

APPENDIX B
PROCEDURES FOR THE OPERATION/CALIBRATION OF THE
METEOROLOGICAL MONITORING SYSTEM

APPENDIX B
PROCEDURES FOR THE OPERATION/CALIBRATION
OF THE METEOROLOGICAL MONITORING SYSTEM

Title

Calibration of the Climatronics EWS Electronic Weather Station

Installation and Operation of the Climatronics EWS Electronic
Weather Station.

TECHNICAL INSTRUCTION

Title: Calibration of the Climatronics EWS Electronic
Weather Station

1.0 Applicability

This procedure describes the steps necessary for calibration of the Climatronics EWS for wind speed and direction.

2.0 Supporting Materials

- calibrated 3 1/2 digit, digital voltmeter
- calibration form

3.0 Instructions

The following procedure will be completed in the laboratory prior to committing the Climatronics EWS to field service, and at least once every 3 months during field use.

3.1 Wind Direction Signal Conditioner Calibration

- a. Set switch S1 in "ZERO" and S2 in "ZERO CAL".
- b. Adjust R26 for zero (0.00 volts) at TP3.
- c. Adjust the recorder mechanical zero for a proper zero indication on the chart.
- d. Set switch S1 in "CAL", S2 in "ZERO CAL".
- e. Adjust R5 for 0.648 volts at TP 3, and a reading of 350° on the chart.
- f. Set switch S1 in "ZERO", S2 in "OP/540°".
- g. Adjust R15 for 0.667 volts at TP 3, and a reading of 360° on the chart.
(Refer to drawing #100248, attached)
- h. Record all data and adjustments on the calibration data sheet.

3.2 Wind Speed Signal Conditioner Calibration

- a. Set the front panel range switch to 0-50 mph.
- b. Place the Cal. Switch, S1, in "zero".
- c. Adjust the R14 for zero (0.00) volts at TP2.
- d. Adjust the recorder mechanical zero for a proper zero indication on the chart.
- e. Place S1 in the "Cal" position, 35 mph.

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- f. Adjust R6 for .7V (35 mph) at TP2. Having adjusted R14 and R6 for the proper voltage levels, the recorder pen should now indicate the expected reading. If the recorder pen does not indicate properly, the "left" meter drive (R51) on the Power Supply and Mux Board should be adjusted to produce the proper deflection. (This is factory set and normally does not require adjustment.)
- g. Place the front panel range switch to 0-100 mph and verify the expected reading. (Refer to drawing #100247, attached).
- h. Record all data and adjustments on the calibration data sheet.

4.0 Acceptance Criteria

- 4.1 All blanks on the calibration data sheet will be filled in or marked "NA".
- 4.2 All voltage readings must be within $\pm 1.5\%$ of the calibration values and all recorder readings must be within 0.5 mph or 5 degrees of the calibration values before the instrument will be accepted for field use.

5.0 Quality Control Check

- 5.1 The zero and calibration checks completed in the lab will be repeated in the field before, after, and at least once every 3 months during field operation. Field checks will be limited to checking the recorder output readings only. Field check data will be recorded in the site log.

6.0 Document Submission

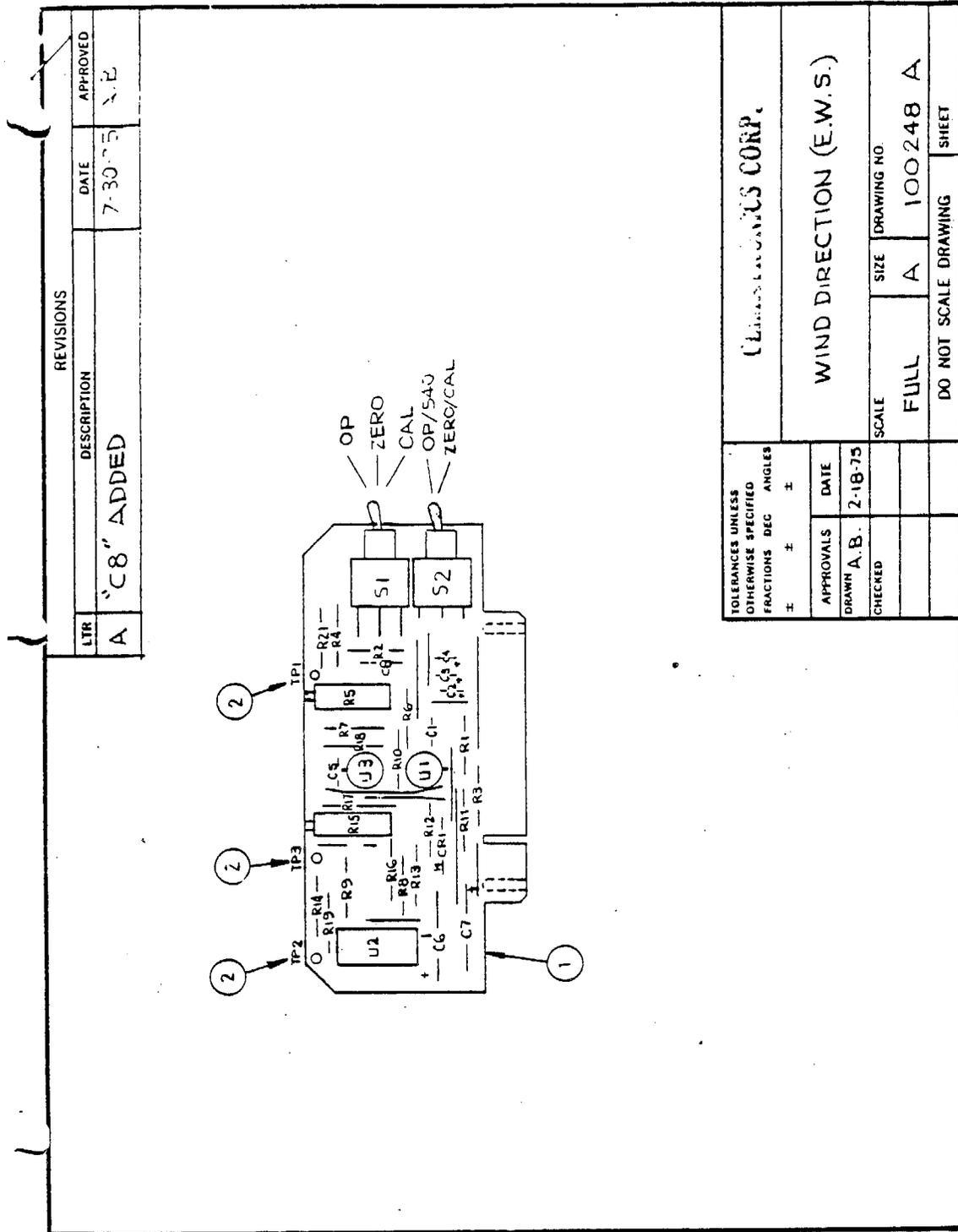
- 6.1 Calibration data sheet will be submitted to the project manager within 3 days of calibration.
- 6.2 Field calibration checks will be recorded and documented in the site log as well as marked on the strip charts.

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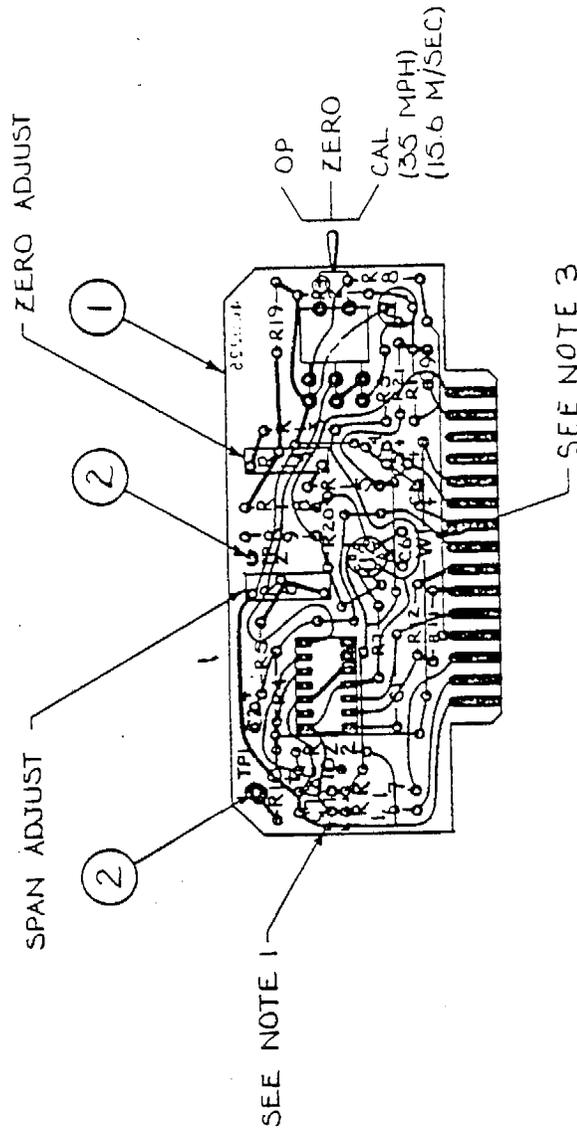
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Title: Calibration of the Climatronics EWS Electronic Weather Station

A100247



- NOTES:
1. ON METRIC UNITS ONLY, ADD RUB-ON LETTER 'M' ON COPPER SIDE OF BOARD.
 2. COAT BOTH SIDES OF BOARD WITH CHEMTRONICS C416/424 OR EQUIV. AFTER PRELIM TEST
 3. INSTALL ONLY WHEN USED WITH 100949 COMPUTER

TOLERANCES (EXCEPT AS NOTED)		REVISIONS		CLIMATRONICS CORP.	
NO.	BY	NO.	BY	EWS WIND SPEED ASSY	
0	1354	1	12/81	DRAWN BY RA	
1	1354	2	12/81	SCALE FULL	
2	1354	3	12/81	DATE 12/14/76	
3	1354	4	12/81	MATERIAL	
4	1354	5	12/81	DRAWING NO	
5	1354	6	12/81	A100247	
6	1354	7	12/81	CHK'D	
7	1354	8	12/81	TRACED	
8	1354	9	12/81	APP'D	
9	1354	10	12/81		

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Title: Calibration of the Climatronics EWS Electronic Weather Station

LABORATORY CALIBRATION DATA SHEET
 CLIMATRONICS EWS ELECTRONIC WEATHER STATION

UNIT S/N: _____ PROJECT#: _____
 DATE: _____ TECHNICIAN: _____

WS CALIBRATION		WD CALIBRATION	
VDC @ TP 2	RECORDER	VDC @ TP 3	RECORDER
_____	ZERO (0.00 VDC)	_____	ZERO (0.00 VDC)
_____	(50 MPH RANGE)	_____	350 DEG CAL
_____	35 MPH (0.70 VDC)	_____	350 DEG (0.648 VDC)
_____	(100 MPH RANGE)	_____	DP/540 CAL
_____	35 MPH (0.35 VDC)	_____	360 DEG (0.667 VDC)

ARE ALL VOLTAGE READINGS WITHIN 1.5% OF SOURCE? Y ___ N ___
 ARE ALL RECORDER READINGS WITHIN 0.5 MPH OF SOURCE? Y ___ N ___
 ARE ALL VOLTAGE READINGS WITHIN 1.5% OF SOURCE? Y ___ N ___
 ARE ALL RECORDER READINGS WITHIN 5 DEG OF SOURCE? Y ___ N ___

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Title: INSTALLATION AND OPERATION OF THE
CLIMATRONICS EWS ELECTRONIC WEATHER STATION

1.0 General Applicability

This procedure describes the installation and field operation of the Climatronics EWS Electronic Weather Station for use in monitoring and recording wind speed (WS) and wind direction (WD).

2.0 Responsibilities

The on-site field technician or operator is responsible for the installation and operation of the meteorological monitoring equipment.

The project field coordinator is responsible for assuring that the instructions found in the procedure are properly followed.

3.0 Materials Required

- Climatronics EWS Electronic Weather Station with strip chart recorder.
- Magnetic compass.
- Local topographic map or other means of determining magnetic declination from true north.
- Extra strip chart paper.
- Field log book.
- Procedure: Calibration of the Climatronics EWS Electronic Weather Station.

4.0 Procedure

4.1 Site Selection

The meteorological monitoring system will be sited in accordance with the guidelines suggested in the EPA Quality Assurance Handbook for Air Pollution Measurement System: Volume IV - Meteorological Measurements (EPA-600/4-82-060). In general, the wind instruments will be mounted 3 to 10-meters above the ground and located at least 10 times the height of obstructions away from those obstructions. The instruments may be tower mounted, or mounted on the roof of a building. If it is necessary to mount the wind instruments on a building roof, it will be mounted high enough to be out of the area in which the air flow is disturbed by the building. The site location; sensor height; and the location, height, and characteristics of all nearby obstructions will be fully documented.

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4.2 Laboratory Calibration and Maintenance

Prior to committing the Climatronics EWS to field service, all preventative maintenance and calibration checks will be completed in the laboratory. Preventative maintenance will be completed following the manufacturer's recommendations. Calibration will be completed following the technical instruction: Calibration of the Climatronics EWS Electronic Weather Station.

4.3 Field Installation and Calibration

After the meteorological monitoring station site location is chosen, the system will be installed and field calibrated as follows:

- a. Carefully unpack the wind set, and place the wind speed and direction transmitters (one unit) on a flat surface. Connect the connector end of the cable to the transmitters, and connect the other end of the cable to the recorder.
- b. After making and checking all connections, turn the recorder on. The wind speed transmitter is located at the end of the crossarm with the connector, and the wind direction transmitter at the opposite end. Rapidly spin the wind speed shaft and note that the recorder stylus moves up scale.
- c. Slowly rotate the wind direction shaft, and note that the wind direction recorder stylus moves. Move the direction shaft slowly until the recorder indicates 90 degrees. Hold the cap steady and place the wind vane on the shaft. Align the vane so that it is parallel to the crossarm, and tighten the set screws in the vane.
- d. Place the cups on the wind speed transmitter and tighten the set screws.
- e. Turn the weather station off and remove the connector from the transmitters.
- f. The wind speed and direction transmitters (sensors) mount on any 3/4-inch pipe (1.05" O.D.). The sensors should be located a minimum of 10 feet (3 meters) above the ground or the roof of a building, if they are located on a building.
- g. Using a compass or using one of the methods recommended in the EPA Quality Assurance Handbook for Air Pollution Measurement Systems: Volume IV. Meteorological Measurements (EPA-600/4-82-060), determine "West" (270°) as related to True North, (as opposed to Magnetic North).

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- h. Install the cable in its final location. Mount the crossarm on the 3/4-inch (1.9 cm) pipe, and rotate the crossarm until the wind speed sensor points west (270°, related to True North). Tighten the set screws in the crossarm mount, and connect the cable to the crossarm.
- i. Using a compass or transit, stand at a distant location from the monitoring station and verify the proper orientation of the crossarm. This should be done from at least two locations at least 90° apart. Record all alignment checks and adjustments in the site log book.
- j. Turn the power to the weather stations "ON" and re-check the laboratory calibration of the signal conditioner boards utilizing the Technical Instruction: Calibration of the Climatronics EWS Electronic Weather Station. For field calibration check, only the recorder readings will be verified. Record all data and adjustments in the site log book and on the strip charts. Return the instrument to "operate".
- k. Using a compass, site the wind direction vane from a distant location and determine the approximate wind direction. Verify this against the recorder reading. Record the results in the site log book.
- l. The unit is now ready for operation.

4.4 Field Operation

- a) Following field installation and calibration, mark the strip charts for date and time.
- b) Assure that the translator and recorder module is in a secure location to prevent damage from weather conditions, site construction work, traffic, etc.
- c) The following checks will be made daily during the program. All notes and data will be recorded in the site log book.
 - Mark each strip chart for date and time. Check to assure that the charts have not jammed and that there is an adequate supply of chart paper in the recorder.
 - Examine the sensors on the mast. Assure that the wind speed and wind direction sensors move freely and that their orientation has not been disturbed.

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- If the unit is operating on batteries, check to assure that the batteries are adequately charged by depressing the "Battery Test" switch on the translator module. The LED will not light if the batteries fall below 9.5 volts, indicating battery replacement.
- d) A field calibration check, as described in the Technical Instruction: Calibration of the Climatronics EWS Electronic Weather Station, will be conducted once weekly during the course of the program. All data and adjustments will be recorded in the site log book and on the strip charts.

A field calibration check, as described in the Technical Instruction: Calibration of the Climatronics EWS Electronic Weather Station, will be conducted at the conclusion of the program. This will be a calibration drift check, and therefore no adjustments will be made. Record the results in the site log book and on the strip charts.

5.0 Documentation

All data, notes, comments, etc., will be documented in the field log book and on the form provided in the Technical Instruction: Calibration of the Climatronics EWS Electronic Weather Station.

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APPENDIX C
SAMPLE COLLECTION PROCEDURES
PS-1 SORBENT SAMPLERS

TECHNICAL INSTRUCTION

Number: 2622-020 Class: A Date of Issue: 1st QTR 1986
Title: Collection of Semi-Volatile Organics in Air Using Solid Sorbents

Organizational Acceptance	Authorization	Date
Originator	<i>Scott M. Whittemore</i>	3-10-86
Department Manager	<i>Jane Henneley</i>	3-11-86
Unit Quality Assurance ^{Manager} Officer	<i>Scott M. Whittemore</i>	3-10-86
Other		

Revisions Changes Authorization Date

Title: Collection of Semi-Volatile Organics in
Air Using Solid Sorbents

1.0 Purpose/Applicability

The objective of this document is to provide a complete, standardized procedure for the collection of semi-volatile organic air contaminants using solid sorbents such as polyurethane foam (PUF), XAD-2 resin or Tenax®. Specific sorbents or combinations of sorbents are selected on a case-by-case basis to optimize collection efficiency for the compounds of interest. The sample air is drawn through the sorbent at constant flowrate for a measured period of time. The exposed sorbent is then solvent extracted and the extract analyzed.

This Techn describes the sorbent preparation, transportation, and exposure procedures. Sampler calibration procedures are given in ERT Techn No. 2622-021. Sample extraction procedures are given in ERT SOP No. 6330. Sample analyses are performed in accordance with the ERT Standard Analytical Method (SAM) or EPA analytical method appropriate for the contaminants of interest.

2.0 Required Materials

- o Sorbent Thimble (65 mm x 125 mm Glass cylinder)
- o Sorbent Material - Selected on the basis of specific sampling objectives
- o Mason Jars (one per cartridge), with teflon lined cap.
- o Particulate Filters - 10 cm dia. glass fiber (Watman EPM 2000, or equivalent)
- o Sampler(s) - General Metals Works Model PS-1, or equivalent
- o Clean white cotton gloves (two pair)
- o Calibration Orifice kit with calibration curve and water manometer
- o ERT Techn 2620-300, Calibration of the GMW Model PS-1 PUF Sampler
- o ERT Techn 6000-201, Filter Processing Method for determination of Total Suspended Particulate

3.0 Procedures

3.1 Sample Collection Media

Semi-volatile organic compounds in the ambient air are collected in a solid sorbent material such as PUF, XAD-2, Tenax®, or a combination of PUF and one of the granular sorbents. Sorbent cartridges are assembled by placing the sorbent media in a glass thimble. Two typical sorbent cartridge configurations are illustrated in Figures 1 and 2.

Particulate matter is collected on a 10cm diameter glass fiber filter upstream of the sorbent cartridge. (See Figure 3).

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3.2 Sorbent Clean-Up

Prior to dispatching for field sampling, the assembled sorbent cartridges must be cleaned in the laboratory to remove potential interferences.

The standard clean-up procedure is soxhlet extraction for at least 16 hours with 5% diethyl ether in hexane, followed by drying at 40°C in a vacuum desiccator or oven. Ten percent of the pre-cleaned sorbent cartridges (or a minimum of one per lot) must be submitted for a quality control check consisting of an extraction and analysis scheme identical to that performed for the actual samples. Acceptance criteria for the results of the QC check will be determined for each project on the basis of the achievable ambient air concentration detection limits. If the quality control acceptance criteria are not satisfied, the cleaning must be repeated for the entire lot.

The pre-cleaned sorbent cartridges are then placed in sealed glass mason jars for dispatching to the field.

3.3 Particulate Filter Preparation

Particulate filters are cut from standard 8" x 10" glass fiber TSP filters. Prior to use, they must be carefully inspected for pinholes, tears and other imperfections. The inspected filters are then equilibrated for 24 hours in a desiccator, tared and placed in individual glass petri dishes for dispatching to the field. Each petri dish is sealed with teflon tape. Filter preparation and gravimetric analysis procedures and quality control are detailed in ERT Techn No. 6000-201.

3.4 Storage and Handling of Sample Collection Media

Extensive precautions must be taken to preserve the integrity of the pre-cleaned collection media during transport and storage. The sorbent cartridges will be stored and transported in sealed mason jars and handled only with clean white cotton gloves or Teflon-tipped tongs. As an additional precaution for light-sensitive species, either the glass sorbent cartridge or the sealed mason jar should be covered with pre-cleaned aluminum foil. Organics particulate filters are handled only with teflon-tipped tongs and are kept in individual glass petri dishes. In addition, the samples are stored and transported under refrigeration to maintain sorbent integrity and minimize artifact release and migration and sorbent contamination. Samples must be removed from the site promptly after collection to avoid contamination. In the laboratory, the organics samples must be stored and handled in a designated organic free area.

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3.5 Chain-of-Custody Procedures

- 1) Chain-of-Custody procedures are initiated by the Laboratory Sample Custodian upon issuance of sample kits. At this time, each sampling kit is sealed with chain-of-custody tape signed and dated by the Sample Custodian, and is accompanied by a chain-of-custody form (Figure 4) containing the preliminary lab sample numbers and particulate filter identification numbers, the chain-of-custody tape numbers (in the signature box), the signature of the Sample Custodian (as "Relinquished By") and the date and time. One chain-of-custody record may be used for up to eight samples as long as those samples are transferred from custodian to custodian as a batch throughout their life. When issuing sample kits, the Laboratory Sample Custodian will retain the back copy of the chain-of-custody record.
- 2) When the field operator receives the sample kits, he or she will sign as "Received By" and enter the date and time. A field notebook entry will be made stating the condition of each chain of custody seal. The samples will be in that person's custody until they are relinquished back to the laboratory.
- 3) Minimum information recorded on the chain-of-custody record in addition to the signatures and dates of all custodians will include:
 - o Sampling site identification
 - o Sampling date and time
 - o Identification of sample collector
 - o Sample identification
 - o Sample description (type and quantity)
- 4) For the return of the completed samples to the laboratory for analysis, each kit will be sealed with chain-of-custody tape and the seals will be signed and dated. The new chain-of-custody seal numbers will be entered on the chain-of-custody form (in the signature box). The current custodian will sign the chain-of-custody record as "Relinquished By", enter the date and time, tear off and keep the back copy and place the remainder in the shipping container with the samples.

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- 5) The samples will be received at the laboratory by the Laboratory Sample Custodian. He will sign the chain-of-custody record as "Received for Laboratory" and enter the date and time. The last copy of the completed record will be sent to the sample collection task manager. The original will be retained in the Laboratory files.
- 6) The laboratory's log-in record will explicitly state the condition of the chain-of-custody seal on each incoming sample.

3.6 Sampler Calibration

Sampler flowrate is measured by means of a venturi built into the flow path between the pump and the sorbent cartridge holder. The pressure differential in the venturi is indicated in inches of water, on a magnehelic gauge mounted inside the body of the sampler. The relationship between the magnehelic gauge reading and the true flowrate in standard liters per minute (SLPM) must be calibrated and documented prior to operation, and should be verified after each sampling round. The calibration is performed at five different flowrates, the range of which must include the operating sample flowrate. Full calibration procedures are detailed in ERT Techn No. 2620-300.

Between sampling rounds, once the sorbent cartridge has been removed, the sampling module (Figure 3b) should be disassembled and decontaminated by soaking in methanol overnight. This is to prevent potential transfer of contamination from the module to the sample once the sorbent cartridge has been reinstated.

3.7 Sample Collection

3.7.1 Installation of Sample Collection Media

Open the sorbent cartridge canister by turning the filter holder support counter-clockwise (see Figure 3). Be careful not to drop the gasket that seals the contact between the sorbent cartridge and the canister. Then open the mason jar containing the sorbent cartridge, take out the cartridge (using the gloves) and slide it into the lower half of the canister on the sampler. Position the gasket (if it is loose) to ensure a good seal, and then close the canister and turn clockwise until it is hand-tight. Promptly close the mason jar.

Unscrew the three wingnuts on the filter retaining ring until the swing-away bolts can be pushed aside, freeing the filter retaining ring. Lift the ring off, being careful

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not to drop the gasket. Take a filter out of its petri dish, using the tongs, and place it, rough side up, on the screen in the filter holder. Position the gasket (if necessary), replace the retainer ring, flip up the bolts and tighten each wingnut finger-tight. Close the petri dish.

The tongs should be kept in a sheath and protected from contamination. If the tongs become soiled or contaminated, clean them immediately by rinsing in methanol or hexane and air drying. The cotton gloves should also be kept clean, and if soiled, they should be replaced.

Fill out the heading information on the Sample Collection Data Sheet (Figure 5), entering the identification numbers of the cartridge and filters just installed, as well as the sampler number, sampling site, date and your name.

3.7.2 Setting the Sampler Flowrate

Turn the sampler on by switching the 7-day timer ON/OFF lever to ON. Record the reading of the elapsed time meter as "start time" on the Sample Collection Data Sheet. Allow several minutes for warm-up.

Look up the desired sample flowrate on the calibration curve for the sampler and find the corresponding value of " I_c ". Record this value as "Sqrt I" on the first line of the "Sample Flowrate" section of the Data Sheet. Record the square of the "Sqrt I" value on the data sheet as "I". Adjust the sampler flowrate to obtain the magnehelic gauge reading just recorded as "I". The flowrate can be adjusted either by turning the voltage variator potentiometer (coarse adjustment) located adjacent to the elapsed time indicator or by turning the ball valve (fine adjustment) located downstream of the venturi. When the desired reading has been achieved, record the time, ambient temperature, barometric pressure and set flowrate on the Data Sheet.

Close the roof of the sampler.

3.7.3 Periodic Sampler Flowrate Checks

The required frequency of flowrate checks varies from one sampling project to another. The Sample Collection Data Sheet is designed to accommodate twelve flowrate readings, including the set point recorded in 3.7.2. Check the project work plan or QA plan for the correct frequency.

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In each flowrate check, record the time, ambient temperature, barometric pressure and magnehelic gauge reading ("I"). Compute and record the square root of "I". On the sampler calibration curve, look up the flowrate corresponding to the "Ic" value just recorded as the square root of "I", and record that flowrate under "SLPM" on the Data Sheet.

If the flowrate just determined differs from the set flowrate by an unacceptable amount, readjust the flowrate (using the ball valve) and note in the margin: "Reset to ___ LPM".

3.7.4 Removal of Sample Collection Media

Record the end time (elapsed time meter reading) and final ambient temperature, barometric pressure and flowrate indication on the Data Sheet. Turn the sampler off by turning the timer ON/OFF switch to the OFF position.

Remove the particulate filter, using the tongs, return it to its original petri dish, and close the petri dish. Seal the petri dish with teflon tape.

Remove the sorbent cartridge, using the gloves, wrap the cartridge with solvent rinsed aluminum foil, return it to its original mason jar, close the jar tightly and seal it with teflon tape.

Place the collected samples in a cooler and remove them from the sampling site promptly.

Dispatch the samples to the laboratory, following the chain-of-custody procedures in Section 3.5.

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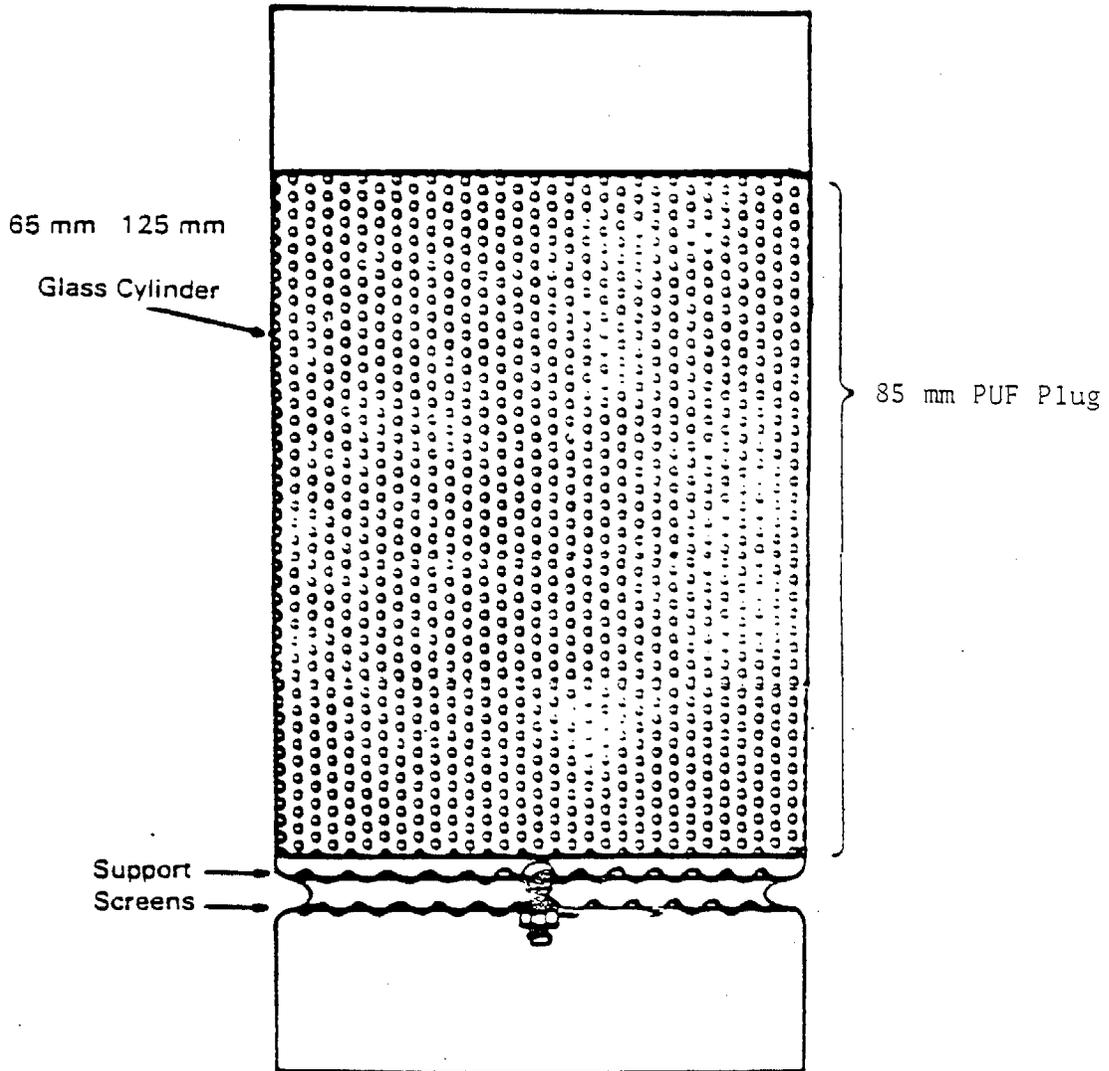


Figure 1 - PUF Sampling Cartridge

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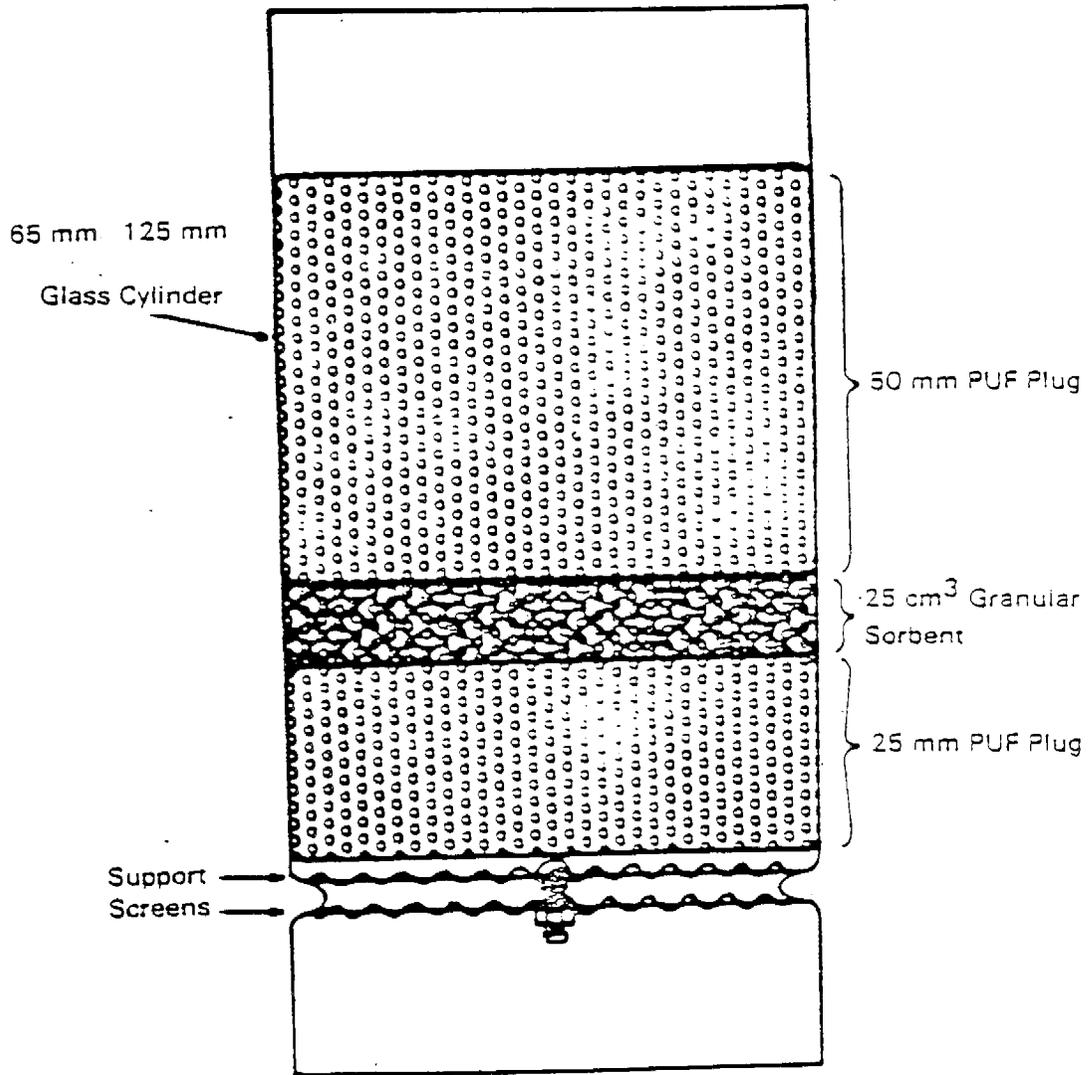


Figure 2 - Dual Sorbent Sampling Cartridge

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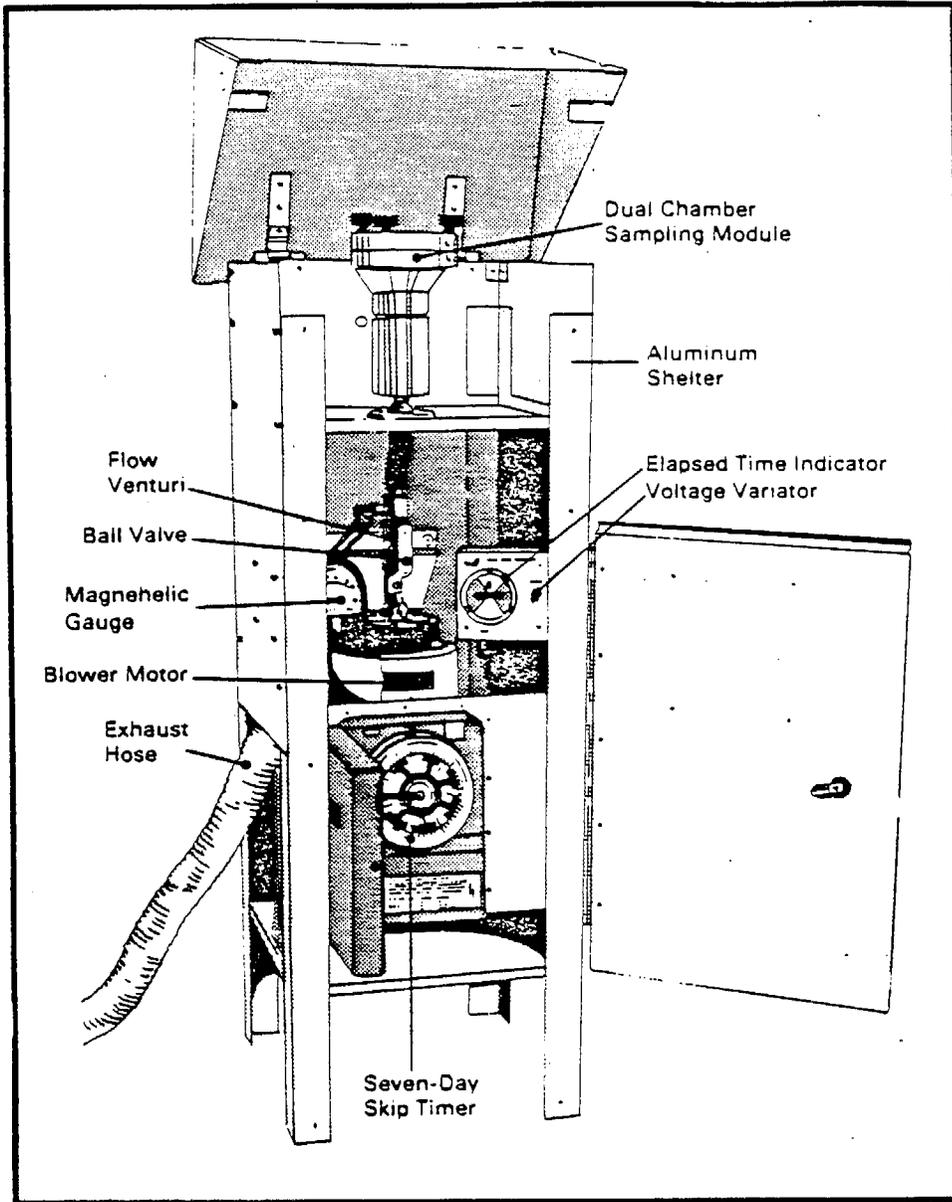


Figure 3a
Sampler

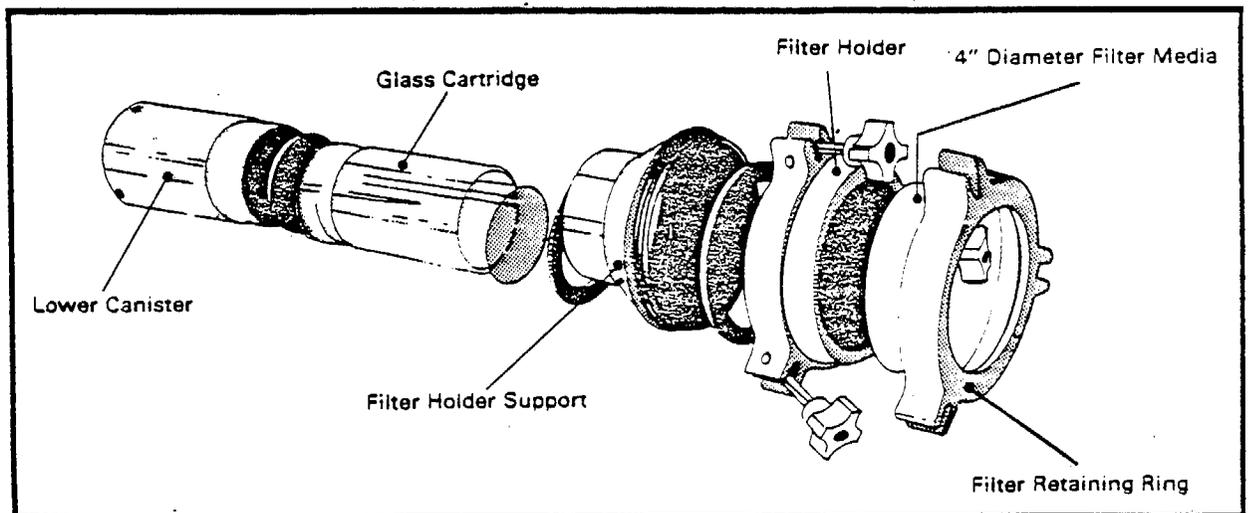


Figure 3b
Dual Chamber
Sampling Module



TECHNICAL INSTRUCTION

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 Number: 2622-020
 Date: 1st Qtr. 1986
 Revision: 0

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Figure 4

CHAIN OF CUSTODY RECORD

Client/Project Name			Project Location			ANALYSES							
Project No.			Field Logbook No.										
Sampler: (Signature)			Chain of Custody Tape No.										
Sample No./ Identification	Date	Time	Lab Sample Number	Type of Sample							REMARKS		
Relinquished by: (Signature)				Date	Time	Received by (Signature)				Date	Time		
Relinquished by: (Signature)				Date	Time	Received by (Signature)				Date	Time		
Relinquished by: (Signature)				Date	Time	Received for Laboratory (Signature)				Date	Time		
Sample Disposal Method:				Disposed of by: (Signature)						Date	Time		
SAMPLE COLLECTOR ERT - A Resource Engineering Company 696 Virginia Road Concord, MA 01742 617-369-8910				ANALYTICAL LABORATORY						ERT			
										No 1663			

1974-3-84

APPENDIX D
PS-1 SAMPLER CALIBRATION PROCEDURES

ERT TECHNICAL INSTRUCTION

2622-021
 Number: ~~2620-300~~ Class: Date of Issue: 3rd Qtr 1984
 Title: Calibration of the GMW PS-1 Poly Urethane Foam (PUF) Sampler

Organizational Acceptance	Authorization	Date
Originator	<i>[Signature]</i>	7-30-84
Department Manager	<i>[Signature]</i>	8-13-84
Unit Quality Assurance ^{Manager} Officer	<i>[Signature]</i>	8-13-84
Other		

Revisions	Changes	Authorization	Date
1	Number changed from 2620-300 to 2622-021	<i>[Signature]</i>	2-3-86

Title: Calibration of the GMW PS-1 Poly Urethane
Foam (PUF) Sampler

1.0 Applicability

This procedure describes the steps necessary for calibration of the General Metal Works model PS-1 Poly Urethane Foam (PUF) Sampler.

2.0 Supporting Materials

- o GMW-40 orifice calibrator which has been calibrated within the past year.
- o Water manometer, Dwyer Model 1221-20-W/M or equivalent; or 0-10" and/or 0-3" and 0-0.25" magnehelic gauge.
- o Thermometer (or equivalent) for ambient temperature readings.
- o Portable aneroid barometer (or equivalent) for ambient pressure readings.
- o Water or unity oil if calibration in freezing weather is expected.
- o Mean barometric pressure for site as determined from Smithsonian tables of elevation vs. mean pressure (see Table 1).
- o Seasonal mean ambient temperature for the site, as determined from reliable climatological information.
- o Flexible ruler, or straight edge and a set of french curves.
- o ERT calibration form.

3.0 Instructions

Note: Avoid calibrating the PS-1 when winds exceed 15 mph.

The PS-1 is usable over the range of 20 SLPM to approximately 250 SLPM. The GMW-40 calibrator must be certified over the range for which the sampler is to be calibrated. The 0-100" H₂O magnehelic gauge supplied with the PS-1 may be used for flows greater than 70 SLPM. Below 70 SLPM a 0-10" H₂O magnehelic gauge must be used. The gauge(s) used during calibration must be the same one(s) employed during actual use of the sampler.

- 3.1 Remove the filter and whatever material is in the glass cartridge of the sample collection unit. Be certain that the glass cartridge is put back into the holder and secured.
- 3.2 Install the GMW-40 calibrator on top of the 4" filter holder.

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Title: Calibration of the GMW PS-1 Poly Urethane
Foam (PUF) Sampler

- 3.3 Connect the water manometer (or equivalent gauge) to the pressure tap of the GMW-40 calibrator. If a manometer is used, fill it (about half full) with water or unity oil and secure in a vertical position. Set the scale to read "0" at the bottom of the meniscus.
- 3.4 Fill out all of the heading information on ERT Calibration form.
- 3.4.1 Place the thermometer in a shaded, well ventilated place and wait for a stable reading. Record as Ambient Temperature (T_1).
- 3.4.2 Barometric Pressure - Obtain a barometric pressure reading from the nearest National Weather Service (NWS) observation station and apply the correction factor that corresponds to your site elevation in Table 2.

$$\text{NWS Pressure} \times \text{Correction Factor} = \text{True Pressure}$$

- 3.5 Connect the appropriate magnehelic gauge (0-100" H₂O or 0-10" H₂O) across the venturii meter located downstream of the motor. Both taps of the magnehelic gauge(s) must be connected. The gauge(s) should be used in the vertical position. Adjust the zero if necessary by turning the zero adjust screw (below meter face).
- 3.6 Turn the PS-1 on by switching the 7 day timer on/off lever to "on". Flow may be regulated by adjusting the voltage variator potentiometer (located next to the elapsed time indicator) and/or by the ball valve located downstream of the venturii meter. The maximum flow desired for the calibration should be set using the potentiometer for a coarse adjustment and the valve for the fine adjustment. Read the differential pressure on the manometer or magnehelic gauge. (Read the bottom of the water meniscus.) Differential pressure equals the sum of the water displacements (in inches) of both sides of the manometer; in other words, the total distance between meniscus levels. Example: if one side reads 3.5" above zero and the other reads 3.4" below zero, then the differential pressure is 6.9". Record the value under "ΔH" on the calibration form. Take the square root of the manometer reading and record it in the "√Δ" column.
- 3.7 Record the magnehelic gauge reading in the "I" column. Take the square root of the magnehelic gauge reading and enter it in the "√I" column.
- 3.8 Repeat steps 3.6 and 3.7 for at least 4 additional flow points.

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3.9 Temperature and Pressure Corrections.

3.9.1 Obtain and record seasonal mean ambient temperature (°C) on calibration sheet. This information should be available from the Program Manager or Meteorologist responsible for the network.

3.9.2 Determine the mean barometric pressure for the site elevation from Table 1.

3.9.3 Determine the correction factor for the manometer readings as follows:

$$CF_1 = 0.626 \left(\frac{P_1}{T_1} \right)^{1/2}$$

where

CF_1 = correction factor for manometer readings

P_1 = barometric pressure during HI-VOL calibration, mmHg

T_1 = ambient temperature during HI-VOL calibration, °K
(°K = °C + 273)

3.9.4 Determine the correction factor for magnehelic gauge readings as follows:

$$CF_2 = \left(\frac{P_1}{P_2} \times \frac{T_2}{T_1} \right)^{1/2}$$

where

CF_2 = correction factor for magnehelic gauge or flow recorder readings, representing seasonal mean temperature and site mean barometric pressure,

P_1 and T_1 = same as defined above,

P_2 = site mean barometric pressure, mmHg

T_2 = seasonal mean temperature for the site, °K.

Title: Calibration of the GMW PS-1 Poly Urethane
Foam (PUF) Sampler

-
- 3.9.5 Record the correction factors. The correction factors will often be close to 1.000, but they should be recorded anyway. Multiply each value of " ΔH " and each value of " V_I " by the corresponding correction factors determined above and enter the resulting corrected values in the " ΔH_c " and " I_c " columns, respectively.
- 3.10 For each value of " ΔH_c ", locate the corresponding true flow rate in standard liters per minute on the orifice calibration curve supplied with the orifice. Record under " Q_{STD} ".
- 3.11 Plot the curve using the standardized magnehelic gauge readings (I_c) as the horizontal scale (abscissa) and Q_{STD} , standardized true flow (SLPM) as the vertical scale (ordinate). Connect the points with a smooth curve. Label the scales to accommodate the range of flows and gauge readings used.
- 4.0 Drawing the Curve
- 4.1 The curve must be either a straight line or a continuous smooth curve.
- 4.2 If a straight line cannot be drawn in such a way that no point is more than two divisions off the line, try a smooth curve using a french curve or flexible ruler.
- 4.3 If neither a straight line nor smooth curve can be drawn in such a way that all points fall within two divisions of it, it will be necessary to redo the "outlier" point.
- 5.0 Acceptance Criteria
- 5.1 All spaces on the calibration form must be filled out or marked N/A.
- 5.2 The plotted curve must be smooth. Only one of the points may be off the curve and that point may not be more than 2 divisions from the curve or the point must be rerun. If rerunning does not improve the reading suspect a leak.
- 5.3 The curve must bracket the range of flows which are anticipated to be employed.
- 6.0 Quality Control Check
- 6.1 A one point calibration check must be performed every week at the flow rate being used during normal sampling conditions. Calculate the $\Delta\%$ between point and the value from the calibration curve. If $\Delta\%$ is $> \pm 7\%$, investigate the cause, and repair and recalibrate as necessary.

TECHNICAL INSTRUCTION

Title: Calibration of the GMW PS-1 Poly Urethane
Foam (PUF) Sampler

Page: 5 of 7
Number: 2622-021
Date: 3rd Qtr. 1984
Revision: 1

7.0 Document Submission

- o Calibration data sheet (2 copies) within 3 days to supervisor.
- o Final cal curve, with QC checks, to sample processing facility.

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Title: Calibration of the GMW PS-1 Poly Urethane
 Foam (PUF) Sampler

TABLE 1

Site Elevation (Feet above sea level)	Approximate Mean Barometric Pressure (mm Hg)
0	760
500	746
1000	733
1500	720
2000	705
2500	694
3000	680
3500	669
4000	656
4500	644
5000	632
5500	620
6000	609
6500	598
7000	586
7500	575
8000	564
8500	554
9000	543
9500	533
10000	523

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TABLE 2
 CORRECTION FACTORS FOR NWS PRESSURES

Site Elevation Above Mean Sea Level		Correction Factor
Ft.	Meters	
11000	3353	0.661
10500	3200	0.674
10000	3048	0.688
9500	2896	0.701
9000	2743	0.715
8500	2591	0.779
8000	2438	0.743
7500	2286	0.757
7000	2134	0.771
6500	1981	0.786
6000	1829	0.801
5500	1676	0.817
5000	1524	0.832
4500	1372	0.848
4000	1219	0.864
3500	1067	0.880
3000	914	0.896
2500	762	0.913
2000	610	0.930
1500	475	0.947
1000	305	0.964
500	152	0.982
0	0	1.000

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P. U. F.
SAMPLER CALIBRATION

Network _____ Site _____ Sys No 1 2 3 4 5

Technician: _____ Date _____ HI-VOL Serial No _____

Orifice SN _____ Cal Date _____

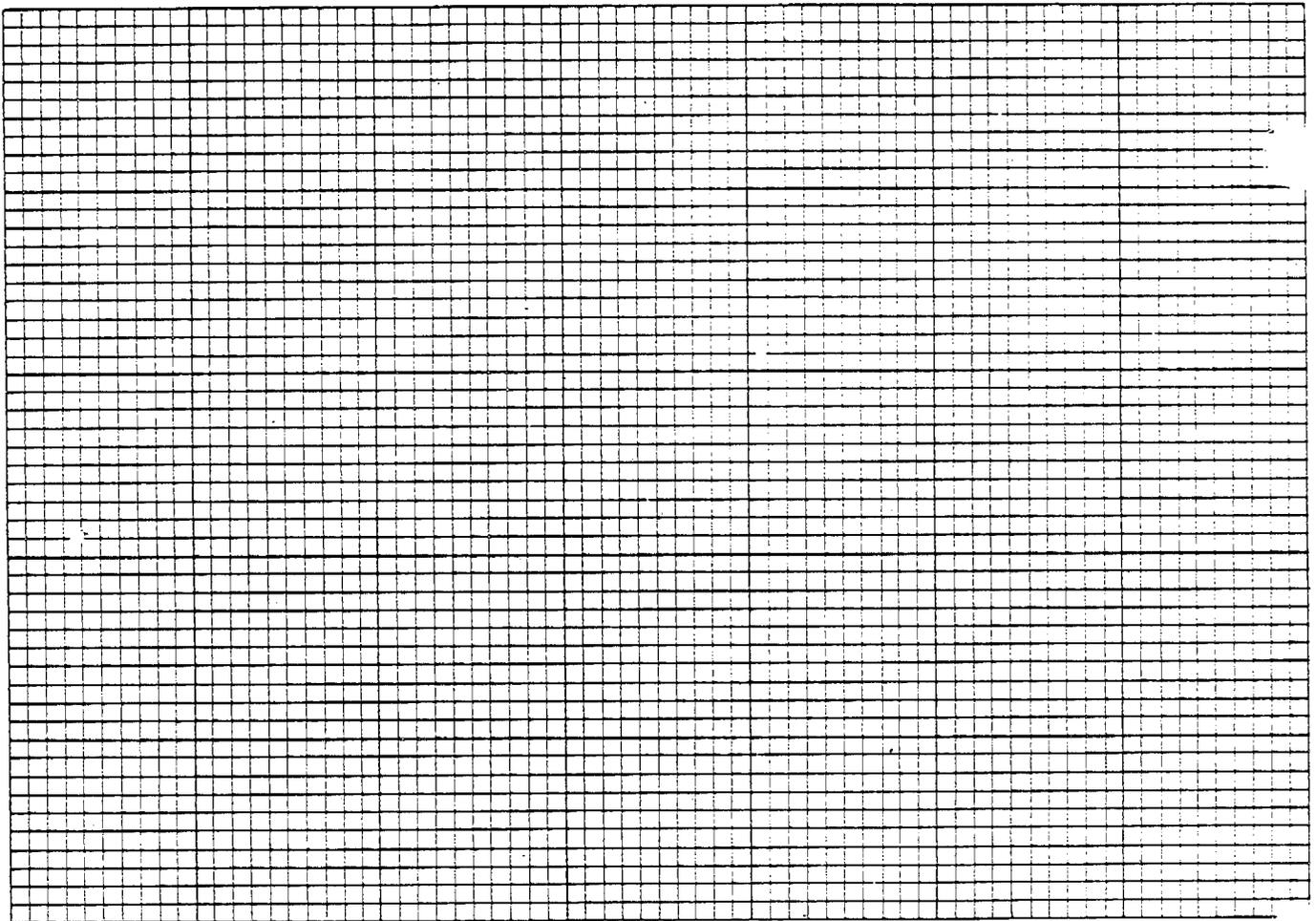
Ambient Temp. (K) _____ (=T₁) Barometric Pressure (mmHg) _____ (=P₁)

Seasonal Avg. Temp. (K) _____ (=T₂) Site Mean Pressure (mmHg) _____ (=P₂)

Reason for Cal. (): Motor/Brush Change: Quarterly Recal New Hi-Vol Other _____

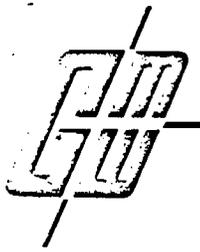
Plate	ORIFICE				LOOK-UP Table	SAMPLER INDICATOR (Logarithmic)			
	ΔH ("H ₂ O)	X 0.392	$\frac{P_1}{T_1} =$	ΔH_c ("H ₂ O)	$\frac{Q_{STD}}{(SLPM)}$	I	\sqrt{I}	X $\sqrt{\frac{P_1}{P_2} \times \frac{T_2}{T_1}}$	= I _c
7									
10									
13									
18									
25									
-									

True Air Flow SLPM (Q_{STD})



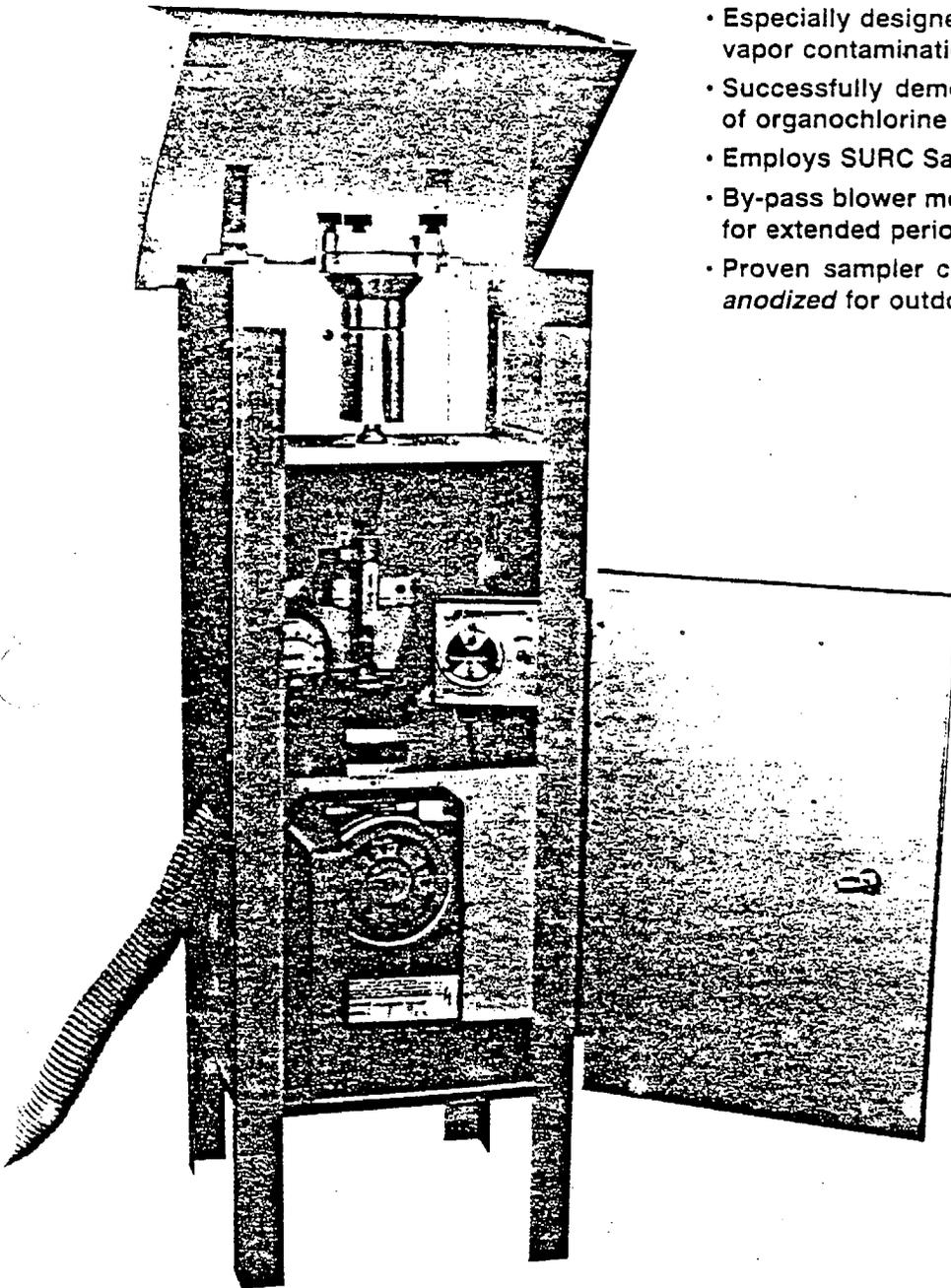
Sampler Indicator Reading (I_c)

QC Review _____ Flow Controller Set Point: _____

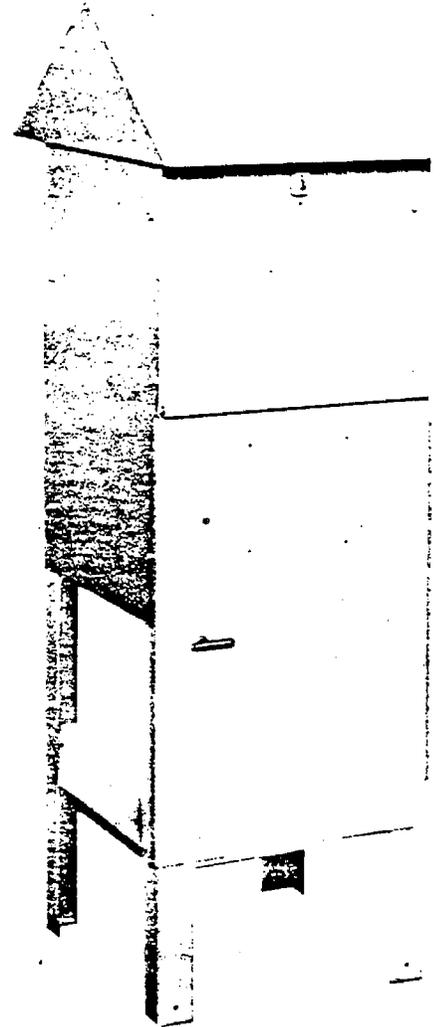


MODEL PS-1 PUF SAMPLER

Pesticide Particulate and Vapor Collection System



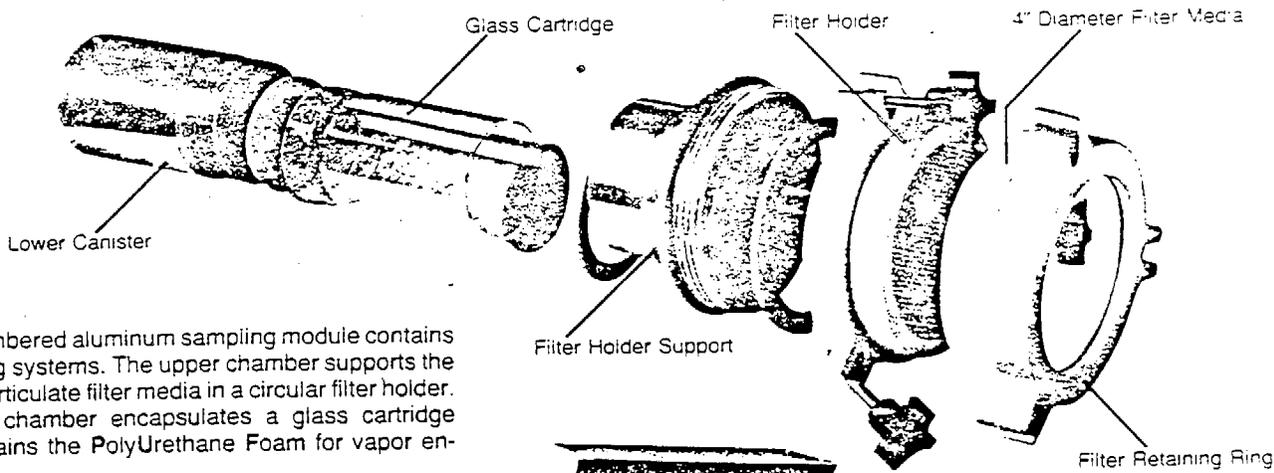
- Especially designed for sampling airborne particulates and vapor contamination from pesticide compounds.
- Successfully demonstrated to efficiently collect a number of organochlorine and organophosphate pesticides.
- Employs SURC Sampler concepts.
- By-pass blower motor design permits continuous sampling for extended periods at rates to 280 liters per minute.
- Proven sampler components housed in aluminum shelter anodized for outdoor service.



General Metal Works' PUF (PolyUrethane Foam) Sampler is a complete air sampling system designed to simultaneously collect suspended airborne particulates as well as trap airborne pesticide vapors at flow rates up to 280 liters per minute. Based on early SURC sampler collection concepts, the Model PS-1 features the latest in technological advances for accurately measur-

ing airborne particulates and vapors.

The GMW PUF Sampler is equipped with a by-pass blower motor arranged with an independent cooling fan. This feature permits the motor to operate at low sampling flow rates for periods of long duration without motor failure from overheating.



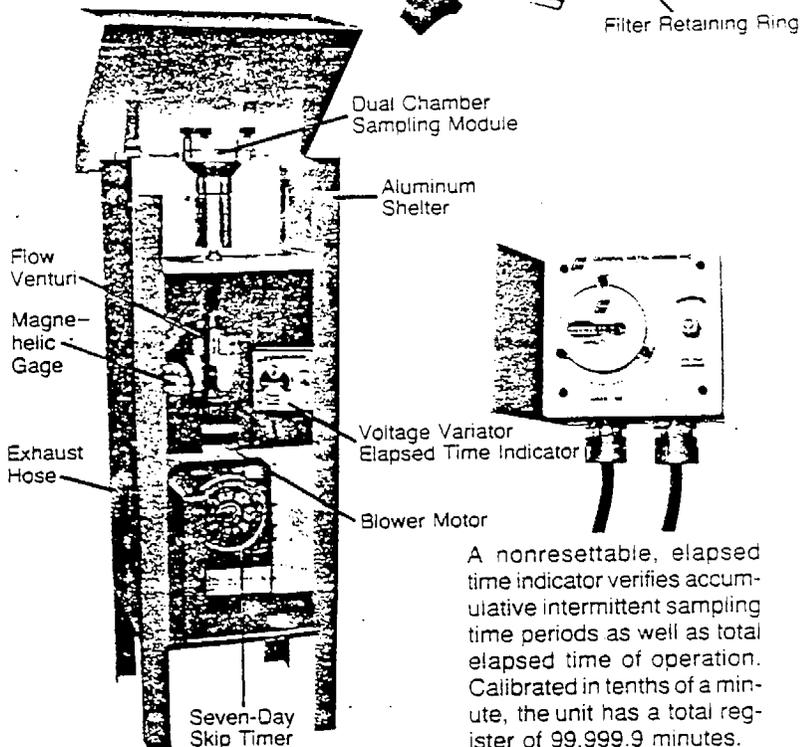
A dual chambered aluminum sampling module contains both filtering systems. The upper chamber supports the airborne particulate filter media in a circular filter holder. The lower chamber encapsulates a glass cartridge which contains the Polyurethane Foam for vapor entrapment.

A wide variety of sorbents can be used in a manner that permits their continual use. Polyurethane foam or wet/dry granular solid media can be used individually or in combination.

The dual chambered sampling module is designed for easy access to both upper and lower media. Swing-away bolts simplify changing the 4" diameter particulate filter media. The threaded lower canister is removed with the cartridge intact for immediate exchange. Filter support screens and module components are equipped with gaskets providing a leak proof seal during the sampling process.

Air flow rates are infinitely variable up to 280 liters per minute. The voltage variator adjusting screw alters the blower motor speed to achieve the flow rate desired. The air flow rate is measured through the flow venturi utilizing a 0-100" Magnehelic Gage. Periodic calibration is necessary to maintain on-site sampling accuracy.

A 7-day skip timer is included as standard and permits weekly scheduling with individual settings for each day and 14 trippers to turn the sampler on and off as desired. Any day or days may be omitted. Day and night periods are distinctly marked. Other timers and timer/programmers are available optionally to suit any sampling requirement.



A nonresettable, elapsed time indicator verifies accumulative intermittent sampling time periods as well as total elapsed time of operation. Calibrated in tenths of a minute, the unit has a total register of 99,999.9 minutes.

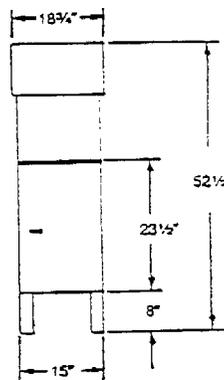


Priced separately, the calibration kit includes a manometer, calibrator and calibration curve nested in a carrying case. The calibrator attaches directly to the top of the filter holder eliminating the need to disassemble the sampling unit. It affords precise calibration of the sampler and is especially recommended for calibrating the Model PS-1 PUF Sampler.

The GMW Model PS-1 PUF Sampler is shipped completely wired and assembled, ready for operation. All components are housed within the anodized aluminum shelter for maximum protection.

SPECIFICATIONS:

- Amperage - 8.0
- Wattage - 960
- Max. Flow Rate - 280 liters per minute
- Power Source - 115V, 1 phase, 60 Hertz (other electrical characteristics available on request)
- Net Weight - 65 lbs.
- Shipping Weight - 75 lbs.



Outside Ohio call toll free 1-800-543-7412



GENERAL METAL WORKS INC.

A Subsidiary of Andersen Samplers, Inc.
145 South Miami Ave. / Village of Cleves, Ohio 45002 / Tel. 513-941-2229

APPENDIX E
SORBENT PRETREATMENT PROCEDURES

PREPARATION OF PUF AIR SAMPLING CARTRIDGES

1.0 SCOPE AND APPLICABILITY

This method describes the preparation of ambient air sampling cartridges for the collection of airborne polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The sorbent cartridge consists of a polyurethane foam (PUF) plug contained in a glass cartridge.

This method is restricted to use by or under the supervision of analysts experienced in the preparation and analysis of sorbent cartridges for semi-volatile organic compounds.

2.0 SUMMARY OF METHOD

PUF is cleaned via soxhlet extraction, dried, and used to prepare sorbent cartridges for use in the collection of airborne PCDDs/PCDFs.

3.0 INTERFERENCES

Method interference may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware which can contribute interfering artifacts precluding proper interpretation of analytical data. Provisions will be made to minimize these interfering substances during the sampling and analysis scheme. All materials that may contact the sorbent media or solvent extracts will be demonstrated to be free of interferences under the actual condition of this analysis by selectively analyzing laboratory method blanks.

4.0 APPARATUS, REAGENTS AND MATERIALS

4.1 Aluminum foil

4.2 Borosilicate glass cartridges, 60 mm I.D. by 120 mm, indented 20 cm from one end with a stainless steel mesh screen.

4.3 Container for PUF cartridges.

4.3.1 Glass jars, tubes or glass bottles with Teflon-lined or aluminum foil-lined screw caps to contain sampling cartridges.

4.3.2 One gallon paint cans with compression lid.

4.4 Die, circular template, 60 mm I.D. -- for cutting PUF plugs

4.5 Disposable gloves - polyester or nylon recommended for handling PUF cartridges and filters.

PREPARATION OF PUF AIR SAMPLING CARTRIDGES

- 4.6 Filters, quartz fiber - Pallflex 2500 QAST, or equivalent.
- 4.7 Forceps - to handle quartz fiber filter samples.
- 4.8 Glass petri dish - for shipment of filters to and from the laboratory.
- 4.9 Polyurethane foam - Porous polyurethane foam, polyether type or equivalent -- 3 inch (7.6 cm) stock material with density of 0.022-0.025 g/cm³ available in 4 ft x4 ft sheets. (Olympic Products, Corp., Greensboro, NC). An alternative source is type 1636 foam available from Flexible Foam Products, Bailey Road, Spencerville, Ohio.
- 4.10 Soxhlet extraction system - including Soxhlet extractors (G size), heating mantels, variable voltage transformers, and cooling water source - for extraction of cartridges before and after sampling. Also for extraction of filter samples.
- 4.11 Vacuum oven connected to water aspirator - for drying extracted PUF cartridges.
- 4.12 Wool felt filter - 4.9 mg/cm² and 0.6 mm thick. To fit sample head for collection efficiency studies. Pre-extracted with 5% diethyl ether in hexane.
- 4.13 Solvents
 - 4.13.1 Acetone - Pesticide or distilled in glass grade.
 - 4.13.2 Dichloromethane - Pesticide or distilled in glass grade.
 - 4.13.3 Toluene - Pesticide or distilled in glass grade.
 - 4.13.4 Benzene - Pesticide or distilled in glass grade.
 - 4.14.5 Methanol - Pesticide or distilled in glass grade.
- 4.14 Nitrogen, UHP grade.

5.0 PREPARATION OF POLYURETHANE FOAM PLUGS

5.1 Cutting:

Polyurethane foam (PUF) plugs are cut from 3-in (7.6 cm) sheet stock of upholstery material (polyether type, density 0.0225 g/cm³) using a 60-mm (id) stainless steel cutting die. This die is turned in a drill-press while a stream of water is directed on

PREPARATION OF PUF AIR SAMPLING CARTRIDGES

it to provide cooling. Each plug is cut with benzene cleaned scissors into 7.6 cm lengths. An alternative approach entails the use of a nichrome wire heated using a variable voltage regulator (variac).

5.2 Cleanup:

PUF plugs are pre-cleaned, if necessary, by Soxhlet extraction:

- a. Soxhlet extract foam plugs for 12-24 hours in benzene or toluene.
- b. Remove excess solvent by pressing the extracted plugs against the inside of the extractor apparatus. Remove the remaining solvent by placing the plugs in a clean vacuum desiccator or oven, heating to 40°C and drawing clean UHP nitrogen or other suitable gas through them.

6.0 PREPARATION OF THE FILTERS

The glass filters will be prepared by baking in a muffle furnace at 245-275°C (500-550°F) for 2-3 hours or rinsing with methylene chloride or air dried in a fume hood. After muffling the filters will be cooled in a drying oven at 103°C (215°F) for half an hour and then desiccated in individual glass petri dishes for 6-8 hours. Three filters will be set aside for the QA/QC check. One filter will also be set aside as a laboratory method blank.

7.0 ASSEMBLY OF THE SAMPLING CARTRIDGES

- 7.1 Carefully place the PUF plug into the benzene rinsed glass sampling cartridge with forceps (see Figure 1). NOTE: It is important not to touch the cleaned PUF with bare hands. Latex gloves should be worn at all times and care should be taken to handle plugs only on benzene cleaned aluminum foil and with benzene cleaned forceps.
- 7.2 Wrap the sampling cartridge in benzene-rinsed aluminum foil and store in benzene-rinsed glass jars until ready for use. The caps of these jars are also lined with benzene-rinsed foil.
- 7.3 The sampling cartridges are now ready for use. It is suggested that each group of cartridges be assigned a lot number. Representative cartridges from each lot should be subjected to a quality control check as described in Section 9.

8.0 QUALITY CONTROL AND ACCEPTANCE TESTING OF PUF CARTRIDGES

Representative cartridges from each assigned lot are submitted for a quality control check, consisting of a sample preparation and analysis scheme identical to that prescribed for actual air samples. Acceptance

PREPARATION OF PUF AIR SAMPLING CARTRIDGES

criteria should be established consistent with the detection limits anticipated for each compound. An upper limit of acceptance criteria of 5 pg per cartridge for each compound has been suggested. It is imperative that all the sampling cartridges from a given lot be recleaned if the quality control sample(s) does not satisfy these established acceptance criteria. In a similar manner, solvents and reagents prescribed in the analytical procedures must also be evaluated using established criteria.

9.0 SAMPLE COLLECTION

Procedures for sample collection shipment and storage are outlined and described in Appendix A of this document.

PREPARATION OF PUF AIR SAMPLING CARTRIDGES

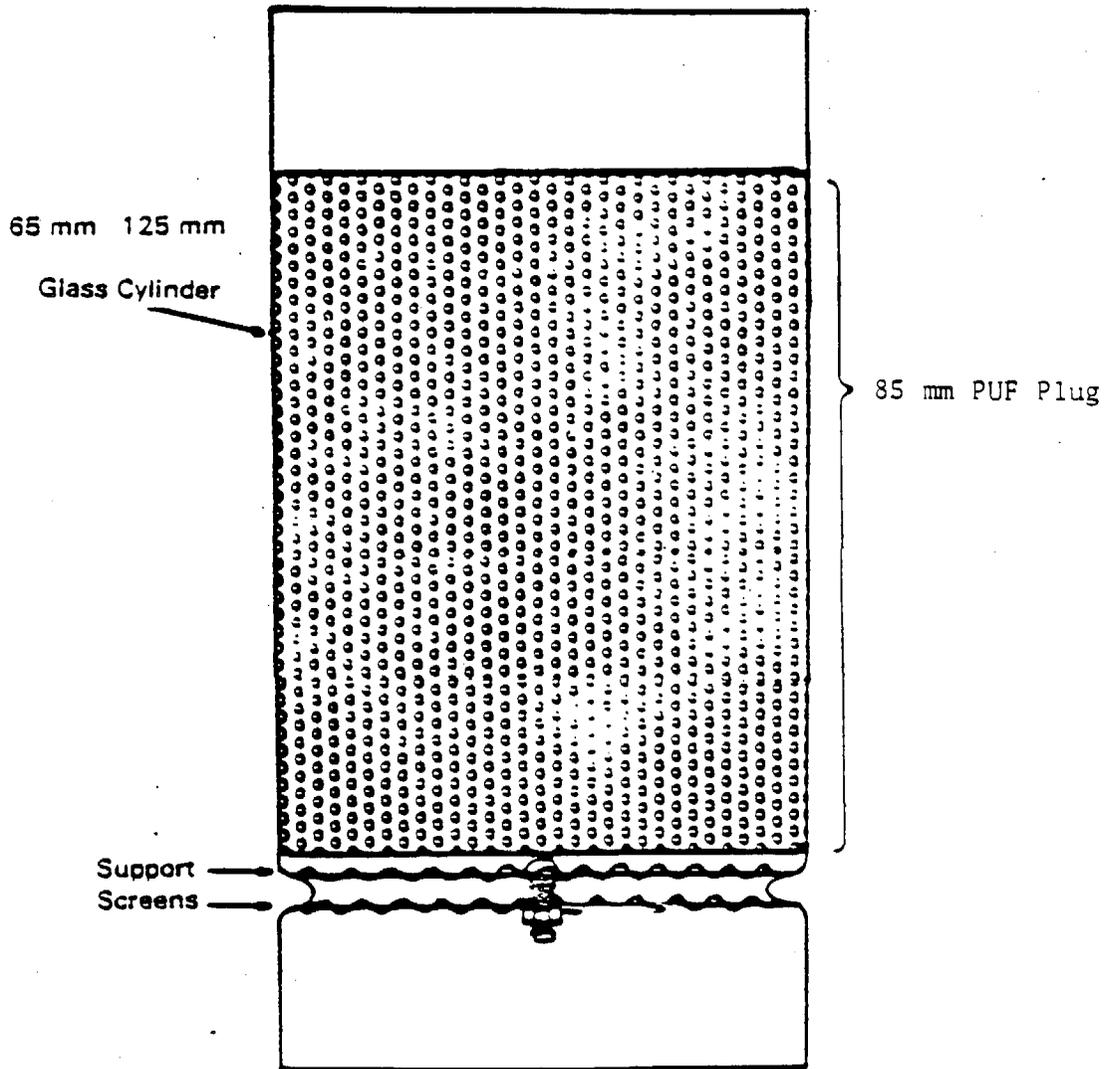


Figure 1 PUF Sampling Cartridge

APPENDIX F
TOTAL AND/OR 2,3,7,8-SUBSTITUTED DIOXIN AND
FURAN ANALYSIS
STATEMENT OF WORK

Total and/or 2,3,7,8-Substituted Dioxin
and Furan Analysis

Statement of Work

6

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1

I. Introduction

The following method is designed for the analysis of chlorinated dioxins, furans, and PCB's in a variety of matrices, including water, sediment, solid wastes, and sampling trains (resins, impingers, etc.), used for stack emissions. The method describes in detail how these analyses are performed at ENSECO-CAL Lab, and include procedures from several different methods, including the Region VII 2,3,7,8-TCDD protocol, Method 8280, and the ASME Analytical Protocol. These methods all depend on the principle of quantitation by isotope dilution for precise and accurate quantitation. An essential part of these analyses is obtaining the necessary $^{13}\text{C}_{12}$ -internal standards, which are currently available through a few select sources.

One key ingredient to this method is the ability to "pick and choose" the appropriate extraction and cleanup options depending on the particular matrix of interest. Any method for dioxins and furans must be designed with the flexibility needed to cope with a variety of extraction and cleanup problems

II. Scope and Applicability of Method

The analytical procedures described here are applicable for the determination of polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF) and polychlorinated biphenyls (PCB's) in stack effluents from combustion processes. These methods are also applicable to residual combustion products such as bottom and precipitator ash, sediments, solid wastes, waters, or rinse/solvent samples. The methods presented entail addition of isotopically-labelled internal standards to all samples in known quantities, extraction of the sample with appropriate organic solvents, preliminary fractionation and cleanup of the extracts using a sequence of liquid chromatography columns, and analysis of the processed extract for PCDD, PCDF and PCB's using coupled gas chromatography/mass spectrometry (GC/MS). Various performance criteria are specified herein which the analytical data must satisfy for quality assurance purposes. These represent minimum criteria which must be incorporated into any program in which PCDD and PCDF are determined in combustion product samples.

The method presented here is designed to indicate the total concentration of the isomers of several chlorinated classes of PCDD and PCDF (that is total C14-C18 dioxins and furans) as well as the total concentration of mono through deca PCB's. It is also designed to yield definitive information on the concentration of individual PCDD and PCDF isomers including isomers with chlorines in the 2,3,7,8-positions. Of the 75 separate PCDD

and 135 PCDF isomers, there are 22 TCDD, 38 TCDF, 14 PeCDD, 28 PeCDF, 16 HxCDF, 2 HpCDD, 4 HpCDF, 4 HxCDF, 1 OCDD and 1 OCDF. Of these isomers the following represents the 2,3,7,8-substituted isomers.

<u>PCDDs</u>	<u>PCDFs</u>
2,3,7,8-TCDD	2,3,7,8-TCDF
1,2,3,7,8-PnCDD	1,2,3,7,8-PnCDF
1,2,3,4,7,8-HxCDD	2,3,4,7,8-PnCDF
1,2,3,6,7,8-HxCDD	1,2,3,4,7,8-HxCDF
1,2,3,7,8,9-HxCDD	1,2,3,6,7,8-HxCDF
1,2,3,4,6,7,8-HpCDD	2,3,4,6,7,8-HxCDF
	1,2,3,7,8,9-HxCDF
	1,2,3,4,6,7,8-HpCDF
	1,2,3,4,7,8,9-HpCDF

The analytical method presented herein is intended to be applicable for determining PCDD/PCDF present in the environmental products at the ppq to ppm level, but the sensitivity which can ultimately be achieved for a given sample will depend upon the types and concentrations of other chemical compounds in the sample, as well as the original sample size and the instrument sensitivity.

This method is restricted to use only by or under the supervision of analysts experienced in the use of gas chromatograph/mass spectrometers and skilled in the interpretation of mass spectra.

Because of the extreme toxicity of these compounds, the analyst must prevent exposure to himself, or to others, by materials known or believed to contain dioxins and furans. Section IV of this method contains guidelines and protocols that serve as minimum safe-handling standard in a limited access laboratory.

a. The abbreviations which are used to designate chlorinated dibenzo-p-dioxins and dibenzofurans throughout this document are as follows:

PCDD-Any or all of the 75 possible chlorinated dibenzo-p-dioxin isomers.

PCDF-Any or all of the 135 possible chlorinated dibenzofuran isomers.

TCDD-Any or all of the 22 possible tetrachlorinated dibenzo-p-dioxin isomers.

TCDF-Any or all of the 38 possible pentachlorinated dibenzofuran isomers.

PeCDD-Any or all of the 14 possible pentachlorinated dibenzo-p-dioxin isomers.

PeCDF-Any or all of the 28 possible pentachlorinated dibenzofuran isomers.

ExCDD-Any or all of the 10 possible hexachlorinated dibenzo-p-dioxin isomers.

ExCDF-Any or all of the 16 possible hexachlorinated dibenzofuran isomers.

HpCDD-Any or all of the 2 possible heptachlorinated dibenzo-p-dioxin isomers.

HpCDF-Any or all of the 4 possible heptachlorinated dibenzofuran isomers.

OCDD-Octachlorodibenzo-p-dioxin.

OCDF-Octachlorodibenzofuran.

Specific Isomers - Any of the abbreviations cited above may be converted to designate a specific isomer by indicating the exact positions (carbon atoms) where chlorines are located within the molecule. For example, 2,3,7,8-TCDD refers to only one of the 22 possible TCDD isomers - that isomer which is chlorinated in the 2,3,7,8-position of the dibenzo-p-dioxin ring structure.

III. Interferences

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated backgrounds at the ions monitored. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running laboratory method blanks as described in Section VIII.

The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

Matrix interference may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerable from source to source, depending upon the nature and diversity of the sample. Dioxins and furans are often associated with other interfering chlorinated compounds which are at concentrations several magnitudes higher than the dioxins or furans of interest. The cleanup procedures in Section X can be used to overcome many of these interferences, but unique samples may require additional cleanup approaches or instrumentation with greater resolving power (HRMS) to eliminate false positives and achieve the required detection limit.

The columns used, DB-5 and/or SP-2331 will resolve 2,3,7,8-substituted dioxins and furans from the other isomers. Positive results obtained using any other GC columns must be shown to be isomer specific.

IV. Safety

ENSECO/CAL Labs follow safety practices as outlined in EPA Method 8280 Section 5 (October 1980 version).

In addition to EPA Method 8280 concerns, the analyst should note that finely divided dry soils or ash contaminated with dioxins or furans are particularly hazardous because of the potential for inhalation and injection. It is recommended that such samples be processed in a confined environment, such as a hood or glove box. Lab personnel handling these types of samples should also wear masks fitted with charcoal absorbent media to prevent inhalation of dust.

V. Apparatus and Materials

All glassware is initially cleaned with aqueous detergent and then rinsed with tap water, deionized water, acetone, toluene, and methylene chloride. Other cleaning procedures may be used as long as acceptable method blanks are obtained.

Grab sample bottle - glass, pint volume, fitted with screw caps lined with Teflon. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed, rinsed with acetone or methylene chloride, and dried before use to minimize contamination.

Clearly label all samples as "FLAMMABLE SOLID" and ship according to DOT requirements. See Appendix B for details.

Concentrator tube, Kuderna-Danish - 10 mL graduated (Kontes-K-570050-1025 or equivalent). Calibration must be checked at the volumes employed in the test. Ground glass stopper is used to prevent evaporation of extracts.

Evaporative flask, Kuderna-Danish - 500 mL (Kontes K-570001-0500 or equivalent). Attach to concentrator tube with springs.

Snyder column, Kuderna-Danish - three-ball macro (Kontes K-503000-0121 or equivalent).

Minivials - 1.0 mL vials; cone shaped inside to enable removing very small samples; heavy wall borosilicate glass; with Teflon faced rubber septa and screw caps.

Soxhlet Apparatus - 1 liter received Kontes #K-601000-0724, 1 liter heating mantle Kontes #K721000-1000, Allihn condenser Kontes #K456000-0022, soxhlet extractor Kontes #K-586100 with modifications.

Gas Chromatograph - An analytical system complete with all required accessories including syringes, analytical columns, and gases. The injection port is designed for capillary columns. Either split, splitless, or on-column injection techniques may be employed.

Rotary Evaporator, Rotovap R (or equivalent), Brinkmann Instruments, Westbury, NY.

Nitrogen blowdown apparatus, N-Evap Analytical Evaporator Model 111 (or equivalent), Organomation Associates Inc., Northborough, MA.

Nitrogen obtained from bleed from liquid nitrogen tank. The appended methods may have additional specialized glassware.

Disposable ipet, 5 3/4 inches x 7.0 mm o.d., Catalog No. 14672-200, VWR Scientific, Inc., Kansas City, MO.

Columns

A. 60 M long x 0.32 mm ID glass, coated with DB-5.

B. 60 M long x 0.32 mm ID fused silica capillary SP-2331 (or SP2330) 0.25 film thickness.

C. Other columns can be used as long as it is demonstrated that 2,3,7,8-TCDD is resolved from the other 21-TCDD isomers.

D. Either a 30 or 60 meter DB-5 fused silica column may be used to analyze tetra through octachlorodibenzodioxins and dibenzofurans. This column is not completely isomer specific but it does allow analysis of hexa, hepta and octachloro compounds with reasonable dispatch.

E. Both a 60 meter DB-5 and a 60 meter SP2330 column are required to do 2,3,7,8-substituted tetra-octa dioxins and furan analysis.

Mass Spectrometer - Either low resolution mass spectrometers (LRMS) or high resolution mass spectrometers (HRMS) may be used. The mass spectrometer must be equipped with a 70 volt (nominal) ion source and be capable of acquiring ion abundance data in real time Selected Ion Monitoring (SIM) for groups of six or more ions. The electron impact ionization mode must be used.

GC/MS interface - Any gas chromatograph to mass spectrometer interface can be used that achieves that the requirements of Section VIII. Glass or glass-lined materials are recommended. Glass surfaces can be deactivated by silanizing with dichlorodimethylsilane. To achieve maximum sensitivity, the exit end of the capillary column should be placed in the ion source. A short piece of fused silica capillary can be used as the interface to overcome problems associated with straightening the exit end of glass capillary columns.

The SIM data acquired during the chromatographic program can be acquired under computer control or as real time analog output. If computer control is used, there must be software available to plot the SIM data and report peak height or area for any ion between specified time or scan number limits.

Balance - Analytical, capable of accurately weighing 0.0001 g.

VI. Reagents

All TCDD standard solutions utilized must be verified by comparison to 2,3,7,8-TCDD check standard solutions available from EPA (Environmental Monitoring Systems Lab - Las Vegas). Surrogate and internal standard solutions of $^{37}\text{Cl}_4$ -2,3,7,8-TCDD (mol wt 328) and $^{13}\text{C}_{12}$ -2,3,7,8-TCDD (mol wt 332), respectively, can be prepared from pure standard materials or purchased as solutions. These standards can be obtained from commercial sources (KOR Isotopes, Fifty-six Rogers Street, Cambridge, MA 02142 and Cambridge Isotope Laboratories, Inc., 141 Magazine Street, Cambridge, MA 02139). The standards should be analyzed to verify the absence of contribution of native 2,3,7,8-TCDD. Prepare a mixed stock solution of $^{13}\text{C}_{14}$ -2,3,7,8-TCDD at 2.5 ng/ μL and $^{13}\text{C}_{12}$ -2,3,7,8-TCDF at 2.5 ng/ μL in isooctane by appropriately diluting the commercial standards. A working solution is then prepared by dilution of the stock solution.

Prepare a mixed solution of $^{13}\text{C}_{12}$ -1,2,3,7,8-PeCDD, $^{13}\text{C}_{12}$ -1,2,3,6,7,8-HxCDD, and ^{13}C -1,2,3,4,6,7,8-HpCDD each at 1.0 ng/ μL in toluene by appropriate dilution of commercial standards.

Prepare separate solutions of $^{13}\text{C}_{12}$ -OCDD and $^{13}\text{C}_{12}$ -OCDF each at 5.0 ng/ μL in toluene by appropriate dilution of commercial standards.

Prepare mixed solutions of 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-ExCDD, and 1,2,3,4,6,7,8-HpCDD at 0.1 ng/ μL and OCDD at 0.5 ng/ μL in toluene by appropriate dilution of commercial standards.

Prepare a mixed solution of 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, and 1,2,3,4,6,7,8-HpCDF at 0.1 ng/uL and OCDF at 0.5 ng/uL in toluene by appropriate dilution of commercial standards.

Calibration Standards

The calibration standard solutions contain amounts of internal standard (2.5 ppb equivalent) and surrogate standard (1.0 ppb equivalent) with variable amounts of native standard. The described solutions are equivalent to native TCDD concentrations of 25, 5 and 1 ppb for 10 gram samples with 50 uL extract volumes. Some samples may require extending the calibration range beyond 25 ppb. This will require the use of commercially supplied native TCDD standards. Additional calibration standards equivalent to 100 ppb (20 ng/uL of native TCDD) and 200 ppb (40 ng/uL) are recommended. Both should contain the internal standard TCDD at 500 pg/uL. It is not necessary to add the surrogate standard to these higher level standards. Some sample sets may require standards which extend to the curve to .1 or .01 ppb.

Standards

The analysis of additional specific chlorodioxin isomers requires the lab have quantitative standards of these isomers. A few isomers are in fact (as opposed to "in catalogue") actually commercially available. We have acquired as many isomers (especially 2,3,7,8-substituted) and other CDE's and CDF's as possible. Most of these come from Chris Rappe of the University of Umea, Sweden. Our collection can be found in Table I and II.

Internal Standards

The analysis of 2,3,7,8-substituted furans at high precision and accuracy is possible only if ^{37}Cl or $^{13}\text{C}_{12}$ -2,3,7,8-substituted internal standards are available. The internal standards are necessary for both precise location (+ 1 scan) on mass chromatograms and correction for losses incurred during extraction and cleanup. CAL Lab has purchased all of the 2,3,7,8-substituted dibenzofurans and dioxins and prepared standards and spiking solutions.

High Level

Combine appropriate volumes of individual and mixed standards solutions with a measured amount of tetradecane to obtain a solution of C_{14} - C_{18} -DD's, C_{14} - C_{18} -DF's, and $^{13}\text{C}_{12}$ -OCDD at 5.0 ng/uL, $^{13}\text{C}_{12}$ - C_{15} - C_{17} -DD's at 1.0 ng/uL, $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and $^{13}\text{C}_{12}$ -2,3,7,8-TCDF at 0.5 ng/uL and ^{37}Cl -2,3,7,8-TCDD at 0.2 ng/uL after excess solvent is removed by nitrogen blowdown.

Medium Level

Combine appropriate volumes of individual and mixed standards solutions with a measured amount of tetradecane to obtain a solution of C_{14} - C_{17} -DD's and C_{14} - C_{17} -DF's at 1.0 ng/uL, OCDD and OCDF both at 2.0 ng/uL, $^{13}\text{C}_{12}$ -OCDD at 5.0 ng/uL, $^{13}\text{C}_{12}$ - C_{15} - C_{17} -DD's at 1.0 ng/uL, $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and $^{13}\text{C}_{12}$ -2,3,7,8-TCDF at 0.5 ng/uL and ^{37}Cl -2,3,7,8-TCDD at 0.2 ng/uL after excess solvent is removed by nitrogen blowdown.

Low Level

Combine appropriate volumes of individual and mixed standards solutions with a measured amount of tetradecane to obtain a solution of C_{14} - C_{17} -DD's and C_{14} - C_{17} -DF's at 0.2 ng/uL, OCDD and OCDF both at 0.5 ng/uL, $^{13}\text{C}_{12}$ -OCDD at 5.0 ng/uL, $^{13}\text{C}_{12}$ - C_{15} - C_{17} -DD's at 1.0 ng/uL, $^{13}\text{C}_{12}$ -2,3,7,8-TCDD and $^{13}\text{C}_{12}$ -2,3,7,8-TCDF at 0.5 ng/uL and ^{37}Cl -2,3,7,8-TCDD at 0.2 ng/uL after excess solvent is removed by nitrogen blowdown.

Spiking Standard Solutions

Internal standard/surrogate solutions are added to all samples prior to extraction.

Those samples designated for native spiking receive aliquots of native isomer solutions (made up of at least one 2,3,7,8-substituted isomer for each congener) in addition to the internal standard/surrogate solutions prior to extraction.

Column Performance Solution

Each vial containing the column performance mixture contains approximately 50 to 100 nanograms each of seven TCDD isomers (2378, 1478, 1234, 1237, 1238, 1278, and 1267). To the solid mixture add 250 microliters of the spiking standard solution containing 250 pg/uL of internal standard and 100 pg/uL of surrogate standard. The approximate concentrations of unlabeled TCDD isomers will thus be in the range of 200 to 400 pg/uL.

All standards must be stored in an isolated refrigerator and protected from light.

Stock standard solutions should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards or spiking solutions from them.

Calibration standard solutions must be replaced after six months.

Sulfuric Acid (Conc.) - (ACS) sp. gr. 1.84.

Methylene chloride, hexane, benzene, methyl alcohol, tetradecane, and other solvents - pesticide quality or equivalent.

Sodium sulfate - (ACS) Granular, anhydrous (purified by heating at 400 C for four hours in a shallow tray or methylene chloride extraction).

Silica gel - for column chromatography, type 60, EM Reagent, 100-200 mesh, or equivalent. Soxhlet extract with methylene chloride, and activate in a foil covered glass container for 24 hours at 130 C.

Alumina - acidic, AG-4, Bio-Rad Laboratories (catalog No. 132-1240 or equivalent), Soxhlet extract with methylene chloride, and activate in a foil covered glass container for 24 hours at 190 C.

Alumina - basic, Woelm activity grade I or equivalent (activate at 600 C for 24 hours), ICN Nutritional Biochemicals, Cleveland, Ohio.

Sulfuric acid - impregnated silica gel (40% w/w) - add two parts concentrated sulfuric acid to three parts silica gel in a screw capped bottle and mix with a glass rod until lump free. Carbowpak C, 80/100 mesh, catalog no. 1-0258, Supelco, Inc. Bellefonte, PA. Celite 545, not acid washed, catalog no. C-212, Fisher Scientific Company, Pittsburgh, PA.

VII. Calibration

Calibration must be done using the internal standard technique. By injecting calibration standards establish ion response factors for Cl₄ - Cl₈ dioxins and furans (D/F) versus the appropriate internal standards.

<u>Native</u>	<u>I.S.</u>
Cl ₄ -Furan	¹³ C-TCDF
Cl ₄ -Dioxin	¹³ C-TCDD
³⁷ Cl ₄ -Dioxin	¹³ C-TCDD
Cl ₅ D/F	¹³ C-PnCDD
Cl ₆ D/F	¹³ C-HxCDD
Cl ₇ D/F	¹³ C-HpCDD
Cl ₈ D/F	¹³ C-OCDD

Using stock standards prepare GC/MS calibration standards equivalent to 1 ppb to 25 ppb (0.2 ng/uL to 5 ng/uL). Use the following three concentrations as the daily working standards.

0.2 ng/uL	Cl ₄ -Cl ₇ D/F
0.5 ng/uL	Cl ₈ D/F
1.0 ng/uL	Cl ₄ D/F
1.0 ng/uL	Cl ₅ -Cl ₇ D/F
2.0 ng/uL	Cl ₈ D/F
5 ng/uL	Cl ₄ -Cl ₇ D/F
5 ng/uL	Cl ₈ D/F

Using injection of 1 to 3 uL (normally 2 uL) tabulate peak area responses against the concentration of the native D/F versus the appropriate internal standard.

Calculate the relative response factor (RRF) for both the native D/F and surrogate using equation 1 and 2.

Equation 1

$$(RRF \text{ for native D/F}) \quad RRF = A_{S}C_{IS}/A_{IS}C_{S}$$

See Table III for appropriate masses to be used in calculation.

Equation 2

$$(\text{RRF for surrogate} - 37\text{Cl}_4\text{-TCDD}) \text{ RRF} = \frac{A_{\text{SSCIS}}}{(A_{\text{ISC}_{\text{SS}}})}$$

The 326 response must be corrected by subtracting 0.009 of the 322 response.

<u>Sample n/e</u>	<u>Internal Standard n/e</u>
Cl4-F 306	318
Cl4--D 322	334
37Cl4-D 328	334
Cl5-F 342	370
Cl5-D 358	370
Cl6-F 376	404
Cl6-D 392	404
Cl7-F 400	438
Cl7-D 426	438
Cl8-F 444	472
Cl8-D 460	472

The RRF Values over the working range for native dioxin/furans must be demonstrated to be constant (<10% RSD). The average RRF must be used for calculations. The RRF must be verified on each work shift of 12 hours or less, by the measurement of one or more calibration standards (one must be the mid-range standard). If the response for D/F varies from the predicted response by more than $\pm 10\%$, then a new calibration must be performed.

The surrogate standard RRF must be determined from the same set of three calibration standards which contain a constant amount (1.0 ppt equivalent) of surrogate standard. The surrogate RRF must also be verified on each work shift of eight (8) hours or less. If the response varies by more than $\pm 10\%$ from the predicted response, the test must be repeated or a new calibration must be performed for the surrogate compound.

VIII. Quality Control Requirements

1. Each sample (10 gm nominal) must be dosed with known quantities of internal standards (Cl₄ [2.5 ppb], Cl₅-Cl₇ [5.0 ppb], Cl₈ [12.5 ppb]) and surrogate standard (equivalent to 1.0 ppt). These values inevitably change depending on sample size and matrix. "Surrogate" spikes vary between 1 ng and 10 ng per sample. Internal standards similarly vary.

The action limits for surrogate standard results will be $\pm 40\%$ of the true value. Samples showing surrogate standard results outside of these limits must be reextracted and reanalyzed, and valid explanations given.

2. A laboratory "method blank" must be run along with each set of samples or lab tickets with similar matrices. A method blank is performed by executing all of the specified extraction and cleanup steps, except for the introduction of the sample. The method blank is also dosed with the internal standard and surrogate standard.

3. The laboratory will perform evaluation samples (i.e., blind field spikes) on a periodic basis throughout the course of a given project. Further sample analyses will not be permitted if the performance criteria are not achieved. Corrective action must be taken and demonstrated before sample analyses can resume.

A method blank native spike can be run in cases where a native spike is not possible, such as segments of the modified method 5 sample train.

4. Qualitative Requirements. The following requirements must be met in order to confirm the presence of native Cl₄ to Cl₉ dioxins and furans (D/F).

a. The monitored mass ratio must be within $\pm 15\%$ of the standard ratio for each mass pair.

b. Ions must all be present and maximize together. The signal to mean noise ratio must be 2.5 to 1 or better for all ions. The level can be pre-determined by the instrument software.

c. The retention time of the native congener must be within ± 0.005 RRT units of the standard RRT. This relationship of native substituted CDD's and CDF's and their isotopically labelled I.S. must be maintained.

d. Isomer specificity must be demonstrated initially and verified once per 12-hour work shift. The verification consists of injecting a mixture containing TCDD isomers which elute close to 2,3,7,8-TCDD. This mixture will be provided by EPA. It contains seven TCDD isomers (2378, 1478, 1234, 1237, 1238, 1278, 1267) including those isomers which are known to be the most difficult to separate on SP2330/SP2331 columns and similar columns containing cyanoalkyl type liquid phases. The column performance solution (Section VI) must also contain both isotopically labeled 2,3,7,8-TCDD standards. The solution must be analyzed using the same chromatographic conditions and mass spectrometric conditions as is used for other samples and standards. The 2,3,7,8-TCDD must be separated from interfering isomers, with no more than a 25% valley relative to the 2,3,7,8-TCDD peak.

Draw a baseline for the isomer cluster representing 1478, 2378, 1237, 1238, and 1234-TCDD. Measure the distance x from the baseline to the valley following the 2,3,7,8-TCDD peak. The distance x over distance y times 100 is the percent valley. This must not exceed 25. An example is given in Figure 1. The criteria: 12348 and 12378 PnCDF; 123478 and 123468 HxCDD must be resolved on a 60 meter column. A 60% valley is attainable.

5. In cases where no native 2,3,7,8-TCDD is detected, the actual detection limit must be estimated and reported based on a signal to noise ratio of 2.5 to 1 at the appropriate mass range. Measure the mean noise for the retention window of each congener mass chromatogram. Multiply the noise by 2.5 and calculate the detection limit according to Equation 3. If an interfering signal is present in the mass window choose the ion not interfered with to calculate a detection limit using equation 3. If both ions have interferences which are more than 2.5 times the noise, compute the detection limit using the mass which will give the most conservative result. (The 2.5 x noise level is indicated by a line on the mass chromatograms, and is controlled by the N command in chro).

The retention window is defined as the period of elution for each of the congener groups starting at the point where the first isomer elutes and ending at the point where the last isomer elutes. Retention time windows for each isomer group can be predetermined by shooting the complete Cl₄-Cl₈ dioxin and furan retention time window. Mix standard prior to sample analysis and whenever the retention times shift significantly.

6. For each sample, the internal standard must be present with at least a 10 to 1 signal to noise ratio for both mass 332 and mass 334. Also, the internal standard 332/334 ratio must be within the range of 0.67 to 0.87.

7. Where appropriate, "field blanks" will be provided to monitor for possible cross contamination of samples in the field. The "field blank" will consist of uncontaminated sample (i.e., background soil taken off-site) and/or equipment rinsate.

IX. Sample Extraction

Caution: When using this method to analyze for dioxins and furans, all of the following operations should be performed in a limited access laboratory with the analyst wearing full protective covering for all exposed skin surfaces.

1. Resin, sediment samples, or highly organic solids (ashes, oily filters) - Soxhlet Method

The soxhlet apparatus should be pre-cleaned by an 8 hr. soxhlet, discard this solvent.

Add 20 g Na₂SO₄ to the thimble.

Weight 10 g of sample on top of the Na₂SO₄.

Mix immediately and add I.S., see flow chart.

Add spike solution if appropriate.

Place thimble in soxhlet apparatus, add 250 mL of extracting solvent (see flow chart) to receiver.

Assemble soxhlet, turn on heating controls and cooling water, allow to extract for 16 hours.

Transfer to a 500 mL round bottom, add ca. 500 uL C14.

Roto-evap to C14, if benzene or toluene was used as the extracting solvent, add 50 mL hexane to the R.B. and roto-evap to C14.

Transfer the extract to an 8 mL test tube with hexane.
Set aside for column cleanups.

2. Water Samples - EPA Method 613 extraction, EPA Method 8280 clean-up.

Place aliquot of sample into appropriate size separatory funnel.

Add I.S., use amount specified by flow chart.

Add spike solution if appropriate.

Extract the sample 3 times with 50 mL portions of MeCl₂.

Combine the extracts and pour through Na₂SO₄ into a round bottom flask, add ca. 500 uL tetradecane.

Roto-evap to the tetradecane.

Transfer the extract to an 8 mL test tube with hexane.

Set aside for column cleanups.

3. Wipes

Transfer wipe to a flask, add I.D.

Add 50 mL benzene and 100 mL hexane.

Shake 1 hour, filter into R.B. add ca. 500 uL C14.

Roto-evap to C14, add 50 mL hexane, roto-evap to C14.

Transfer the extract to an 8 mL test tube with hexane.

Set aside for column cleanups.

4. Solvent or Rinse Samples

Measure 100 μ L of an appropriate volume sample into a 250 mL R.E. flask.

Add internal standard and roto-evap to ca. 5 mL.

(if the aliquot does not concentrate, pass through Na₂SO₄ with excess hexane, add ca. 0.5 mLs C14, roto-evap to C14)

Transfer to an 8 mL test tube, add 50 μ L C14. N₂ to C14 and submit for GC/MS analysis.

5. Sediment or Soil Samples - Region VII EPA Protocol or EPA/CAL 8280

Weigh 10 gm sample into a 250 mL flask.

Add I.S., use amount specified by flow chart.

Add spike solution if appropriate.

Add 20 gm Na₂SO₄.

Add 20 mL MeOH and 150 mL hexane.

Place on shaker for 3 hours.

Filter extract into a round bottom flask.

Add ca. 500 μ L tetradecane.

Roto-evap to the tetradecane.

Set aside for column cleanup.

X. Cleanup Options (see following pages for details)

1. IFE
2. Basic Alumina
3. Option D
4. Option D2
5. "Stallings Method"
6. Option C
7. Florisil

XI. GC/MS Analysis

1. Immediately before analysis by GC/MS, adjust the sample extract volume to approximately 50 μ L or 10 μ L as dictated by desired detection limits. This adjustment may include the addition of ¹³C₁₂-1,2,3,4-TCDD which is used to monitor absolute recovery of the ¹³C₁₂-2,3,7,8-TCDD and/or ¹³C₁₂-2,3,7,8-TCDF.

2. Table I summarizes typical gas chromatographic capillary columns and operating conditions. Other columns and/or conditions may be used as long as isomer specificity is demonstrated. Thereafter a calibration mixture of isomers should be analyzed on a daily basis in order to verify the performance of the system.

3. Analyze standards and samples with the mass spectrometer operating in the selected ion monitoring (SIM) mode using a scan time to give at least five points per peak. For LRMS, use accurate masses to one decimal place from Table IV for the C14 to C18 congeners, and their appropriate internal standards. If HRMS is desired than accurate masses to four decimal places should be used.
4. Calibrate the system daily as described in Section VII. The volume of calibration standard injected should be approximately the same as all sample injection volumes.
5. Inject a 1 to 3 uL (normally 2 uL) aliquot of the sample extract.
6. The presence of C14-C18 congeners is qualitatively confirmed if the criteria of Section VIII, Part 7, are achieved.
7. For quantitation, measure the response of the native congener and the internal standard mass (see Table III). A correction must be made for contribution to m/e 328 by any native TCDD which may be present. To do this, subtract 0.009 of the 332 response from the 328 response. Calculate the concentration of native congener using the relative response factor (RRF) and Equation 3. If the calculated concentration is above the upper calibration range, a smaller sample aliquot must be extracted and analyzed or the sample extract could be diluted if the internal standard signal to noise ratio is satisfied. If the native congener is not present, calculate the detection limit as described in previous sections.

Equation 3 (Calculation of concentration of native 2,3,7,8-TCDD)

$$\text{Concentration, ng/g} = (A_s)(I_s) / (A_{is})(RRF)(W)$$

where: A_s = SIM response for native ion at m/e (see Table III)
 A_{is} = SIM response for the internal standard ion (See Table III)
 I_s = Amount of internal standard added to each sample (ng)
 W = Weight of sample in grams, or liters if appropriate

Equation 4 (Calculation of amount of surrogate standard $^{37}\text{Cl}_{14}$ 2,3,7,8-TCDD)

$$\text{Amount in ng} = (\text{Ass})(\text{Is})/(\text{Ais})(\text{RRF})$$

where: Ass = SIM response for surrogate $^{37}\text{Cl}_{14}$ 2,3,7,8-TCDD ion at m/e 328*

Ais = SIM response for the internal standard ion at m/e 322 + 334

Is = Amount of internal standard added to each sample (ng)

*When using $^{37}\text{Cl}_{14}$ -TCDD, subtract 0.009 of any 322 response.

8. Co-eluting impurities are suspected if all criteria except the isotope ratio criteria are achieved. If broad background interference restricts the sensitivity of the GC/MS analysis, the analyst must employ additional cleanup procedures and reanalyze by GC/MS.

9. Calculation of Percent Accuracy of surrogate standard.

$$\% \text{Accuracy} = (\text{amount measured in ng}/10 \text{ ng}) (100).$$

10. Calculation of Absolute Recovery is the same as Equation 3 but substitute $^{13}\text{C}_{12}$ -1,2,3,4-TCDD for AIS. Is and W are not applicable.

An RRF must be generated in a similar fashion.

CLEAN UP OPTIONS

IFB COLUMN CLEAN UP

Use 15mm column for top column.
Use 11mm column for bottom column.



- | | | |
|---|--|--------------------|
| | | # of 15ml capsfull |
| 1 cm Na ₂ SO ₄ | | 1 |
| 2g Silica gel | | 2 |
| 4g 44% H ₂ SO ₄ /Silica gel | | 2 |
| 1g Silica gel | | 1 |
| 2g 33% 1M NaOH/silica gel | | 1 |
| 1g Silica gel | | 1 |
| glasswool | | |

- 1 cm Na₂SO₄
- 6g Acid alumina
- glasswool

- Pre-rinse both columns with hexane
- Put one column above the other
- Add extract to the top column
- Elute the top column directly onto the bottom column with 90ml hexane
- Elute the bottom column with 20 mls of hexane -- discard in dioxin waste
- Elute with 20ml of 20% MeCl₂/hexane
- Use tetradecane and N₂ as appropriate per flow chart

BASIC ALUMINA CLEANUP (9/20, Rp)



Use 11mm id short column

1cm Na₂SO₄

5g basic alumina
(>12 hour at 600 C, fresh, < 5 days old)

glasswool

- Add sample with hexane
- Elute with 20ml hexane (discard)
- Elute with 20ml 3:1 MeCl₂/hexane (save)
- Elute with 35ml 50% MeCl₂/hexane.
Use tetradecane and N₂ as appropriate
per flow chart.

OPTION D

SEPT 1983

dispo-pipet
2cm charcoal/silica gel
glasswool

Pre-elute:

2ml Toluene
1ml 75:25 MeCl₂:MeOH
1ml 1:1 Cyclohexane:MeCl₂
2ml hexane

Discard these column rinses.

TRANSFER SAMPLE CONCENTRATE WITH HEXANE

Elute:

1ml hexane
1ml hexane
1ml 1:1 Cyclohexane:MeCl₂
1ml 75:25 MeCl₂:MeOH

SAVE ALL ABOVE ELUATES COMBINED

SAVE NEXT ELUATE ALONE

2ml Toluene

Use tetradecane and N₂ with the toluene eluate as appropriate per flow chart.

PACKING:

3.6g carbopak
16.4g silica gel



OPTION D2

DEC 1984

5ml dispo pipet
(cut off 1cm of tip)
glasswool
0.3g charcoal/silica gel
glasswool (at the 2.5ml mark)

Pre-rinse:
5ml hexane in direction A
Turn column over
5ml hexane in direction B

Pre-elute: in direction B
2ml Toluene
1ml 75:20 MeCl₂:MeOH
1ml 1:1 Cyclohexane:MeCl₂
2ml hexane
Discard these column rinses.

TRANSFER SAMPLE CONCENTRATE WITH HEXANE

Elute:
1ml hexane
1ml hexane
1ml 1:1 Cyclohexane:MeCl₂
1ml 75:20 MeCl₂:MeOH

Discard above eluates into dioxin waste solvent container.

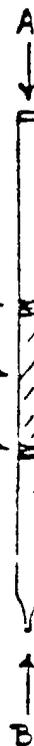
Turn column over; eluate in direction A

SAVE NEXT ELUATE ALONE

4ml Toluene
(gentle blow out)

Use tetradecane and N₂ with the toluene
eluate as appropriate per flow chart.

PACKING:
3.6g carbopak
16.4g silica gel



STALLING'S METHOD (COLUMBIA FISHERIES)

Crab, shrimp, crayfish, snail, etc., commercial molluscs, etc.

From: Determination of Polychlorinated Biphenyl Levels of Environmental Contaminants and Bioaccumulation in Aquatic Organisms of the Columbia River, Oregon, Columbia River Fishery Research Laboratory, U.S. Fish and Wildlife Service, 6001 East 10th St., Astoria, OR 97103.

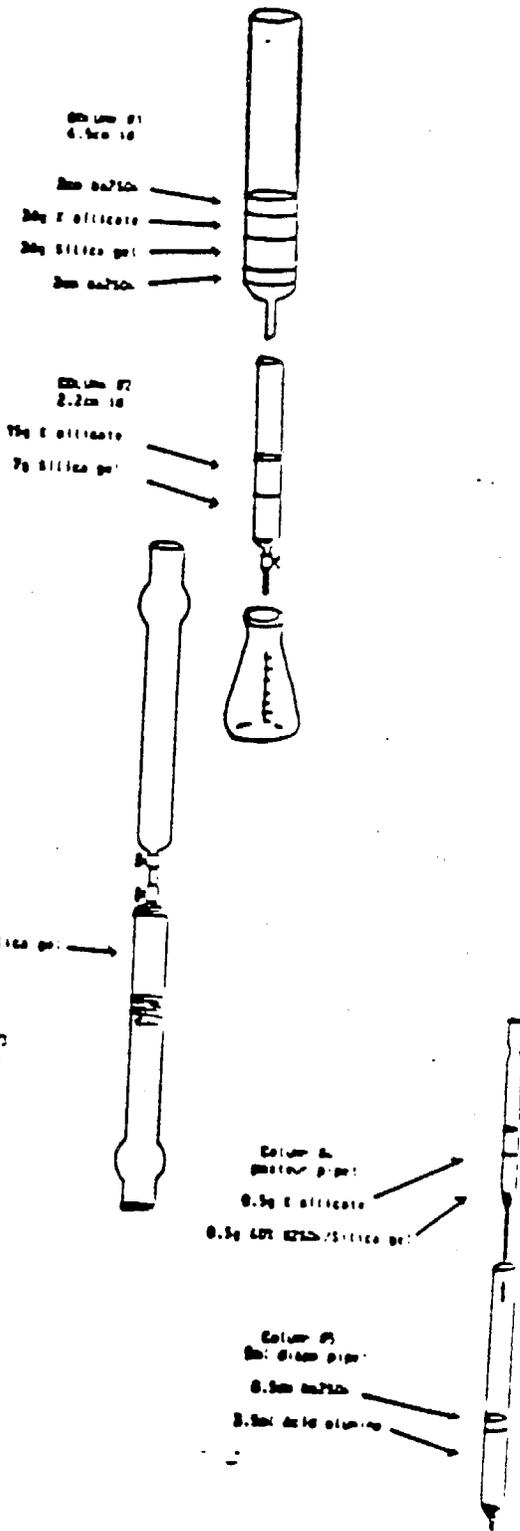
Use of 50% of each of, bring into a waste, bring into a new 1000g plastic bottle.
 - 100g ca. 25g NaOH to be a transfer sample into the beaker.
 - Break with spatula 25g portion of NaOH.
 - Add ca. 150g NaOH to the beaker and stir like crazy, cover with aluminum foil and allow to bring overnight.
 - Break up clumps and bring until free, transfer to a bottle until ready to use.

- Fill each column with packing, discard sample.
 - For each column #2 with 20g of solvent A (10% cyclohexane + 90% DCM) discard waste.
 - Add 100g solvent A to the beaker, and 1.5L, stir to break up clumps.
 - Transfer sample to the top of column #1, seal with NaOH.
 - Stack columns as pictured, pinch sides of column #1 with fingers & solvent A.
 - Add 50g of solvent A and adjust the film of column #1 such that the top of column #2 is always wet with column #1 eluate.

- Put 10g of P2 21/100g gel in a 150ml beaker with 75ml solvent A and pour into column #1.
 - After the packing has settled, start draining solvent, when when it reaches within 2cm of the bottom, pinch the side with each hand, pour a large amount of solvent into column #2 onto the gel top, drain solvent down to the packing.
 - Repeat the column with a thin portion of each followed by a 20g portions of solvent A.
 - Pour the eluate from column #1 into column #2, discard eluate.
 - Elute the column with the solvent A then 50g 75/25 hex/2/mch. Save these for eluate collection in an Erlenmeyer.
 - Insert column #2 and connect the reservoir as pictured.
 - Elute the gel in column #2 with 40g solvent into a round bottom flask, and ca. 170g solvent and run down to D1.

- Pack column #1 and #2, transfer each with beakers, discard eluate, then stack columns as pictured.
 - Transfer concentrate in 20 portions of beaker that totals 5.0g.
 - Eluate column #1
 - Eluate column #2 with
 - 5.0g hexane
 - 15.0g 75 hex/2/mch
 - 15.0g 50 hex/2/mch
 - 20.0g 25 hex/2/mch
 - Save the first 25ml "oil"
 - Collect the rest using 170g and concentrate to final volume in D1 on top the film sheet.

PACKAGING: Once prepared, they are kept at 130 C.
 - 100g of
 - 50g hexane
 - 50g 75/25 hex/2/mch
 - 50g 50/50 hex/2/mch
 - 50g 25/75 hex/2/mch



OPTION C

- Pour the un-concentrated extract into a separatory funnel (filter thru a large glasswool plug if there are particulates).
- Wash the organic extract two times with 50ml portions of 10N NaOH, discard the washes.
- Wash the organic layer once with 50ml blank water, discard the wash.

—CAUTIOUSLY—

- Wash the organic extract two times with 25ml portions of con. H₂SO₄, discard the wash.
- Wash the organic layer once with 50ml blank water, discard the wash.
- Pass the organic extract thru Na₂SO₄ into a round bottom flask and add ca. 500ml tetradecane.
- Rotary evaporate as necessary to remove excess solvent down to the tetradecane.
- Clean up as per flow chart.

FLORISIL (OPTION-F)

APPLICATION: Separation of PCB's and TCDD/TCDF.

Place 20g of florisil (activated overnight at 130 C-190 C) in a glasswool plugged 15mm x 300mm column fitted with a teflon stopcock, add 2cm of Na₂SO₄ to the top of the column. Rinse the packed column with 60ml hexane (discard). Place up to 10ml of sample extract (in hexane or isooctane) on the column with ca. 2ml hexane (discard). Elute with the following: 200ml of hexane, 200ml 6% diethyl ether/hexane, 200ml 15% diethyl ether/hexane. Collect the hexane and the 6% fractions together. Collect the 15% fraction separate.

Add the sample and elution volumes just as the previous volume has reached the Na₂SO₄.

The hexane/6% fraction is to be exchanged into isooctane and concentrated to an appropriate final volume for PCB analysis.

The 15% fraction is to be concentrated to an appropriate final volume for TCDD/TCDF analysis.

3/20/86

Table I

TRICHLORODIBENZO-P-DIOXIN

UNLABELED

12-TricDD

TETRACHLORODIBENZO-P-DIOXINS

LABELED

13C-2376-TCDD

37CL-2376-TCDD

13C-1234-TCDD

UNLABELED

2376-TCDD

1234-TCDD

1366-TCDD

1476-TCDD

1276-TCDD

1267-TCDD

1237/1236-TCDD

PENTACHLORODIBENZO-P-DIOXINS

LABELED

13C-12376-PeCDD

UNLABELED

12376-PeCDD

HEXACHLORODIBENZO-P-DIOXINS

LABELED

13C-123476-HxCDD

13C-123676-HxCDD

UNLABELED

123476-HxCDD

123676-HxCDD

HEPTACHLORODIBENZO-P-DIOXINS

LABELED

13C-1234676-HpCDD

UNLABELED

1234676-HpCDD

OCTACHLORODIBENZO-P-DIOXINS

LABELED

13C-OCDD

UNLABELED

OCDD

DICHLORODIBENZOFURANS

27-DCDF

28-DCDF

TETRACHLORODIBENZOFURANS

LABELED

13C-2376-TCDF

UNLABELED

1246-TCDF

1279-TCDF

1267-TCDF

1367-TCDF

1368-TCDF

2367-TCDF

1379-TCDF

2376-TCDF

2368-TCDF

1467-TCDF

1469-TCDF

2468-TCDF

2467-TCDF

1278-TCDF

1239-TCDF

1247-TCDF

1346-TCDF

2347-TCDF

2348-TCDF

1236-TCDF

1269-TCDF

PENTACHLORODIBENZOFURANS

LABELED

13C-12376-PeCDF
13C-23476-PeCDF

UNLABELED

12346-PeCDF
12466-PeCDF
23466-PeCDF
23476-PeCDF
12476-PeCDF
12376-PeCDF
12376-PeCDF
12479-PeCDF
12369-PeCDF

HEXACHLORODIBENZOFURANS

LABELED

13C-123476-HxCDF

UNLABELED

124669-HxCDF
124676-HxCDF
123466-HxCDF
234676-HxCDF
123476-HxCDF
123479-HxCDF
123676-HxCDF
123769-HxCDF
123669-HxCDF

HEPTACHLORODIBENZOFURANS

LABELED

13C-1234576-HpCDF

13C-1234789-HpCDF

UNLABELED

1234689-HpCDF

1234576-HpCDF

1234789-HpCDF

1234579-HpCDF

OCTACHLORODIBENZOFURANS

LABELED

13C-OCDF

UNLABELED

OCDF

TABLE II

2,3,7,8-Substituted Furans and Dioxins

In-House (3-15-86)	Reference
<u>Furans:</u>	
2,3,7,8-TCDF	2,3,7,8-TCDF
1,2,3,7,8-PnCDF	1,2,3,7,8-PnCDF
2,3,4,7,8-PnCDF	2,3,4,7,8-PnCDF
1,2,3,4,7,8-HxCDF	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	2,3,4,6,7,8-HxCDF
1,2,3,7,8,9-HxCDF	1,2,3,6,7,8-HxCDF
*1,2,3,4,6,7,8-HpCDSF	1,2,3,4,6,7,8-HpCDF
1,2,3,4,6,7,8-HpCDF	1,2,3,4,7,8,9-HpCDF
OCDF	OCDF
<u>Dioxins:</u>	
2,3,7,8-TCDD	2,3,7,8-TCDD
1,2,3,7,8-PnCDD	1,2,3,7,8-PnCDD
1,2,3,4,7,8-HxCDD	1,2,3,4,7,8-HxCDD
1,2,3,6,7,8-HxCDD	1,2,3,6,7,8-HxCDD
1,2,3,7,8,9-HxCDD	1,2,3,7,8,9-HxCDD
1,2,3,4,6,7,8-HpCDD	1,2,3,4,6,7,8-HpCDD
OCDD	OCDD

TABLE III
Ion Masses used in Calculations

304/306 = TCDF
316/318 = Labeled TCDF (Internal Standard)
320/322 = TCDD
332/334 = Labeled TCDD (Internal Standard)
340/342 = PCDF
356/358 = PCDD
368/370 = ¹³C-PCDD (Internal Standard)
374/376 = HxCDF
390/392 = HxCDD
402/404 = ¹³C-HxCDD (Internal Standard)
408/410 = HpCDF
424/426 = HpCDD
434/436 = ¹³C-HpCDD (Internal Standard)
442/444 = OCDF
458/460 = OCDD
470/472 = Labeled OCDD (Internal Standard)

TABLE IV

Recommended GC Capillary Conditions

Column	60 meter (SP 2331)	60 meter DE-5	30M DE-225
2,3,7,8-TCDD R.T.	12 min	10.0 min	11.0 min
Helium Linear Velocity		30 cm/sec	
Initial Temperature	190 C	190 C	190 C
Initial Time	1 min	1 min	1 min
Splitless Time	0.6 min	0.5 min	1.0 min
Program Rate	10 C/min	8 C/min	8 C/min
Final Temperature	250 C	300 C	240 C
Final Hold Time	15 min	7 min	7 min
Split Flow	30 ml/min	30 ml/min	30 ml/min
Septum Purge Flow	5 ml/min	5 ml/min	5 ml/min
Capillary Head Pressure	28 psi	15 psi	15 psi

The above GLC conditions are employed for both classification and the isomer specific analysis of tetra through octa chlorodioxins and dibenzofurans.

The 60 meter DE5 is appropriate for total C14-C18 D/F classification. Isomer specific analysis of all 2,3,7,8-substituted chlorinated dibenzodioxins and dibenzofurans required a 60 meter DE-5 and a 60 meter SP 2331. If 2,3,7,8-TCDF is suspected it must be analyzed as well on DE-225.

TABLE V
 Selected Data for the Polychlorinated Dibenzofurans
 and
 Polychlorinated Dibenzo-P-Dioxins of Interest

Compound	Accurate Mass		Theoretical Isotope Ratio	Limit of Detection	
	Low Mass	High Mass		Water	Total Nanograms
Di-CDF	235.980	237.977	1.5		
Di-CDD	235.974	251.974	1.5		
Tri-CDF	269.941	271.938	1.01		
Tri-CDD	319.897	321.894	1.01		
Tetrachlorodibenzofuran	303.9016	305.8987	0.77	100 ppq	0.1
Tetrachlorodibenzo-p-dioxin	319.8965	321.8936	0.77	100 ppq	0.1
¹³ C ₁₂ -2,3,7,8-TCDD	331.9368	333.9339	0.77		
¹³ C ₁₂ -2,3,7,8-TCDF	317.9390	319.937	0.77		
Pentachlorodibenzofuran	339.8597	341.8567	1.54	400 ppq	0.4
Pentachlorodibenzo-p-dioxin	355.8546	357.8517	1.54	400 ppq	0.4
[¹³ C ₁₂ -12378-PnCDD ¹³ C ₁₂ -12378 or 23478-PnCDF	367.8947 351.9000	369.8918 353.8970	1.54 1.54		
Hexachlorodibenzofuran	371.8237	373.8207	1.23	500 ppq	0.5
	373.8207	375.8178			
	387.8185	389.8156			
Hexachlorodibenzo-p-dioxin	389.8156	391.8127	1.23	500 ppq	0.5
	383.8640	375.8610			
[¹³ C ₁₂ -HCDF] ¹³ C ₁₂ -HCDD	(385.8610 391.8559	(376.8581] 393.8530	1.23 1.23		
Heptachlorodibenzofuran	407.7817	409.7788	1.03	1500 ppq	1.5
Heptachlorodibenzo-p-dioxin	423.7766	425.7737	1.03	1500 ppq	1.5
¹³ C ₁₂ -Hepta-CDD	435.8169	437.8140	1.03		
[¹³ C ₁₂ -Heptachlorodibenzofurans 419.8220 421.8191]			1.03		
Octachlorodibenzofuran	441.7428	443.7398	0.88	5000 ppq	5
Octachlorodibenzo-p-dioxin	457.7377	459.7347	0.88	5000 ppq	5
¹³ C ₁₂ -Octa-CDD	469.7780	471.7750	0.88		
¹³ C ₁₂ -Octachlorodibenzofuran	443.7831	457.7801	0.88		

[] Not Monitored

05-55 CROSS SCAN REPORT, RUN: GENIKC0801

FIGURE 1

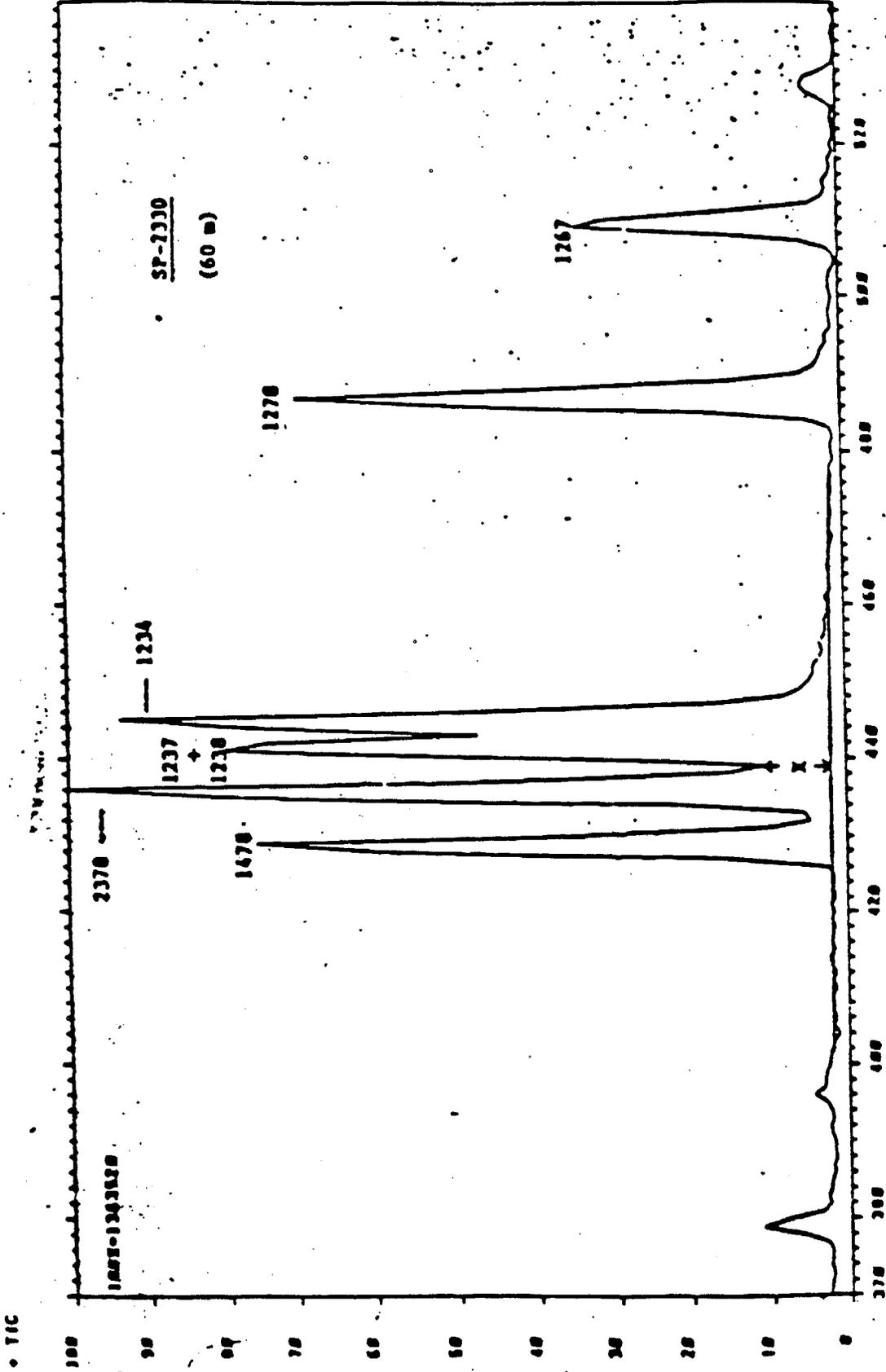


Figure 2. Selected ion current profile for m/a 370 and 372 produced by MS analysis of performance check solution using a 60-m SP-2330 fused silica capillary column and conditions listed in Table 1.

DIOXIN AND DIBENZOFURANS
STANDARD OPERATION PROCEDURES

(REVISED 3/87 SKV)

(REVISED 3/87 SKV)

Glassware Washing

Glassware that have been in direct contact with the samples or with the extracts should be rinsed with copious quantities of TOLUENE. Allow the toluene to dry in hood before setting in tub for washing.

Wash all glassware in soapy water. Wash flasks, beakers, and graduates in the dishwasher. Separatory funnels stopcocks should be disassembled for proper cleaning. Using a plastic dishpan, wash other odd size/shape items by hand with the aid of brushes to clean all interior parts.

Rinse all glassware well with tap water.

Allow the glassware to drain well and air dry.

Solvent rinse all glassware with Acetone, Toluene, Hexane and Methylene Chloride.

Put cleaned glassware away.

Note: All High Hazard marked glassware should be rinsed twice with each of the solvents and stored in a area for high hazard glassware.

(REVIEWED 3/87 SKV)

DIOXIN LABORATORY SAFETY PROCEDURES

- Consider ALL surfaces to be contaminated

- Always wear a lab coat when in lab.
- Notify the lab manager of any accidents or spills.
- When weighing samples wear :
 - Dispo Gloves
 - Lab coat
 - Paper jacket
 - Particulate mask
- TCDD GARBAGE :
 - Special trash can for garbage that has contacted samples or extracts
 - This special trash can is to be double bagged before use. Only allow it to be filled half full. Then remove the bags and tie shut or twist and tape closed. Throw secured bag into the yellow waste can.
- Solvent eluates, extracts, concentrates, standards, etc. should be rinsed into a special waste container and when full, the contents analyzed for dioxin/furan. After this analysis a decision is made as to proper disposal.

- Wipe tests should be performed periodically. an area of approximately a square foot should be wiped with a gauze pad or filter paper dampened with hexane. The wipe is then extracted by the "Wipe" method and cleaned up by the IFB method. The extracts may be analyzed by GC/ECD or GC/MS on FSCC. If GC/ECD is used do not add the I.S. to the wipes and confirm any possible positives by GC/MS. Also if there are interferences at the retention time of 2378-TCDD the extract needs to be sent to GC/MS. Less than 0.1ug 2378-TCDD per wipe indicates acceptable cleanliness, anything higher warrants further cleaning of the lab. More than 10 ug per wipe indicates an acute hazard and requires prompt decontamination. some factors necessary to consider to make judicious selection of the area to wipe are:
 - Is the area exposed to:
 - a. Samples or sample containers?
 - b. Internal standard or spiking solutions ?
 - c. Cleanup column eluates or packings?
 - d. Waste disposal?

Also consider doing wipe tests on areas that the chemist uses frequently that may seem to be away from possible contamination.

5. SAFETY

- 5.1 The human toxicology of PCDD's/PCDF's are not well defined at present, although the 2,3,7,8-TCDD isomer has been found to be acrogenic, carcinogenic, and teratogenic in the course of laboratory animal studies. The 2,3,7,8-TCDD is a solid at room temperature, and has a relatively low vapor pressure. The solubility of this compound in water is only about 200 parts-per-trillion, but the solubility in various organic solvents ranges from about 0.001 percent to 0.14 percent. The physical properties of the 135 other tetra- through octa-chlorinated PCDD's/PCDF's have not been well established, although it is presumed that the physical properties of congeners are generally similar to those of the 2,3,7,8-TCDD isomer on the basis of the available toxicological and physical property data for TCDD, this compound, as well as the other PCDD and PCDF, should be handled only by highly-trained personnel who are thoroughly versed in the appropriate procedures, and who understand the associated risks. Additional references to laboratory safety are identified. 1-3
- 5.2 Each laboratory must develop a strict safety program for handling PCDD's and PCDF's. The following laboratory practices are recommended:
- 5.2.1 Contamination of the laboratory will be minimized by conducting all manipulations in a hood.
- 5.2.2 The effluents of sample splitters for the gas chromatograph and vacuum pumps on the GC/MS should pass through either a column of activated charcoal or through a trap containing oil or high-boiling alcohols.
- 5.3 The following precautions for safe handling of PCDD's/PCDF's in the laboratory are presented as guidelines only. The precautions for safe handling and use are necessarily general in nature because detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual usage. Assistance in evaluating the health hazards of particular laboratory conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. Although some PCDD's and PCDF's are extremely toxic to laboratory animals, it has been handled for years without injury in analytical and biological laboratories. Techniques used in handling radioactive and infectious materials are applicable to PCDD's/PCDF's.

- 5.3.1 Protective Equipment--Eye protection equipment (preferably full face shields), throw-away latex gloves, plastic-backed absorbent bench top paper, shoe covers, apron or lab coat, and lab hood adequate for radioactive work.
- 5.3.2 Training--Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces. Operating of respirator equipped with activated carbon filters when sampling aerosols or dusts.
- 5.3.3 Personal Hygiene--Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and sniffs) with any mild soap and plenty of scrubbing action.
- 5.3.4 Confinement--Well-ventilated, controlled-access laboratory is required. Posted with signs. Separate glass-are and tools.
- 5.3.5 Waste--Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors should not handle wastes.
- 5.3.6 Disposal of Wastes--Low level waste, such as the absorbent paper and plastic gloves, may be burned in a good incinerator. Waste containing gross quantities (milligrams) of PCDD's/PCDF's should be packaged securely and disposed of in approved steel hazardous waste drums fitted with heavy gauge polyethylene liners. Liquids should be allowed to evaporate in an efficient hood and in a disposable container; residues may then be handled as above.
- 5.3.7 Glassware, Tools, and Surfaces--Satisfactory cleaning may be accomplished by rinsing with 1,1,1-Trichloroethane, then washing with any detergent and water. Dishwater may be disposed to the sewer (also see Section 6.5).
- 5.3.8 Laundry--All laboratory safety clothing contaminated with PCDD's/PCDF's in the course of analyses must be carefully secured and subjected to proper disposal (see Section 5.3.6). Lab coats or other clothing worn in dioxin work may be laundered. Clothing should be collected in a plastic bag. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a washer without contact if the launderer knows the problem. The washer should be run through a cycle before being used again for other clothing. Disposable garments may be used to avoid a laundry problem, but they must be properly disposed of or incinerated.
- 5.3.9 Wipe Tests--Surfaces of laboratory benches, apparatus and other appropriate areas should be periodically subjected to surface wipe tests using solvent-wetted filter paper which is then analyzed to check for PCDD/PCDF contamination in the

laboratory. Typically, if the detectable level of PCDD's or PCDF's from such a test is greater than 50 ng/m², this indicates the need for decontamination of the laboratory. A typical action limit in terms of surface contamination of the other PCDD/PCDF (summed) is 500 ng/m². In the event of a spill within the laboratory, absorbent paper is used to wipe up the spilled material and this is then placed into a hazardous waste drum. The contaminated surface is subsequently cleaned thoroughly by washing with appropriate solvents (methylene chloride followed by methanol) and laboratory detergents. This is repeated until wipe tests indicate that the levels of surface contamination are below the limits cited.

- 5.3.10 Inhalation--Any procedure that may produce airborne contamination should be performed with good ventilation when finely divided samples (dust, soils, dry chemicals) are being processed; removal of these from sample containers, as well as other operations, including weighing, transferring, and mixing with solvents should all be accomplished in a hood or glove box. Laboratory personnel should wear respirator or masks fitted with a particulate filter and charcoal sorbent. Handling of the dilute solutions normally used in analytical work presents no inhalation hazards except in case of an accident.
- 5.3.11 Accidents--In the unlikely event that analytical personnel experience skin contact with PCDD's/PCDF's or samples containing these, the contaminated skin area should immediately be thoroughly scrubbed using mild soap and water. Personnel involved in any such accident should subsequently be taken to the nearest medical facility, preferably a facility whose staff is knowledgeable in the toxicology of chlorinated hydrocarbons. Again, disposal of contaminated clothing is accomplished by placing it in hazardous waste drums.
- 5.3.12 Personal Health--It is desirable that personnel working in laboratories where PCDD's/PCDF's are handled be given periodic physical examinations (at least yearly). Such examinations should include specialized tests, such as those for urinary porphyrins and for certain blood parameters which, based on published clinical observations, are appropriate for persons who may be exposed to PCDD's/PCDF's. Periodic facial photographs to document the onset of dermatologic problems are also advisable.

6. APPARATUS AND EQUIPMENT

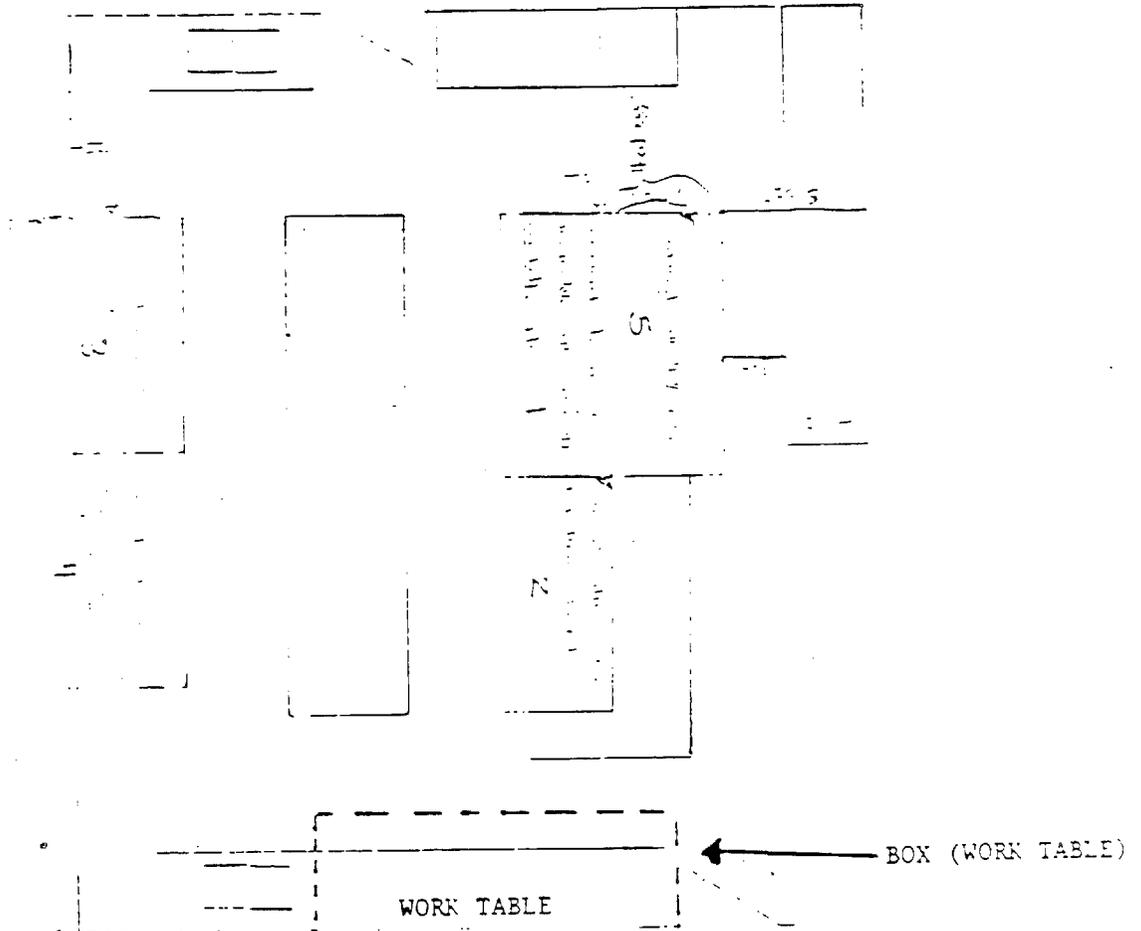
6.1 Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS)

- 6.1.1 The GC must be capable of temperature programming and be equipped with all required accessories, such as syringes, gases, and a capillary column. The GC injection port must be designed for capillary columns. Splitless or on-column injection technique

(REVIEWED 3/87 SKV)

DIOXIN SAFETY

FRONT HALL



-NO ITEMS IN CONTACT WITH DIOXINS ARE ALLOWED IN DIOXIN WORK SPACE INDICATED BY BOX ON MAP.

-NO EXTRACTS ARE ALLOWED ON WORK TABLE.

-FOLDERS SHOULD BE CLIPPED TO THE SHELF, SUCH THAT THE FLOW CHART CAN BE SEEN.

(REVISED 3/87 SKV)

WIPE TEST METHOD

WIPE AN AREA 30CM X 30CM WITH THREE HEXANE SOAKED GAUZE PADS.
SELECT DIFFERENT AREAS WHERE POSSIBLE DIOXIN CONTAMINATION COULD BE
PRESENT.
TRANSFER WIPE TO A FLASK, ADD I.S., IF APPROPRIATE, NATIVE SPIKE.
ADD 50ML BENZENE AND 100ML HEXANE.
SHAKE FOR 1 HOUR, FILTER INTO 250ML ROUND BOTTOM AND ADD ABOUT 500ML
TETRADECANE.
ROTO-EVAP TO TERADECANE, ADD 50ML HEXANE, ROTO-EVAP TO TERADECANE.
SET ASIDE FOR COLUMN CLEAN-UPS.
IF POSSIBLE, DO WIPE TEST EVERY SIX MONTHS OR WHEN APPROPRIATE.

(REVISED 3/87 BY SKV)

DISPOSAL METHOD FOR SAMPLES SUBMITTED BY SAMPLE CONTROL

DISPOSAL OF AQUEOUS DIOXINS AND DIBENZOFURANS SAMPLES

- 1.) All aqueous samples received for disposal from sample control will be disposed by the following method:
 - a.) The samples are poured into an appropriate size separatory funnel. All bottles and/or containers are rinsed out with MECL₂ into the separatory funnel.
 - b.) The samples are extracted with three portions of 50 ml MECL₂ and the extracts combined in a container labelled as " DIOXIN WASTE ONLY. "
 - c.) The aqueous portion can be discarded into the sink and flushed with large amounts of running water.
 - d.) All bottles and/or containers can be discarded into the regular trash.

(REVIEWED 3/87 SKV)

DIOXIN NOTES

EXTRACTIONS:

IFB = 10G soil/sediment, Na₂SO₄, MeOH, hexane, shake.

Jar = IFB

Sox = sample size will be specified
solvent will be specified
Na₂SO₄ mixed with sample in thimble
soxhlet for 16 hours

HXCP = hexachlorophene method

613 = EPA Method 613, 11, neutral pH, 3x60ml MeCl₂

WIPE = WIPE METHOD

RINSEATE= REINSEATE METHOD

SOLV. DIL. = SOLVENT DILUTION

- 8280= EPA METHODS AS PUBLISHED
-SLUDGE (DEAN-STARK EXTRACTION)
-STILL BOTTOM (SOLVENT DILUTION)
-FLY ASH (TOLUENE SOXLET)
-SOIL (JAR SHAKE USING PET. ETHER)
-AQUEOUS SAMPLES (MECL₂ H₂O EXTRACTION)
- 8280= CAL (MODIFIED CAL LAB METHODS)
-SLUDGE (BENZENE SOXLET)
-STILL BOTTOM (SOLVENT DILUTION)
-FLY ASH (BENZENE SOXLET)
-SOIL (IFB METHOD)
-AQUEOUS (613 METHOD)

INTERNAL STANDARDS

IFB = add 100ul TS I or DS I to "NS" sample
add 100ul TS II or DS II to all other samples

Otherwise all I.S. will be specified and all samples (including "NS") will receive the same Internal Standards. The "NS" will, in addition, have the native spike compound/compounds added.

Internal Standards are always labelled compounds:
Carbon-13 or Chlorine-37

NOTATIONS TO BE ADDED TO THE LABEL.

After doing	Add this to the label
H ₂ SO ₄	H+
Option A	a
Option B	b3% or b50%
Option D	d
Basic Alumina	3% or 50%
IFB	IFB
Further clean up	FC followed by the Notation used for the clean up used
Re-extraction	rx
Recovery standard	rs

(REVISED 3/87 SKV)

DIOXIN PACKING MATERIALS

Silica gel-

Kieselgel 60, activate for >12 hours at 130C before use. Store at 130 C in covered flask.

Acid alumina-

Bio-Rad Ag-4, activate for >12 hours at 130C before use. Store at 130 C in covered flask.

Basic alumina-

Bio-Rad Ag-10, kiln at 600 C for >24 hours before use. Store at 130 C in covered flask. DO NOT USE IF OLDER THAN 5 DAYS!

Carbopack/silica gel-

Mix 3.6g carbopack (Supelco 1-0257) and 16.4g activated silica gel. Activate mix for >12 hours at 130 C before use. Store at 130 C in covered flask.

44% H₂SO₄/silica gel-

Mix 24ml con. H₂SO₄ and 56g activated silica gel. Stir and shake until free flowing. Store at room temperature.

33% NaOH/silica gel-

Mix 34ml 1N NaOH and 67g activate silica gel. Stire and shake until free flowing. Store at room temperature.

K-silicate-

Dissolve 168g KOH in 700ml MeOH. Mix in 300g unactivated silica gel. Heat for 90 minutes at 60 C, swirling often.

PX-21/silica gel-

Mix 0.6g PX-21 charcoal and 100g activated silica gel. Stir and shake until uniform. Activate for >12 hours at 130 C before use. Store at 130 C in covered flask.

(REVIEWED 3/87 SKV)

TCDD EXTRACTION PROCEDURE

Water samples: (EPA method 613)

Place aliquot of sample into appropriate size separatory funnel.

Add I.S., use amount specified by flow chart.

Add spike solution if appropriate.

Extract the sample 3 times with 50ml portions of MeCl_2 .

Combine the extracts and pour thru Na_2SO_4 into a round bottom flask, add ca. 500ul tetradecane.

Roto-evap to the tetradecane.

Transfer the extract to an 8ml test tube with hexane.

Set aside for column clean ups.

Sediment samples: (Region VII EPA Protocol Sept, 83; JAR, IFB)

Weigh 10gm sample into a 250 ml flask.

Add I.S., use amount specified by flow chart.

Add spike solution if appropriate.

Add 20gm Na_2SO_4 .

Add 20ml. MeOH and 150ml hexane.

Place on shaker for 3 hours.

Filter extract into a round bottom flask.

Add ca. 500ul tetradecane.

Roto-evap to the tetradecane.

Set aside for column cleanup.

Sediment Samples: (soxhlet)

The soxhlet apparatus should be pre-cleaned by an 8hr. soxhlet, discard this solvent.

Add 20g Na_2SO_4 to the thimble.

Weigh 10g of sample on top of the Na_2SO_4

Mix immediately and add I.S., see flow chart.

Add spike solution if appropriate.

Place thimble in soxhlet apparatus, add 250ml of

extracting solvent (see flow chart) to receiver.

Assemble soxhlet, turn on heating controls and cooling water, allow to extract for 16 hours.

Transfer to a 500ml round bottom, add ca. 500ul C_{14} .

Roto-evap to C_{14} , if benzene or toluene was used as the extracting solvent, add 50ml hexane to the R.B. and roto-evap to C_{14} .

Transfer the extract to an 8ml test tube with hexane.

Set aside for column clean ups.

(REVISED 3/87 SKV)

Hexachlorophene Extraction Method:

Add 50ml MEOH to a 1L separatory funnel.
Weigh 10 grams of sample into the separatory funnel.
Rinse the spatula and sides of separatory funnel with about 25ml MEOH.
Add INTERNAL STANDARD and if appropriate, native spike.
Add 10ml of 10N NAOH to the separatory funnel, mix until sample dissolves.
Add 225ml blank water, shake well, vent frequently.
Extract with 150ml hexane.
Collect the aqueous layer into a 500ml flask.
Pass the hexane extract thru Na₂SO₄ into a 500ml round bottom flask.
Pour aqueous portion back into the separatory funnel and extract with another 150ml hexane.
Combine second extract with first thru Na₂SO₄.
Add about 200ul tetradecane, rotoevap to the tetradecane.
Set aside for clean-up as per flow chart.

Wipes:

Transfer wipe to flask, add I.S.
Add 50ml benzene and 100ml hexane.
Shake 1 hour, filter into R.B. add ca. 200ul C14.
Roto-evap to C14, add 50ml hexane, roto-evap to C14.
Transfer the extract to a 8ml test tube with hexane.
Set aside for clean up as per flow chart.

Rinsates:

Measure 100ml of the rinsate into a 250ml r.b. flask.
Add I.S. and roto-evap to ca. 5ml
(if the aliquot does not concentrate, pass thru Na₂SO₄ with excess hexane, add ca. 200ul C14, roto-evap to C14.)
Transfer to an 8ml test tube, add 50ul C14.
N₂ to C14 and submit for GC/MS analysis.

(REVIEWED 3/87 SKV)

SDS METHOD

- Put ca. 25ml MeCl₂ into a 250ml separatory funnel.
- Add ca. 2g of sample (record weight), swirl until sample is dissolved.
- Add 125ml hexane.
- Add I.S.
- Wash:
 - 2x with 20ml 10N NaOH
 - 1x with 50ml blank water
 - 3x with con. H₂SO₄
 - 1x with 50ml blank water
- Discard these washes.
- Pass the organic phase thru Na₂SO₄ into a round bottom.
- Add ca. 1/2 ml tetradecane, roto evaporate to the C14.

CLEANUP FOR SDS SAMPLES:

IFB

BASIC ALUMINA (using 10g basic alumina
and 2x elution volume)

OPTION D2
FV 50ul

(REVISED 3/87 SKV)

CARB METHOD

FILTER + HOLDER

- Transfer filter to a 250ml flask.
- Rinse holder with acetone, benzene, and hexane into flask.
- Add I.S. as per flow chart.
- Add 50ml benzene and 75ml hexane.
- Shake 1 hour, filter into round bottom flask.
- Add ca. 200ul C14, roto-evap to C14.
- Set aside for column clean-up.

XAD-2 RESIN AND FLOROSIL

- Transfer XAD-2 resin or florisil to a precleaned soxhlet and cover with glasswool.
- Add I.S. as per flow chart.
- If more than one thimble is used per sample, then split the I.S. evenly between thimbles.
- Place thimble in soxhlet apparatus.
- Pour 50ml MeOH into the thimble.
- Charge the receiver with 300ml toluene, soxhlet 16 hours.
- Transfer extract to a 500ml round bottom flask.
- Add ca. 200ul C14, roto-evap to C14.
- Set aside for column clean-up.

ASSORTED GLASSWARE + LIQUIDS

- Empty liquids into sep. funnel.
- Rinse glassware with acetone, benzene, and MeCl₂ into same sep. funnel.
- Add I.S. as per flow chart.
- If more than one sep. funnel is used per sample series, then split the I.S. evenly between sep. funnels.
- Shake 2 minutes.
- Drain solvent into flask.
- Extract aqueous layer with 3x 50ml MeCl₂.
- Combine all solvents in a flask.
- Pass thru Na₂SO₄ into a round bottom flask.
- Add ca. 200ul C14, roto-evap to C14.
- Set aside for column clean-up.

COLUMN CLEAN-UP

- ASSORTED GLASSWARE + LIQUIDS AND FILTER + HOLDER
IFB-->D OR D2-->FV
- XAD-2 RESIN AND FLOROSIL
IFB-->D OR D2-->FV

Note: ALL GLASSWARE IS CLEANED WITH ACETONE, BENZENE, HEXANE, AND MECL₂.

(REVIEWED 3/87 SKV)

IFB-LAMPARSKI MODIFICATION
(Anal. chem., 52(13), 1980, 2045-54)

- The sample extract solvent is benzene either from an extraction with benzene (soxhlet) or exchanged into benzene.
- Adjust the sample extract volume to ca. 25ml.
- Add 25ml hexane, mix well.
- Pre-rinse the top column of IFB with hexane, discard rinse.
- Put all 50ml thru the top column of IFB, rinse RB with 3-5ml portions of hexane, add to column.
- Put 90 ml hexane thru the column.
- Collect all eluate from the column in a round bottom, add 1/2ml tetradecane, roto evap to the C14.
- Add 50ml hexane, roto evap to C14.
- Repeat this step as necessary to remove ALL traces of benzene.
- Pre-rinse the bottom column of IFB with hexane.
- transfer the C14 solution to the bottom column of IFB with small portions of hexane.
- Elute the column with 20 ml hexane
- Eluate the column with 20ml 20% MeCl₂/hexane.
- Use N₂ and tetradecane on the 20% eluate as appropriate per flow chart.

(REVIEWED 3/87 SKV)

STALLING'S METHOD (COLUMBIA FISHERIES)

(fish, worms, crayfish, mouse, mole, opossum belly, 7)

From:

Determination of Part-per-Trillion Levels of polychlorinated Dibenzofurans and Dioxins in Environmental Samples. Smith, Stallings, and Johnson. Columbia National Fisheries Research Laboratory, U.S. Fish and Wildlife Service. Anal. Chem. 1984, 56, 1830-1842.

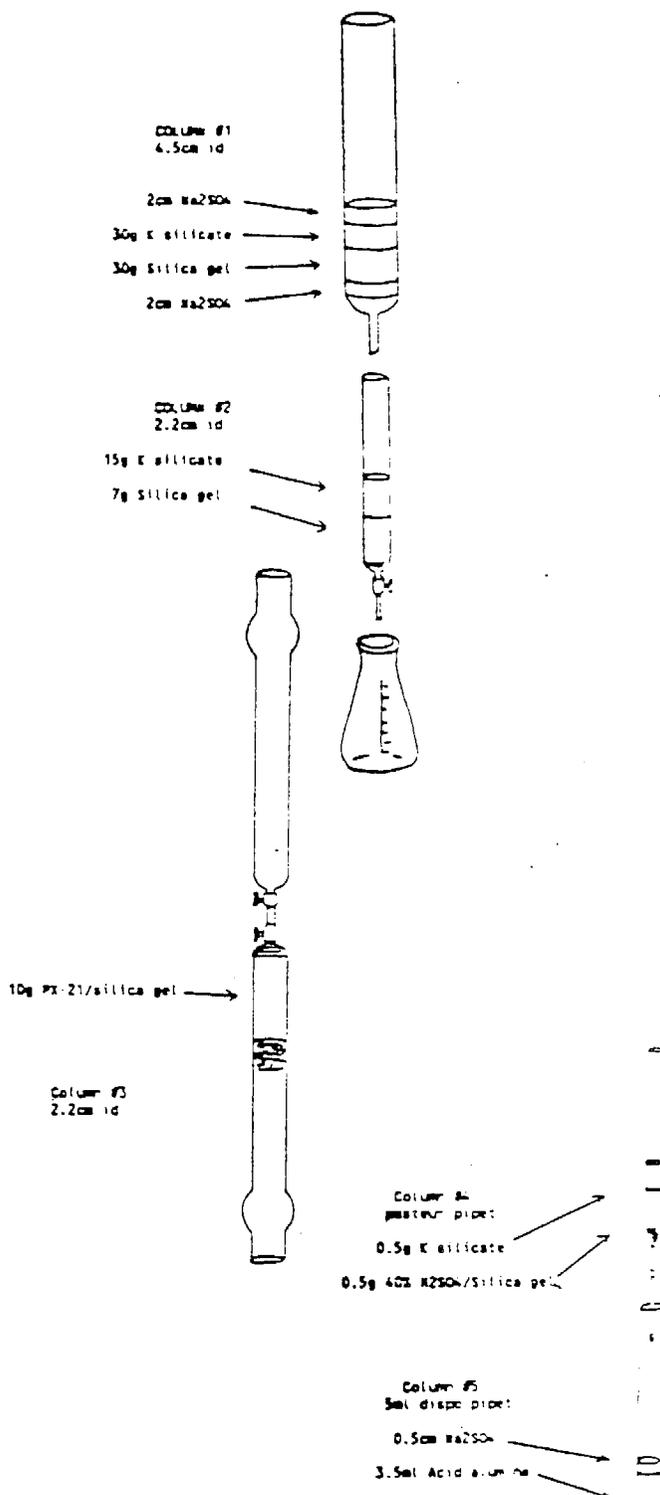
- Weigh 50g of sample, blend into a paste, scrap into a new 1000m plastic beaker.
- Blend ca. 25g $\text{K}_2\text{S}_2\text{O}_8$ to help transfer sample into the beaker.
- Repeat with another 25g portion of $\text{K}_2\text{S}_2\text{O}_8$.
- Add ca. 150g $\text{K}_2\text{S}_2\text{O}_8$ to the beaker and stir like crazy, cover with aluminum foil and allow to stand overnight.
- Break up clumps and blend until lump free, transfer to a soft jar until ready to work up.

- Fill each column with packings, except sample.
- Pre-wash column #2 with 30ml of solvent A (1:1 cyclohexane + Me_2C) discard wash.
- Add 100ml solvent A to the sample, add I.S., stir to break up clumps.
- Transfer sample to the top of column #1, top with $\text{K}_2\text{S}_2\text{O}_8$.
- Stack columns as pictured, rinse sides of column #1 with several portions of solvent A.
- Add 650ml of solvent A and adjust the flow of column #1 such that the top of column #2 is always wet with column #1 eluate.

- Put 10g of PX-21/silica gel in a 150ml beaker with 75ml toluene, mix and pour into column #3.
- After the packing has settled, start draining solvent, when when it reaches within 2cm of the packing, rinse the walls with Me_2C , then push a large plug of glasswool into column #3 onto the packing. Drain solvent down to the packing.
- Wash the column with 4-15ml portions of Me_2C followed by 4-20ml portions of solvent A.
- Pour the eluate from column #1/#2 onto column #3, discard eluate.
- Elute the column with 75ml solvent A then 30ml 75/20 $\text{Me}_2\text{C}/\text{Me}_2\text{C}$. Save these two eluates conc. red in an 8oz. bottle.
- Invert column #3 and connect the reservoir as pictured.
- Elute the upside down column #3 with 40ml toluene into a round bottom flask, add ca. 1/2ml tetradecane and rotovap to C14.

- Pack columns #4 and #5, prewash each with hexane, discard eluate, then stack columns as pictured.
- Transfer concentrate with portions of hexane that totals 5.0ml.
- Discard column #4.
- Elute column #5 with:
 - 5.0ml hexane
 - 15.0ml 2:1 $\text{Me}_2\text{C}/\text{hexane}$
 - 15.0ml 5:1 $\text{Me}_2\text{C}/\text{hexane}$
 - 20.0ml 8:1 $\text{Me}_2\text{C}/\text{hexane}$
- Save the first 23ml "as is"
- Collect the remaining 37ml and concentrate to final volume in C14 as per the flow chart.

PACKINGS: Once prepared these are kept at 130 C.
Kiesel gel 60
B-D Bed AD-4 acid alumina
40% $\text{K}_2\text{S}_2\text{O}_8$ /silica gel (w/w)
PX-21/silica gel (0.6g PX 21/100g silica gel)



(REVIEWED 3/87 SKV)

PAPER/PULP METHOD

SAMPLE SIZE IS 10g OR WHATEVER FITS INTO SOXHLET THIMBLE.

IF SAMPLES ARE DRY, OR MOIST, THEN THEY ARE EXTRACTED BY A 300ml BENZENE SOXHLET.
(see attached method)

IF SAMPLES ARE EXTREMELY WET SLUDGES THEN PREPARE FOR EXTRACTION BY THE FOLLOWING:

- WEIGH 10g OF DRAINED SLUDGE INTO A BEAKER
- ADD 20g Na_2SO_4
- MIX WELL AND LET STAND FOR 2 HOURS
- BREAK UP CLUMPS, USE BLENDER IF NECESSARY
- ADD TO THIMBLE CONTAINING A 1/2-INCH GLASSWOOL PLUG
- CONTINUE WITH ATTACHED SOXHLET METHOD
- DO NOT TRANSFER TO 500ml ROUND BOTTOM FLASK
- TRANSFER EXTRACT TO 500ml SEP. FUNNEL

CLEANUP FOR PAPER/PULP SAMPLES

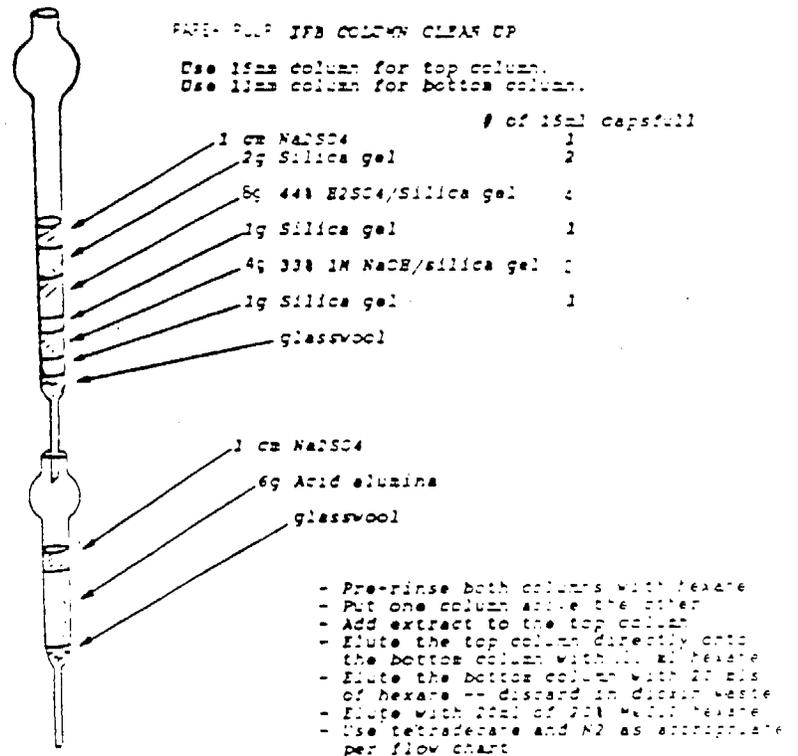
OPT. C CLEANUP

PAPER/PULP IFC COLUMN CLEANUP

BASIC ALUMINA (using 10g basic alumina
and 2X elution volumes)

OPT. D2

F.V. = 10ul



(REVISED 3/87 SKV)

MODIFIED EPA METHOD 8280
EXTRACTION AND CLEAN-UP PROCEDURE

1.1 EXTRACTION

1.1.1 SLUDGE. Weigh aqueous sludge sample (e.g. 2g) into a 250ml round bottom flask. Add internal standard as per flow chart. Add 50ml of toluene and fit flask with a Dean-Stark water separator. Reflux the sample until all of the water has been removed. Cool the sample and filter the toluene extract through Whatman No. 1 filter paper or equivalent, into a 250ml round bottom flask. Rinse the filter paper with 10ml of toluene, combine the extract and rinseate. Add ca. 1/2ml C14. Concentrate the combined solution to C14 using a rotary evaporator at 75 C. Proceed with step 1.1.4.

1.1.2. STILL BOTTOM. Extract still bottom samples by mixing a sample (e.g. 0.1g) with 10ml toluene. Add internal standard as per flow chart. Filter the solution through Whatman No. 1 filter paper (or equivalent) into a 50ml round bottom flask. Rinse the filter with 10ml of toluene. Add ca. 1/2 ml C14. Concentrate the combined toluene solution to C14 using a rotary evaporator at 75 C. Proceed with step 1.1.4.

1.1.3. FLY ASH. Extract fly ash by placing a sample (e.g. 10g) and an equivalent amount of Na_2SO_4 in a Soxhlet thimble. Add internal standard as per flow chart. Charge the receiver with 300ml of toluene and soxhlet for 16 hours using a three cycle/hour schedule. Cool and filter the toluene extract through Whatman No. 1 filter paper or equivalent, into 500ml round bottom flask. Rinse the filter paper with 5ml toluene. Add ca. 1/2ml C14. Concentrate the combined toluene solution to C14 using a rotary evaporator at 75 C. Proceed with step 1.1.4.

1.1.4. Transfer the residue to a 125ml separatory funnel using 15ml of hexane. Rinse the flask with two 5ml aliquots of hexane and add the rinses to the funnel. Shake two minutes with 50ml of 5% NaCl solution. Discard the aqueous layer and proceed with step 1.2.

1.1.5. SOIL. Extract soil samples by placing the sample (e.g. 10g) and an equivalent amount of Na_2SO_4 in a 250ml Erlenmeyer flask. Add internal standard as per flow chart. Add 20ml of methanol and 80ml petroleum ether in that order, to the flask. Shake on a wrist-action shaker for two hours. The solid portion of sample should mix freely. If a smaller soil aliquot is used, scale down the amount of methanol proportionally.

1.1.5.1. Filter the extract from 1.1.5. through a glass funnel fitted with filter paper (Whatman No.1 or equivalent) and filled with Na_2SO_4 into a 250ml round bottom flask. Add 50ml of petroleum ether to the Erlenmeyer flask, swirl the sample gently and decant the solvent through the funnel as above. Wash the Na_2SO_4 on the funnel with two additional 5ml portions of petroleum ether.

1.1.5.2. Add ca. 1/2 ml C14 to the round bottom flask. Concentrate the extract to C14 using a rotary evaporator at 60 C. Add 50ml hexane to the 250ml round bottom flask. Concentrate to C14 using rotary evaporator at 60 C.

1.1.5.3 Transfer the residue to a 125 ml separatory funnel using 15 ml hexane. Rinse the flask with two 5 ml aliquots of hexane add the rinses to the separatory funnel. Proceed to step 1.2.

1.1.6. AQUEOUS SAMPLES. Mark the meniscus on the side of the sample bottle for later determination of the exact sample volume. Pour the entire sample (approximately 1L) into a 2L separatory funnel. Add internal standard as per flow chart. Note: A continuous liquid-liquid extractor may be used in place of a separatory funnel.

1.1.6.1. Add 60ml methylene chloride to the sample bottle, seal and shake 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for two minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, the analyst must employ mechanical techniques to complete the phase separation. Extract with 3 times 50ml MeCl_2 in a 250ml flask. Pass the sample extract through a filter funnel packed with Na_2SO_4 into a 250ml erlenmeyer flask. Rinse the Na_2SO_4 with an additional 30ml of MeCl_2 to ensure quantitative transfer.

1.1.6.2 Transfer the extract to a 250ml separatory funnel using 15 ml hexane. Rinse the flask with two 5 ml aliquots of hexane, add the rinses to the separatory funnel.

1.1.6.3. Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000ml graduated cylinder. Record the sample volume to the nearest 5ml. Proceed with step 1.2.

1.2. Partition the solvent against 40ml of 20% (w/v) potassium hydroxide. Shake for two minutes. Remove and discard the aqueous layer (bottom). Repeat the base washing until no color is visible in the bottom layer (perform base washings a maximum of four times)

1.3. Partition the solvent against 40ml distilled water. Shake for 2 minutes. Remove and discard aqueous layer (bottom layer).

1.4. Partition the solvent against 40ml of concentrated sulfuric acid. Shake for 2 minutes. Remove the aqueous layer (bottom). Repeat the acid washings until no color is visible in the acid layer (perform acid washings a maximum of four times).

1.5. Partition the extract against 40ml distilled water. Shake for 2 minutes. Remove and discard aqueous layer (bottom). Dry the organic layer by pouring through a funnel containing Na_2SO_4 , wash with two 5ml portions of hexane. Add ca. 1/2 ml Cl_4 . Concentrate the hexane solution to Cl_4 using a rotary evaporator (75 C water bath), making sure that all traces of toluene are removed. Use of an inert gas to concentrate is also permitted.

1.6. Pack a silica gel column (glass 300mm x 10.5mm), fitted with a Teflon stopcock, in the following manner:

Insert a glasswool plug into the bottom of the column. Add a 4g layer of Na₂SO₄. Add a 4g layer of Woelm super 1 neutral alumina. Tap the top of the column gently. Woelm super 1 neutral alumina need not be activated or cleaned prior to use but should be stored in a sealed dessicator. Add a 4g layer of Na₂SO₄ to cover the alumina. Elute with 10ml of hexane and close the stockcock just prior to the exposure of the Na₂SO₄ 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.

1.7. Dissolve the residue from 1.5 in 2ml of hexane and apply the hexane solution to the top the column. Use enough hexane (3-4ml) to complete the transfer of the sample cleanly to the surface of the alumina. Discard the eluate.

1.7.1. Elute with 10ml of 8% (v/v) MeCl₂ in hexane. As a quality assurance step, check that no PCDD's or PCDF's are eluted in this fraction.

1.7.2. Elute the PCDD's and PCDF's from the column with 15ml of 60% (v/v) MeCl₂ in hexane and collect this fraction in a 40ml VOA vial. Add ca. 1/2ml C14 and using nitrogen, concentrate the extract to the C14.

1.8. CARBON COLUMN CLEAN-UP

1.8.1. Follow attached d or d2 clean-up procedures (whichever is applicable) using 0.30g of normal d/d2 active carbon Carbopack C (Supleco 1-0257) material.

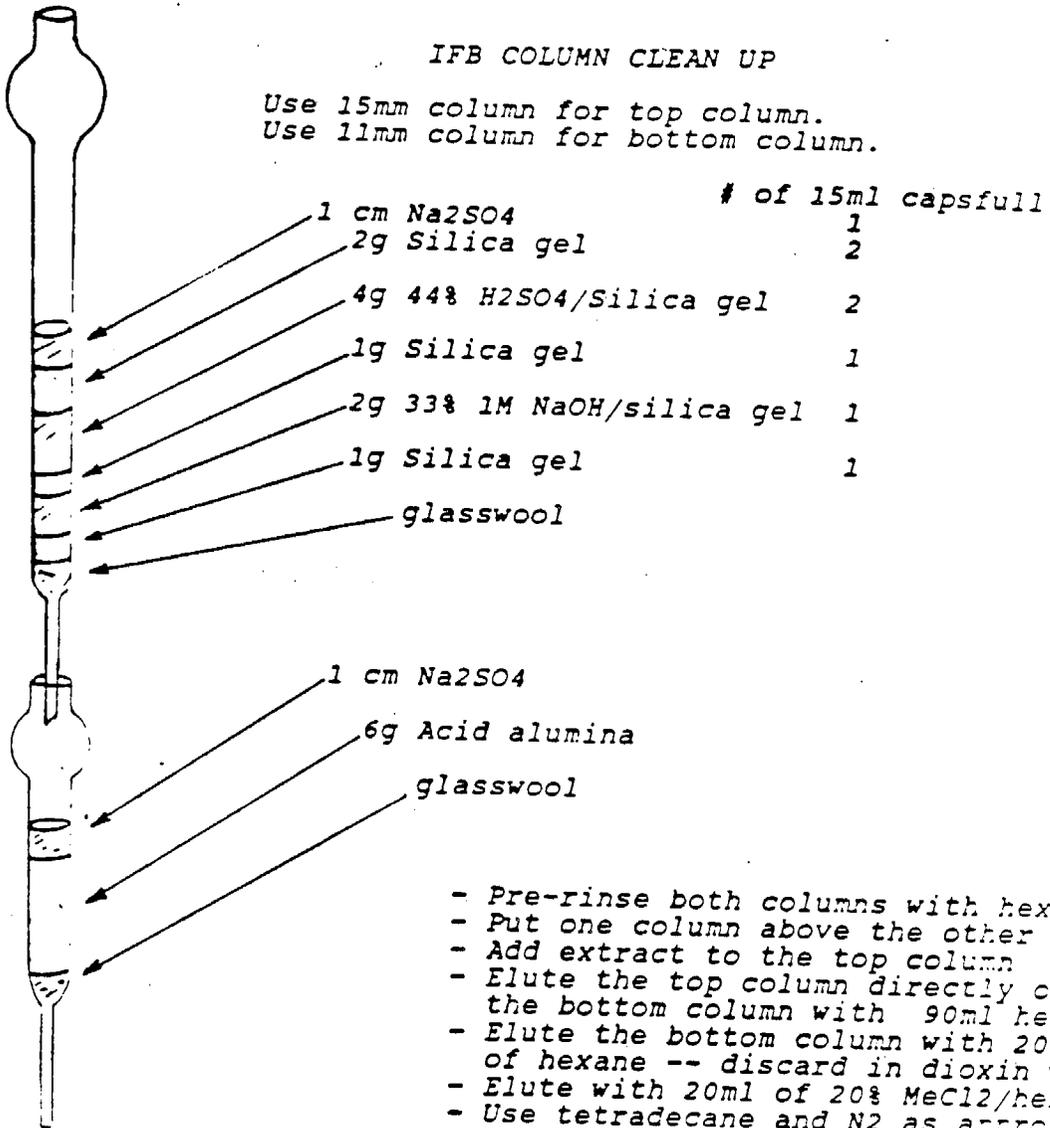
1.8.2. Add the specified amount (see flow chart) of C14. N2-->C14.

1.9. Approximately 1 hour before HRGC/LRMS analysis, add to the extract an amount of 13C-1,2,3,4-TCDD equivalent to the amount of 13C-2,3,7,8-TCDD added as an internal standard. N2-->C14.

(REVIEWED 3/87 SKV)

IFB COLUMN CLEAN UP

Use 15mm column for top column.
Use 11mm column for bottom column.



- Pre-rinse both columns with hexane
- Put one column above the other
- Add extract to the top column
- Elute the top column directly onto the bottom column with 90ml hexane
- Elute the bottom column with 20 ml of hexane -- discard in dioxin waste
- Elute with 20ml of 20% MeCl₂/hexane
- Use tetradecane and N₂ as appropriate per flow chart

(REVIEWED 3/87 SKV)

BASIC ALUMINA CLEANUP

Use 11mm id short column



1cm Na₂SO₄

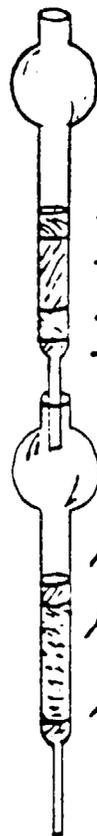
5g basic alumina

(>12 hour at 600 C, fresh, < 5 days old)

glasswool

- Add sample with hexane
 - Elute with 20ml hexane (discard)
 - Elute with 8ml 3% MeCl₂/hexane (save)
 - Elute with 35ml 50% MeCl₂/hexane.
- Use tetradecane and N₂ as appropriate per flow chart.

(REVIEWED 3/87 SKV)



OPTION A

use 11mm dia. columns (top & bottom)

1cm Na₂SO₄

4g 44% H₂SO₄/Silica gel

1g Silica gel

glasswool

1cm Na₂SO₄

6g Acid Alumina

glasswool

Collect 20ml 20% MeCl₂/hexane
in a VOA vial.

Use tetradecane and N₂ as appropriate
per flow chart.

-Transfer extract
with 2 x 0.5ml
hexane.

-Elute with 45ml
hexane. Discard.

-Remove top col.

-Elute with 20ml
hexane. Discard.

-Elute with 20ml

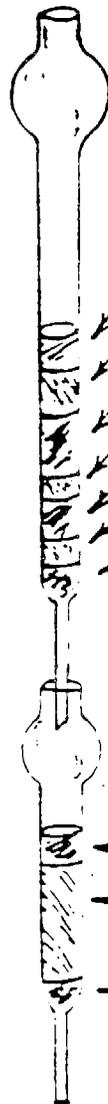
-20% MeCl₂/hexane.

(REVIEWED 3/87 SKV)

OPTION B

Use a 15mm id column

of 15ml capsfull



1 cm Na ₂ SO ₄	1
2g Silica gel	2
4g 44% H ₂ SO ₄ /Silica gel	2
1g Silica gel	1
2g 33% 1M NaOH/Silica gel	1
1g Silica gel	1
glasswool	

- Pre-wash both columns with 20ml hexane (discard).
- Transfer extract to the column with hexane.
- Elute with 90ml hexane.
- Run the eluate directly onto the basic alumina column.

Use a 11 mm id column

- 1cm Na₂SO₄
- 3g Basic alumina
- glasswool

- Remove top column.
- Elute bottom column with 10ml 3% MeCl₂/hexane. Save eluate.
- Elute with 30ml 50% MeCl₂/hexane.
- Use tetradecane and N₂ as appropriate per flow chart.

(REVIEWED 3/87 SKV)

OPTION C

- Pour the un-concentrated extract into a separatory funnel (filter thru a large glasswool plug if there are particulates).
- Wash the organic extract two times with 50ml portions of 10N NaOH, discard the washes.
- Wash the organic layer once with 50ml blank water, discard the wash.
- CAUTIOUSLY----
- Wash the organic extract two times with 25ml portions of con. H₂SO₄, discard the wash.
- Wash the organic layer once with 50ml blank water, discard the wash.
- Pass the organic extract thru Na₂SO₄ into a round bottom flask and add ca. 500ml tetradecane.
- Rotary evaporate as necessary to remove excess solvent down to the tetradecane.
- Clean up as per flow chart. .

(REVIEWED 3/87 SKV)

OPTION D

dispo-pipet

2cm charcoal/silica gel

glasswool

Pre-elute:

2ml Toluene

1ml 75:20 MeCl₂:MeOH

1ml 1:1 Cyclohexane:MeCl₂

2ml hexane

Discard these column rinses.

TRANSFER SAMPLE CONCENTRATE WITH HEXANE

Elute:

1ml hexane

1ml hexane

1ml 1:1 Cyclohexane:MeCl₂

1ml 75:20 MeCl₂:MeOH

Discard above eluates into dioxin waste solvent container

SAVE NEXT ELUATE ALONE

2ml Toluene

Use tetradecane and N₂ with the toluene eluate as appropriate per flow chart.

PACKING:

3.6g carbopak

16.4g silica gel



(REVIEWED 3/87 SKV)

OPTION D2

5ml dispo pipet
(cut off 1cm of tip)

glasswool

0.3g charcoal/silica gel

glasswool (at the 2.5ml mark)

Pre-rinse:

5ml hexane in direction A
Turn column over
5ml hexane in direction B

Pre-elute; in direction B

2ml Toulene
1ml 75:20 MeCl₂:MeOH
1ml 1:1 Cyclohexane:MeCl₂
2ml hexane

Discard these column rinses.

TRANSFER SAMPLE CONCENTRATE WITH HEXANE

Elute:

1ml hexane
1ml hexane
1ml 1:1 Cyclohexane:MeCl₂
1ml 75:20 MeCl₂:MeOH

Discard above eluates into dioxin waste solvent container.

Turn column over; eluate in direction A

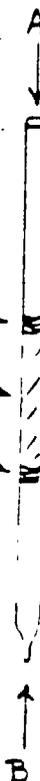
SAVE NEXT ELUATE ALONE

4ml Toluene
(gentle blow out)

Use tetradecane and N₂ with the toluene
eluate as appropriate per flow chart.

PACKING:

3.6g carbopak
16.4g silica gel



(REVIEWED 3/87 SKV)

FLORISIL (OPTION-F)

APPLICATION: Separation of PCB's and TCDD/TCDF.

Place 20g of florisil (activated overnight at 130 C-190 C) in a glasswool plugged 19mm x 300mm column fitted with a teflon stopcock, add 2cm of Na₂SO₄ to the top of the column. Rinse the packed column with 60ml hexane (discard). Place up to 10ml of sample extract (in hexane or isooctane) on the column with ca. 2ml hexane (discard). Elute with the following: 200ml of hexane, 200ml 6% diethyl ether/hexane, 200ml 15% diethyl ether/hexane. collect the hexane and the 6% fractions together. Collect the 15% fraction separate.

Add the sample and elution volumes just as the previous volume has reached the Na₂SO₄.

The hexane/6% fraction is to be exchanged into isooctane and concentrated to an appropriate final volume for PCB analysis.

The 15% fraction is to be concentrated to an appropriate final volume for TCDD/TCDF analysis.

(REVISED 3/87 SKV)

VOLUME REDUCTION OF TETRADECANE

Pack a dispo-pipet with 2cm basic alumina.
Pre-elute with 1ml hexane. Discard.
Transfer concentrate with hexane.
Elute with 1ml hexane. Discard.
Elute with 2ml MeCl₂. Save.
Add the appropriate amount of tetradecane and
use N₂ to final volume. Use excess N₂ to assure
complete removal of MeCl₂. Submit for GC/MS
analysis.

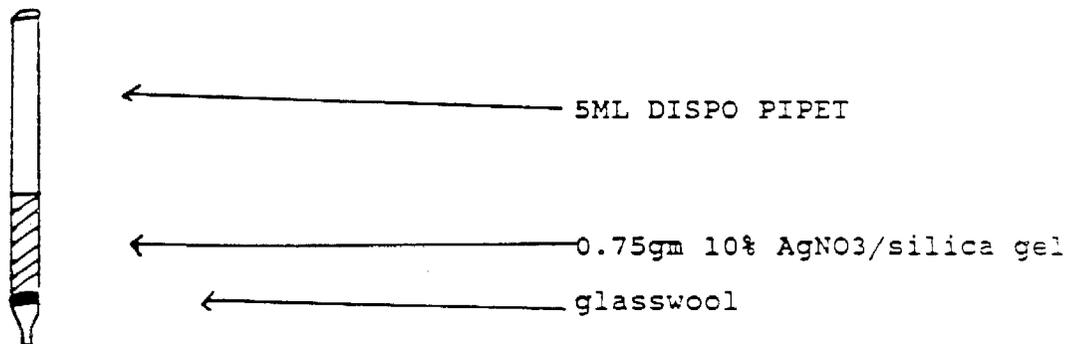
(REVISED 3/87 SKV)

AgNO₃ CLEAN-UP COLUMN
(Anal. Chem. 1979, 54, 1453, Lamparski, Nestruck, Stehl)

1. PREPARATION OF 10% AgNO₃/SILICA GEL COLUMN PACKING MATERIAL

Dissolve 5.5 gm AgNO₃ in 21.4 ml water, add this solution to 50 gm silica gel. Mix well and allow to stand 30 minutes. Place in a 125 degree C oven, shake frequently. Keep in oven for 15 hours after the water has evaporated. Can be stored at ambient temperature in desiccator or well sealed bottle.

2. AgNO₃ CLEAN-UP COLUMN



-TRANSFER EXTRACT TO COLUMN WITH 3X 0.5ML HEXANE.

-ELUTE WITH 16ML HEXANE.

-COLLECT ALL ELUATE IN VOA VIAL.

-N₂ AS APPROPRIATE.

APPENDIX G
ANALYTICAL PROCEDURES AND QUALITY ASSURANCE
FOR MULTIMEDIA ANALYSIS OF
POLYCHLORINATED DIBENZO-p-DIOXINS AND
POLYCHLORINATED DIBENZOFURANS

ANALYTICAL PROCEDURES AND QUALITY ASSURANCE
FOR MULTIMEDIA ANALYSIS

OF

POLYCHLORINATED DIBENZO-p-DIOXINS

AND

POLYCHLORINATED DIBENZOFURANS

BY

HIGH-RESOLUTION GAS CHROMATOGRAPHY/HIGH-RESOLUTION MASS
SPECTROMETRY

(Exhibits D and E)

by

Yves Tondeur

January 1987

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NOTICE

This document is a preliminary draft. It has not been formally released by the University of Nevada Environmental Research Center or the U.S. Environmental Protection Agency, and it should not at this stage be construed to represent University or Agency policy. It is circulated for comments on its technical merit and policy implications.

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FOREWORD

In January 1986, the Environmental Protection Agency published an analytical protocol, Protocol for the Analysis of 2,3,7,8-Tetrachlorodibenzo-p-Dioxin (TCDD) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS) (EPA 600/4-86-004), aimed at the determination of part per trillion and sub-part per trillion levels of 2,3,7,8-TCDD and of total TCDD in soil, sediment and aqueous samples. The January 1986 document was intended to be a stepping stone for the realization of a more comprehensive method that would include all the polychlorinated dibenzodioxin (PCDD) and polychlorinated dibenzofuran (PCDF) congeners present in a broader spectrum of environmentally significant matrices.

The present report constitutes a draft addressing the analytical procedures (Exhibit D) and quality assurance (Exhibit E, quality assessment and control) requirements sections of the future analytical protocol for the analysis of PCDDs and PCDFs by HRGC/HRMS; i.e., Method 8280 (HRMS). At times, reference to other exhibits (e.g., Exhibit C) are made even though these sections have not been prepared. The format

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used for this report is similar to the format used for other EPA TCDD protocols. Figures and tables are however grouped at the end of Exhibit D. A final version of Method 8280 (HRMS) is expected following peer review of this draft report and the completion of the single laboratory evaluation. Elements included in this Method 8280 (HRMS) have been inspired from a variety of sources such as the EPA Region VII low-resolution mass spectrometry (LRMS) TCDD protocol, the aforementioned high-resolution mass spectrometry TCDD protocol, the RCRA Method 8280 (LRMS), the method evaluation study final report by Midwest Research Institute on "Analysis for Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans in Human Adipose Tissue" (EPA-56015-86-020), the National Dioxin Study Analytical Procedures and Quality Assurance Plan for the Analysis of 2,3,7,8-TCDD in Tier 3-7 Samples (EPA/600/3-85/019), and the analytical protocol for the analysis of PCDDs and PCDFs by HRGC/HRMS submitted recently for review by Region VII. Also, we wish to acknowledge the contributions from experts in the analysis of PCDDs and PCDFs in environmental samples. The cooperation of P.W. Albro (National Institute of Environmental Health Sciences, Research Triangle Park, NC), L. Alexander (Center for Disease Control, Atlanta, GA), J.R. Hass and D.J. Harvan (Triangle Laboratories, Inc.; Research Triangle Park, NC), R. Harless (US-EPA, Research Triangle Park, NC), R.D. Kleopfer (US-EPA, Region VII, Kansas City, MO), D.W. Kuehl (US-EPA,

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Duluth, MN), M.J. Mille (California Analytical Laboratories, Sacramento, CA), R.W. Noble (Monsanto Company, Dayton, OH), T.M. Sack and J.S. Stanley (Midwest Research Institute, Kansas City, MO) is particularly appreciated.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

A	--	Integrated ion abundance
AX-21	--	Type of carbon adsorbent
C	--	Concentration
CDC	--	Center for Disease Control
CDWG	--	Chlorinated Dioxins Workgroup
⁰ C	--	Degree centigrade
¹³ C	--	Carbon-13 labeled
cm	--	centimeter
DB-5	--	Type of fused-silica capillary column
DS	--	Data system
EDL	--	Estimated Detection Limit
EMPC	--	Estimated Maximum Possible Concentration
EMSL-LV	--	Environmental Monitoring System Laboratory, Las Vegas
EPA	--	Environmental Protection Agency
g	--	gram
GC	--	Gas Chromatography or Gas Chromatograph
GC/MS	--	Gas Chromatography/Mass Spectrometry
HEPA	--	High-efficiency particulate air
HpCDD	--	Heptachlorodibenzodioxin
HpCDF	--	Heptachlorodibenzofuran
HRGC/HRMS	--	High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry
HxCDD	--	Hexachlorodibenzodioxin
HxCDF	--	Hexachlorodibenzofuran
IFB	--	Invitation for Bid
IS	--	Internal Standard
KD	--	Kuderna - Danish
L	--	Liter
MCL	--	Method Calibration Limit
mL	--	Milliliter
mm	--	Millimeter
M/ΔM	--	Mass spectrometer resolving power
OCDD	--	Octachlorodibenzodioxin
OCDF	--	Octachlorodibenzofuran
OSHA	--	Occupational Safety and Health Administration
PCB	--	Polychlorinated biphenyl
PCDD	--	Polychlorinated dibenzodioxin
PCDPE	--	Polychlorinated diphenylether
PCDF	--	Polychlorinated dibenzofuran
PE	--	Performance Evaluation
PeCDD	--	Pentachlorodibenzodioxin
PeCDF	--	Pentachlorodibenzofuran
PFK	--	Perfluorokerosene
pg	--	picogram

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ppm -- part per million
 ppt -- part per trillion
 Q -- amount of substance
 QA -- Quality Assurance or Quality Assessment
 QA/QC -- Quality Assessment/Quality Control
 rpm -- revolutions per minute
 RPD -- Relative Percent Difference
 RRF -- Relative Response Factor
 \overline{RRF} -- Mean Relative Response Factor
 RRT -- Relative Retention Time
 RS -- Recovery Standard
 S -- EPA reference standard solution
 SAS -- Special Analytical Service
 SES -- Site Evaluation Sheet
 SICP -- Selected Ion Current Profile
 SIM -- Selected Ion Monitoring
 SMO -- Sample Management Office
 S/N -- Signal-to-noise ratio
 SOP -- Standard Operating Procedure
 SP-2330 -- Type of fused-silica capillary column
 Still-
 bottom -- Name of a matrix that is used as a noun
 TCDD -- Tetrachlorodibenzodioxin
 TEF -- Toxicity Equivalency Factor
 V -- Volume
 v/v -- volume/volume
 W -- weight or laboratory working standard
 WTE -- Wipe Test Experiment
 uL -- microliter

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ANALYTICAL METHODS

(EXHIBIT D)

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EXHIBIT D

1. Scope and Application

1.1 This method provides procedures for the detection and quantitative measurement of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), polychlorinated dibenzo-p-dioxins (tetra- through octa-chlorinated homologues; PCDDs), and poly-chlorinated dibenzofurans (tetra- through octa-chlorinated homologues; PCDFs) in a variety of environmental matrices and at part per trillion (ppt) concentrations. The analytical method calls for the use of high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) on purified sample extracts. Table 1 lists the various sample types covered by this analytical protocol, the 2,3,7,8-TCDD-based Method Calibration Limits (MCLs) and other germane information. Analysis of a one-tenth aliquot of the sample permits measurement of concentrations up to 10 times the upper MCL (Table 1). Samples containing concentrations of specific congeneric analytes (PCDDs and PCDFs) considered within

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the scope of this method that are greater than the upper MCL must be analyzed by a protocol designed for such concentration levels. An optional method for reporting the analytical results using a 2,3,7,8-TCDD toxicity equivalency factor (TEF) is described.

- 1.2 The sensitivity of this method is dependent upon the level of interferences within a given matrix. Actual limits of detection and quantitation will be provided following the single or multilaboratory evaluation of this proposal, and from examining the data gathered by the Sample Management Office (SMO) from Special Analytical Services (SAS) performed over the past few years.
- 1.3 This method is designed for use by analysts who are experienced with residue analysis and skilled in high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS).
- 1.4 Because of the extreme toxicity of these compounds, the analyst must take the necessary precautions to prevent exposure to himself or herself, or to others, of materials known or believed to contain PCDDs or PCDFs. It is the laboratory's responsibility to ensure that safe handling procedures are employed.

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2. Summary of the Method

2.1 This procedure uses a matrix-specific extraction, analyte-specific cleanup, and high-resolution capillary column gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) techniques.

2.2 If interferences are encountered, the method provides selected cleanup procedures to aid the analyst in their elimination. The analysis flow chart is shown in Figure 1.

2.3 An aliquot (see Table 1) of soil, sediment, fly-ash, water, sludge, still-bottom, fuel oil, reactor residue, fish, or human adipose tissue is spiked with a solution containing specified amounts of each of the nine isotopically ($^{13}\text{C}_{12}$) labeled PCDD/PCDFs listed in Table 2. The sample is then extracted according to a matrix-specific extraction procedure. The extraction procedures are: a) toluene (or benzene) Soxhlet extraction for soil, sediment and fly-ash samples; b) methylene chloride liquid-liquid extraction for water samples; c) toluene (or benzene) Dean-Stark extraction for fuel oils and aqueous sludges; d) toluene (or benzene) extraction for still-bottoms; e)

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hexane extraction for fish; and f) methylene chloride extraction for human adipose tissue. The decision for the selection of an extraction procedure for reactor residue samples is based on the appearance (consistency, viscosity) of the samples. Generally, they can be handled according to the procedure used for still-bottom (or chemical sludge) samples.

2.4 The extracts are then submitted to an acid-base washing treatment and dried. Following a solvent exchange step, the residue is cleaned up with column chromatography on neutral alumina and carbon on silica gel. The extract from adipose tissue is first treated with sulfuric acid impregnated silica gel before chromatography on acidic silica gel, neutral alumina, and carbon on silica gel. The preparation of the final extract for HRGC/HRMS analysis is accomplished by adding, to the concentrated carbon column eluate, 10-to-50 uL (depending on the matrix type) of a tridecane solution containing 50 pg/uL of each the two recovery standards $^{13}\text{C}_{12}$ -1,2,3,4-TCDD and $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD (Table 2). The former is used to determine the percent recoveries of tetra- and penta-chlorinated PCDD/PCDF congeners while the latter is used for the determination of hexa-, hepta- and octa-chlorinated PCDD/PCDF congeners percent recoveries.

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NOTE: As an additional retention time and instrumental switching time quality control checks, the recovery standard solution will contain $^{13}\text{C}_{12}$ -1,2,8,9-TCDD and $^{13}\text{C}_{12}$ -1,3,4,6,8-PeCDF (10 pg/uL each).

[OFF-THE-RECORD NOTE: These labeled standards are not available at the present time. However, Cambridge Isotope Laboratories will prepare these labeled compounds if the EPA indicates interest in implementing this additional QC requirement.]

2.5 One-to-two uL of the concentrated extract are injected into an HRGC/HRMS system capable of performing selected ion monitoring at resolving powers of at least 10,000 (10 percent valley definition).

2.6 The identification of OCDD and nine of the 15 most-toxic congeners (Table 3), for which a ^{13}C -labeled standard is available in the sample fortification and recovery standard solutions (Table 2), is based on their elution at their exact retention time (-1 to +3 seconds from the respective internal or recovery standard signal) and the simultaneous detection of the two most abundant molecular ions. The remaining six most toxic congeners (i.e.,

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2,3,4,7,8-PeCDF; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDF; 1,2,3,7,8,9-HxCDF; 2,3,4,6,7,8-HxCDF, and 1,2,3,4,7,8,9-HpCDF), for which no carbon-labeled internal standard is available in the sample fortification solution, are identified by their retention times falling within their respective PCDD/PCDF retention time windows as established by using a GC column performance evaluation solution and the simultaneous detection of the two most abundant molecular ions. Identification of OCDF is based on its retention time relative to $^{13}\text{C}_{12}$ -OCDD and the simultaneous detection of the two most abundant molecular ions. All other identified PCDD/PCDF congeners (not presenting a 2,3,7,8-lateral substitution pattern) must have a retention time falling within their respective PCDD/PCDF retention time windows as established by using a GC column performance evaluation solution and the simultaneous detection of the two most abundant molecular ions. Confirmation is based on a comparison of the ratio of the integrated ion abundance of these molecular ion species to their theoretical abundance ratio.

- 2.7 Quantification of the individual congeners, total PCDDs and PCDFs is achieved in conjunction with the establish-

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ment of a multipoint (seven points) calibration curve for each homologue, and during which each calibration solution is analyzed once.

3. Definitions

3.1 Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are compounds (Figure 2) that contain from one to eight chlorine atoms. The 15 most toxic of these PCDDs (totaling 75) and PCDFs (totaling 135) are shown in Table 3. The number of isomers at different chlorination levels is shown in Table 4.

3.2 An "homologue" is defined here as a group of chlorinated dibenzodioxins or dibenzofurans having a specific number of chlorine atoms.

3.3 An "isomer" is defined by the arrangement of chlorine atoms within an "homologue". For example, 2,3,7,8-TCDD is a TCDD isomer.

3.4 The term "congener" is used to mean any isomer of any homologue.

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3.5 **Internal Standard** Nine internal standards are used in this method. There is one for each of the dioxin and furan homologues with the degree of chlorination ranging from four to eight. An internal standard is a $^{13}\text{C}_{12}$ -labeled analogue of a congener chosen from the compounds listed in Table 3 and of OCDD. Internal standards are added to all samples including method blanks and quality control samples before extraction, and they are used to measure the concentration of the analytes.

3.6 **Recovery Standard** Two recovery standards are used to determine the percent recoveries for PCDDs and PCDFs. The $^{13}\text{C}_{12}$ -1,2,3,4-TCDD is used to measure the percent recoveries of tetra- and penta-chlorinated dioxins and furans while $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD permits the determination of hexa-, hepta- and octa-chlorinated homologues' recoveries. They are added to the sample final residue before HRGC/HRMS analysis. Furthermore, $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD is used for the identification of the native analogue present in sample extracts (this exhibit, Section 2.6).

3.7 **High-Resolution Concentration Calibration Solutions** (Table 5) Solutions (tridecane) containing known amounts of 17

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selected PCDDs and PCDFs, nine internal standards ($^{13}\text{C}_{12}$ -labeled PCDD/PCDFs), and two carbon-labeled recovery standards (this exhibit, Section 3.6); the set of seven solutions is used to determine the instrument response of the native analytes relative to the internal standards and of the internal standards relative to the recovery standards.

3.8 **Sample Fortification Solution** (Table 2) Solution (isooctane) containing the nine internal standards, which is used to spike all sample before extraction and cleanup.

3.9 **Recovery Standard Spiking Solution** (Table 2) Tridecane solution containing the two recovery standards, which is used to prepare the final sample residue before HRGC/HRMS analysis. This solution also contains $^{13}\text{C}_{12}$ -1,2,8,9-TCDD and $^{13}\text{C}_{12}$ -1,3,4,6,8-PeCDF as retention time markers (see Exhibit D, Section 2.4 note).

3.10 **Field Blank** A portion of a sample representative of the matrix under consideration, which is free of any PCDD/PCDFs.

3.11 **Laboratory Method Blank** This blank is prepared in the laboratory through performing all analytical procedures

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except the addition of a sample aliquot to the extraction vessel.

3.12 **Rinsate** A portion of solvent used to rinse sampling equipment; the rinsate is analyzed to demonstrate that samples were not contaminated during sampling.

3.13 **GC Column Performance Check Mixture** A tridecane solution containing a mixture of selected PCDD/PCDF standards (first and last eluters for each homologue), which is used to demonstrate continued acceptable performance of the capillary column (i.e., \leq 25 percent valley separation of 2,3,7,8-TCDD from all the other 21 TCDD isomers) and to define the homologous PCDD/PCDF retention time windows.

3.14 **Performance Evaluation Materials** A representative aliquot sample containing known amounts of certain unlabeled PCDD/PCDF congeners (in particular the ones having a 2,3,7,8-substitution pattern). Representative interferences may be present. PEMS are obtained from the EPA EMSL-LV and submitted to potential contract laboratories, who must analyze it to obtain acceptable results before

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being awarded a contract for sample analyses (see IFB Pre-Award Bid Confirmations). PEMS are also included as an unspecified ("blind") quality control (QC) sample in any sample batch submitted to a laboratory for analysis.

3.15 Relative Response Factor Response of the mass spectrometer to a known amount of an analyte relative to a known amount of an internal standard.

3.16 Estimated Level of Method Blank Contamination The response from a signal occurring in the homologous PCDD/PCDF retention time windows and at any of the masses monitored is used, as described in Section 14 (Exhibit D), to calculate the level of contamination in the method blank. The results from such calculations must be reported along with the data obtained on the samples belonging to the batch, associated with the method blank. Reporting a method blank contamination level for any of the 2,3,7,8-substituted congeners listed in Table 3 (i.e., the following statement does not apply to OCDD and OCDF) that either equals or exceeds the level present in any one sample from the batch would invalidate the results and

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require automatic sample reruns (Exhibit C) for all positive samples found in that batch of samples. A positive sample is defined as a sample found to contain at least one 2,3,7,8-substituted PCDD/PCDF congener.

- 3.17 **Sample Rerun** Extraction of another aliquot of the sample followed by extract cleanup and extract analysis.
- 3.18 **Extract Reanalysis** Analysis by HRGC/HRMS of another aliquot of the final extract.
- 3.19 **Mass Resolution Check** Standard method used to demonstrate a static resolving power of 10,000 minimum (10 percent valley definition).
- 3.20 **Method Calibration Limits (MCLs)** For a given sample size, a final extract volume, and the lowest and highest concentration calibration solutions, the lower and upper MCLs delineate the region of quantitation for which the HRGC/HRMS system was calibrated with standard solutions.
- 3.21 **HRGC/HRMS Solvent Blank** This additional QC check analysis corresponds to a 2-uL injection of pure tridecane into the GC column and a complete (tetra- through octa-chlorinated congeners) HRGC/HRMS analysis. Such QC check

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is required following a calibration run and before the daily analysis of the first sample extract. Acceptable HRGC/HRMS solvent blanks (see Exhibit D, Section 3.16 for guidelines) must be obtained before pursuing the analysis of subsequent sample extracts.

3.22 **Toxicity Equivalency Factor GC Mixture** This is a tridecane solution containing selected native and carbon-labeled 2,3,7,8-substituted PCDD/PCDF congeners. The mixture is used exclusively on the 60-m SP-2330/31 fused-silica column for the sole purpose of confirming relative retention times during TEF measurements. (Identification criteria; Section 14.7.1.3, Exhibit D.)

4. Interferents

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

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- 4.2 The use of high-purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.
- 4.3 Interferents co-extracted from the sample will vary considerably from source to source, depending upon the industrial process being sampled. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs) and polychlorinated diphenyl ethers (PCDPEs) that may be found at concentrations several orders of magnitude higher than the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established in Section 8.1.3 (Exhibit D). While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup techniques to achieve lower detection limits.
- 4.4 A high-resolution capillary column (60 m DB-5) is used to resolve as many PCDD and PCDF isomers as possible; however, no single column is known to resolve all the isomers. Several capillary columns will, in fact, be necessary during the determination of the TEFs (this Exhibit D, Section 14.7).

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5. Safety

5.1 The following safety practices are excerpted directly from EPA Method 613 Section 4 (July 1982 version) and amended for use in conjunction with this method.

In addition to 2,3,7,8-TCDD, other PCDDs and PCDFs containing chlorine atoms in positions 2,3,7,8 are known to have comparable toxicities. The analyst should note that finely divided dry soils contaminated with PCDDs and PCDFs are particularly hazardous because of the potential for inhalation and ingestion. It is recommended that such samples be processed in a confined environment, such as a hood or a glove box. Laboratory personnel handling these types of samples should also wear masks fitted with charcoal filter absorbent media to prevent inhalation of dust.

5.2 The toxicity or carcinogenicity of each reagent used in this method is not precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in

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this method. A reference file of material data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are given in references 1-3 (see end of Section 5, Exhibit D). Benzene and 2,3,7,8-TCDD have been identified as suspected human or mammalian carcinogens.

5.3 Each laboratory must develop a strict safety program for the handling of 2,3,7,8-TCDD. The following laboratory practices are recommended.

5.3.1 Contamination of the laboratory will be minimized by conducting all manipulations in a hood.

5.3.2 The effluents of sample splitters for the gas chromatograph and roughing pumps on the HRGC/HRMS system should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols.

5.3.3 Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light with wavelength less than 290 nm for several days (Use F

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40 BL lamps or equivalent). Using this analytical method, analyze the liquid wastes and dispose of the solutions when 2,3,7,8-TCDD can no longer be detected (at what level?).

5.4 Some of the following precautions were issued by Dow Chemical U.S.A. (revised 11/78) for safe handling of 2,3,7,8-TCDD in the laboratory and amended for use in conjunction with this method.

5.4.1 The following statements on safe handling are as complete as possible on the basis of available toxicological information. The precautions for safe handling and use are necessarily general in nature since detailed, specific recommendations can be made only for the particular exposure and circumstances of each individual use. Inquiries about specific operations or uses may be addressed to the Dow Chemical Company. Assistance in evaluating the health hazards of particular plant conditions may be obtained from certain consulting laboratories and from State Departments of Health or of Labor, many of which have an industrial health service. The 2,3,7,8-TCDD isomer is extremely toxic to laboratory animals. However, it has been handled for years without injury

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in analytical and biological laboratories. Techniques used in handling radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

- 5.4.1.1 Protective Equipment: Throw-away plastic gloves, apron or lab coat, safety glasses and lab hood adequate for radioactive work.
- 5.4.1.2 Training: Workers must be trained in the proper method of removing of contaminated gloves and clothing without contacting the exterior surfaces.
- 5.4.1.3 Personal Hygiene: Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).
- 5.4.1.4 Confinement: Isolated work area, posted with signs, segregated glassware and tools, plastic-backed absorbent paper on benchtops.
- 5.4.1.5 Waste: Good technique includes minimizing contaminated waste. Plastic bag liners should be used in waste cans. Janitors must be trained in safe handling of waste.

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5.4.1.6 Disposal of Hazardous Wastes: Refer to the November 7, 1986 Issue of the Federal Register on Land Ban Rulings for details concerning the handling of dioxin-containing wastes.

5.4.1.7 Decontamination: Personal - any mild soap with plenty of scrubbing action; Glassware, Tools and Surfaces - Chlorothene NU Solvent (Trademark of the Dow Chemical Company) is the least toxic solvent shown to be effective. Satisfactory cleaning may be accomplished by rinsing with Chlorothene, then washing with any detergent and water. Dish water may be disposed to the sewer after percolation through a charcoal bed filter. It is prudent to minimize solvent wastes because they require special disposal through commercial sources that are expensive.

5.4.1.8 Laundry: Clothing known to be contaminated should be disposed with the precautions described under "Disposal of Hazardous Wastes". Lab coats or other clothing worn in 2,3,7,8-TCDD work area may be laundered. Clothing should be collected in plastic bags. Persons who convey the bags and launder the clothing should be advised of the hazard and trained in proper handling. The clothing may be put into a

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washer without contact if the launderer knows the problem. The washer should be run through a cycle before being used again for other clothing.

5.4.1.9 Wipe Tests: A useful method of determining cleanliness of work surfaces and tools is to wipe the surface with a piece of filter paper.

NOTE: Appendix A describes a procedure for the collection, handling, analysis, and reporting requirements of wipe tests performed within the laboratory. The results and decision making processes are based on the presence of 2,3,7,8-substituted PCDD/PCDFs.

5.4.1.10 Inhalation: Any procedure that may produce airborne contamination must be done with good ventilation. Gross losses to a ventilation system must not be allowed. Handling of the dilute solutions normally used in analytical and animal work presents no inhalation hazards except in case of an accident.

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5.4.1.11 Accidents: Remove contaminated clothing immediately, taking precautions not to contaminate skin or other articles. Wash exposed skin vigorously and repeatedly until medical attention is obtained.

References:

1. "Carcinogens - Working with Carcinogens", Department of Health, Education, and Welfare. Public Health Service. Center for Disease Control. National Institute for Occupational Safety and Health. Publication No. 77-206, August 1977.
 2. "OSHA Safety and Health Standards, General Industry", (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).
 3. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety, (3rd Edition, 1979.)
6. Apparatus and Equipment
- 6.1 High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/Data System (HRGC/HRMS/DS).

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6.1.1 The GC must be equipped for temperature programming, and all required accessories must be available, such as syringes, gases, and capillary columns. The GC injection port must be designed for capillary columns. The use of splitless injection techniques is recommended. On-column injection techniques can be used on the 60-m DB-5 column. The use of a moving needle injection port is also acceptable. When using the method described in this protocol, a 2-uL injection volume is used consistently (i.e., the injection volumes for all extracts, blanks, calibration solutions and the performance check samples are 2 uL). One-uL injections are allowed; however, laboratories are encouraged to remain consistent throughout the analyses by using the same injection volume at all times.

6.1.2 Gas Chromatograph/Mass Spectrometer (GC/MS) Interface

The GC/MS interface components should withstand 350° C temperatures. The interface must be designed so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. Cold spots or active surfaces (adsorption sites) in the GC/MS in-

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terface can cause peak tailing and peak broadening. It is recommended that the GC column be fitted directly into the mass spectrometer ion source without being exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb the PCDDs and PCDFs. VespelTM or equivalent ferrules are recommended.

6.1.3 Mass Spectrometer

The static resolving power of the instrument must be maintained at a minimum of 10,000 (10 percent valley). The mass spectrometer must be operated in a selected ion monitoring (SIM) mode with a total cycle time (including the voltage reset time) of one second or less (this exhibit, Section 9.1.4.1). At a minimum, the ions listed in Table 6 for each of the five SIM descriptors must be monitored. Note that with the exception of the last descriptor (OCDD/OCDF), all the descriptors contain 10 ions. The selection (Table 6) of the molecular ions M and M+2 for ¹³C-HxCDF and ¹³C-HpCDF rather than M+2 and M+4 is to eliminate, even under high-resolution mass spectrometric conditions, interferences occurring in these two ion channels for samples containing high

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levels of native HxCDDs and HpCDDs. It is important to maintain the same set of ions for both calibration and sample extracts analyses. The selection of the lock-mass ion is left to the performing laboratory. The recommended mass spectrometer tuning conditions (this exhibit, Section 8.2.3) are based on the groups of monitored ions shown in Table 6.

6.1.4 Data System

A dedicated data system is employed to control the rapid multiple ion monitoring process and to acquire the data. Quantification data (peak areas or peak heights) and SIM traces (displays of intensities of each ion signal being monitored including the lock-mass ion as a function of time) must be acquired during the analyses and stored. Quantifications may be reported based upon computer-generated peak areas or upon measured peak heights (chart recording). The data system must be capable of acquiring data at a minimum of 10 ions in a single scan. It is also recommended to have a data system capable of switching to different sets of ions (descriptors) at specified times during an HRGC/HRMS acquisition. The data system should be able to provide hard copies of

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individual ion chromatograms for selected gas chromatographic time intervals. It should also be able to acquire mass-spectral peak profiles (this exhibit, Section 8.2.4) and provide hard copies of peak profiles to demonstrate the required resolving power. The data system should also permit the measurement of noise on the base line.

NOTE: The detector zero setting must allow peak-to-peak measurement of the noise on the base line of every monitored channels. Figure 3 illustrates the effect of electronic noise setting upon the estimation of the resolving power.

6.2 GC Column

In order to have an isomer-specific determination for 2,3,7,8-TCDD and to allow the detection of OCDD/OCDF within a reasonable time interval in one HRGC/HRMS analysis, the 60-m DB-5 fused-silica capillary column is recommended. Minimum acceptance criteria must be demonstrated and documented (this exhibit, Section 8.1). At the beginning of each 12-hour period (after mass resolution is demonstrated) during which sample

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extracts or concentration calibration solutions will be analyzed, column operating conditions must be attained for the required separation on the column to be used for samples. Operating conditions known to produce acceptable results with the recommended column are shown in Table 7.

6.3 Miscellaneous Equipment and Materials

The following list of items does not constitute an exhaustive compendium of the equipment needed for this analytical method.

- 6.3.1 Nitrogen evaporation apparatus with variable flow rate.
- 6.3.2 Balances capable of accurately weighing 0.01 g and 0.0001 g.
- 6.3.3 Centrifuge.
- 6.3.4 Water bath -- equipped with concentric ring covers and capable of being temperature-controlled within $\pm 2^{\circ}$ C.

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- 6.3.5 Stainless steel or glass container large enough to hold contents of one-pint sample containers.
- 6.3.6 Glove box.
- 6.3.7 Drying oven.
- 6.3.8 Stainless steel spoons and spatulas.
- 6.3.9 Laboratory hoods.
- 6.3.10 Pipets - disposable, Pasteur, 150-mm long x 5-mm ID.
- 6.3.11 Pipets - disposable, serological 10 mL for the preparation of the carbon column specified in Section 7.1.2.
- 6.3.12 Reacti-vial, 2 mL, silanized amber glass.
- 6.3.13 Stainless steel meat-grinder with a 3 to 5-mm hole size inner plate.
- 6.3.14 Separatory funnels, 125 mL.
- 6.3.15 Kuderna-Danish, 500 mL, fitted with 10-mL concentrator tube and three-ball Snyder column.

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- 6.3.16 TeflonTM boiling chips (or equivalent), washed with hexane before use.
- 6.3.17 Glass chromatographic column, 300 mm x 10.5 mm, fitted with Teflon stopcock.
- 6.3.18 Adaptors for concentrator tubes.
- 6.3.19 Glass fiber filters.
- 6.3.20 AX-21 carbon (Anderson Development Co., Adrain, Michigan).
- 6.3.21 Dean-Stark trap, 5 or 10 mL with T joints, condenser and 125-mL flask.
- 6.3.22 Continuous liquid-liquid extractor.
- 6.3.23 All-glass Soxhlet apparatus, 500 mL flask.
- 6.3.24 Glass funnels, sized to hold 170 mL of liquid.
- 6.3.25 Desiccator.

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- 6.3.26 Solvent reservoir (125 mL) Kontes; 12.35 cm diameter (special order item), compatible with gravity carbon column.
- 6.3.27 Rotary evaporator with a temperature-controlled water bath.
- 6.3.28 High-speed tissue homogenizer -- equipped with an EN-8 probe or equivalent.
- 6.3.29 Glass wool -- extracted with methylene chloride, dried and stored in a jar.

NOTE: Reuse of glassware should be minimized to avoid the risk of contamination. All glassware that is reused must be scrupulously cleaned as soon as possible after use, applying the following procedure. Rinse glassware with the last solvent used in it then with high-purity acetone and hexane. Wash with hot detergent water. Rinse with copious amounts of tap water and several portions of distilled water. Drain, dry and heat in a muffle furnace at 400° C for 15 to 30 minutes. Volumetric glassware must not be heated in a muffle furnace, and some thermally stable materials (such as PCBs) may not be removed by heating in a

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muffle furnace. In these cases, rinsing with high-purity acetone and hexane may be substituted for muffle-furnace heating. After the glassware is dry and cool, rinse with hexane, and store inverted or capped with solvent-rinsed aluminum foil in a clean environment.

7. Reagents and Standard Solutions

7.1 Column Chromatography Reagents

- 7.1.1 Alumina, neutral, Super 1, Woelm^R, 80/200 mesh. Store in a sealed container at room temperature in a desiccator over self-indicating silica gel.
- 7.1.2 AX-21 carbon (Anderson Development Co., Adrian, Michigan). Carbon column (gravity flow): Prepare the carbon on silica gel packing material by mixing five percent (by weight) active carbon AX-21, prewashed with methanol and dried in vacuo at 110° C and 95 percent (by weight) silica gel (Type 60, EM Reagent, 70 to 230 mesh, CMS No 393-066) followed by activation of the mixture at 130° C for six hours. Prepare a 10-mL disposable serological pipet by cutting off each end to give a 4-inch long column. Fine polish both ends and

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flare if desired. Insert a glass-wool plug at one end and pack with 1 g of the carbon and silica gel mixture to form a 2-cm long adsorbant bed. Cap the packing with a glass-wool plug.

7.2 Reagents

7.2.1 Sulfuric acid, concentrated -- ACS grade, specific gravity 1.84.

7.2.2 Potassium hydroxide -- ACS, 20 percent (w/v) in distilled water.

7.2.3 Sodium chloride -- Analytical reagent, 5 percent (w/v) in distilled water.

7.3 Desiccating Agent

7.3.1 Sodium sulfate -- granular, anhydrous; use as such.

7.4 Solvents

7.4.1 High-purity, distilled-in-glass or highest available purity: methylene chloride, hexane, benzene, methanol, tridecane, isooctane, toluene, cyclohexane, and

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acetone.

7.5 Calibration Solutions

7.5.1 High-Resolution Concentration Calibration Solutions (Table 5) -- Seven tridecane solutions containing native (totaling 17) and carbon-labeled (totaling 11) PCDDs and PCDFs at known concentrations used to calibrate the instrument. The concentration ranges are homologue dependent with the lowest values associated with the tetra- and penta-chlorinated dioxins and furans (2.5 pg/uL) and the highest for the octachlorinated congeners (1000 pg/uL).

7.5.2 These high-resolution concentration calibration solutions may be obtained from the Quality Assurance Division, US EPA, Environmental Monitoring System Laboratory (EMSL-LV), Las Vegas, Nevada. However, additional secondary standards must be obtained from commercial sources, and solutions must be prepared in the contractor laboratory. Traceability of standards must be verified against EPA supplied standard solutions. Such procedures will be documented by laboratory standard operating procedures (SOP) as required in IFB Pre-award Bid Confirmations, part 2.f.(4). It is the

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responsibility of the laboratory to ascertain that the calibration solutions received (or prepared) are indeed at the appropriate concentrations before they are used to analyze samples. A recommended traceability procedure for PCDD/PCDF standards is described in Appendix B.

7.5.3 Store the concentration calibration solutions in 1-mL minivials at 4° C.

7.6 GC Column Performance Check Solution -- This solution contains the first- and last-eluting isomers for each homologue from tetra- through hepta-chlorinated congeners. The solution also contains a series of other TCDD isomers for the purpose of documenting the chromatographic resolution. The $^{13}\text{C}_{12-2,3,7,8}\text{-TCDD}$ is also present. The laboratory is required to use tridecane as the solvent and adjust the volume so that the final concentration does not exceed 100 pg/uL per congener. Table 8 summarized the qualitative composition (minimum requirement) of this performance evaluation solution.

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NOTE: The use of a PCDD/PCDF-containing fly-ash extract is allowed but the qualitative equivalency of the fly-ash extract to the EPA solution should be demonstrated for each fly-ash extract.

7.7 Sample Fortification Solution -- This isooctane solution contains the nine internal standards at the nominal concentrations that are listed in Table 2. The solution contains at least one carbon-labeled standard for each homologue, and it is used to measure the concentrations of the native substances. (Note that $^{13}\text{C}_{12}$ -OCDF is not present in the solution.)

7.8 Recovery Standard Spiking Solution -- This tridecane solution contains two recovery standards ($^{13}\text{C}_{12}$ -1,2,3,4-TCDD and $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HxCDD) at a nominal concentration of 50 pg/uL per compound. Two additional carbon-labeled standards (1,2,8,9-TCDD and 1,3,4,6,8-PeCDF) will be included in this solution once they are available. Ten-to-fifty uL of this solution will be spiked into each sample extract before the final concentration step and HRGC/HRMS analysis.

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