatory funnel.

11.5.2 Spike the sample aliquot with 20 uL of the internal standard spiking solution. Allow the spiked sample to equilibrate 1-2 hours with occasional shaking.

11.5.3 For each sample or sample set (up to 10) to be extracted in the same twenty four hour shift, measure two 100 mL aliquots of de-ionized water into clean separatory funnels. If larger batches (up to 20) are to be extracted, include an additional aliquot of the reference matrix material. Spike as described in 11.2.6.

11.5.4 Add 300 mL of 1.5M potassium oxalate solution and 600 mL of de-ionized water to each sample in the separatory funnel.

11.5.5 Gently shake the separatory funnel for 8-10 minutes.

11.5.6 Add 150 mL of 1:1:1 ethanol/ether/hexane to the sample and shake gently for 3-4 minutes.

11.5.7 Allow the layers to separate 15-20 minutes.

11.5.8 Collect the milk (bottom layer) and emulsion layers in a clean 2 L beaker. (The emulsion layer can be reduced by adding small volumes (10-30 mL) of the 1:1:1 solvent mixture to the separatory funnel after separation of the layers.)

11.5.9 Transfer the clear organic layer directly to a Kuderna-Danish concentrator and set aside.

11.5.10 Transfer the milk and emulsion back to the separatory funnel and repeat the extraction two more times. Combine the organic layers to the K-D flask and save the emulsion layer in a 500 mL separatory funnel.

11.5.11 After the final extraction, rinse the 2 L separatory funnel with 60 mL of the 1:1:1 solvent mixture and add to the K-D flask.

11.5.12 Concentrate the extract to 2 mL and allow to cool.

11.5.13 Quantitatively transfer the extract into the separatory funnel containing the emulsion and add 80 mL hexane.

11.5.14 Perform the acid washes and cleanup as described. For milk samples, acid cleanup is not considered optional.

NOTE: Do not shake the first acid wash. Slowly pour the first 50 mL of sulfuric acid into the separatory funnel and allow to separate for 15 minutes. Drain the acid and perform the remaining washes in the normal manner.

11.6 Preparation and extraction of Tissue Samples (Environmental)

11.6.1 If the sample is supplied as whole fish or fillets, grind the sample using a meat grinder or blender.

11.6.2 Weigh a 10 gram aliquot of the homogenized sample into a clean beaker. Using a larger sample size increases lower limits of detection. Mix in enough extracted anhydrous sodium sulfate to dry the sample (usually approximately 20 grams). If the sample is extracted using Soxhlet Dean-Stark apparatus (with toluene), no sodium sulfate is added.

11.6.3 Quantitatively transfer the sample into a clean Soxhlet thimble and top with extracted glass wool.

11.6.4 Spike the sample aliquot with 20 uL of the internal standard spiking solution. Allow the spiked sample to equilibrate 12-24 hours, remix before extraction to prevent clumping.

11.6.5 Prepare batch QC as described above, using 10 grams of clean fish tissue or corn oil for each QC sample. Sample material is used for matrix spikes and sample duplicates.

11.6.6 Store any remaining sample in the freezer at approximately -18°C.

11.6.7 If the sample is extracted using Soxhlet Dean-Stark apparatus (with toluene), no sodium sulfate is added.

11.6.8 Place the loaded thimble into the Soxhlet apparatus.

11.6.9 Add 250 mL of hexane/methylene chloride (1:1 v/v) and reflux for 16-18 hours.

11.6.10 Cool and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. The extract can otherwise be quantitatively transferred to a K-D flask and concentrated on a steam bath.

11.6.11 Concentrate to approximately 10 mL. Remove and allow to cool for 5 minutes.

11.6.12 Rinse Snyder column down into the flask with three 2 mL portions of hexane.

11.6.13 Perform the acid washes and cleanup. For tissue and food samples, acid cleanup is not considered optional. The column acid wash procedure is preferable to the separatory funnel procedure.

11.6.14 NOTE: Do not shake the first acid wash. Slowly pour the first 50 mL of sulfuric acid into the separatory funnel and allow to separate for 15 minutes. Drain the acid and perform the remaining washes in the normal manner.

11.6.15 Concentrate to 1 mL using KD and N-evap apparatus and proceed with sample cleanup.

11.6.16 Alternatively, the sample can be extracted using Soxhlet Dean-Stark apparatus and toluene. No sodium sulfate is used with this option.

11.7 High Fat Food and Feed Samples

11.7.1 Preparation

11.7.1.1 Fatty samples containing over 10% lipids use a blender to extract the lipid (or use same procedure as low fat foods). A ratio of approximately 1 part sample:2 parts sodium sulfate:3 parts methylene chloride is used for the extraction. The lipid extraction is performed in triplicate with two minutes of blending per extraction and the extracts are combined. The solvent volume is be reduced to 1-2 parts on the second and third extractions. When performed in this manner, an aliquot of the lipid (after solvent removal) is spiked with internal standards and treated as the sample (see below for spiking and QC procedures). The lipid aliquot is then be dissolved with hexane (5x wt.) and taken directly to the analyte enrichment procedures. Note that petroleum ether is a substitute for methylene chloride during the lipid extraction. Food samples requiring the EU TEQ levels are extracted using the sample weights described in Attachment III. The food project dilutions of the labeled standards are substituted for the normal level standards.

11.7.1.2 Corn oil is used as the reference matrix for fatty food and feed matrices. An amount approximately equivalent to the lipid weight of the field sample is used.

11.7.1.3 Weigh out an aliquot (see Attachment III) of the extracted lipid sample into a clean beaker and spike the aliquot with the diluted internal standard spiking solution. Dissolve the sample in hexane using approximately 5x the weight of lipid sample.

11.7.1.4 Quantitatively transfer the sample into a clean drying column.

11.7.1.5 Prepare batch QC as described above, using corn oil for each QC sample. Use approximately the same amount of reference sample material as is used for sample extraction. Sample material is used for matrix spikes and sample duplicates.

11.7.1.6 Store any remaining sample in the freezer at approximately -18°C

11.7.2 Extraction

11.7.2.1 Place the loaded thimble into the Soxhlet apparatus

11.7.2.2 Add 250 mL of hexane/methylene chloride (1:1 v/v) and reflux 16 – 18 hours.

11.7.2.3 Cool the Soxhlet apparatus and place a pre-rinsed Snyder column on the 500 mL round bottom flask for concentration. The extract can otherwise be quantitatively transferred to a K-D flask and concentrated on a steam bath.

11.7.2.4 Concentrate to approximately 10 mL. Remove and allow to cool for 5 minutes.

11.7.2.5 Rinse Snyder column down into the flask with three 2 mL portions of hexane.

11.7.2.6 Perform the column acid washes and cleanup. For food samples, acid cleanup is not considered optional.

11.7.2.7 Alternatively, the sample can be extracted using Soxhlet Dean-Stark apparatus and toluene. No sodium sulfate is used with this option.

11.8 Low Fat Food and Feed Samples

11.8.1 Preparation

11.8.1.1 Low fat and non-fat samples are prepared for extraction as described below. Food samples required to meet the EU TEQ levels are extracted using the sample weights described in Attachment III. The food project dilutions of the labeled standards are substituted for the normal level standards.

11.8.1.2 Sodium sulfate or sand is used as the reference matrix for non-fat food and feed samples. Again, the amount used is equivalent to the amount of field sample being extracted

11.8.1.3 If the sample is to be Soxhlet extracted and is not already finely ground, grind the sample using a grinding bar, meat grinder or hand blender.

11.8.1.4 Weigh an aliquot (see Attachment III) of the homogenized sample into a clean beaker. Mix in enough extracted anhydrous sodium sulfate to dry the sample. If the sample is extracted using Soxhlet Dean-Stark apparatus (with toluene), do not add sodium sulfate.

11.8.1.5 Quantitatively transfer the sample into a clean Soxhlet thimble and top with extracted glass wool.

11.8.1.6 Spike the sample aliquot with the diluted internal standard spiking solution. Allow the spiked sample to equilibrate 1-2 hours with occasional shaking.

11.8.1.7 Prepare batch QC as described above, using sodium sulfate or sand for each QC sample. Sample material is used for matrix spikes and sample duplicates. Use approximately the same amount of reference sample material as is used for sample extraction.

11.8.1.8 Store any remaining fat based samples in the freezer at approximately –18°C.

11.8.1.9 Extract samples as described for high fat feed samples.

11.9 Blood and Serum Samples

11.9.1 Preparation

11.9.1.1 Quantitatively transfer approximately 50 grams of blood or serum into a 250-mL glass jar using 3 x 5-mL rinses of ethanol. If the aliquot represents the entire sample, spike the sample with the internal standard spiking solution and equilibrate for 1 hour prior to the transfer. Otherwise, spike after transfer.

11.9.1.2 Determine the weight of the sample by difference using the weight of the sample container before and after the sample is removed. If the sample was completely removed from the original container, also measure the volume of sample extracted.

11.9.1.3 For each sample or sample set (up to 10) to be extracted in the same twenty four hour shift, weigh two similarly sized aliquots of de-ionized water and place each into separate jars. If larger batches are to be extracted, include an additional aliquot of the reference material. If available, aliquots of pooled blood are used as reference material Spike as described in 11.2.6.

11.9.2 Extraction

11.9.2.1 Add 50 mL of saturated ammonium sulfate. 35 additional mL of methanol and 50 mL of hexane to the sample. Extract by shaking or tumbling for 30 minutes.

11.9.2.2 Allow the hexane layer to separate (centrifuge if necessary) and remove the hexane (top) layer.

11.9.2.3 Dry the hexane by passing it through a sodium sulfate column or funnel and collect in a KD receiver.

11.9.2.4 Repeat the hexane extraction two additional times with fresh 50 mL aliquots of hexane.

11.9.2.5 Concentrate down and transfer to a small vial. Concentrate to dryness and determine the percent lipid in the sample by weight. This is typically 0.1 to 0.3 grams per 50 mL sample.

11.9.2.6 Re-dissolve the sample in hexane, spike with the cleanup standard, and proceed to extract enrichment (11.11).

11.9.2.7 Store any remaining blood samples in the freezer at < 0° C.

11.10 Preparation of Oil Based Food Product Samples

11.10.1 Corn oil is used as the reference matrix for oil based food and feed matrices.

11.10.2 Weigh out a 10-gram aliquot (use 20 grams if EU requirements apply) of the oil based sample into a clean 8 ounce soil jar and spike the aliquot with the internal standard spiking solution.

11.10.3 Add 50 mL of hexane to the sample and dissolve by sonication.

11.10.4 Prepare batch QC as described above, using corn oil for each QC sample. Sample material is used for matrix spikes and sample duplicates.

11.10.5 Proceed to "Super Carbon First" enrichment.

11.11 Extract Enrichment/Cleanup Procedures

11.11.1 Back Extraction with Acid – Micro scale

NOTE: This enrichment step is optional. It is used on extracts based on appearance and color. If the extract is cloudy, emulsive, or multi-layered, this back extraction is employed. It is also used when the extract is not clear or if the sample appears particularly dirty (i.e. multi-layer, sludge-like) or contains various organic materials (i.e. milk, fish, vegetation, etc.). Most samples undergo this procedure.

11.11.1.1 Spike each extract with 250 µL of the clean-up std. Prior to concentration using KD and N-evap apparatus.

11.11.1.2 Quantitatively transfer H_2O and Soxhlet extract with 15 mL of hexane to 40 mL vials. Extracts obtained using the MAE method are concentrated to almost dryness (~1mL) and 15 mL of hexane added.

11.11.1.3 Partition the extract against 2-3 mL concentrated sulfuric acid. Shake for two minutes with periodic venting into a hood. Remove and discard the acidic bottom layer. Emulsions are broken down by mechanical or chemical means.

11.11.1.4 Repeat the acid washing, until no color is visible in the aqueous layer, to a maximum of four washings.

11.11.1.5 Acid waste is collected, and then stored in labeled containers for disposal. Use caution when handling.

11.11.1.6 Repeat step 11.11.1.3, but substitute buffer solution (100 mL 0.5 M KH_2PO_4 and 31 mL 1:0 NaOH).

11.11.1.7 Concentrate extract to approximately 1 mL on the N-evap and proceed with column cleanup. DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS!

11.11.2 Back Extraction with Acid – Macro scale

NOTE: This enrichment step is optional. It is used on extracts based on appearance and color. of the extract is cloudy, emulsive, or multi-layered, this back extraction is employed. It is also used when the extract is not clear or if the sample appears particularly dirty (i.e. multi-layer, sludge-like) or contains various organic materials (i.e. milk, fish, vegetation, etc.). Most samples undergo this procedure.

11.11.2.1 Spike the separatory funnel with 250 µL of the cleanup standard (CCl4-#).

11.11.2.2 Quantitatively transfer with 100 mL of hexane and partition the extract in 50 mL 1N-sodium hydroxide. Shake for two minutes with periodic venting into a hood. Remove and discard the aqueous bottom layer. Emulsions are be broken down by mechanical or chemical means. The sodium hydroxide wash is optional at the discretion of the technician.

11.11.2.3 Only one NaOH rinse is needed.

11.11.2.4 Partition the extract against 50 mL of the 5%(w/v) sodium chloride solution in the same way and number of repetitions as with base. Discard the aqueous layer

11.11.2.5 Quantitatively transfer and partition the extract in 50 mL concentrated sulfuric acid. Shake for two minutes with periodic venting into a hood. Remove and discard the aqueous bottom layer. Emulsions are broken down by mechanical or chemical means.

11.11.2.6 Repeat the acid washing until no color is visible in the aqueous layer, to a maximum of four washings.

11.11.2.7 Partition the extract against 50 mL of the 5%(w/v) sodium chloride solution in the same way as with acid. Discard the aqueous layer.

11.11.2.8 Acid waste is collected, and then stored in labeled containers for disposal. Use caution when handling.

11.11.2.9 Pour the extract through a drying column containing 7 to 12 cm of anhydrous sodium sulfate and a pre-rinsed glass wool plug. Rinse the separatory funnel with three 20 mL portions of hexane and add to the column. Collect the extract in a 500 mL KD evaporator flask.

11.11.2.10 Add 1 to 2 clean boiling chips to the receiver and attach a three ball macro Snyder column. Preset the column by adding approximately 1 mL of hexane through the top. Place the KD apparatus in a hot water bath so the entire lower rounded surface of the flask is bathed in steam.

11.11.2.11 Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. At the proper rate of distillation, the balls of the column actively chatter but the chambers do not flood. DO NOT ALLOW THE EXTRACT TO GO TO DRYNESS.

11.11.2.12 When the liquid has reached an apparent volume of 1 mL, remove the KD apparatus from the steam bath and allow draining and cooling for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1-2 mL of hexane.

11.11.2.13 Remove the concentrator tube from the apparatus, concentrate to approximately 1 mL on the N-evap and proceed with column cleanup.

11.11.3 Back Extraction with Acid – Column Method

NOTE: This enrichment step is the preferred approach for food and feed matrices. Acid washes are not considered optional for food and feed matrices.

11.11.3.1 If the sample has not already been quantitatively transferred to a drying column, do so at this time. The sample is dissolved in hexane at a 1:5 weight to weight ratio or to a minimum volume of 100 mL, whichever is greater. Slowly pour the first 50 mL of sulfuric acid into the drying column containing the sample extract, stir gently and allow separating for 15 minutes. Drain the acid and perform the remaining washes in a similar manner until the extract is free from color. Emulsions are broken down by mechanical or chemical means. The column acid wash procedure is preferable to the separatory funnel procedure for non-food matrices as well.

11.11.3.2 Acid waste is collected, and then stored in labeled containers for disposal. Use caution when handling.

11.11.3.3 The washed extract can then be collected in a beaker prior to silica or allowed to drip directly onto a pre-washed silica column (described below). If allowed to drip, fill the macro silica column to approximately 50% of the available solvent volume with sample material and allow the silica column to flow. Collect the hexane extract in a clean 500 mL beaker. Adjust the sample extract flow rate to a rate similar to that of the silica column.

11.11.3.4 When the sample has eluted through the silica to a point where the hexane extract just covers the silica, elute the silica with another 500 mL of hexane. Again, after filling approximately 50% of the available solvent volume, adjust the reservoir flow rate to a rate similar to that of the silica column. Collect the entire hexane elution volume in the 500 mL beaker.

11.11.4 High Fat Clean-up Using Carbon First

11.11.4.1 Prepare and elute a carbon column as described below with the following exceptions:

11.11.4.2 Prepare the column in a 12 mm wide glass tube rather than the normal 8 mm tube used for carbon.

11.11.4.3 Double the amount of carbon/Celite used to 1 gram.

11.11.4.4 The lipid sample is typically dissolved in hexane (1:1 V:V) prior to addition to the carbon column. Additional hexane or the application of heat is sometimes required to prepare a non-viscous sample for the column. Allow the sample to equilibrate for 30 minutes to ensure that a stable solution has been achieved.

11.11.4.5 When the sample elution is near completion, the column is washed with an additional 60 mL of hexane.

11.11.4.6 The analytes are eluted with 50 mL of toluene rather than the standard 30 mL.

11.11.4.7 After the carbon procedure, the extract is taken through the macro silica and standard alumina columns described below.

11.11.5 "Super Carbon First" Column

11.11.5.1 Prepare carbon/Celite packing by mixing 18% (by weight) 100–400 mesh active carbon (pre-washed in methanol and dried in a vacuum oven at 110°C) and 82% (by weight) Celite. Mix thoroughly.

11.11.5.2 Bake the mixture at 130°C for 6 hours. Store in desiccator.

11.11.5.3 The column is prepared in the same glassware used for jumbo silica cleanup. Rinse the tube three times with 1 mL portions of hexane.

11.11.5.4 Insert a silanized glass wool plug at one end (~10 cm from the end of the column) and pack with 1 cm of Celite followed by 3.0 g of the carbon/Celite mixture. Cap the end with a silanized glass wool plug. Note: Tap the column between layers to level out the resins.

11.11.5.5 Rinse the column "clean (Celite)" side up with 30 mL of hexane. The flow rate must be less than 0.5 mL/minute. If the flow rate is greater than 0.5 mL/minute, discard the column. Discard the rinses.

11.11.5.6 While the column is still wet with hexane, quantitatively transfer the sample extract to the top of the column and rinse the jar with two 10 mL aliquots of hexane. If necessary use a 3rd 10 mL hexane rinse to completely transfer the sample to the column. Note: Add the sample and rinses slowly using sonication or vortexing as needed to keep the sample dissolved.

11.11.5.7 Collect the hexane containing the sample matrix as waste, periodically rinsing the bottom of the column with fresh hexane to remove any residual oil matrix from the column.

11.11.5.8 Carefully turn the column upside down and elute the PCDDs and PCDFs with 50 mL of toluene. If carbon is present in the eluate, filter through a 0.45 µm glass fiber filter rinsing with an additional 2 mL of toluene.

11.11.5.9 Evaporate the toluene to near dryness, add 1 mL of hexane and spike the sample with cleanup standard before proceeding to the jumbo silica column and alumina column cleanups described below.

11.11.5.10 A substitution with an equivalent carbon column is acceptable as long as the data meets method requirements.

11.11.6 Silica Column

11.11.6.1 Vertically clamp a disposable glass column, 12 mm ID x 35 cm. Rinse three times with hexane, air dry, and place a pre-extracted silanized glass wool plug into bottom.

11.11.6.2 Pack the column in the following order (bottom to top): 1 g neutral silica, 2 g basic silica, 4 g acidic silica and 2 g neutral silica. Between each layer, tap the column to settle the silica. Wet column with 10 mL hexane after the basic silica layer is added. Plug the end of the column with a septa when it starts dripping. Check the column for channeling. If channeling is observed, discard the column. DO NOT allow the column to go dry. Adding an additional 2 gram layer of 22% acidic silica just above the 44% acidic silica layer lessens the possibility of charring.

11.11.6.3 Spike the extract with the cleanup standard (CCl4-#), if it has not already been added.

11.11.6.4 Quantitatively transfer the sample extract onto the column using 2-2 ml rinses of hexane. Break off the tip of the column containing the septum. Elute until the solvent just covers the silica. Do NOT let the column go dry.

11.11.6.5 Elute the column with 90 mL hexane. Collect the eluant in a 100 mL beaker.

11.11.6.6 A substitute silica column is appropriate as long as the data meets method requirements.

11.11.6.7 Jumbo-silica columns are prepared using roughly three times the amount of the silica noted above in each layer of the column. Larger macro-silica columns are prepared using nine times the amount of the silica noted above in each layer of the column. These columns are prepared in drying tubes and are eluted with approximately 300 mL or 500 mL of hexane, respectively.

11.11.6.8 Problematic matrices (i.e., adipose tissue, waste samples, etc.) are optionally processed by mixing up to 100 grams of acid silica into the sample extract. The extract is then processed through the above silica column and remaining cleanup steps.

11.11.6.9 Concentrate the extract to approximately 1 mL using KD and N-evap apparatus or ambient air conditions

11.11.7 Alumina Column

11.11.7.1 Pack a silanized glass wool plug into the bottom of a disposable glass column (12 mm ID x 35 mm). Pack the column in the following order: 4 g of anhydrous sodium sulfate, 7 g of neutral alumina, and 4 g of anhydrous sodium sulfate to cover the alumina. Between layers, tap the top of the column gently to settle the adsorbents.

11.11.7.2 Elute with 10 mL hexane. Plug the bottom of the column with a septum just before exposure of the sodium sulfate layer to the air. Discard the eluate. Check the column for channeling. If channeling is present, discard the column. DO NOT TAP A WETTED COLUMN AND DO NOT LET THE COLUMN GO DRY.

11.11.7.3 Quantitatively transfer the sample to the top of the column with 2-2 ml of hexane. Elute the sample with 10 mL hexane to complete the transfer of the sample cleanly to the surface of the alumina. Archive the eluate until after sample analysis.

11.11.7.4 Elute with 35 ml of 60% (v/v) methylene chloride in hexane and collect this fraction in a 12 dram vial.

11.11.7.5 Concentrate the extract to near dryness using an N-evap apparatus.

11.11.7.6 A substitute alumina column is appropriate so long as the data meet method requirements.

11.11.8 Carbon Column

11.11.8.1 Prepare carbon/Celite packing by mixing 18% (by weight) 100–400 mesh active carbon (pre-washed in methanol and dried in a vacuum oven at 110°C) and 82% (by weight) Celite. Mix thoroughly.

11.11.8.2 Bake the mixture at 130°C for 6 hours. Store in desiccator.

11.11.8.3 Prepare an 8 mm glass tube about one foot in length. Rinse the tube three times with 1 mL portions of hexane.

11.11.8.4 Insert a silanized glass wool plug at one end and pack with 1 cm of Celite followed by 0.5 g of the carbon/Celite mixture. Cap the end with a silanized glass wool plug.

11.11.8.5 Rinse the column "clean (Celite)" side up sequentially with 5 mL of toluene, 2 mL of methylene chloride/methanol/toluene (75:20:5 v/v), 2 mL of cyclohexane/methylene chloride (1:1 v/v) and 5 mL hexane. The flow rate must be less than 0.5 mL/minute. If the flow rate is greater than 0.5 mL/minute, discard the column. Discard the rinses.

11.11.8.6 While the column is still wet with hexane, quantitatively transfer the sample extract to the top of the column with two 2 mL aliquots of hexane.

11.11.8.7 Elute the column sequentially with 2 mL of cyclohexane/methylene chloride (1:1 v/v) and 2 mL of methylene chloride/methanol/toluene (75:20:5 v/v). Archive these eluates until after sample analysis.

11.11.8.8 Turn the column upside down and elute the PCDDs and PCDFs with 10 mL of toluene. If carbon is present in the eluate, filter through a 0.45 µm glass fiber filter rinsing with an additional 2 mL of toluene.

11.11.8.9 A substituted carbon column is appropriate so long as the data meet method requirements.

11.12 Final Extract Preparation

11.12.1 Extract Transfer

11.12.1.1 Concentrate the extract under a gentle stream of nitrogen to a volume of less than 1 mL. Do NOT blow the sample so the portions of the solvent "ride" up the sides of the glass vial. The temperature of the N-evap bath must be <42 °C.

11.12.1.2 Add 10 µL of tridecane to an autosampler vial using a calibrated Eppendorf pipettor to act as a keeper solvent. The keeper solvent is not used for food samples.

11.12.1.3 Quantitatively transfer the extract to the autosampler vial. Rinse the original vial with less than 1 mL of methylene chloride/hexane (60:40 V: V). Transfer rinsate to the autosampler vial. Repeat rinse of the autosampler vial with two additional aliquots (<1 mL) of methylene chloride/hexane. Then blow down extract to the level of the 10 µL keeper solvent or to near dryness for food samples.

11.12.1.4 Add the 10 µL of recovery standard (CR3-#) to the extract with a calibrated Eppendorf pipettor for a final volume of 20 µL and cap. Any unwanted solvent remaining is removed using the N-evap. A final volume of 20 uL, 10 uL for food and feed samples, is verified at this time based on solvent height in the vial. Cap and vortex each sample vial.

11.12.1.5 Transfer the extracts to the analytical laboratory for analysis. Extracts must be stored in the dark at approximately <-10°C.

11.13 Instrument Maintenance

11.13.1 There is no set schedule for the maintenance listed in this section. It is performed on an as needed basis. Regular preventative maintenance is performed by Pace Analytical's service engineer. If the instrument needs to be vented, do the following in this order: close the analyzer isolation valve, turn off the source ion gauge, close the source isolation valve, close all source rough pump valves, allow air into the source chamber through the bleed valve while watching vacuum gauges to ensure leakage does not occur. If any leakage is seen, close the bleed valve and open the main roughing pump valve. Determine the cause of the problem and correct.

11.13.2 The rough pump oil must be changed if the pump fails to produce a vacuum lower than 10^{-1} mbar or if the pump oil becomes excessively dark. To do so, turn off the ion gauge, isolate and turn off the diffusion pump and allow it to cool. When the diffusion pump is cool, isolate and turn off the rough pump. Now drain the oil into a waste container and recap the drain. Add oil up to the full line and turn on the pump. When the gurgling sound stops, open the valve to pump on the instrument. After several minutes, turn on the diffusion pump. Wait another 10-15 minutes and turn on the ion gauge. If it is a source linked pump, the source needs to be evacuated.

11.13.3 When the carrier gas, helium, pressure gets below 500 psi, replace the tank.

11.13.4 The chromatographic column used for these analyses is the DB-5MS in a 60 meter length. As with any column, these degrade in time. Once this degradation reaches the point where EPA Method 1613B criteria are not met, the column needs to be replaced. Similar results are required for the DB-225 or other confirmation column.

11.13.5 The injector liner and baseplate require periodic cleaning or replacement. This maintenance is performed either as a preventative measure or when analyte response factors indicate that injector maintenance is required. A low response factor for the heavier labeled analytes is a typical indicator that injector maintenance is required.

11.13.6 Air leaks are a common source of problems in mass spectrometry. If the system seems unstable or shows arching, the first step is to check for air leaks. This is done by comparing the signal at m/z 28 to historic levels or by monitoring the mass of a gas or solvent which is then applied to potential leaking locations. Correct any leaks before proceeding to other measures.

11.13.7 Source/ion volume cleaning is also be done either as a preventative measure or to correct issues with instrument operation. Source cleaning is performed when tuning parameters no longer offer the desired affect, when arcing occurs, or for a number of other reasons. Instructions for removing, cleaning and reassembly of the source are provided in the instrument operation manuals.

11.13.8 All maintenance must be documented. Routine maintenance, such as changing septa, is recorded in the instrument run log. Other 'major' maintenance is documented in the maintenance log specific to each system.

11.14 Sample Analysis

11.14.1 Introduce PFK into the batch inlet and tune the instrument to a resolution of ≥ 10,000 (M/ΔM, 10% valley) using a PFK peak within the analysis mass range (M/Z 331 or 381).

Typical Operating conditions include:

Trap current:	500-700 µA
Electron Energy:	32 ± 5 eV
Source Temperature:	270 °C
Emmision/Trap Ratio:	≤ 3
Accelerating Voltage:	8000 eV

11.14.2 After calibration and column performance have been established, (per Quality Control Section Guidelines) any spikes are typically analyzed. A blank must be analyzed between calibration standards and client samples.

11.15 Data Processing

11.15.1 Data is collected using MassLynx Version 4.0 or Xcalibur Version 2.0 software. The software is run on personal computers running Microsoft Windows XP.

11.15.2 The raw data files are imported into the Avalon Version 3.0 data processing program for integration. Information on how to use Avalon is available in the Avalon manual that can be accessed on the HRMS group computers. Also, since the DB-5MS capillary column gives partial resolution of 2,3,7,8-TCDF isomer (typically 30-40% valley), second column confirmation analyses are only performed if coelution is exhibited or based upon project requirements.

11.15.3 Note that the window mixture does not need to be queued. Visually inspect the chromatographic data to ascertain the elution times of the first and last eluting isomers of each congener class and chromatographic resolution.

11.15.4 With the elution time information recorded, adjust the method file times so that the group changes occur at points between the elution time of the last isomer of a given class and the first isomer of the following class. The first PeCDF isomer is monitored in Group 1 with the group change set approximately 30 seconds later.

11.16 Calculations

11.16.1 The PCDD/PCDF isomers (native or labeled) are quantified by comparison of their responses to those of the corresponding/appropriate internal standard. Relative response factors are calculated from analyses of standard mixtures containing representatives of each of the PCDD/PCDF congener classes at five concentration levels, and each of the internal and recovery standards at one concentration level. The PCDD/PCDF response factors are calculated by comparing the sum of the responses from the two ion masses monitored for each chlorine congener class to the sum of the responses from the two ion masses of the corresponding isotopically labeled standard. The formula for the response factor calculation:

$$Rf = \frac{Aa \times Qs}{As \times Qa}$$

Where:

Rf = Response factor
Aa = Sum of integrated areas for analyte
Qs = Quantity of labeled standard
As = Sum of integrated areas for labeled standard
Qa = Quantity of analyte

11.16.2 The levels of PCDD/PCDF in the samples are quantified using the following equation:

$$C = \frac{An \times Qis}{Ais \times W \times Rf}$$

where:

C = Concentration of target isomer or congener class
An = Sum of integrated areas for the target isomer or congener class
Qis = Quantity of labeled internal standard added to the sample
Ais = Sum of integrated areas for the labeled internal standard

W = Sample amount
Rf = Response factor

11.16.3 A Practical Reporting Limit (PRL), equivalent to the practical quantitation limit, is determined based on the amount of sample extracted, the volume of the final extract, and the concentration of the lowest level in the standard curve. Levels detected below the PRL are reported as not detected at the PRL. Blanks may be reported to 1/3 the PRL (Method 1613 Section 17.6.1.4), to the PRL or to the LOD, based on project requirements. A PRL was calculated for isomer/isomer group using the following equation:

$$PRL = \frac{C \times V}{W}$$

where:

PRL = Pace Reporting Limit
C = Concentration of lowest level standard
V = Volume of final extract
W = Initial sample weight or volume

If based on project requirements, lower reporting limits are needed, results are reported as low as the signal to noise based limits of detection. Any values outside the calibration range must be flagged as estimated values.

11.16.4 A limit of detection (LOD) may be calculated based on the signal to noise ratio of the noise level of the ion of interest versus the appropriate standard, is calculated for each sample and isomer. The equation used for calculating the LOD is:

$$LOD = \frac{Hn \times Qis \times 2.5}{His \times W \times Rf}$$

Where:

LOD = Limit of Detection
Hn = Sum of noise heights for target isomer
Qis = Quantity of labeled internal standard added to the sample
His = Sum of signal heights from labeled internal standard
W = Initial sample weight or volume
Rf = Response factor

11.16.5 The recovery of the 2,3,7,8-TCDD-$^{37}Cl_4$ cleanup efficiency standard and each $^{13}C_{12}$-labeled internal standard, relative to either 1,2,7,8-TCDD-$^{13}C_{12}$ or 1,2,3,7,8,9-HxCDD-$^{13}C_{12}$, is calculated using the following equation:

$$\%R = \frac{Ais \times Qrs \times 100}{Rfr \times Ars \times Qis}$$

where:

%R = Percent recovery of labeled internal standard

Ais = Sum of integrated areas of labeled internal standard

Qrs = Quantity of recovery standard

Ars = Sum of integrated areas of recovery standard

Rfr = Response factor of the specific labeled internal standard relative to the recovery standard

Qis = Quantity of the labeled internal standard added to the sample

12 QUALITY CONTROL

12.1 The quality of the sample processing steps and instrument performance are monitored on a routine basis. The procedures and criteria are summarized below.

12.1.1 Internal standards are spiked into each sample prior to extraction in order to monitor the level of recovery that is achieved for each individual sample. Acceptable recoveries ranges for the internal standards are included in Attachment II and are used unless a deviation is due to variation in instrument response as a result of analytical interferences. Results outside the target range must be flagged. The analysis is repeated based on project requirements.

12.1.1.1 Since the method is based on isotope dilution, the accuracy of native congener determinations is generally not affected when an internal standard recovery falls outside the target range. If a small number of internal standards fail, it is possible the data is narrated. If a large number of internal standards have low recoveries, the lab re-extracts (if possible). If the failures appear to be attributable to the analysis (not the extraction), re-analyze the extract.

Note: Ohio VAP requires corrective action be taken for failing internal standards. Samples must be re-analyzed and/or re-extracted to confirm failures. Data must not just be qualified without investigation.

12.1.1.2 If recoveries are outside of the target range and it appears that matrix interferences are the cause, samples can be diluted or processed through further clean-up steps and re-analyzed. If recoveries are still outside of the target ranges, it is possible the data is reported with flags.

12.1.2 Prior to each analysis, the resolution of the mass spectrometer is verified to be 10,000 or greater. Hardcopies of the reference peaks are printed at the beginning and end of each analytical shift.

12.1.3 The resolving power of the DB-5MS chromatographic column is checked daily using a standard solution containing 2,3,7,8-TCDD and the adjacent TCDD isomers. When second column confirmations are performed, the DB-225 (or equivalent) column resolution is checked using a standard solution containing 2,3,7,8-TCDF and the adjacent TCDF isomers. Acceptable performance is achieved when 2,3,7,8-TCDD or 2,3,7,8-TCDF is resolved from the adjacent isomers by a valley of 25% or less.

12.1.4 The group times for the selected-ion-monitoring data acquisitions are also checked daily using the column performance mix that contains the first and last eluting isomers of each congener class. In this way one is assured of collecting data representative of the total PCDD/PCDF content and the 2,3,7,8-substituted isomers are suitably resolved. The isomers described above are also available as part of the CS-3 calibration solution (EPA 1613 CS3 WT).

12.1.5 Initial calibrations are generated using standard solutions containing target native and labeled PCDD/PCDF compounds. Response factors are calculated and averaged for each compound.(See Equation 1) These averages are used for quantification and for comparison to the daily continuing calibration. The relative standard deviation for each native compound must be 20% or less (30% or less for the labeled compounds) as specified in method 1613B

12.1.5.1 Typically samples are not be analyzed until the above criteria can be met. In the event that samples are analyzed using an unacceptable curve, the samples are re-analyzed with an acceptable initial calibration. If this is not possible, data is qualified accordingly.

12.1.5.2 Note: For Ohio VAP analysis, the initial calibration must meet all criteria prior to sample analysis. All necessary corrective action must be taken to obtain a passing Ical and associated samples would require reanalysis. See section 11.13 – Instrument Maintenance for corrective action procedures.

12.1.6 A continuing calibration standard (or VER) is analyzed at the beginning of each 12-hour shift on days when initial calibrations are not performed.

12.1.6.1 The initial calibration is considered to be valid when the response factors from the continuing calibration analysis agree to within the acceptance limits described in Attachment II.

12.1.6.2 If the continuing calibration does not meet method criteria, correct the problem and repeat the continuing calibration or initiate a new initial calibration. See section 11.13, Instrument Maintenance for corrective actions.

12.1.6.3 The absolute retention time of the recovery standards is variable from that of the ICAL after column maintenance is performed.

12.1.6.4 Calculate the RF values as described in Equation 1. Then calculate the %Difference using Equation 4.

Equation 4

$$\%\,Difference = \frac{RF_1 - RF_c}{RF_1} x100$$

Where:
RF1=Average response factor from initial calibration.
RFc=Response factor from current verification check standard.

12.1.6.5 Typically samples are not analyzed until the above criteria is met. In the event that samples are analyzed using an unacceptable curve, the samples are re-analyzed with an acceptable initial calibration. If this is not possible, results are qualified accordingly.

12.2 Qualitative Analysis

In order for a peak to be accepted as a PCDD/PCDF isomer, the following criteria must be met:

12.2.1 Intensity ratios must be within 15% of the theoretical isotope ratio.

12.2.2 The signal to noise of the peak versus the background noise must be >2.5:1.

12.2.3 A PCDF peak cannot have a co-eluting peak in the mass window monitored for polychlorinated diphenylethers.

12.2.4 The peak elutes within the retention time determined from the analysis of the column performance window mix standard.

12.3 Data Acceptance/Rejection Criteria and Corrective Action

12.3.1 Extraction Corrective Action

12.3.1.1 If a laboratory error occurs during the extraction process that results in the loss of an extract prior to final concentration and transfer of the sample, a new aliquot is re-extracted and added to the original batch. The new aliquot must be set up within 24 hours for the set up of the first sample in the extraction batch or it must be put into a new batch, including QC aliquots.

12.3.1.2 Make note of any error and corrective action on the extraction sheet. Include times of laboratory error and re-set up of the aliquot.

12.3.2 Method Blank

12.3.2.1 One method blank is typically prepared with each twenty samples of any given matrix.

12.3.2.2 A method blank or solvent blank must be analyzed between standards and samples to demonstrate lack of PCDD/PCDF carryover.

12.3.2.3 If the blank contains PCDDs/PCDFs, find and correct the source of the problem.

12.3.2.3.1 If the contamination appears to be instrument related, correct the problem, analyze a solvent blank, and reanalyze the method blank before proceeding with samples.

12.3.2.3.2 If the contamination appears to be from the extraction or enrichment steps, continue with the analysis of samples. If the sample shows similar contamination it must be re-extracted, if possible. All associated sample results are qualified for blank contamination when any analyte is detected in the method blank at 10% of more of the sample concentration.

12.3.2.3.3 If the blank shows no contamination above levels of the lowest calibration solution, continue the analysis of samples. However, all associated sample results are qualified for blank contamination when any analyte is detected in the method blank at 10% of more of the sample concentration. Blank levels within the extended calibration range used for food and feed samples are acceptable if levels do not impact the usefulness of results for their intended purpose (samples are within acceptance range or significantly above acceptance range).

NOTE: For Ohio VAP samples, if the detection is above the reporting limit and corrective actions do not result in acceptable data, the samples must be re-extracted. If re-extraction is not possible due to depleted sample volume, then contact the client for further instructions. The client has the option to re-submit the sample or have the lab qualify the data and narrate as appropriate.

12.3.3 Laboratory Control Spike (OPR)

12.3.3.1 At a minimum, one laboratory control spike (OPR) is prepared with each batch of samples (up to 20) of any given matrix. The recoveries of the native PCDD/PCDF analytes in the spiked samples are monitored verses performance-based limits calculated annually. Method specific limits are noted in Attachment II. Matrix spikes are not required by this method, if performed, they must meet the criteria described in Method 8290 (within 20% relative percent difference, unless affected by sample levels).

NOTE: Recoveries of up to 2 native analytes outside the acceptable range do not invalidate the data but provide information that is used by the laboratory to monitor recovery trends and to assure optimization of the method. Any failure cannot occur for the same set of analytes in two consecutive batches. Affected samples must be re-extracted and reanalyzed if possible, or the data is qualified with a detailed explanation of data impact in the narrative section of the final report.

12.3.3.2 Calculate the %recovery using Equation 5 and the RPD using Equation 6. Control limits can be found in Attachment II.

Equation 5

$$\text{Percent Recovery} = \frac{C_q}{C_a}(100)$$

where, C_q=Quantitated concentration of compound x in ppbv;
C_a=Actual concentration of compound x in ppbv.

Equation 6

$$RPD = \frac{|R1 - R2|}{\frac{R1 + R2}{2}}(100)$$

where, $R1$=result for sample 1
$R2$=result for sample 2

12.3.3.3 For Ohio VAP samples, if the outlier is an analyte of interest and corrective actions do not result in acceptable data, the samples must be re-extracted. If re-extraction is not possible due to depleted sample volume, then contact the client for further instructions. The client has the option to re-submit the sample or have the lab qualify the data and narrate as appropriate.

12.3.4 Accuracy of the standard spiking solutions must be verified with each initial calibration by comparison of the solutions to certified native materials obtained from a second source or batch.

12.3.4.1 A set of four (4) spikes are analyzed when the method is first set up or if any significant change to the analytical procedure is made. The results from these analyses must meet the criteria for the IPR as described in section 9.2 of Method 1613.

12.3.4.2 For food and feed matrices, three low level spikes (approximately 0.5, 1 and 2 times the given acceptance TEQ limit) are required in lieu of the IPRs and MDLs. These spikes must agree to within the limits set by the regulatory agency (currently TEQs that agree to within 20% and yield coefficients of variation of 15% or less for European Union samples).

12.3.5 Ongoing participation in food based performance studies and ISO 17025 accreditation are also required for samples requiring acceptance by the European Union.

12.3.6 Method detection limit studies must be performed annually for selected matrices: solids, aqueous, tissue and any others deemed appropriate by QA and management personnel.

12.4 Reporting and Review

12.4.1 Reports are generated using the Avalon software package. Reporting options are chosen to match the requirements for individual clients.

12.4.2 Units/Significant Figures

12.4.2.1 Values are reported to two significant figures. Aqueous samples are routinely reported in units of pg/L and solid matrices are reported in ng/Kg. Other units are available upon request.

12.4.3 Data Qualifiers/Flags

12.4.3.1 The information typically reported is summarized below.

12.4.3.2 Base Report

12.4.3.2.1 Case Narrative including client name, address, and project information, introduction, sample information, and discussion of results.

12.4.3.2.2 Copies of chain of custody documents and analytical requests

12.4.3.2.3 Data summary tables

12.4.3.3 Full Report

12.4.3.3.1 Those items listed in base report summary

12.4.3.3.2 Raw data including sample, QC sample and standards

12.4.3.3.3 Selected ion current profiles (chromatograms)

12.4.3.3.4 Communications records

12.4.3.3.5 Extraction and login forms

12.4.3.3.6 Instrument resolution checks

12.4.3.3.7 Calibration Results

12.5 Levels of Review

12.5.1 Each sample work-up must be rechecked for work-up, header information, and data entry accuracy. The results of this review are recorded on the data review sheet.

12.5.2 All data generated during analysis are peer reviewed and a review checklist is completed. The project manager reviews the data prior to inclusion in the final report.

12.6 Data Archiving or Filing

12.6.1 Initial and Continuing Calibration standard data are stored in a QA notebook located near each instrument.

12.6.2 After reporting, the complete project file is archived in the permanent chemistry archive.

13 METHOD PERFORMANCE

13.1 There are several requirements that must be met to insure that this procedure generates accurate and reliable data. A general outline of requirements has been summarized below. Further specifications are found in the Laboratory Quality Manual and specific Standard Operating Procedures.

13.1.1 The analyst must read and understand this procedure with written documentation maintained in his/her training file which is located in the QA Office.

13.1.2 An initial demonstration of capability (IDC) must be performed. A record of the IDC must be maintained in his/her file with written authorization from the Laboratory Manager and Quality Manager. Results are stored in the QA office.

13.1.3 An annual minimum detection limit (MDL) study following SOP ALL-Q-004 must be completed for this method and whenever there is a major change in personnel or equipment. Results are stored in the QA Office.

13.1.4 Periodic performance evaluation (PE) samples are analyzed to demonstrate continuing competence. Results are stored in the QA office.

14 POLLUTION PREVENTION AND WASTE MANAGEMENT

14.1 The quantity of chemicals purchased is based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes reflect anticipated usage and reagent stability.

14.2 The Environmental Protection Agency (USEPA) requires that laboratory waste management practice be consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are characterized and disposed of in an acceptable manner. For further information on waste management consult SOP ALL-C-001.

15 REFERENCES

15.1 USEPA Method 1613: Tetra- through Octa- Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS (September 1997, Revision B)

15.2 USEPA Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, 3rd Edition, Method 8290, September, 1994

15.3 Commission Directive 2002/70/EC: Establishing Requirements for the Determination of Levels of Dioxins and Dioxin-like PCBs in Feedingstuffs., July 26, 2002.

15.4 Commission Directive 2002/69/EC: Laying Down the Sampling Methods and Methods of Analysis for the Official Control of Dioxins and the Determination of Dioxin-like PCBs in Feedstuffs., July 26, 2002.

16 TABLES, DIAGRAMS, FLOWCHARTS, APPENDICES, ADDENDA, ETC.

16.1 Attachment I: Dioxin Extraction Worksheet

16.2 Attachment II: Acceptance Criteria

16.3 Attachment III: Food and Feed Extraction Amount

16.4 Attachment IV: Method 8290 Analyte List

16.5 Attachment V: Theoretical Ion Abundance Ratios and QC limits

17 REVISIONS

Document Number	Reason for Change	Date
MN-H-002-Rev.4	**Additions made to include food matrices:** 6.21 Added definitions of food and feed sample, food, and feed 8.1 Sample size instructions added in attachment VI and noted in this section 10.4.6, 10.7.6, 10.10.6, 10.13.8 Add instructions for low level food spiking solution 10.5.2, 10.8.2, 10.11.2 Add "diluted food native standard solution may be substituted for BN1-# for food samples 10.15 Added directions for calibration and spiking levels for food and feed matrices 10.16 Directions for bringing the calibration range down to a lower level for food and feed matrices. 11.1.1 An exception is made for low level food standards; they require 3:1 signal to noise intensity 12.1.1 Added this section to include glassware used with food matrices and to include extra precautions to follow while cleaning glassware 12.2.3.1 Added "Fatty food samples are reported based on the lipid weight of the sample. Non-fatty food and all feed samples are reported based on the total weight of the sample extracted." 12.2.14 Added this section to include the preparation of high fat food and feed samples 12.2.15 Added this section to include the preparation of low fat food and feed samples 12.3.9 Added "food and feed samples prepared for Soxhlet extraction" 12.4.3 Added section "Back Extraction with Acid – Column Method" as the preferred enrichment step for food and feed matrices 13.3.1.3.3 Added "Blank levels within the extended calibration range used for food and feed samples may be acceptable if levels do not impact the usefulness of results for their intended purpose (samples are within acceptance range or significantly above acceptance range)" 13.3.2.5&6 Added performance studies, MDLs, and accreditation Added Attachment VI **Other changes made:** 4.7 Changed wording of chromatographic interference guidelines to "the area from least affected signal of the pair"; to be more specific 6.40 Added an exception to the definition of Reporting Limit when signal to noise based limits of detection are used. 11.2.1.5 Remove 25:00 timeframe for elution of 1,2,3,4-TCDD 12.3.8.7 Remove "If acid washes are not required, transfer the extract through a drying column containing a 10 cm plug of glass wool and sodium sulfate, and combine with the filtrate portion of the extract (if applicable). Rinse the flask with hexane (3 x 30 mL) and add to the drying column." 12.4.3 Added section for Back Extraction with Acid – Column Method 12.4.5.8 Added section for Jumbo-silica and larger macro-silica columns 12.9.4 Added LOD section Updated attachments	09Sep2004
MN-H-002-Rev. 5 MN-H-002-Rev. 6	Sections 12.1.16 and 12.3.10 added for preparation and extraction of blood samples, respectively 10.5 Delete preparation of Internal Standard Spiking solution 13 Clarify levels of data review and delete annual review of control limits.	07 Mar 05 **11Jul2006**
S-MN-H-002-Rev.07	Updated front page format Added Sec; 12.2.17 and 12.4.5	30July2007
S-MN-H-002-Rev.08	Added Attachment 5 Removed wording to record volume of water from sections 12.3.2.4.2, 12.3.3.3.2, 12.3.5.2 Section 12.4.7.1 changed 4g to 7g Section 12.4.7.3 Changed 20mL to 10mL Section 12.4.7.4 Changed 20mL to 35mL and 8 dram to 12 dram Added 13.3 Laboratory Error Corrective Action process	27Aug2007
S-MN-H-002-Rev.09	Removed Responsibilities and Distribution section Removed ASE procedure section Moved all extraction procedures to follow preparation procedures.	04Feb2008

	Consolidated some of the redundant preparation procedures and put them at the beginning pf section 11. Added additional equations for calculations (%Recovery RPD) Updated SOP reference in waste section Added corrective actions to 12.1.1 12.3.2.6 Added caveat to method blank section for Ohio VAP criteria Added additional corrective actions to 12.1.5 and referenced them in section 10.2.2 Corrected concentration of 13C12-OCDD in 9.13.4 Added attachment 6 with reference in 10.2.1 Added reference to Percent Lipid Determination SOP in 11.2.4.	
S-MN-H-002-Rev.10	Changed should to must where action was required Made corrective actions for Ohio VAP work more specific	15April2008
S-MN-H-002-Rev.11	Added additional information for residual chlorine and pH confirmation to section 7 Updated ion monitoring criteria in Table 9 Removed section 11.15.9 Updated Table 9	16May2008
S-MN-H-002-Rev.12	Added additional Ohio VAP corrective action criteria to the QC section Added final volume is achieved with an Eppendorf pipettor	30Jun2008
S-MN-H-002 Rev.13	Added Microwave extraction procedure (11.3.3) Temp requirement now "above freezing but below 6°C" instead of "4°C±2°C" Updated standards information ICAL solution table updated in 9.5 11.2.5.2 – mortar and pestle changed to metal bar Now using Avalon software (12.4), software versions added Attachment II – Package checklist removed; Avalon is now used for packages. Updated all attachments and attachment references to roman numerals (formatting) MSDS electronically located on Groupwise (section 5) All verbage updated to present tense	03Sep2009

ATTACHMENT I: Dioxin Extraction Worksheet (example of solids)

DIOXIN EXTRACTION WORKSHEET

DummyForQCForms_1

Setup By _____

Extraction Batch : EB-02837

Extraction On (Date/Time): _____

Extraction Off (Date/Time): _____

Client(s):

Extract Solvents
Toluene Lot # _____
Hexane Lot # _____
MeCl Lot # _____

Acid Base:
Sulphuric Acid Lot # _____
Buffer Soln # _____

Silica:
Neutral Batch # _____
Basic Batch # _____
Acid Batch # _____

Standards
Internal Std _____
Cl-37 Std _____
Recovery Std _____
Tridecane _____
Native _____
Others _____
Alumina Lot _____

Alumina:
Date _____
Initials _____
Temp _____
Hexane Lot # _____
60% Batch # _____
Humidity _____

Silica:
Date _____
Initials _____
Temp _____
Hexane Lot # _____
Humidity _____

Carbon:
Date _____
Initials _____
Temp _____
Toluene Lot # _____
75% Batch # _____
50% Batch # _____
Hexane Lot # _____
Humidity _____

Method EPA 8290 Method 1613 TO9 Method23 PCB1668
Matrix PUF XAD Solid Water Tissue Other _____

	Sample #	Labeled Stds	Native Stds	mL or g Extracted	Filtered	Cl-37 Std	Mineral Oil	Acid	Buffer Soln	Silica	Alumina	Carbon	Rec Std	Glassware Set	Comments
1	BLANK-5445														Extraction QC
2	BLANK-5446														Extraction QC
3	BLANK-5447														Extraction QC
4	BLANK-5448														Extraction QC

Extracts Relinquished By: _____ **Received By:** _____ **Date:** _____

ATTACHMENT I (continued): Dioxin Extraction Worksheet (example of solids)

DIOXIN EXTRACTION WORKSHEET

DummyForQCForms_1

Extraction Batch : EB-02837

Extraction Notes

ATTACHMENT I (continued): Dioxin Extraction Worksheet (example of water)

DIOXIN EXTRACTION WORKSHEET

Setup By _____

Dummy-Water-QC

Extraction Batch : EB-02838

Extraction On (Date/Time): _____

Extraction Off (Date/Time): _____

Client(s):

Extract Solvents
Toluene Lot # _____
Hexane Lot # _____
MeCl Lot # _____

Acid Base:
Sulphuric Acid Lot # _____
Buffer Soln # _____

Silica:
Neutral Batch # _____
Basic Batch # _____
Acid Batch # _____

Standards
Internal Std _____
Cl-37 Std _____
Recovery Std _____
Tridecane _____
Native _____
Others _____
Alumina Lot _____

Alumina:
Date _____
Initials _____
Temp _____
Hexane Lot # _____
60% Batch # _____
Humidity _____

Silica:
Date _____
Initials _____
Temp _____
Hexane Lot # _____
Humidity _____

Carbon:
Date _____
Initials _____
Temp _____
Toluene Lot # _____
75% Batch # _____
50% Batch # _____
Hexane Lot # _____
Humidity _____

Method EPA 8290 Method 1613 TO9 Method23 PCB1668
Matrix PUF XAD Solid Water Tissue Other _____

	Sample #	Labeled Stds	Native Stds	Full Bottle Wt.	Empty Bottle Wt.	Filtered	Cl-37 Std	Mineral Oil	Acid	Buffer Soln	Silica	Alumina	Carbon	Rec Std	Glassware Set	Comments
1	BLANK-5449															Extraction QC
2	BLANK-5450															Extraction QC
3	BLANK-5451															Extraction QC
4	BLANK-5452															Extraction QC

Extracts Relinquished By: _____ Received By: _____ Date: _____

ATTACHMENT I (continued): Dioxin Extraction Worksheet (example of water)

DIOXIN EXTRACTION WORKSHEET

Dummy-Water-QC

Extraction Batch : EB-02838

Extraction Notes

ATTACHMENT II – Acceptance Criteria

A. Acceptance Criteria for Performance Tests When All CDDs/CDFs are Tested[1]

CDD/CDF	Test Conc. (ng/mL)	s (ng/mL)	IPR[2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.8	8.3-12.9	6.7-15.8	7.8-12.9
2,3,7,8-TCDF	10	2.0	8.7-13.7	7.5-15.8	8.4-12.0
1,2,3,7,8-PeCDD	50	7.5	38-66	35-71	39-65
1,2,3,7,8-PeCDF	50	7.5	43-62	40-67	41-60
2,3,4,7,8-PeCDF	50	8.6	36-75	34-80	41-61
1,2,3,4,7,8-HxCDD	50	9.4	39-76	35-82	39-64
1,2,3,6,7,8-HxCDD	50	7.7	42-62	38-67	39-64
1,2,3,7,8,9-HxCDD	50	11.1	37-71	32-81	41-61
1,2,3,4,7,8-HxCDF	50	8.7	41-59	36-67	45-56
1,2,3,6,7,8-HxCDF	50	6.7	46-60	42-65	44-57
1,2,3,7,8,9-HxCDF	50	6.4	42-61	39-65	45-56
2,3,4,7,8,9-HxCDF	50	7.4	37-74	35-78	44-57
1,2,3,4,6,7,8-HpCDD	50	7.7	38-65	35-70	43-58
1,2,3,4,6,7,8-HpCDF	50	6.3	45-56	41-61	45-55
1,2,3,4,7,8,9-HpCDF	50	8.1	43-63	39-69	43-58
OCDD	100	19	89-127	78-144	79-126
OCDF	100	27	74-146	63-170	63-159
$^{13}C_{12}$-2,3,7,8-TCDD	100	37	28-134	20-175	82-121
$^{13}C_{12}$-2,3,7,8-TCDF	100	35	31-113	22-152	71-140
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	39	27-184	21-227	62-160
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	34	27-156	21-192	76-130
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	38	16-279	13-328	77-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	41	29-147	21-193	85-117
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	38	34-122	25-163	85-118
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	43	27-152	19-202	76-131
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	35	30-122	21-159	70-143
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	40	24-157	17-205	74-135
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	37	29-136	22-176	73-137
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	35	34-129	25-166	72-138
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	41	32-110	21-158	78-129
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	40	28-141	20-186	77-129
$^{13}C_{12}$-OCDD	200	95	41-276	26-397	96-415
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.6	3.9-15.4	3.1-19.1	7.9-12.7

[1] All specifications are given as concentration in the final extract assuming a 20-µL volume.
[2] s = standard deviation of the concentration
[3] X = average concentration

ATTACHMENT II (Continued)

B. Acceptance Criteria for Performance Tests When Only Tetra Compounds are Tested [1]

CDD/CDF	Test Conc. (ng/mL)	s (ng/mL)	IPR[2,3] X (ng/mL)	OPR (ng/mL)	VER (ng/mL)
2,3,7,8-TCDD	10	2.7	8.7-12.4	7.3-14.6	8.2-12.3
2,3,7,8-TCDF	10	2.0	9.1-13.1	8.0-14.7	8.6-11.6
$^{13}C_{12}$-2,3,7,8-TCDD	100	35	32-115	25-141	85-117
$^{13}C_{12}$-2,3,7,8-TCDF	100	34	35-99	26-126	76-131
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.4	4.5-13.4	3.7-15.8	8.3-12.1

C. Labeled Compound Recovery in Samples When All CDDs/CDFs are Tested

CDD/CDF	Test Conc. (ng/mL)	Labeled Compound Recovery (ng/mL)[1]	Labeled Compound Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	25-164	25-164
$^{13}C_{12}$-2,3,7,8-TCDF	100	24-169	24-169
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	25-181	25-181
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	24-185	24-185
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100	21-178	21-178
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100	32-141	32-141
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	28-130	28-130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100	26-152	26-152
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	26-123	26-123
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	100	29-147	29-147
$^{13}C_{12}$-2,3,4,6,7,8-HxCDF	100	28-136	28-136
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	23-140	23-140
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	28-143	28-143
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100	26-138	26-138
$^{13}C_{12}$-OCDD	200	34-313	17-157
$^{37}Cl_4$-2,3,7,8-TCDD	10	3.5-19.7	35-197

[1] All specifications are given as concentration in the final extract assuming a 20-µL volume.
[2] s = standard deviation of the concentration
[3] X = average concentration

ATTACHMENT II (Continued)

D. Labeled Compound Recovery in Samples When Only Tetra Compounds are Tested

CDD/CDF	Test Conc. (ng/mL)	Labeled Compound Recovery (ng/mL)[1]	Labeled Compound Recovery (%)
$^{13}C_{12}$-2,3,7,8-TCDD	100	31-137	31-137
$^{13}C_{12}$-2,3,7,8-TCDF	100	29-140	29-140
$^{37}Cl_4$-2,3,7,8-TCDD	10	4.2-16.4	42-164

[1] All specifications are given as concentration in the final extract assuming a 20-µL volume.
[2] s = standard deviation of the concentration
3 X = average concentration

ATTACHMENT III - Food and Feed Extraction Amount

Food and Feed Extraction Amounts, 10 uL Final Volume

Food or Feed Type	EU Limit	Target PQL	Amount	Weight Basis
Meat, Ruminants	2.0 pg/g	0.4 pg/g	20 grams	Lipid
Meat, Poultry	1.5 pg/g	0.3 pg/g	28 grams	Lipid
Meat, Pig	0.6 pg/g	0.12 pg/g	35 grams	Lipid
Meat, Liver	4.0 pg/g	0.8 pg/g	10 grams	Lipid
Fish, Muscle	3.0 pg/g	0.6 pg/g	15 grams	Lipid
Milk/Milk Products	2.0 pg/g	0.4 pg/g	20 grams	Lipid
Eggs/Egg Products	2.0 pg/g	0.4 pg/g	20 grams	Lipid
Oils & Fats, Ruminants	2.0 pg/g	0.4 pg/g	20 grams	Lipid
Oils & Fats, Poultry	1.5 pg/g	0.3 pg/g	28 grams	Lipid
Oils & Fats, Pigs	0.6 pg/g	0.12 pg/g	35 grams	Lipid
Oils & Fats, Mixed	1.5 pg/g	0.3 pg/g	28 grams	Lipid
Vegetable Oil	0.5 pg/g	0.1 pg/g	40 grams	Lipid
Fish Oil	1.5 pg/g	0.3 pg/g	28 grams	Lipid
Fruits	0.4 pg/g	0.08 pg/g	100 grams	Total
Vegetables	0.4 pg/g	0.08 pg/g	100 grams	Total
Cereals	0.4 pg/g	0.08 pg/g	100 grams	Total
Feed Materials, Plant	0.5 pg/g	0.1 pg/g	80 grams	Total
Minerals	0.5 pg/g	0.1 pg/g	80 grams	Total
Animal Fat, Incl. Milk & Eggs	1.2 pg/g	0.24 pg/g	34 grams	Total
Animal Products	0.5 pg/g	0.1 pg/g	80 grams	Total
Fish Oil	4.5 pg/g	0.9 pg/g	10 grams	Total
Fish	1.0 pg/g	0.2 pg/g	40 grams	Total
Compound Feedstuffs	0.4 pg/g	0.08 pg/g	100 grams	Total
Pet Food	1.5 pg/g	0.3 pg/g	28 grams	Total

ATTACHMENT IV - Method 8290 Analyte List

Compound Name	CAS No[a]
2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD)	1746-01-6
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	40321-76-4
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	57653-85-7
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	39227-28-6
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD)	19408-74-3
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin (HpCDD)	35822-39-4
1,2,3,4,6,7,8,9-Octachlorodibenzo-p-dioxin (OCDD)	3268-87-9
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	51207-31-9
1,2,3,7,8-Pentachlorodibenzofuran (PeCDF)	57117-41-6
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	57117-31-4
1,2,3,6,7,8-Hexachlorodibenzofuran (HxCDF)	57117-44-9
1,2,3,7,8,9-Hexachlorodibenzofuran (HxCDF)	72918-21-9
1,2,3,4,7,8-Hexachlorodibenzofuran (HxCDF)	70648-26-9
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	60851-34-5
1,2,3,4,6,7,8-Heptachlorodibenzofuran (HpCDF)	67562-39-4
1,2,3,4,7,8,9-Heptachlorodibenzofuran (HpCDF)	55673-89-7
1,2,3,4,6,7,8,9-Octachlorodibenzofuran (OCDF)	39001-02-0

[a] Chemical Abstract Service Registry Number

ATTACHMENT V - Theoretical Ion Abundance Ratios and QC limits

Table 9. Theoretical Ion Abundance Ratios and QC Limits

Number of Chlorine Atoms	M/Z's Forming Ratio	Theoretical Ratio	QC Limit[1] Lower	Upper
4[2]	M/(M+2)	0.77	0.65	0.89
5	(M+2)/(M+4)	1.55	1.32	1.78
5[3]	M/(M+2)	0.61	0.52	.70
6	(M+2)/M+4)	1.24	1.05	1.43
6[4]	M/(M+2)	0.51	0.43	0.59
7	(M+2)/(M+4)	1.05	0.88	1.20
7[5]	M/(M+2)	0.44	0.37	0.51
8	(M+2)/(M+4)	0.89	0.76	1.02

1 QC limits represent ±15% windows around the theoretical ion abundance ratios.

2 Does not apply to the clean up standard ($^{37}Cl_4$-2,3,7,8-TCDD)

3 used for native PeCDD only

4 used for $^{13}C_{12}$-HxCDF Only

5 used for $^{13}C_{12}$-HpCDF Only

ATTACHMENT VI – Method Deviations

Table of Modifications

2.1.1.2+ Particulate filtered	Particulate is separated by centrifuge
2.1.2+ SDS used for extraction	Soxhlet is optional substitute for SDS
4.2.2 Glassware washing	Glassware wash sequence is modified
4.2.4 Pre-extraction with toluene	Methylene chloride is an optional substitute for toluene
5.3.1 Samples weighed in hood	Sample are homogenized in a hood and weighed outside of the hood
6.1.1 Bottles are cleaned	Pre-cleaned bottles are an optional substitute
6.7 GPC cleanup	GPC is not currently available at this facility
6.7.4 Chromatographic columns	Some column size varies from those listed
6.8 Rotary evaporator for concentration	Other options used for concentration
6.9 DB-5 column specified	Optionally substitute a DB-5MS column
7.5 Silica activated at 180 C	Silica activated at 400 C
7.5 Acid or basic silica options	Neutral silica is an optional substitute
7.15 Column performance mix	Optionally combined with CS-3
8.2 Solids stored frozen	Stored at 0-6 C
9.5.1 Order of analysis	Blanks are treated like samples and analyzed at any point in a sequence. Some type of blank must be analyzed before samples to demonstrate that the system is clean.
10.1.1 GC program	The GC program does not match the one in the method
10.2.4 Minimum retention time	Advances in chromatographic columns allow shorter retention times.
11.2.1 Aqueous percent solids	Percent solids determinations are not performed on samples obviously containing less than 1% solids.
11.4.2 Marking bottle volumes	Since weights are used for sample calculations, the sample volume is not marked.
12.1 Solvent volumes for extraction	Some sample extraction volumes vary from those in the method.
12.4.1.9 Lipid determination	Lipids are otherwise determined and described in the Lipid Determination SOP.
13. Extract cleanup	Cleanup column preparation and elution volumes were modified from those described in this method. The columns more closely resemble those from Method 8290A.
15. Laboratory performance	Depending on project requirements, QC outliers are sometimes flagged and reported.
16.5 Second column confirmations	Confirmations are not performed unless specifically required for a project.
16.6/18.3 Interferences	The presence of interferences are flagged and narrated.
17.5 Dilution	Samples with levels above the calibration range are diluted.
17.6.1.4.1 Reporting limit	Results below the calibration range are reported and flagged as estimated.

APPENDIX C

U.S. ENVIRONMENTAL RENTAL CALIBRATION SOPS

YSI 600 Series Calibration With the 650 MDS

1. Make sure all cable connections with the sonde and display are tight and secured correctly.
2. Turn 650 MDS on.
3. Press enter on sonde menu. (Sonde will connect with display.)
4. Scroll down sonde menu and highlight Report. Press enter and scroll down to DO CHG and Ph mV and press enter. When there is a solid dot next to the parameter that means it is turned on. Ph mV, and DO CHG are only needed for calibration and checking the status of the probes, and are not needed for field reports.
5. Press escape to return to sonde menu and scroll up to Calibrate. Press enter.
6. We recommend using our calibration procedures, using our calibration solutions. Failure to use our procedures with our solutions may compromise the accuracy of your results.
7. Start your calibration with conductivity first.
   A. Using our conductivity calibration solution, 1000 microsiemens, completely submerge probes in solution. Highlight Cond and press enter.
   B. Highlight SpCond and press enter.
   C. "Enter value" screen appears. Hold down enter and press escape to enter the Uncal mode.
   D. Highlight yes and press enter. Highlight SpCond and press enter.
   E. Now at "enter value" screen enter the value, (If using our solutions enter 1 milisiemen, and it will calibrate to 1000 microsiemens.) Press enter once value is entered.
   F. Here is where you need to check your DO CHG. It should be within the ranges of 25 – 75.
   G. Check your SpCond, and Cond readings. If they display a drastic spike every four seconds here are some procedures to fix that.
      - Pull membrane and o-ring off DO probe.
      - Use sandpaper discs and sand the conductors on the probe. Use a match lighting motion going with the conductors 7-10 times in

each direction. Do not sand the conductors excessively. This will wear down the probe life. Rinse end of probe off in clean water and use a q-tip to dry.

- Place drops of KCL (DO) Solution until there is a nice meniscus on the end of the probe.
- Stretch membrane over the end of the probe. Seal membrane in place by pushing the o-ring on the end of the probe. Be careful not to push out the solution under the membrane. (Some will leak out.)
- Make sure there are no air bubbles under the membrane or any wrinkles in the membrane. These will cause faulty readings.
- Trim excess membrane away leaving about ¼ of an inch excess. The membrane will relax after a while so it will need a little slack.
- You may also need to change your KCL Solution. (6 month shelf life mixed)

H. If SpCond reading seems to high, (1100+), you might want to change your cal solutions.

I. When the SpCond and Cond readings have become stable, count to ten and press enter.

J. The values for SpCond, and Cond will calibrate.

K. Press enter to return to calibration parameters screen.

L. Rinse and dry probes thoroughly.

8. Calibrate Ph Second

A. Highlight Ph and press enter.

B. Highlight 3 point cal and press enter.

C. When "enter value" screen comes up hold down enter and press escape to enter uncal mode.

D. Highlight yes and press enter.

E. Highlight 3 point cal and press enter.

F. Enter 7. Always start your Ph calibration with 7. Press enter.

G. Check your Ph mV readings and make sure they are within specifications on the chart. (See Appendix 1.)

H. When the Ph readings have become stable, count to ten and press enter.

I. Once calibrated press enter again to proceed to the next "enter value" screen. Rinse and dry probes thoroughly between each solution.

J. Enter 4, (DO NOT UNCAL FOR EVERY PH, ONLY FIRST VALUE), and press enter.

K. Repeat steps G – I.

L. Enter 10 for last Ph value and press enter.

M. Repeat step G - H.

N. Press enter again to return to the 1, 2, and 3 point cal screen. Press escape to return to calibration parameters screen. Rinse and dry probes thoroughly.

9. ORP Calibration

A. Before you do your ORP calibration you need to be aware of the temperature so you can enter the correct value. Refer to chart. (Appendix 2).

B. Place Orp container on Ph/Orp combo probe. Orp solution in calibration cup needs to be changed after 3 – 5 uses. Mixed Zobell solution has a shelf life of six months from the day it was mixed. Unmixed Zobell solution has an expiration date on the bottle.

C. Highlight Orp and press enter. "Enter value" screen will appear. Press enter and exit to enter uncal mode.

D. Highlight yes and press enter for uncal.

E. Highlight Orp and press enter. Enter correct value corresponding with temperature on chart and press enter.

F. When the Orp value has become stable, count to ten and press enter.

G. Press enter to continue to calibration parameter screen.

H. Remove Orp container, being careful not to disturb the DO o-ring and membrane, rinse and dry probes thoroughly.

I. Put on probe guard, and put on white storage/calibration container. (Make sure there is a wet sponge in the container.)

10. DO Calibration

A. With sensor probe guard, and the white plastic storage/calibration container on, highlight DO and press enter.

B. Highlight DO%, and press enter.

C. When "enter value" screen appears, press enter and exit to enter uncal mode. Highlight yes and press enter for uncal.

D. Highlight DO% and press enter. Enter 760 for your barometric pressure to get a DO% calibration of a 100% saturation.

E. When the DO% value has become stable, count to ten and press enter.

F. Press enter to return to calibration parameter screen.

11. Exiting Calibration Mode

A. Press escape from calibration parameter screen to return to sonde menu screen.

B. Scroll down and highlight Report and press enter.

C. Scroll down to Ph mV and DO CHG, and turn them off by highlighting them and pressing enter. No solid dot next to the parameter means that it is turned off. Ph mV, and DO CHG are only needed for calibration and checking the status of the probes, and are not needed for field reports.

D. Once parameters are selected for field reports and are turned on, press escape and return to the sonde menu.

E. Your YSI is now calibrated and ready for field use.

RFB: ENVIRONMENTAL MONITORING, LABORATORY ANALYSIS AND REPORTING SERVICES FOR CRRA LANDFILLS

CRRA Visitor's Center and Trash Museum, 211 Murphy Road, Hartford Connecticut 06114
9:00 a.m., Wednesday, March 13, 2013

(PLEASE PRINT)

Initial if in Attendance	Name	Company	Address	Email Address	Telephone Number
	Rachel Rosen	Burns & McDonnell	108 Leigus Road, Campus at Greenhill Wallingford, CT	rmrosen@burnsmcd.com	(203) 284-8590
PC	Paul Connelly	CCA LLC	40 Old New Milford Road Brookfield, CT 06804	paulconnelly@ccaengineering.com	(203) 775-6207
	Russell Anderson	Civil & Environmental Consultants, Inc.	31 Bellows Road Raynham, MA 02767	randerson@cecinc.com	(774) 501-2176
JV	Graham Curtis Jean Vossler	Diversified Technology Consultants	2321 Whitney Avenue, Suite 301	graham.curtis@teamdtc.com jean.vossler@teamdtc.com	(203) 239-4200
S.D.	Steve Daniels	Facility Support Services LLC	2685 State Street Hamden CT 06517	sdaniels.fss@snet.net	(203) 288-1281
C.P.	Christina Pollock Christina Pollock	Geo-Environmental Management Services, MBE	173 Suffolk Court Meriden CT 06450	gems@geoenviro.com	(203) 631-3384
KH	Douglas Liddell Karen Harris	Groundwater & Environmental Services, Inc.	425B Hayden Station Road	dliddell@gesonline.com kharris@gesonline.com	(800) 220-6119 x3530
	Jason Krechko	GZA GeoEnvironmental, Inc.	655 Winding Brook Drive, Suite 402 Glastonbury, CT	jason.krechko@gza.com	(860) 286-8900
BM GB	Alicia Mojica	HRP Associates	197 Scott Swamp Road Farmington, CT 06032	alicia.mojica@hrpassociates.com	(860) 674-9570

RFB: ENVIRONMENTAL MONITORING, LABORATORY ANALYSIS AND REPORTING SERVICES FOR CRRA LANDFILLS

CRRA Visitor's Center and Trash Museum, 211 Murphy Road, Hartford Connecticut 06114
9:00 a.m., Wednesday, March 13, 2013

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Initial if in Attendance	Name	Company	Address	Email Address	Telephone Number
	Ken Gaynor	Jacobs Engineering Group	6 Otis Park Drive Bourne MA 02532	ken.gaynor@jacobs.com	(508) 743-0214 x 257
TT FOR JAMES DAVIS	~~James~~ ~~Davis~~ TERRY THOMASSON	Northern Engineering	37 Corneau Way South Windsor, CT 06074	northernengineering@comcast.net	(860) 528-7652
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	W. Scott Burrus	Soverign Consulting Inc.	1 Tarby Lane Oxford, CT 06478	sburrus@sovcon.com	(203) 828-1640
MJH	Freddie Ferreira, CPG, MBA Michael Horton	Tetra Tech, Inc.	250 Andover Street, Suite 200 Wilmington, MA	freddie.ferreira@tetratech.com	(978) 474-8444
	Matt Calvert	CME Associates	32 Crabtree Lane Woodstock CT 06281	mcalvert@cmeengineering.com	860 928 7848
TRH	Thomas Hughes	Sound Environmental Solutions	77 Havemeyer Ln Apt 424 Stamford, CT 06902	thughes30@optonline.net	203 962-1270

MANDATORY SITE TOUR SIGN-IN SHEET

RFB: ENVIRONMENTAL MONITORING, LABORATORY ANALYSIS AND REPORTING SERVICES FOR CRRA LANDFILLS – HARTFORD LANDFILL

Hartford Landfill, 180 Leibert Road, Hartford, Connecticut 06120
12:30 p.m., Wednesday, March 13, 2013

(PLEASE PRINT)

Initial if in Attendance	Name	Company	Address	Email Address	Telephone Number
	Rachel Rosen	Burns & McDonnell	108 Leigus Road, Campus at Greenhill Wallingford, CT	rmrosen@burnsmcd.com	(203) 284-8590
PC	Paul Connelly	CCA LLC	40 Old New Milford Road Brookfield, CT 06804	paulconnelly@ccaengineering.com	(203) 775-6207
GAC	~~Russell Anders~~on Glen Cote	Civil & Environmental Consultants, Inc.	31 Bellows Road Raynham, MA 02767	randerson@cecinc.com gcote@cecinc.com	(774) 501-2176
JV	Graham Curtis Jean Vossler	Diversified Technology Consultants	2321 Whitney Avenue, Suite 301	graham.curtis@teamdtc.com jean.vossler@teamdtc.com	(203) 239-4200
S.D.	Steve Daniels	Facility Support Services LLC	2685 State Street Hamden CT 06517	sdaniels.fss@snet.net	(203) 288-1281
	Christina Pollock	Geo-Environmental Management Services, MBE	173 Suffolk Court Meriden CT 06450	gems@geoenviro.com	(203) 631-3384
KH	Douglas Liddell Karen Harris	Groundwater & Environmental Services, Inc.	425B Hayden Station Road	dliddell@gesonline.com kharris@gesonline.com	(800) 220-6119 x3530
JAK	Jason Krechko	GZA GeoEnvironmental, Inc.	655 Winding Brook Drive, Suite 402 Glastonbury, CT	jason.krechko@gza.com	(860) 286-8900
AM	Alicia Mojica	HRP Associates	197 Scott Swamp Road Farmington, CT 06032	alicia.mojica@hrpassociates.com	(860) 674-9570

MANDATORY SITE TOUR SIGN-IN SHEET
RFB: ENVIRONMENTAL MONITORING, LABORATORY ANALYSIS AND REPORTING SERVICES FOR CRRA LANDFILLS – HARTFORD LANDFILL

Hartford Landfill, 180 Leibert Road, Hartford, Connecticut 06120
12:30 p.m., Wednesday, March 13, 2013

(PLEASE PRINT)

Initial if in Attendance	Name	Company	Address	Email Address	Telephone Number
	Ken Gaynor	Jacobs Engineering Group	6 Otis Park Drive Bourne MA 02532	ken.gaynor@jacobs.com	(508) 743-0214 x 257
TT	~~James Davis~~ TERRY THOMASSON	Northern Engineering	37 Corneau Way South Windsor, CT 06074	northernengineering@comcast.net	(860) 528-7652
	Chris Downey	Northwest Environmental Water Labs	450 Meriden Road Waterbury, CT 06705	nwlabs_ct@yahoo.com	(203) 437-4110
	W. Scott Burrus	Soverign Consulting Inc.	1 Tarby Lane Oxford, CT 06478	sburrus@sovcon.com	(203) 828-1640
MJH	Freddie Ferreira, CPG, MBA Michael Horton	Tetra Tech, Inc.	250 Andover Street, Suite 200 Wilmington, MA	freddie.ferreira@tetratech.com	(978) 474-8444
MPC	CME Associates Matt Calvert	CME Associates	32 Crabtree Lane Woodstock CT 06281	mcalvert@cmengineering.com	860 928 7839
FH	Frank Hyde	Terrecon Consultants Inc	201 Hall Mill Rd Rocky Hill	fhyde@terrecon.com	860-929-7861
TRH	Tom Hughes	SES	Stamford		

MANDATORY SITE TOUR SIGN-IN SHEET
RFB: ENVIRONMENTAL MONITORING, LABORATORY ANALYSIS AND REPORTING SERVICES FOR CRRA LANDFILLS –ELLINGTON LANDFILL
Ellington Landfill, 217 Sadds Mill Road (State Route 140), Ellington, Connecticut 06029
3:00 p.m., Wednesday, March 13, 2013

(PLEASE PRINT)

Initial if in Attendance	Name	Company	Address	Email Address	Telephone Number
	Rachel Rosen	Burns & McDonnell	108 Leigus Road, Campus at Greenhill Wallingford, CT	rmrosen@burnsmcd.com	(203) 284-8590
	Paul Connelly	CCA LLC	40 Old New Milford Road Brookfield, CT 06804	paulconnelly@ccaengineering.com	(203) 775-6207
GAC	~~Russell Anderson~~ Glen Cote	Civil & Environmental Consultants, Inc.	31 Bellows Road Raynham, MA 02767	~~randerson@cecinc.com~~ gcote@cecinc.com	(774) 501-2176
	Graham Curtis	Diversified Technology Consultants	2321 Whitney Avenue, Suite 301	graham.curtis@teamdtc.com	(203) 239-4200
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JML	Douglas Liddell Jill Lore	Groundwater & Environmental Services, Inc.	425B Hayden Station Road	dliddell@gesonline.com jlore@gesonline.com	(800) 220-6119 x3530
JAK	Jason Krechko	GZA GeoEnvironmental, Inc.	655 Winding Brook Drive, Suite 402 Glastonbury, CT	jason.krechko@gza.com	(860) 286-8900
	Alicia Mojica	HRP Associates	197 Scott Swamp Road Farmington, CT 06032	alicia.mojica@hrpassociates.com	(860) 674-9570

MANDATORY SITE TOUR SIGN-IN SHEET
RFB: ENVIRONMENTAL MONITORING, LABORATORY ANALYSIS AND REPORTING SERVICES FOR CRRA LANDFILLS –ELLINGTON LANDFILL

Ellington Landfill, 217 Sadds Mill Road (State Route 140), Ellington, Connecticut 06029
3:00 p.m., Wednesday, March 13, 2013

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Initial if in Attendance	Name	Company	Address	Email Address	Telephone Number
	Ken Gaynor	Jacobs Engineering Group	6 Otis Park Drive Bourne MA 02532	ken.gaynor@jacobs.com	(508) 743-0214 x 257
TM	~~James Davis~~ TERRY THOMASSON	Northern Engineering	37 Corneau Way South Windsor, CT 06074	northernengineering@comcast.net	(860) 528-7652
	Chris Downey	Northwest Environmental Water Labs	450 Meriden Road Waterbury, CT 06705	nwlabs_ct@yahoo.com	(203) 437-4110
	W. Scott Burrus ROBERT COLBERT	Soverign Consulting Inc.	1 Tarby Lane Oxford, CT 06478	sburrus@sovcon.com	(203) 828-1640
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MPC	Matt Calvert	CME Associates	32 Crabtree Lane Woodstock CT 06281	mcalvert@cmeengineering.com	860 928 7845
TRH	Tom Hughes	Sound Environmental	Stamford	thughes3@optonline.net	203 962-1276

MANDATORY SITE TOUR SIGN-IN SHEET

RFB: ENVIRONMENTAL MONITORING, LABORATORY ANALYSIS AND REPORTING SERVICES FOR CRRA LANDFILLS – WALLINGFORD LANDFILL

Wallingford Landfill, Pent Road (off of South Cherry Street), Wallingford, Connecticut 06492
9:30 a.m., Thursday, March 14, 2013

(PLEASE PRINT)

Initial if in Attendance	Name	Company	Address	Email Address	Telephone Number
	Rachel Rosen	Burns & McDonnell	108 Leigus Road, Campus at Greenhill Wallingford, CT	rmrosen@burnsmcd.com	(203) 284-8590
PSC	Paul Connelly	CCA LLC	40 Old New Milford Road Brookfield, CT 06804	paulconnelly@ccaengineering.com	(203) 775-6207
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	Graham Curtis Jan Vossler	Diversified Technology Consultants	2321 Whitney Avenue, Suite 301	graham.curtis@teamdtc.com jan.vossler@tenera.com	(203) 239-4200
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	Christina Pollock David Lehnus	Geo-Environmental Management Services, MBE	173 Suffolk Court Meriden CT 06450	gems@geoenviro.com	(203) 631-3384
JLL	Douglas Liddell Jill Lore	Groundwater & Environmental Services, Inc.	425B Hayden Station Road	dliddell@gesonline.com jlore@gesonline.com	(800) 220-6119 x3530
JAK	Jason Krechko	GZA GeoEnvironmental, Inc.	655 Winding Brook Drive, Suite 402 Glastonbury, CT	jason.krechko@gza.com	(860) 286-8900
AM	Alicia Mojica	HRP Associates	197 Scott Swamp Road Farmington, CT 06032	alicia.mojica@hrpassociates.com	(860) 674-9570

MANDATORY SITE TOUR SIGN-IN SHEET
RFB: ENVIRONMENTAL MONITORING, LABORATORY ANALYSIS AND REPORTING SERVICES FOR CRRA LANDFILLS – WALLINGFORD LANDFILL

Wallingford Landfill, Pent Road (off of South Cherry Street), Wallingford, Connecticut 06492
9:30 a.m., Thursday, March 14, 2013

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	Ken Gaynor	Jacobs Engineering Group	6 Otis Park Drive Bourne MA 02532	ken.gaynor@jacobs.com	(508) 743-0214 x 257
JM	~~James Davis~~ TERRY THOMASSON	Northern Engineering	37 Corneau Way South Windsor, CT 06074	northernengineering@comcast.net	(860) 528-7652
	Chris Downey	Northwest Environmental Water Labs	450 Meriden Road Waterbury, CT 06705	nwlabs_ct@yahoo.com	(203) 437-4110
WSB	W. Scott Burrus	Soverign Consulting Inc.	1 Tarby Lane Oxford, CT 06478	sburrus@sovcon.com	(203) 828-1640
	Freddie Ferreira, CPG, MBA	Tetra Tech, Inc.	250 Andover Street, Suite 200 Wilmington, MA	freddie.ferreira@tetratech.com	(978) 474-8444
TRH	Tom Hughes	SES	Stamford, CT		203 962-1270
	Wayne Bugden	CME	32 ~~Crabtree~~ Lane Woodstock CT 06281	mcalvert@cmeengineering.com	860-928784[illegible]

MANDATORY SITE TOUR SIGN-IN SHEET

RFB: ENVIRONMENTAL MONITORING, LABORATORY ANALYSIS AND REPORTING SERVICES FOR CRRA LANDFILLS – SHELTON LANDFILL

Shelton Landfill, 866 River Road (State Route 110), Shelton, Connecticut 06484
1:00 p.m., Thursday, March 14, 2013

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Initial if in Attendance	Name	Company	Address	Email Address	Telephone Number
	Rachel Rosen	Burns & McDonnell	108 Leigus Road, Campus at Greenhill Wallingford, CT	rmrosen@burnsmcd.com	(203) 284-8590
	Paul Connelly	CCA LLC	40 Old New Milford Road Brookfield, CT 06804	paulconnelly@ccaengineering.com	(203) 775-6207
	Russell Anderson	Civil & Environmental Consultants, Inc.	31 Bellows Road Raynham, MA 02767	randerson@cecinc.com	(774) 501-2176
JV	Graham Curtis jean vossler	Diversified Technology Consultants	2321 Whitney Avenue, Suite 301	graham.curtis@teamdtc.com Jean.vossler@teamdtc.com	(203) 239-4200
KB	Steve Daniels Kevin Bogue	Facility Support Services LLC	2685 State Street Hamden CT 06517	sdaniels.fss@snet.net KBogue.fss@snet.net	(203) 288-1281
	Christina Pollock Christina Pollock	Geo-Environmental Management Services, MBE	173 Suffolk Court Meriden CT 06450	gems@geoenviro.com	(203) 631-3384
JMK	Douglas Liddell Jill Lore	Groundwater & Environmental Services, Inc.	425B Hayden Station Road	dliddell@gesonline.com jlore@gesonline.com	(800) 220-6119 x3530
JAK	Jason Krechko	GZA GeoEnvironmental, Inc.	655 Winding Brook Drive, Suite 402 Glastonbury, CT	jason.krechko@gza.com	(860) 286-8900
AM	Alicia Mojica	HRP Associates	197 Scott Swamp Road Farmington, CT 06032	alicia.mojica@hrpassociates.com	(860) 674-9570

MANDATORY SITE TOUR SIGN-IN SHEET

RFB: ENVIRONMENTAL MONITORING, LABORATORY ANALYSIS AND REPORTING SERVICES FOR CRRA LANDFILLS – SHELTON LANDFILL

Shelton Landfill, 866 River Road (State Route 110), Shelton, Connecticut 06484
1:00 p.m., Thursday, March 14, 2013

(PLEASE PRINT)

Initial if in Attendance	Name	Company	Address	Email Address	Telephone Number
	Ken Gaynor	Jacobs Engineering Group	6 Otis Park Drive Bourne MA 02532	ken.gaynor@jacobs.com	(508) 743-0214 x 257
JM	~~James Davis~~ TERRY THOMASSON	Northern Engineering	37 Corneau Way South Windsor, CT 06074	northernengineering@comcast.net	(860) 528-7652
	Chris Downey	Northwest Environmental Water Labs	450 Meriden Road Waterbury, CT 06705	nwlabs_ct@yahoo.com	(203) 437-4110
WSB	W. Scott Burrus	Soverign Consulting Inc.	1 Tarby Lane Oxford, CT 06478	sburrus@sovcon.com	(203) 828-1640
~~TRH~~	Freddie Ferreira, CPG, MBA	Tetra Tech, Inc.	250 Andover Street, Suite 200 Wilmington, MA	freddie.ferreira@tetratech.com	(978) 474-8444
TRH	Tom Hughes	SES	Stanford, CT	thughes3@optonline.net	203 962-1270