SUMMARY SHEET 23

			Run #1	Run #2	Run #3	Avg
Client/Plant Name		FDS 23				
Job No.		FDS 23				
Sampling Location		FDS 23				
Sample ID#		FDS 23				
Test Date		FDS 23				
Run Start Time		FDS 23				
Run Finish Time		FDS 23				
Traverse Points (if applicable)		FDS 1				
Net Run Time, min	θ	FDS 23				
Dry Gas Meter Calibration Factor	Y	FDS 23				
Avg Pressure Differential Across Orifice, in. H_2O	ΔH	FDS 23				
Barometric Pressure, in. Hg	P_b	FDS 05				
Absolute Average Temperature, R	T_m	FDS 05				
Volume of Metered Gas Sample, dcf	V_m	FDS 05				
Volume of Metered Gas Sample, dscf	$V_{m(std)}$	SS 05				
Gas Sample ($V_{m(std)}$ x 0.02832), dscm	$V_{m(std)}$	SS 05				
Concentration of PCDD/PCDF, pg/m^3						
2,3,7,8-TCDD	C_i	LDS 23				
2,3,7,8-TCDF	C_i	LDS 23				
1,2,3,7,8-PeCDD	C_i	LDS 23				
1,2,3,7,8-PeCDF	C_i	LDS 23				
2,3,4,7,8-PeCDF	C_i	LDS 23				
1,2,4,5,7,8-HxCDD	C_i	LDS 23				
1,2,3,6,7,8-HxCDD	C_i	LDS 23				
1,2,3,7,8,9-HxCDD	C_i	LDS 23				
1,2,3,4,7,8-HxCDF	C_i	LDS 23				
1,2,3,6,7,8-HxCDF	C_i	LDS 23				
1,2,3,7,8,9-HxCDF	C_i	LDS 23				
2,3,4,6,7,8-HxCDF	C_i	LDS 23				
1,2,3,4,6,7,8-HpCDD	C_i	LDS 23				
1,2,3,4,6,7,8-HpCDD	C_i	LDS 23				
OCDD	C_i	LDS 23				
OCDF	C_i	LDS 23				
Total Concentration of PCDD's/PCDF's, pg/m^3	C_{Tr}	SS 23				

$$C_{Tr} = \sum_{i=1}^{n} C_i$$

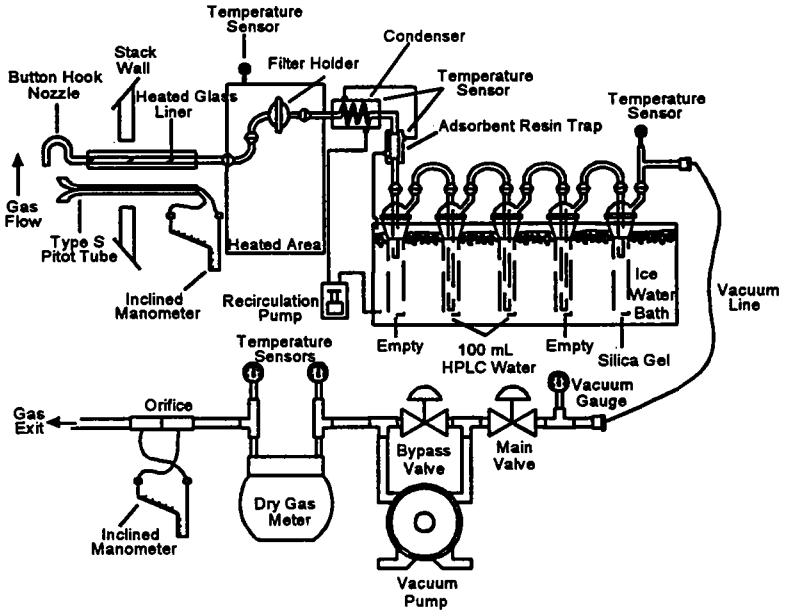

Figure F23-1. Sampling Train.

FIELD PROCEDURE 23
Polychlorinated Dibenzo-p-dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF)

Note: This sampling procedure is basically the same as that of Method 5. Preclean components according to LP 23a.

A. Major Exceptions

1. Do not use sealing greases in assembling the train.
2. Use nozzle material made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.
3. Use pesticide quality for acetone, methylene chloride, and toluene.
4. As sample storage containers of washes, use amber glass bottles with leak-free Teflon-lined caps.

B. Pretest Preparation

1. See LP 23a for pre-test procedures.
2. Soak for several hours in chromic acid cleaning solution all glass components of the train upstream of and including the adsorbent module. Then clean the components as described in section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." Especially ensure the removal of residual silicone grease sealants on ground glass connections of used glassware.
3. Load the adsorbent trap in a clean area (never in the field) to avoid contamination. Fill the trap with 20 to 40 g XAD-2. Follow with glass wool and tightly cap both ends of the trap.
4. Add ***100 µL of each of the five surrogate standards*** (see Table 23-1) to each trap.
4. Prepare the sampling train as follows:
    a. Place ~100 mL water in the second and third impingers.
    b. Leave the first and fourth impingers empty.
    c. Transfer ~200 to 300 g preweighed silica gel from its container to the fifth impinger.

C. Sampling

1. Assemble the train as shown in Figure F23-1. Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature.
2. Ensure proper sorbent temperature gas entry temperature before proceeding and before initiating sampling. Never exceed 50°C because thermal decomposition of the XAD-2 adsorbent resin will occur. During testing, do not exceed 20°C for the XAD-2 (necessary for efficient capture of PCDD and PCDF).

D. Sample Recovery

Follow the general procedure in Method 5. Use aluminum foil or Teflon tape to close off both ends of the probe. Close off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil. Do not smoke (possible contaminating source) in the cleanup area. Treat the samples as follows:

1. Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container.
2. Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store on ice for transport to the laboratory.
3. Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, as follows:
    a. Brush the probe while rinsing three times each with acetone and then rinse three times with methylene chloride.
    b. Rinse the back half of the filter holder and connecting line between the filter and condenser three times with acetone.
    c. Soak the connecting line with three separate portions of methylene chloride for 5 min each.
    d. If used, rinse the condenser in the same manner as the connecting line.
    e. Mark the level of the liquid on the container and label.
4. Container No. 3. Follow step D3 using toluene as the rinse solvent. Mark the liquid level on the container and label.
5. Impinger Water. Treat as in Method 5.
6. Silica Gel. Treat as in Method 5.

Method _____ **FIELD DATA SHEET 23** 9/30/94: FD23-1

Client/Plant Name _____ Date _____ Job # _____

City/State _____ Bar P_b _____ in. Hg Stk P_g _____ in. H_2O

Test Location/Run # _____ Personnel _____

Equipment Checks	Equipment ID#'s	Leak-Checks
Pitot Leak-Chk: Pre ____ Post ____ Nozzle: Pre ____ Post ____	Rgnt Box _____ Sampl'g Box # _____ Meter Box _____ Y _____ Umbilical _____ Pitot _____ C_p _____ Tedlar Bag _____ Noz'l _____ D_n _____ Orsat Pump _____ TC Readout _____ TC Probe _____	Vac., in. Hg _____ _____ _____ _____ DGM init, cf _____ _____ _____ _____ DGM finl, cf _____ _____ _____ _____ Leak Rate, cfm _____ _____ _____ _____

	Isokinetic Set-Up Data	Silica Gel
Filter # _____ Probe Liner _____ XAD I.D. # _____ Htr sett'g _____ Amb temp _____ Time: Start _____ End _____ Est M_d _____	$\Delta H_@$ _____ _____ _____ _____ Metr temp _____ _____ _____ _____ Est $\%H_2O$ _____ _____ _____ _____ Stk temp _____ _____ _____ _____ Ref Δp _____ _____ _____ _____ C factor _____ _____ _____ _____ K factor _____ _____ _____ _____	SG + (check) ___ Container ____ Impinger Initial wgt _____ g Final wgt _____ g

LINE	Sampl Pt #	Clock Time	DGM Rdg (cf)	DGM t_i (°F)	DGM t_o (°F)	Pitot Δp (in. H_2O)	Stk temp (°F)	Orifice (in. H_2O) Act'l	Orifice (in. H_2O) Ideal	Gauge Vac. (in. Hg)	Gas Temperatures (°F) Filter	Gas Temperatures (°F) Imping exit	Gas Temperatures (°F) Cond. <68°F
1													
2													
3													
4													
5													
6													
7													
8													
9													
10													
11													
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25													

QA/QC Check

Completeness ____ Legibility ____ Accuracy ____ Specifications ____ Reasonableness ____

Checked by: _____ _____

Personnel (Signature/Date) Team Leader (Signature/Date)

LABORATORY PROCEDURE 23
Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans

Note: Extract all samples within 30 days of collection and analyze within 45 days of extraction. Preclean components according to LP 23a.

A. Reagent Preparation

1. Chromic Acid Cleaning Solution. Dissolve 20 g sodium dichromate in 15 mL of water, and then carefully add 400 mL of conc. sulfuric acid.
2. Potassium Hydroxide, 2%. Prepare in the ratio of 2 g KOH/100 mL water.
3. Sodium Hydroxide, 1.0 N. Dissolve 40 g NaOH in water, and dilute to 1 L with water.
4. Basic Alumina. Before use, activate the alumina by heating for 16 hr at 130°C. Store in a desiccator. Pre-activated alumina, purchased from a supplier, may be used as received.
5. Silica Gel Impregnated with H_2SO_4. Combine 100 g silica gel with 44 g conc. H_2SO_4 in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon lined screw cap.
6. Silica Gel Impregnated with NaOH. Combine 39 g 1 N NaOH with 100 g silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.
7. Carbon/Celite. Combine 10.7 g AX-21 carbon with 124 g Celite 545 in a 250-mL glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.
8. ***Unlabelled and Internal Standards.*** Prepare 100 pg/μL in 10-mL nonane containing the unlabelled analytes and isotopically labelled PCDD and PCDF as shown in Table L23-1.
9. ***Surrogate Standards.*** Prepare 100 pg/μL in 10-mL nonane containing the isotopically labelled PCDD and PCDF as shown in Table L23-1.
10. ***Recovery Standards.*** Prepare 500 pg/μL in 10-mL nonane containing the isotopically labelled PCDD and PCDF as shown in Table L23-1.

B. Sample Extraction System Preparation

1. Place an extraction thimble, 1 g silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for ≥3 hr. Remove the toluene and discard it, but retain the silica gel.
2. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

C. Sample Preparation and Extraction

The items in steps C1, C2, C3, and C4 are extracted simultaneously.

1. Container No. 1 (Filter). Transfer contents directly to the glass thimble of the extraction system.
2. Adsorbent Cartridge. With the glass frit in the up position, suspend the adsorbent module directly over the extraction thimble in the beaker. Using a Teflon squeeze bottle, flush the XAD-2 with toluene into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module, and catch the rinsings in the beaker containing the thimble. If the resin is wet, loosely pack the resin in the thimble to increase extraction efficiency. Add the XAD-2 glass wool plug into the thimble.
3. Container No. 2 (Acetone and Methylene Chloride). Concentrate the sample to about 1-5 mL using the rotary evaporator apparatus at <37°C. Rinse the sample container three times with small portions of methylene chloride ($MeCl_2$) and add these to the concentrated solution and evaporate to near dryness. Add this concentrate to the extraction apparatus.
4. Internal Standards. Add ***100 μL of the internal standards*** (see Table L23-1) to the extraction thimble.
5. Extraction. Extract as follows:
   a. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD-2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor.
   b. Add the toluene from the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir ~2/3 full.
   c. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hr.

d. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-mL rinses to the rotary evaporator. Concentrate the extract to ~10 mL. (At this point the analyst may split the sample; store one half for future use and analyze the other.)

f. Using a nitrogen evaporative concentrator, reduce the sample volume being analyzed to near dryness. Dissolve the residue in 5 mL hexane.

6. Container No. 3 (Toluene Rinse). Add ***100 µL of the internal standard*** solution. Concentrate the sample to about 1-5 mL using the rotary evaporator apparatus at <37°C. Rinse the sample container apparatus at <37°C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and evaporate further to near dryness. Analyze this extract separately according to steps D and E, except use a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

D. Sample Cleanup and Fractionation

1. Silica Gel Column

   a. Pack one end of a glass column, 20 mm x 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g NaOH impregnated silica gel, 1 g silica gel, 4 g acid-modified silica gel, and 1 g silica gel. Wash the column with 30 mL hexane and discard it.

   b. Dissolve the sample extract in 5 mL hexane, and add to the column with two additional 5-mL hexane rinses. Elute the column with an additional 90 mL hexane and retain the entire eluate.

   c. Concentrate the eluate to about 1 mL using the nitrogen evaporative concentrator.

2. Basic Alumina Column

   a. Shorten a 25-mL disposable Pasteur pipette to about 16 mL. Pack the lower section with glass wool and 12 g basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column, and elute the column sequentially with 120 mL 0.5% $MeCl_2$ in hexane followed by 120 mL 35% $MeCl_2$ in hexane.

   b. Discard the first 120 mL eluate. Collect the second 120 mL eluate and concentrate it to about 0.5 mL using the nitrogen evaporative concentrator.

3. AX-21 Carbon/Celite 545 Column

   a. Remove the bottom 0.5 in. from the tip of a 9-mL disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2-cm column. Top with a glass wool plug. Add a celite plug to the exit end of the column to prevent AX-21 carbon fines from washing through the glass wool plug and into the sample.

   b. Rinse the column in sequence with 2 mL 50% benzene in ethyl acetate, 1 mL 50% $MeCl_2$ in cyclohexane, and 2 mL hexane. Discard these rinses.

   c. Transfer the concentrate in 1 mL hexane from the basic alumina column to the carbon/celite column along with 1 mL hexane rinse.

   d. Elute the column sequentially with 2 mL 50% $MeCl_2$ in hexane and 2 mL 50% benzene in ethyl acetate and discard these eluates.

   e. Invert the column and elute in the reverse direction with 13 mL toluene. Collect and concentrate this eluate in a rotary evaporator at 50°C to about 1 mL.

   f. Transfer the concentrate to a ReacM-vial using a toluene rinse and concentrate to 200 µL using a stream of N_2.

   g. Store extracts at room temperature, shielded from light, until the analysis is performed.

E. Initial GC/MS Calibration

1. Set up the GC/MS system; set mass spectrometer lock channels as specified in Table L23-2. Monitor the quality control check channels specified in Table L23-2 to verify instrument stability during analysis.

2. Calibrate the system using ***five concentrations, 2.5, 5, 25, 250, and 500 pg/µL, of the unlabeled analytes and internal standards, surrogate standards, and alternate*** (see Table L23-1).

3. Determine the relative standard deviation of the average response factors for each compound. The specifications for the RSDs are given in Table 23-1 (initial cal).

4. Determine the signal to noise ratio for the GC. The ratio should be ≥2.5.

5. Determine the ion abundance ratios (limits are given in table in CDS 23).

F. Analysis

1. Immediately before analyzing any sample, add ***20 µL of the two recovery standards*** from Table L23-1 to each sample.
2. Inject 2 µL of the extract into the GC using the DB-5 capillary column to determine the concentration of each isomer of PCDD and PCDF (tetra-through octa-). If any TCDF is detected, then inject 2 µL of the extract using the DB-225 column to measure the 2,3,7,8 TCDF isomer.
3. Identify and quantify the PCDD and PCDF. Sum the peak areas for the two ions monitored for each analyte. Use each internal standard to quantify the indigenous PCDD or PCDF in its homologous series. For example, use:
   a. $^{13}C_{12}$ -2,3,7,8-tetra chlorinated dibenzodioxin to calculate the concentrations of all other tetra chlorinated isomers.
   b. $^{13}C_{12}$ -1,2,3,4-TCDD to calculate the recoveries of the tetra- and penta- internal standards.
   c. $^{13}C_{12}$ -1,2,3,7,8,-HxCDD to calculate the recoveries of the hexa- through octa- internal standards.
   d. Corresponding homolog from the internal standard to calculate the recoveries of the surrogate standards.
4. Analyze the toluene QA rinse separately from the total sample catch; do not add it to the total sample.

G. Daily Performance Check

1. Calibration Check. Inject ***1.0 µL of the 25 pg/µL*** of the ***unlabelled, internal, surrogate and alternate standards (see CDS 23a).*** Calculate the RRF for each compound and compare each RRF to the corresponding mean RRF from the initial calibration. Acceptable limits are given in Table L23-1. The daily check must also meet the ion abundance specifications (see CDS 23).
2. Column Separation Check
   a. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8 TCDD and other TCDD isomers. Identify and record the retention time windows for each homologous series.
   b. Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

Table L23-1. Minimum Requirements for Initial and Daily Calibration Response Factors.

Compound	Relative response factors	
	Initial Calibration RSD	Daily Calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25
Recovery Standards:		
$^{13}C_{12}$-1,2,3,4-TCDD	NA	NA
$^{13}C_{12}$-1,2,3,7,8,9-HxDD	NA	NA

Table L23-2. Elemental Compositions and Exact Masses of the Ions Monitored by High Resolution Mass Spectrometry for PCDD's and PCDF's.

Descriptor No.	Accurate Mass	Ion Type	Elemental Composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF(S)
	317.9389	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF(S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD(S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD(S)
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl^{37}ClO_2$	TCDD(S)
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF(S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl^{37}Cl_2O$	PeCDF(S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_3{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD(S
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_2{}^{35}Cl_6O$	HxCDF(S
	385.8610	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF(S
	389.8157	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD(S
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD(S
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
	417.8253	M	$^{13}C_{12}H^{35}Cl_7O$	HpCDF(S
	419.8220	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF(S
	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD(S
	437.8140	M+4	$^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD(S
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD(S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD(S)
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

LABORATORY PROCEDURE 23a
Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans (PCDF)
Pre-Test Procedures

Note: Clean all glassware as described in section A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples."

A. Filter Precleaning

Clean all filters before using as follows:

1. Prepare the extraction system (see LP 23, step B1).
2. Place ≤50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool.
3. Charge the Soxhlet with toluene and reflux for 16 hr.
4. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream.
5. Store the filters in a glass petri dish sealed with Teflon tape.

B. Adsorbent Precleaning

Clean thoroughly the adsorbent resin (Amberlite XAD 2) before using as follows:

1. Use a giant Soxhlet extractor with an all-glass filter thimble containing an extra-course frit. Recess the frit 10-15 mm above the crenelated ring at the bottom of the thimble to facilitate drainage.
2. Carefully retain the resin in the extractor cup with a glass wool plug and a stainless steel ring (resin floats on methylene chloride).
3. Sequentially extract the resin as shown in the following Table:

Solvent	Procedure
Water	Place resin in a beaker, rinse once with water, and discard water. Fill with water a second time, let stand overnight, and discard water.
Water	Extract for 8 hr.
Methanol	Extract for 22 hr.
Methylene Chloride	Extract for 22 hr.
Toluene	Extract for 22 hr.

4. Dry the adsorbent resin as follows:
   a. Connect a standard commercial liquid N_2 cylinder to the drying column with a length of cleaned copper tubing, 0.95-cm ID, coiled to pass through a heat source (e.g., water-bath heated from a steam line).
   b. Purge the resin with warmed N_2 (warm to the touch but not over 40°C) until all the residual solvent is removed. Adjust the flow rate to gently agitate the particles but not so excessive as to cause the particles to fracture.
5. Check the resin for residual toluene as follows:
   a. Weigh 1.0 g dried resin into a small vial, add 3 mL toluene, cap the vial, and shake it well.
   b. Inject 2-μL sample of the extract into a gas chromatograph operated under the following conditions:

Column	6 ft x 1/8 in. stainless steel containing 10% OV-101 on 100/120 Supelcoport.
Carrier Gas	Helium at a rate of 30 mL/min.
Detector	Flame ionization detector operated at a sensitivity of 4 x E-11 A/mV.
Injection Port Temp.	250°C
Detector Temp.	305°C
Oven Temp.	30°C for 4 min; programmed to rise at 40°C/min until it reaches 250°C; return to 30°C after 17 min

   c. Inject 2.5 μL methylene chloride into 100 mL toluene to obtain 100 μg/g, and analyze as in step B5b.
   d. Compare the chromatograms from steps B5b and B5c (methylene chloride must be ≤1000 μg/g of adsorbent).
6. Store the adsorbent in a wide mouth amber glass container with a Teflon-lined cap or in one of the glass adsorbent modules (tightly seal with glass stoppers).
7. Use resin within 4 weeks of cleaning or, if precleaned adsorbent is purchased in sealed containers, use within 4 weeks after the seal is broken.

C. Glass Wool Precleaning

1. Immerse sequentially in three aliquots of methylene chloride
2. Dry in a 110°C oven.

3. Store in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

D. Water Storage Container

Rinse glass container with methylene chloride before storing water.

E. Sodium Sulfate

1. Rinse granulated, reagent grade sodium sulfate with $MeCl_2$.
2. Oven dry. Store the cleaned material in a glass container with a Teflon-lined screw cap.

F. Silica Gel (Bio-Sil A)

1. Activate the silica gel by heating for ≥30 min at 180°C.
2. After cooling, rinse the silica gel sequentially with methanol and $MeCl_2$.
3. Heat the rinsed silica gel at 50°C for 10 min, then increase the temperature gradually to 180°C over 25 min and maintain at 180°C for 90 min.
4. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

CALIBRATION DATA SHEET 23
Polychorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans
Initial Calibration

Calibration Sol'n	#1 (2.5 pg/μL)			#2 (5.0 pg/μL)			#3 (25.0 pg/μL)			#4 (250 pg/μL)			#5 (500 pg/μL)			Avg. RF	RSD	Avg. Relative RF
COMPOUND	Mass pg	Ion current	Respns Factor	Mass pg	Ion current	Respns Factor	Mass pg	Ion current	Respns Factor	Mass pg	Ion current	Respns Factor	Mass pg	Ion current	Respns Factor			
Unlabeled Analytes:	m	A	RF	m	A	RF	m	A	RF	m	A	RF	m	A	RF	$\overline{RF}$		$\overline{RRF}$
2,3,7,8-TCDD																		
2,3,7,8-TCDF																		
1,2,3,7,8-PeCDD																		
1,2,3,7,8-PeCDF																		
2,3,4,7,8-PeCDF																		
1,2,4,5,7,8-HxCDD																		
1,2,3,6,7,8-HxCDD																		
1,2,3,7,8,9-HxCDD																		
1,2,3,4,7,8-HxCDF																		
1,2,3,6,7,8-HxCDF																		
1,2,3,7,8,9-HxCDF																		
2,3,4,6,7,8-HxCDF																		
1,2,3,4,6,7,8-HpCDD																		
1,2,3,4,6,7,8-HpCDF																		
OCDD																		
OCDF																		
Internal Standards	m^*	A^*	RF^*	m^*	A^*	RF^*	m^*	A^*	RF^*	m^*	A^*	RF^*	m^*	A^*	RF^*	$\overline{AF}^*$		
$^{13}C_{12}$-2,3,7,8-TCDD																		
$^{13}C_{12}$-1,2,3,7,8-PeCDD																		
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD																		
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD																		
$^{13}C_{12}$-OCDD																		
$^{13}C_{12}$-2,3,7,8-TCDF																		
$^{13}C_{12}$-1,2,3,7,8-PeCDF																		
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF																		
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF																		

Continued

CALIBRATION DATA SHEET 23
Polychorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans
Initial Calibration

Calibration Sol'n	#1			#2			#3			#4			#5					Avg. Re
COMPOUND	Mass pg	Ion Current	Respns Factor	Mass pg	Ion Current	Respns Factor	Mass pg	Ion Current	Respns Factor	Mass pg	Ion Current	Respns Factor	Mass pg	Ion Current	Respns Factor	Avg RF	RSD	Relative RF
Surrogate Standards	m_s	A_s	RF_s	m_s	A_s	RF_s	m_s	A_s	RF_s	m_s	A_s	RF_s	m_s	A_s	RF_s	RF_s		RRF
$^{37}Cl_4$-2,3,7,8-TCDD																		
$^{13}C_{12}$-2,3,4,7,8-PeCDF																		
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD																		
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF																		
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF																		
Alternate Standard	m	A	RF	m	A	RF	m	A	RF	m	A	RF	m	A	RF	RF		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF																		

_____ S/N ratio in every selected ion current profile ≥2.5?

Calculate:

$$RF = \frac{m}{A} \qquad \overline{RF} = \frac{\Sigma\, RF}{5}$$

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}} \qquad \overline{RRF} = \frac{\overline{RF}*}{\overline{RF}}$$

Acceptable ranges for ion abundance ratios of PCDD's and PCDF's

No. of chlorine atoms	Ion Type	Theoretical ratio	Control Limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6a	M/M+2	0.51	0.43	0.59
7b	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

a = Used only for ^{13}C-HxCDF b = Used only for ^{13}C- HpCDF

_____ All Ion abundance ratios within control limits?

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by: _____ Personnel (Signature/Date) _____ Team Leader (Signature/Date)

CALIBRATION DATA SHEET 23a
Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans
Daily Calibration

COMPOUND	25pg/μL					
	Mass, (pg)	Ion Current	RRF	Initial Avg.RRF	% Difference	Ion Abundance Ratio
Unlabeled Analytes	m^*_d	A^*_d				
2,3,7,8-TCDD						
2,3,7,8-TCDF						
1,2,3,7,8-PeCDD						
1,2,3,7,8-PeCDF						
2,3,4,7,8-PeCDF						
1,2,4,5,7,8-HxCDD						
1,2,3,6,7,8-HxCDD						
1,2,3,7,8,9-HxCDD						
1,2,3,4,7,8-HxCDF						
1,2,3,6,7,8-HxCDF						
1,2,3,7,8,9-HxCDF						
2,3,4,6,7,8-HxCDF						
1,2,3,4,6,7,8-HpCDD						
1,2,3,4,6,7,8-HpCDF						
OCDD						
OCDF						
Internal Standards	m_q	A_q				
$^{13}C_{12}$-2,3,7,8-TCDD						
$^{13}C_{12}$-1,2,3,7,8-PeCDD						
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD						
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD						
$^{13}C_{12}$-OCDD						
$^{13}C_{12}$-2,3,7,8-TCDF						
$^{13}C_{12}$-1,2,3,7,8-PeCDF						
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF						
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF						

Continued

CALIBRATION DATA SHEET 23a
Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans
Daily Calibration (Continued)

COMPOUND	Cal Sol'n #3					
	Mass, (pg)	Ion Current	RF	Initial Avg. RRF	% Difference	Ion Abundance Ration
Surrogate Standards	m_{si}	A_{csi}				
$^{37}Cl_4$-2,3,7,8-TCDD						
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD						
$^{13}C_{12}$-2,3,4,7,8-PeCDF						
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF						
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF						
Recovery Standards	m_{rs}	A_{rs}				
$^{13}C_{12}$-1,2,3,4-TCDD						
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD						
Alternate Standard	m_{ci}	A_{cij}				
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF						

$$\text{Average Relative } RF_i = \frac{1}{n}\sum_{j=1}^{n}\frac{A_{cij}\,m_{ci}^{*}}{A_{cij}^{*}\,m_{ci}}$$

$$C_i = \frac{m_i^{*}\,A_i}{A_i^{*}\,RRF_i\,V_{mstd}}$$

_____ RRF's for the calibration within the limits of the mean values?

_____ Ion abundance ratios within control limits?

_____ Column separation check performed? (Retention time)

_____ Monitored ions reached their maximum peak within 2 sec. of each other?

_____ S/N ratio for all monitored ions >2.5?

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by:

_____
Personnel (Signature/Date)

_____
Team Leader (Signature/Date)

LABORATORY DATA SHEET 23
Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans

COMPOUND	Sample #1							Sample #2							Sample #3						
	Mass pg	Ion current	Peak Height 1	2	Total	Ret. time	Conc pg/m^3	Mass pg	Ion current	Peak Height 1	2	Total	Ret. time	Conc pg/m^3	Mass pg	Ion current	Peak Height 1	2	Total	Ret. time	Conc pg/m^3
Unlabeled Analytes	m_1	A_1					C_1	m_1	A_1					C_1	m_1	A_1					C_1
2,3,7,8-TCDD																					
2,3,7,8-TCDF																					
1,2,3,7,8-PeCDD																					
1,2,3,7,8-PeCDF																					
2,3,4,7,8-PeCDF																					
1,2,4,5,7,8-HxCDD																					
1,2,3,6,7,8-HxCDD																					
1,2,3,7,8,9-HxCDD																					
1,2,3,4,7,8-HxCDF																					
1,2,3,6,7,8-HxCDF																					
1,2,3,7,8,9-HxCDF																					
2,3,4,6,7,8-HxCDF																					
1,2,3,4,6,7,8-HpCDD																					
1,2,3,4,6,7,8-HpCDF																					
OCDD																					
OCDF																					
Internal Standards	m_1	A_1						m_1	A_1						m_1	A_1					
$^{13}C_{12}$-2,3,7,8-TCDD																					
$^{13}C_{12}$-1,2,3,7,8-PeCDD																					
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD																					
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD																					
$^{13}C_{12}$-OCDD																					
$^{13}C_{12}$-2,3,7,8-TCDF																					
$^{13}C_{12}$-1,2,3,7,8-PeCDF																					
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF																					
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF																					

Continued

LABORATORY DATA SHEET 23
Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans

COMPOUND	Sample #1							Sample #2							Sample #3						
	Mass pg	Ion Current	Peak Height 1	2	Total	Ret. time	Conc	MAss pg	Ion current	Peak Height 1	2	Total	Ret. time	Conc	Mass pg	Ion current	Peak Height 1	2	Total	Ret. time	Conc
Surrogate Standards	m_{si}	A_{si}						m_{si}	A_{si}						m_{si}	A_{si}					
$^{37}Cl_4$-2,3,7,8-TCDD																					
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD																					
$^{13}C_{12}$-2,3,4,7,8-PeCDF																					
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF																					
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF																					
Recovery Standards	m_{ri}	A_{ri}						m_{ri}	A_{ri}						m_{ri}	A_{ri}					
$^{13}C_{12}$-1,2,3,4-TCDD																					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD																					
Alternate Standard	m_i	A_i						m_i	A_i						m_i	A_i					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF																					

$$C_i = \frac{m_i^* A_i}{A_i^* RRF_i V_{mstd}}$$

Column separation check performed? (Retention time)

_____ Monitored ions reached their maximum peak within 2 sec. of each other?

_____ S/N ratio for all monitored ions >2.5?

QA/QC Check

Completeness _____ Legibility _____ Accuracy _____ Specifications _____ Reasonableness _____

Checked by:

_____
Personnel (Signature/Date)

_____
Team Leader (Signature/Date)