

Title: Dioxins/Furans in Ambient Air Samples (PM-Dioxin)		Copy No: ##
Method No.: 3.02/4.1/M	Effective Date: October 9, 2013	Location: ###

QSM Approval: _____

Dioxins / Furans in Ambient Air Samples (PM - Dioxin)

1. SUMMARY

A High Resolution Mass Spectrometric (HRMS) method has been developed for measuring ultra trace amounts (fg/m^3) of PCDDs/PCDFs in ambient air samples.

2. INTRODUCTION

Levels of PCDD/PCDF in the ambient air of several selected Canadian cities have been monitored by Environment Canada since 1987. One of the main objectives of this monitoring effort is to assess the environmental impact associated with the operation of municipal solid waste incinerators in the vicinity of urban areas. Hi-volume ambient air samples collected in these areas had been routinely analyzed by Analysis and Air Quality Division of the Environmental Technology Centre using a Low Resolution Mass Spectrometric (LRMS) method until late 1989. Since that time, a High Resolution Mass Spectrometric (HRMS) method has been developed and applied to the analysis of these ambient air samples.

This method describes the latest analytical techniques employed by the Analysis and Air Quality Division for the determination of PCDD/PCDF in ambient air. Various aspects of the procedures, including personnel safety, waste disposal, sample preparation, GC/MS analysis and quality assurance are briefly outlined in the following sections. Detailed descriptions can be found in References 1-3.

3. CONTAMINATION AND INTERFERENCES

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines that could lead to elevated detection limits and/or loss of ability to detect PCDDs/PCDFs that may be present. Reagents should be of the highest available purity and in some cases, may require further purification before use.

Proper cleaning of glassware is extremely important. Glassware should be rinsed with solvent before and after washing with a detergent solution and as soon after use as is practical. Glassware is also rinsed after washing, upon delivery to the lab before being put away in drawers. Sonication of glassware filled with a detergent solution can also be performed as an aid to cleaning.

It shall be demonstrated that all materials used in the analysis are free from interferences by running reference matrix blanks (use precleaned PUFs), with each sample set.

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Interferences co-extracted from samples will vary considerably from source to source depending upon the exact nature of the sample matrix. Interfering compounds may be present at concentrations several orders of magnitude higher than any PCDDs/PCDFs that may be present. For PCDF determination, response for the chlorinated diphenyl ether ion must be absent at retention times coincident with analyte peaks. Interfering co-extractants must therefore be eliminated or reduced to the maximum extent practicable in order to ensure reliable quantification of trace amounts of PCDDs/PCDFs. The cleanup procedures described in this method can effectively remove many potential interferents.

Despite rigorous cleanup procedures, matrix interference will still be a possibility. If detection limits are seriously affected by excessive background (non-discrete interference), the sample extract will have to be re-processed using alternative cleanup techniques (Creaser and Haddad, 1989; NCASI Method, June 1990).

4. PERSONNEL SAFETY

Because of the highly toxic properties of PCDD/PCDFs, special precautions must be taken to minimize the risk of human exposure, either through direct contact with contaminated materials, or through inhalation of contaminated air. All work related to PCDD/PCDF analysis, including the preparation, handling, and storage of all samples and standards, should be conducted within a specially designed laboratory. This facility would include the following design features:

- restricted access area;
- sufficient ventilation;
- negative pressure relative to surrounding areas;
- all exhaust air ducting routed to a common, scrubbed outlet;
- segregation, via doors and air pressure differentials, into low and high hazard areas;
- an independent back-up air supply system designed to come into operation whenever a shut-down of the building's air supply system occurs;
- capability on auxiliary power in the event of a commercial power failure;
- capability to visually monitor ventilation system performance;
- devices to monitor indoor air levels of organic vapours generated from solvent use;
- a system of distinctive audio and visual alarms to alert lab personnel to potentially hazardous conditions

Lab workers must wear protective clothing consisting of safety glasses, disposable coveralls or clean buttoned labcoats, disposable foot coverings (optional) and disposable gloves. Other personal protective devices, such as face masks and cartridge or canister respirators, should be available in the laboratory in the event of a spill or other accident with potential to generate toxic fumes. Common laboratory safety equipment and facilities, such as safety showers, first-aid kits, eye wash stations and fire extinguishers,

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must be easily accessible.

5. APPARATUS AND REAGENTS

5.1 Equipment and Supplies

- 5.1.1 **Extraction Apparatus:** 200-mL Soxhlet body (Dean-Stark moisture trap optional), condenser, 500-mL boiling flask, and a temperature-controlled heating mantle
- 5.1.2 **Evaporative Concentrator:** Buchi R-110 rotary evaporator or equivalent
- 5.1.3 **Balance:** Top-loading macro balance, capacity to 1600 g, readability to 0.01 g, for weighing samples and reagents
- 5.1.4 **Pipettes:** Electronic or mechanical pipettes with capacities from 10 to 1000 µL
- 5.1.5 **Oven:** Range to 225⁰C, for conditioning carbon, silica, reagent-coated silica, sodium sulphate, and glass wool
- 5.1.6 **Tube Furnace:** Lindberg or equivalent, for activating alumina at 350°C
- 5.1.7 **Pumps:** Pressure/Vacuum with vacuum to 85 kPa (25 in. Hg) for rotary evaporation and suction filtration
- 5.1.8 **Weighing Paper**
- 5.1.9 **Forceps, Spatulas, Scoops**
- 5.1.10 **Ultrasonic Bath**
- 5.1.11 **Desiccators**
- 5.1.12 **Automatic Glassware Washing Equipment**
- 5.1.13 **HRGC/HRMS/DS**

5.2 Glassware

- 5.2.1 **Beakers:** Assorted volumes from 150 to 2000 mL
- 5.2.2 **Boiling Flasks:** 250 and 500 mL
- 5.2.3 **Erlenmeyer Flasks:** 500 mL with glass stopper
- 5.2.4 **Powder Funnels:** 7 cm diameter
- 5.2.5 **Graduated Cylinders:** 10, 50, 100, 250 mL
- 5.2.6 **Pasteur Pipettes:** 22 cm, disposable
- 5.2.7 **Glass Column:** Minimum 1 L capacity, Teflon stopcock, for solvent washing of silica, sodium sulphate, and glass wool
- 5.2.8 **Cleanup Columns:** Acid/Base, Alumina
- 5.2.9 **Alumina Conditioning Column**
- 5.2.10 **Measuring Pipettes:** 5.0 mL and 10.0 mL, graduated at 0.1 mL intervals, for preparing PCDD/PCDF standard mixtures
- 5.2.11 **Sample Extract Vials:** 1 mL capacity, internally-tapered, screw cap vials with Teflon-faced septa
- 5.2.12 **Vials:** Assorted capacities from 1.5 to 40 mL, amber glass, screw cap with Teflon-faced septa

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5.3 Reagents

- 5.3.1 Standards:** Certified native PCDD/PCDF standard solutions, carbon-13-labeled standards, window defining mixtures and column performance mixtures are available from Cambridge Isotope Laboratories, Woburn, MA and Wellington Laboratories, Guelph, Ontario. Refer to SOP 3.09/*.*S for preparation, use and storage of standard solutions.
- 5.3.2 Solvents:** All solvents are distilled-in-glass quality. Those required include hexane, toluene, cyclohexane, dichloromethane and acetone.
- 5.3.3 Gases:** Ultra-high purity grade nitrogen and helium
- 5.3.4 Water:** An in-house supply of high purity distilled or deionized water is used (Millipore Milli-Q Water System or equivalent system using a carbon filtration stage).
- 5.3.5 Others:** Silica (100 to 200 mesh) and basic alumina (AG 10, 100 to 200 mesh) are commercially available. AX-21 carbon is available from Anderson Development Company, Adrian, MI. All other reagents, including sulphuric acid, sodium hydroxide, silver nitrate, and sodium sulphate are A.C.S. reagent grade or better.
- 5.3.6** Prepared reagents have an expiry date of 90 days from the date of preparation except for silver nitrate which is 30 days (refer to SOP 3.13/*.*S).

6. SAMPLE REQUIREMENTS

6.1 Sample Handling and Custody

Upon arrival at the laboratory, samples must be inspected immediately for their physical condition and to ensure proper labelling. Typically the PUF and associated filter are received wrapped in foil and enclosed in a polyethylene bag. Inform the client of any potential problem concerning the integrity of samples. After logging and labelling with laboratory code numbers, samples should be processed within six months. **Any sample-tracking report sheets submitted with samples are completed and signed by authorized lab personnel and retained for auditing. The laboratory's analysis-tracking documents must also be available for auditing.**

Samples are stored in the freezer below -10°C from the time of receipt until extraction.

7. PROCEDURE

7.1 Glassware and Material Preparation

7.1.1 Glassware

All reusable glassware must be scrupulously cleaned within 24 hours

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of use. Glassware is sequentially rinsed with the last solvent used, followed by hexane and acetone. This is followed by washing with hot detergent solution and sequential rinsing with hot water, deionized water, and three portions each of acetone, hexane, and dichloromethane. For severely contaminated glassware, treatment in an ultrasonic bath filled with detergent solution is often beneficial. If a brush is used to scrub glassware, great care must be taken to ensure that glass surfaces are not scratched. Glassware is either air-dried or dried in an oven, and then stored in a contaminant-free area.

A glassware proofing sample is taken before actual test samples are processed. Each piece of glassware to be used with test samples, including Soxhlet bodies and condensers, flasks, funnels, columns, vials and rotary evaporators, must be rinsed with three portions each of acetone and dichloromethane. The final rinse of each piece of glassware is combined into one sample, which is archived. This combined rinse could be spiked with surrogates, cleaned up (optional) and analyzed by GC/MS to determine potential interferents and any amounts of PCDD/PCDF that may be present.

7.1.2 Glass Wool

Compress a quantity of glass wool into a large glass column (1 L capacity or larger) and wash sequentially with hexane and dichloromethane. The volume of solvent used for each wash should be twice the estimated volume of glass wool in the column. Transfer the washed glass wool into a large beaker. Loosely cover the mouth of the beaker with hexane and dichloromethane-rinsed aluminum foil, allow the glass wool to air dry in a fume hood, and then condition overnight at approx. 225°C in a vented oven. Store in a clean, wide-mouth, glass-stoppered bottle.

7.1.3 Sodium Sulphate

Wash the granular, anhydrous sodium sulphate in the same column used for preparing glass wool. Sequentially wash the sodium sulphate twice with hexane and twice with dichloromethane. The volume of solvent used for each washing should be twice the estimated volume of sodium sulphate in the column. Transfer to a large beaker, cover the mouth loosely with solvent-rinsed aluminum foil, and oven dry at approx. 50°C for a minimum of one hour before conditioning overnight at approx. 225°C. Store in a desiccator in a clean, screw-capped bottle, dated and fitted with a Teflon-lined cap.

7.1.4 Silica

Transfer approximately 350 g of silica (enough silica for 35 cleanup

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columns) to the large glass column used for preparing glass wool and sodium sulphate. Sequentially wash with hexane and dichloromethane as previously described. Oven dry the silica at approx. 50°C for a minimum of one hour in a beaker loosely covered with solvent-rinsed aluminum foil, then condition at approx. 180°C for a minimum of four hours. Store the clean silica in a desiccator, in a clean, screw-capped glass bottle, dated and fitted with a Teflon-lined cap.

7.1.5 44% (w/w) H₂SO₄ on Silica

Add 78.6 g of concentrated H₂SO₄ in a stepwise manner (5 mL at a time), to 100 g of freshly-conditioned silica in a 500-mL glass-stoppered Erlenmeyer flask. After each addition, shake the flask vigorously to remove all clumps. Store in the stoppered flask and labelled with the preparation date. This amount of material is sufficient for 40 cleanup columns. Preparation of larger batches is not recommended. (**Caution:** This material has all the properties of concentrated H₂SO₄. Handle with care).

7.1.6 33% (w/w) of 1 M NaOH on Silica

Add 24.6 g of a 1 M NaOH solution, in a stepwise manner, to 50 g of freshly-conditioned silica in a glass-stoppered Erlenmeyer flask. After each addition, shake the flask to remove all clumps. Store in a screw-capped bottle, dated and fitted with a Teflon-lined cap.

7.1.7 10% (w/w) AgNO₃ on Silica

Dissolve 5.6 g of silver nitrate in 21.5 mL of deionized water. Add this solution, in a stepwise manner, to 50 g of freshly-conditioned silica in a glass-stoppered Erlenmeyer flask. Between additions, shake the flask until a uniformly-coated, free-flowing powder is produced. When all silver nitrate has been added, allow the material to stand for approximately 30 minutes, cover the mouth of the flask with solvent-rinsed aluminum foil, and place in an oven at approx. 30°C. Over a five-hour period, gradually raise the oven temperature to approx. 180°C, and continue to condition overnight at this temperature. Cool to room temperature and immediately transfer to an amber glass, screw-capped bottle, dated and fitted with a Teflon-lined cap. Minimize exposure of this material to light. Store in a desiccator until use.

7.1.8 5% AX-21 Carbon/Silica

Wash 7 g of AX-21 carbon powder by suspending in 100 mL of methanol, then vacuum filter through a glass fibre filter (Gelman A/E or equivalent) fitted in a Buchner funnel. Follow with two 100 mL methanol rinses and

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continue suction until methanol flow stops completely. Dry the washed AX-21 carbon in an oven for several hours at approx. 30°C and then maintain at approx. 130°C for a minimum of 72 hours.

Combine 5.0 g of prepared AX-21 carbon with 95 g of prepared silica gel in a wide-mouth bottle, dated and fitted with a Teflon-lined screw cap. Blend by shaking until a uniform colour is achieved. Activate the blended AX-21 carbon/silica at approx. 130°C for a minimum of 24 hours, then cap and store in a desiccator. Reactivation of the carbon/silica may be required after several weeks of storage.

7.1.9 Basic Alumina

Weigh out 2 to 3 g more alumina than is required (2.5 g/sample) for the number of samples to be batch-processed at one time. Add the alumina to the conditioning column and wash with dichloromethane then hexane. The volume of solvent used for each wash should be two to three times the estimated volume of alumina in the conditioning column. After draining, insert a pre-cleaned glass wool plug into the column to immobilize the alumina. Drain as much solvent as possible from the wet alumina by applying suction at the end of the column, then place the column in the tube furnace. Connect the glass-jointed end of the column to a cylinder of pre-purified nitrogen. With the furnace off, purge the alumina with nitrogen at 200 to 400 mL/min. for approximately 30 minutes. While maintaining the nitrogen purge, condition the alumina at approx. 350°C for a minimum of two hours. Conditioned alumina should be used immediately after removal from the tube furnace. Do not store for later use. (**Caution:** Hot glass.)

7.1.10 Field Supplies

The Polyurethane foam (PUF) plugs (8.5 cm diameter x 9 cm long) are cut in the Organic laboratory on a drill press fitted with a die. The density of the foam is 22.4 kg/m³ having a compression ratio of 1531. The PUF are pre-cleaned in the Organic laboratory following SOP 4.21/*.*/*S. Two PUFs are placed into stainless steel sleeves (7.5 cm diameter x 15 cm long) and forwarded to the Air Toxics Section for shipment to various sampling locations following SOP 3.19/*.*/*S.

7.2 Sample Preparation

Field samples consisting of polyurethane foam (PUF) and Teflon-coated glass fibre filters are prepared for ultimate mass spectrometric analysis through a series of comprehensive extraction and cleanup steps. These procedures are briefly described in the following sections. Sample processing of each set of samples is

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recorded on a copy of the 'Ultra Trace Lab PCDD/F Extraction and Cleanup Flowsheet' found at the back of the method. Before loading the samples confirm that the filter number matches the PUF number and the number stamped on the filter. If any discrepancies that could invalidate the sample are observed, contact the supervisor before proceeding. Use Ultra Trace Lab PCDD/F Extraction and Cleanup Flowsheet 1 for samples that only require analysis for PCDD/F and Ultra Trace Lab PCDD/F Extraction and Cleanup Flowsheet 2 for samples that are split for PCDD/F analysis and other analytes.

7.2.1 Extraction

7.2.1.1 The sample (PUF and filter) is first spiked with 100uL of surrogate solution containing 9 carbon -13-labelled, PCDD/PCDF congeners (2,3,7,8-substituted), at concentrations of 10-20 pg/μL (see Table 1). After 30 minutes of air drying, the sample is loaded into a soxhlet apparatus and extracted for 16 to 20 hours with toluene. The extract is then dried by passage through sodium sulphate followed by three 5 mL toluene rinses of the flask and the sodium sulphate. The extract is then concentrated to 2 mL by rotary evaporation at 72°C or lower. After adding 100 mL of hexane, the extract is concentrated again to 2 mL and is ready for sample cleanup.

7.2.1.2 **For samples that require analysis for both PAH and PCDD/PCDF:** Spike the sample with twice the amount of the 9 ¹³C₁₂ -labelled PCDD/F compounds for a total of 2-4 ng. In addition, the sample is spiked with 1000 ng each of 17 isotopically-labelled PAH compounds. The sample is extracted with a cyclohexane/toluene (80/20) mixture instead of toluene.

Then the sample is dried by passage through sodium sulphate and concentrated to approximately 3 mL. The solvent is exchanged to cyclohexane by adding 100 mL of cyclohexane and concentrating to 3-5 mL. Transfer the extract into a 12 or 15 mL centrifuge tube with 3 cyclohexane rinses of the flask and make up to a maximum final volume of 12.0 mL. The sample extract is mixed well then split by removing 6.0 mL of the extract for PAH analysis (see Method 3.03/*.*/*M).

The extract for PCDD/PCDF analysis is then processed following the cleanup procedure that follows.

7.2.2 Cleanup

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Cleanup columns required in this method are described below. A column control sample containing each of the 17 PCDD/F natives, is processed with each set of samples. This control is analysed using GC/ECD and the results are entered onto the column control chart in the laboratory.

7.2.2.1 The first Acid/Base column contains layers of sodium sulphate, silica, 44% (w/w) sulphuric acid on silica, 33% (w/w) of 1M sodium hydroxide on silica and 10% (w/w) silver nitrate on silica. By chemical reaction, this column removes easily oxidized organics and sulphurous compounds from the raw extract. The prepared Acid/Base column is first washed with 30 mL of 3 % dichloromethane (DCM) in hexane. The concentrated raw extract is then transferred onto the column followed by three sequential rinses of the sample flask using 3% DCM. The solvent is eluted from the column to bed dry and then 50 mL of 3% DCM in hexane is added. Column eluent is collected and concentrated to 2mL by rotary evaporation. Finally, it is exchanged to hexane by adding 100mL of hexane and repeating the concentration step.

7.2.2.2 The second column is a basic alumina column which can isolate PCDD/PCDF from most potential interferents by using absorbent column chromatography. After pre-washing the activated basic alumina column with 15 mL of hexane, the concentrated extract from the Acid/Base column is transferred onto the basic alumina column, followed by three 5 mL hexane rinsings of the sample flask. An additional 30 mL of hexane is added to the column. Then, just as the solvent drains to the top of the sodium sulphate layer, 20 mL of 2% DCM in hexane is added.

7.2.2.3 The basic alumina column eluent, collected to this point, is labelled as fraction 2 and archived. When the solvent level in the column again just reaches the top of the sodium sulphate layer, 30 mL of 50% DCM in hexane is added and allowed to drain completely to a new flask. This fraction of eluent (fraction 3), containing the PCDD/PCDF, is concentrated to 2 mL and exchanged to hexane by adding 100 mL of hexane to the sample flask and repeating the concentration step, if required. Cleanup procedures may be repeated once more on a second alumina column. Fractions 2 from the alumina column(s) may be assessed for PCDD/PCDF if poor surrogate recovery is observed. Fraction 3, containing the PCDD/PCDF is transferred to a 1 mL conical vial and concentrated to a small volume under a gentle stream of pre-purified nitrogen. Prior to GC/MS analysis, the sample is blown down just to dryness. An exact volume of 20 µL of the recovery standard solution, containing 50 pg/µL each of ¹³C₁₂-

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1,2,3,4-TCDD and -1,2,3,7,8,9-H6CDD in toluene, is added to the sample vial. The capped sample vial is then sonicated in an ultrasonic bath for ten minute before GC/MS analysis.

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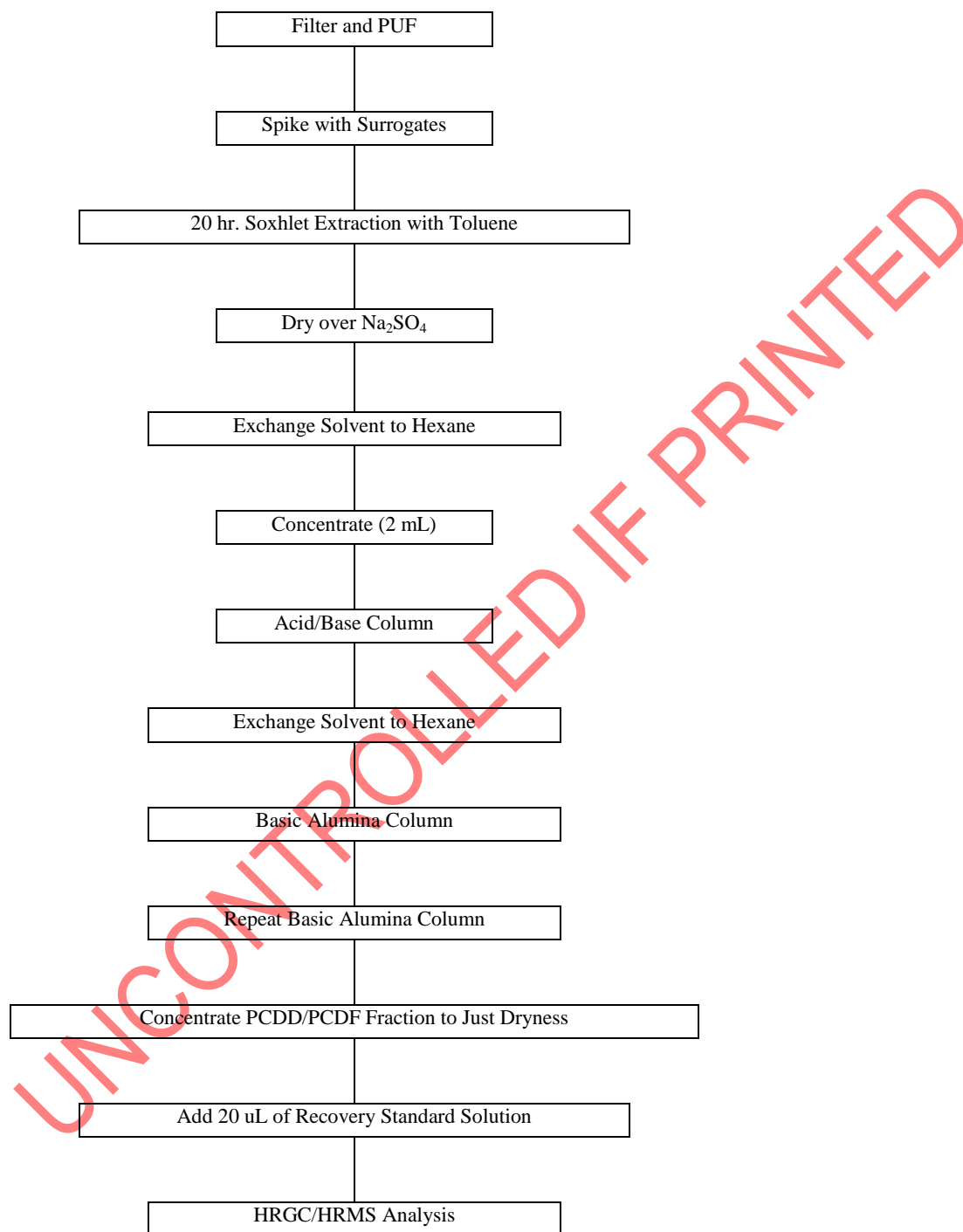


Figure 1 Extraction, Cleanup and Analysis Schematic

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7.3 Instrumental Analysis

Instrumental analysis of the prepared sample extracts is carried out using a high resolution gas chromatograph (HRGC) coupled to a high resolution mass spectrometer (HRMS). The gas chromatograph is equipped with a capillary column and is directly coupled to the mass spectrometer. The mass spectrometer is a double focusing unit supported by a dedicated computerized data system (DS). Sample analysis and data collection is carried out with the spectrometer operating in electron impact (EI) mode under the selected ion monitoring (SIM) technique. This sophisticated analytical device (HRGC/HRMS/DS) is capable of measuring extremely small quantities (femtogram amounts) of the target PCDD/PCDF analytes in the cleaned sample extracts.

7.3.1 Gas chromatographic parameters

A commercially-available Window Defining Mixture (WDM), which contains the earliest and latest eluting congeners in each PCDD/PCDF homologous group, is used to establish optimal gas chromatographic parameters and precise retention time windows for the time-sequenced SIM mode analysis of PCDD/PCDFs.

The order of elution on a 60 meter DB-5 or equivalent column is such that five retention time windows can be defined, corresponding to the five levels of chlorine substitution (4 CI to 8 CI) without any overlap.

This mixture should be analyzed at regular intervals for verification of retention time windows. The WDM must be analyzed following any deliberate change in GC parameters; following any condition or upset, which requires disconnecting the GC column; and following replacement of the carrier gas cylinder.

To achieve acceptable gas chromatographic separation one can use the following set of experimental parameters as a starting point:

- Injector temperature: 280°C for split-splitless or ambient for on-column;
- Interface temperature: 290°C;
 - Temperature program: 1) Initial temperature at 130°C for split-splitless or 70°C for on-column and hold for 1 minute; 2) 100°C (or 70°C) to 200°C @ 35°C min⁻¹ and hold for 8 min; 3) 200°C to 280°C @ 4°Cmin⁻¹ and hold for 15 min; 4) 280°C to 300°C @ 10°Cmin⁻¹ and hold for 5 min.

7.3.2 Isomer-Specific Separation

Using helium as carrier gas with an appropriate column velocity and oven temperature program as defined above, a 60-meter DB-5 or equivalent

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column (0.25 mm ID, 0.25 um film thickness) can adequately separate 2,3,7,8-TCDD from neighbouring isomers 1,2,3,7-/1,2,3,8- and 1,2,3,9-TCDD. In addition, this column easily separates to baseline both hepta-CDD isomers (1,2,3,4,6,7,8- and 1,2,3,4,6,7,9-) and the four hepta-CDF isomers (1,2,3,4,6,7,8-, 1,2,3,4,6,7,9-, 1,2,3,4,6,8,9- and 1,2,3,4,7,8,9-). However, on a DB-5 column 2,3,7,8-TCDF cannot be resolved from its neighbouring isomers (1,2,4,9-, 2,3,4,8- and 2,3,4,6-). In order to quantify 2,3,7,8-TCDF accurately, use of an additional column (DB-225) is required. On a 30 m DB -225 column 2,3,7,8-TCDF can be resolved from its neighbouring 2,3,4,7- and 1,2,3,9-isomers.

For 2,3,7,8-TCDD and 2,3,7,8-TCDF analysis, a column performance test mixture, containing the target analyte and its neighbouring isomers at equal concentration, should be analyzed daily to confirm acceptable chromatographic separation. It is recommended that these isomers be included in the Window Defining Mixture. The peak/valley criterion between 2,3,7,8-TCDD and its neighbouring isomers should be equal to or less than 25% of the 2,3,7,8-TCDD peak height. The corresponding peak/valley criterion for 2,3,7,8-TCDF is 30% or less. Results for these analytes must be flagged if these criteria cannot be met in order to acknowledge the possibility of co-eluting isomers.

7.3.3 Mass spectrometric Parameters

The mass spectrometer is operated in the electron impact mode with the ionization energy kept constant at a value ranging between 28 and 40 eV. The mass spectrometer must be tuned using PKF, to achieve a resolution of at least 5,000 (10% valley definition). A lock-mass is assigned and monitored for each homologue window and its intensity must not vary by more than 10% throughout its respective window.

Sample components are identified as PCDD/PCDFs if their GC/MS data satisfy the following criteria:

- (a) Peak responses for each of the two selected molecular cluster ions must be at least three times the background noise level;
- (b) Chlorine isotope ratio for the two molecular cluster ions must be within $\pm 15\%$ of the correct ratio;
- (c) Peak maxima for both quantitation ions must coincide within two seconds;
- (d) Response of the chlorinated diphenyl ether ion must be absent or insignificant relative to analyte peaks for PCDF determination;
- (e) The relative retention time for 2,3,7,8-substituted congeners must agree with the calibration standards within 0.2%.

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7.3.4 Calibration

Calibration standards should contain:

- (a) all seventeen 2,3,7,8-substituted PCDD/PCDF congeners;
- (b) the set of carbon -13-labeled congeners added to samples as surrogates;
- (c) the labelled congeners $^{13}\text{C}_{12}$ -1,2,3,4-TCD and $^{13}\text{C}_{12}$ -1,2,3,7,8,9-HCDD which are added to sample extracts as (i) recovery standards to calculate surrogate recoveries; and (ii) reference peaks for assigning sample peak identities on the bases of relative retention times.

The linear calibration range for each analyte should be established by running a series of five multi-point calibration standards, in triplicate, prior to initial sample analysis. The recommended concentration levels for HRMS calibration standard solutions are presented in Table 1.

An Internal Standard method is recommended for quantitation of sample data. This method relies upon consistent linearity of MS response over the intervals between multi-point calibration checks and is easily integrated into automated routines for data quantitation (see Reference 3 for detailed procedures).

Internal Standard quantitation is based on the use of Relative Response Factors (RRF). A RRF is the ratio of analyte response factor (area counts per unit mass) to the response factor of the corresponding labelled surrogate. These RRFs remain unchanged over the range of concentration for which MS response is linear. Using these RRFs, along with surrogate responses from the sample run, concentrations of PCDD/PCDFs can be calculated directly, without the necessity of calculating surrogate recoveries. Recoveries should nevertheless be calculated separately and reported, as these values serve to indicate the overall quality of the concentration data being reported.

For homologues represented by more than one isomer in the calibration standard solutions, the “homologue-average” RRF is used to quantify all target analytes that are not 2,3,7,8-substituted congeners.

The calibration data from which RRFs are calculated must be of good and definable quality. For initial calibration, RRFs are calculated by analyzing the series of four calibration standard solutions, the compositions of which are given in **Table 1**. The Relative Standard Deviation (RSD) of the four

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RRFs must be less than 20% for each native analyte. If this criterion is met, then the calibration is successful, and the mean RRF values are used for quantification of subsequent target analyte data. This value effectively corresponds to a response linearity criterion. The established calibration curve must be verified by analyzing the calibration verification standard (CAL 1.0 or CAL 5.0) at least once during every 12-hour period in which sample analysis occurs. The RRF values from the verification standards must be within 20 % of the values obtained from the initial calibration.

Calibration standard CAL 1.0 or CAL 5.0 is used to assess instrumental detection limits. Minimum acceptable detection limits (i.e., S/N ≥ 15) at 10,000 resolution are 0.2 and 0.8 pg for TCDD and OCDD, respectively. If these levels cannot be detected, then instrument parameters are to be adjusted accordingly, while maintaining acceptable resolution.

8. METHOD VALIDATION AND DETECTION LIMIT

The Sample Detection Limit (SDL) for PCDD/PCDF analysis is defined as the minimum concentration of analyte in the sample extract that will produce a clearly defined peak with an acceptable chlorine isotope ratio, and with a signal-to-noise ratio equal 3 -to- 1. Variables such as sample matrix, sample size, final extract volume, injection volume used in analysis, surrogate recovery, GC column performance, chromatographic parameters, electronic noise and instrument sensitivity can directly influence the SDL.

Reported SDL must be corrected for surrogate recovery and is calculated as follows:

$$SDL = \frac{3 * N * A/H * Q_s}{A_s * RRF_n * V}$$

where:

N= estimated sum of electronic and chemical (matrix) noise expressed in peak height;

A/H= area/height ratio for the surrogate standard peak;

Q_s= mass of the surrogate standard added (pg);

A_s= surrogate peak area;

RRF_n= relative response factor (native standard to surrogate standard);

V= sample size (m³);

Sample Detection Limits should be determined on a homologue and sample by sample basis. In cases where a quantitation ion chromatogram contains at least one peak that is sufficiently large to prevent observation of noise, the ion chromatogram should be re-scaled to allow for measurement of noise amplitude.

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This current method has been used by the Analysis and Air Quality Division for approximately the past 15 years. During this time there have been some changes in the methodology such as changing the analytical tool from low resolution mass spectroscopy to high resolution mass spectroscopy. The sample detection limit is currently 1 to 4 fg/m³ for a typical 800 m³ sample. (This has been based on the results of hundreds of samples analyzed over the years).

This method is fit for its intended use.

9. ESTIMATION OF UNCERTAINTY OF MEASUREMENT

Refer to SOP 2.10/*./S for the detailed estimation approach. The uncertainty sources of the method and the QC data used for uncertainty estimation are listed in Appendix A. The estimated uncertainty of the method above the quantitation limit is presented in Appendix B. Uncertainty was estimated using method control samples consisting of SRM 1649a, Urban Dust.

10. QUALITY ASSURANCE

Key elements of an acceptable quality assurance program that must be followed are summarized below.

- 10.1 Prior to the processing of actual test samples, all pre-cleaned glassware (including Soxhlet apparatus, concentrators, columns, flasks, and vials) are rinsed with acetone and dichloromethane. Rinses are combined and may be processed in the same manner as test samples. Contamination levels of individual 2,3,7,8 substituted tetra, penta, hexa, hepta and octa dioxin and furan congeners must not exceed 5,10,10,15, and 50 pg respectively. All glassware is washed again with appropriate solvents and a second proof rinse sample is collected for analysis, if these criteria are not met.
- 10.2 A method blank sample, consisting of clean sampling media spiked with surrogates, is processed with each batch of 10 test samples to demonstrate freedom from PCDD/PCDF cross-contamination.
- 10.3 Prior to Soxhlet extraction, each sample is spiked with a mixture of 9 isotopically-labelled surrogates to assess the degree of analyte loss during sample work-up.
- 10.4 A control sample, consisting of a standard reference material (SRM 1649a, Urban Dust), is processed and analyzed along with each batch of 20 routine samples. The analyte recoveries achieved gives an indication of the accuracy of the analyses.
- 10.5 A known concentration of ¹³C₁₂-1,2,3,4-TCDD and ¹³C₁₂-1,2,3,7,8,9-H6CDD are added to each sample extract immediately prior to GC/MS analysis. These two compounds serve as retention time references for labelled surrogates and as the basis for calculation of surrogate recoveries.

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- 10.6 A Window Defining Mixture, containing the first and last eluting isomer within each congener group of PCDD/PCDFs, is used daily to define retention time window for Selected Ion Monitoring of individual congeners.
- 10.7 Prior to sample analysis, calibration curves are constructed to verify linearity of MS response for all congeners over the concentration range of 0.25 to 400 pg/μL for PCDD/PCDF.
- 10.8 The established calibrations are verified by analysing the calibration verification standard (CAL 1.0 or CAL 5.0 at least once during every 12 hour period in which sample analysis occurs. The calculated concentration of each analyte must be within $\pm 20\%$ of the design value. Recalibration is required if this criterion is not met.
- 10.9 As a check on accuracy, NIST Reference Material 1614 (2,3,7,8-TCDD in solution) or Reference Material EN-1948 from Wellington is periodically analyzed as a sample. The values obtained must be within 20 % of the certified values. This aspect of the QA program should be enhanced by the use of other reference materials, as they become commercially available.
- 10.10 For 2,3,7,8-TCDD/TCDF analysis, acceptable chromatographic separation between these target analytes and their closest neighbouring isomers must be confirmed daily. This solution may be combined with the Window Defining Mixture.
- 10.11 Reported sample results are fully documented in terms of detection limits, surrogate recoveries, and number of isomer peaks contributing to reported homologue concentrations. All QA/QC documents and raw GC/MS data must be available for auditing.
- 10.12 The pipette ID's for all electronic pipettes used are recorded.

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Table 1 Composition of PCDD/PCDF Calibration Solution for HRMS

	ng/ml				
	CAL 0.1 ^a	CAL 1.0 ^b	CAL 2.5	CAL 5.0	CAL 25.0
2,3,7,8 – TCDD	0.086	0.89	2.30	4.9	27.4
2,3,7,8 – TCDF	0.086	0.89	2.30	4.9	27.4
1,2,3,7,8-P ₅ CDD	0.173	1.8	4.7	10	54.25
1,2,3,7,8-P ₅ CDF	0.173	1.8	4.7	10	54.25
2,3,4,7,8-P ₅ CDF	0.173	1.8	4.7	10	54.25
1,2,3,4,7,8-H ₆ CDD	0.173	1.8	4.7	10	54.25
1,2,3,6,7,8-H ₆ CDD	0.173	1.8	4.7	10	54.25
1,2,3,7,8,9-H ₆ CDD	0.173	1.8	4.7	10	54.25
1,2,3,4,7,8-H ₆ CDF	0.173	1.8	4.7	10	54.25
1,2,3,6,7,8-H ₆ CDF	0.173	1.8	4.7	10	54.25
2,3,4,6,7,8-H ₆ CDF	0.173	1.8	4.7	10	54.25
1,2,3,7,8,9-H ₆ CDF	0.173	1.8	4.7	10	54.25
1,2,3,4,6,7,8-H ₇ CDD	0.33	3.5	9.3	20.15	111.5
1,2,3,4,6,7,8-H ₇ CDF	0.33	3.5	9.3	20.15	111.5
1,2,3,4,7,8,9-H ₇ CDF	0.33	3.5	9.3	20.15	111.5
OCDF	0.33	3.5	9.3	20.15	111.5
OCDD	0.33	3.5	9.3	20.15	111.5
Surrogates					
¹³ C ₁₂ -2,3,7,8-TCDD	50	50	50	50	50
¹³ C ₁₂ -2,3,7,8-TCDF	50	50	50	50	50
¹³ C ₁₂ -1,2,3,7,8-P ₅ CDD	50	50	50	50	50
¹³ C ₁₂ -1,2,3,7,8-P ₅ CDF	50	50	50	50	50
¹³ C ₁₂ -1,2,3,6,7,8-H ₆ CDD	50	50	50	50	50
¹³ C ₁₂ -1,2,3,4,7,8-H ₆ CDF	50	50	50	50	50
¹³ C ₁₂ -1,2,3,4,6,7,8-H ₇ CDD	50	50	50	50	50
¹³ C ₁₂ -1,2,3,4,6,7,8-H ₇ CDF	50	50	50	50	50
¹³ C ₁₂ -OCDD	100	100	100	100	100
Recovery Standards					
¹³ C ₁₂ -1,2,3,4-TCDD ^c	50	50	50	50	50
¹³ C ₁₂ -1,2,3,7,8,9-H ₆ CDD ^d	50	50	50	50	50

^a used to assess detection limits; ^b used daily to verify calibration; ^c retention time reference and recovery standard for tetra- and penta-CDD/CDF; ^d retention time reference and recovery standard for hexa-, hepta- and octa-CDD/CDF.

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11. APPLICABLE SOPs

- 4.04/*./S “Glassware”
- 4.21/*./S “Preparation of Polyurethane Foam Plugs (PUF) for Ambient Air Sampling”
- 3.09/*./S “The Preparation, Storage and Use of Standard Solutions”
- 3.13/*./S “Reagents”
- 3.19/*./S “Procedures for Preparing and Receiving PAH Canisters”

12. REVISIONS

- March 2006: Section 7.1.1: State that glassware proof is archived and could be used to assess contamination
 Section 7.2: Add the use of Flowsheets to monitor the sample prep
 Section 7.2.2: Add the use of column control samples and control charting with each set of samples
 Section 7.3.4: Add requirement that CS-1 have s/n = 15
 Section 10.9: Add SRM 1613
 Attach Flowsheet to back of method
- May 2008: Lead Reviewers: Jennifer Verner and Alison Walkey
 Replaced Table 1
 Section 4: Added “or clean buttoned labcoats”
 Section 12: Added Oct. 1997 and Nov. 1997
 Section 12: Deleted author from August 1999, and added to October 1997
- Dec. 2009: Lead Reviewers: Benoit Thibert, Alison Walkey and Jennifer Verner
 Replace value in Table 1
 Section 7.3.1 change the GC temperature program
 Section 7 Added “or equivalent”
 Section 10.9 Deleted NIST 1613, and added EN-1948 from Wellington
 Section 7.3 Deleted CS2, and added CAL 1.0 or CAL 5.0
 Section 7.3 Deleted 8, and added 12
 Section 10.8 Deleted CS2, and added CAL 1.0 or CAL 5.0
 Section 10.8 Deleted 8, and added 12
 Modified section 7.2 to include the paragraph regarding checking that PUF and filter numbers match, etc.
 Section 7.2.1 Changed 20 hrs to 16 to 20 hours
 Section 7.2.2.2 Corrected spelling of alumina
 Deleted Revisions history between Oct. 1997 and Oct. 2005
- Aug. 2010 Lead Reviewer: Benoit Thibert
 Replaced value in Table 1
- May 2011 Lead Reviewer: Michael Lister

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- Section 3 Added extra rinsing procedure
- Section 7.1: Added extra rinsing procedure and preparation dates for reagents where applicable, made changes to field supplies section to reflect new procedures.
- Section 7.2: Changed rinse volume to 5 mL from 50 mL, Added maximum volume to split procedure for PAH's. Changed flow chart order to reflect actual procedure.
- Section 10: Changed solvents to reflect current practice, added "may be" in reference to solvent proofs.
- Oct. 2011 Lead Reviewer: Alison Walkey
 - Added Section 5.3.6
 - Added Section 10.12
 - Added reference SOP to Section 11
 - Deleted reference SOP's 4.16, 4.17, and 4.19 from Section 11
 - Analyse window defining mixture daily
 - Set acceptance limit values of 20 % for Wellington EN 1938 reference standard
- Jan. 2013 Lead Reviewer: May Siu
 - Section 7: Added "approx." to oven temperature
 - Section 7.1.3: Corrected spelling mistake 'desiccator'
 - Section 7.2: Added 'Teflon-coated' to glass fiber filter

12. REFERENCES

"Environmental Screening Self-Assessment/High Hazard Facility", Chemistry Division, RRETC, Technology Development Branch, Environment Canada, June, 1982.

"A Method for the Analysis of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans in Ambient Air Samples", Chemistry Division, Ref# CD 890201, RRETC, Technology Development Branch, Environment Canada, Feb. 1989.

"Reference Method for the Determination of PCDDs and PCDFs in Pulp and Paper Mill Effluents" Report EPS 1/RM/19, Environment Canada, February 1992.

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Lead Reviewer: Alison Walkey
Title: Chemical Technologist

Date:

Approved by: Gary Poole
Title: Organic Laboratory Supervisor

Date:

**** Appendices follow starting on the next page ****

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APPENDIX A

Dioxins/Furans in Ambient Air: 3.02/3.6/M)

Uncertainty Estimation – Major Sources

Measurement Steps	Uncertainty Sources	QC Data Used
Matrix Sample	Sample preparation Spike preparation Instrument response Preparation method Matrix interference Purity	Control Samples, consisting of SRM 1649a Urban Dust
Standard Preparation	Bias	
Sample size	Mass, Volume	

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APPENDIX B

Reported Uncertainty, November, 2005 – Summary

Congener	<i>n</i>	Median (ng/g)	Average (ng/g)	SD	RSD, %	U	"t" value
2378-TCDD	20	0.008	0.008	0.001	14.426	30.1	2.086
12378-P5CDD	23	0.085	0.088	0.011	12.203	25.1	2.060
123478-H6CDD	23	0.242	0.238	0.016	6.728	13.9	2.060
123678-H6CDD	23	0.598	0.608	0.059	9.706	20.0	2.060
123789-H6CDD	19	0.545	0.576	0.112	19.465	40.7	2.093
1234678-H7CDD	23	17.914	17.742	1.200	6.762	13.9	2.060
OCDD	23	196.130	196.088	16.428	8.378	17.3	2.060
2378-TCDF	22	0.124	0.126	0.015	11.619	23.9	2.060
12378-P5CDF	23	0.082	0.086	0.016	18.674	38.5	2.060
23478-P5CDF	23	0.305	0.304	0.033	10.877	22.4	2.060
123478-H6CDF	23	1.038	1.017	0.137	13.454	27.7	2.060
123678-H6CDF	23	0.392	0.392	0.020	5.116	10.5	2.060
234678-H6CDF	23	0.629	0.654	0.094	14.349	29.6	2.060
123789-H6CDF	21	0.041	0.041	0.005	11.611	24.2	2.086
1234678-H7CDF	23	3.604	3.585	0.213	5.938	12.2	2.060
1234789-H7CDF	23	0.486	0.484	0.043	8.791	18.1	2.060
OCDF	22	6.314	6.239	0.958	15.352	31.6	2.060
TOTAL TCDD	23	0.129	0.128	0.027	21.341	44.0	2.060
TOTAL P5CDD	23	0.874	0.864	0.109	12.566	25.9	2.060
TOTAL H6CDD	23	6.588	6.515	0.613	9.405	19.4	2.060
TOTAL H7CDD	23	32.923	32.156	2.495	7.761	16.0	2.060
TOTAL TCDF	23	238.499	237.274	19.610	8.265	17.0	2.060
TOTAL P5CDF	23	0.731	0.699	0.198	28.292	58.3	2.060
TOTAL H6CDF	23	1.639	1.643	0.185	11.270	23.2	2.060
TOTAL H7CDF	23	4.644	4.566	0.449	9.826	20.2	2.060
TOTAL DIOXINS	23	8.823	8.830	0.607	6.870	14.2	2.060
TOTAL FURANS	23	22.325	21.870	2.375	10.861	22.4	2.060

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APPENDIX C Form 3.02M/F1-ver*.*

Tracking sheet #:

OTHER SPLIT

CS#:

ULTRA TRACE LAB PRE-CLEANUP DATA SHEET PBDE/CoPCB/DX

Reference Method 3.02/x.x/M

Project name:

Batch #:

Targets compounds:

Glassware: HL or LL

LIMS CODE(S):

SPIKE (Surrogate(s)-Volume-Date-Initials)

Pipette ID:

SEQUENCE COMPLETE

_____	_____	Extraction (Type-Solvent-Date-Initials)
_____	_____	
_____	_____	Pass through Na ₂ SO ₄
_____	_____	Rotavap Exchange to Hexane
_____	_____	Acid/Base Column
_____	_____	Rotavap Exchange to Hexane
_____	_____	Split for _____ analysis
_____	_____	Update LIMS (Extract & _____EXT)-Print Tracking Sheet
_____	_____	Deliver _____ Split to _____ Lab (Date-Time-Initials)
_____	_____	Alumina Column
_____	_____	2nd Clean-Up
		F1 (PCB or HCB)
_____	_____	Archive
_____	_____	Concentrate to 500 mL
_____	_____	Add recovery standard
_____	_____	Pipette ID:
_____	_____	Update LIMS (PCBEXT or OCEXT)-Print Tracking Sheet
		F2 (PCDD/F, PBDE)
_____	_____	Concentrate to dryness in Reacti-vials
_____	_____	Add recovery standard
_____	_____	Pipette ID:
_____	_____	Update LIMS (DIOEXT)-Print Tracking Sheet

SUBMISSION DATE:

Remarks:

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APPENDIX D Form 3.02M/F2-ver*.*

Tracking sheet #:

NO SPLIT

ULTRA TRACE LAB PCDD/F EXTRACTION and CLEANUP FLOWSHEET 1

Project name:
Targets compounds:

Batch #:
Glassware: HL or LL

LIMS CODE(S):

SPIKE (Surrogate(s)-Volume-Date-Initials)

Pipette ID:

<u>SEQUENCE</u>	<u>COMPLETE</u>	
_____	_____	Extraction (Type-Solvent-Date-Initials)
_____	_____	
_____	_____	Pass through Na2SO4
_____	_____	Rotavap Exchange to Hexane
_____	_____	Update LIMS (Extract)
_____	_____	Acid/Base Column
_____	_____	Rotavap Exchange to Hexane
_____	_____	Alumina Column
_____	_____	2nd Clean-Up
_____	_____	F2
_____	_____	Archive
_____	_____	F3 (PCDD/F)
_____	_____	Concentrate to dryness in Reacti-vials
_____	_____	Add recovery standard
_____	_____	Update LIMS (DIOEXT)-Print Tracking Sheet

SUBMISSION DATE:

Remarks:

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APPENDIX E Form 3.02M/F2-ver*.*

Tracking sheet #: _____ PAH SPLIT

ULTRA TRACE LAB EXTRACTION and CLEANUP FLOWSHEET 2

Project name: _____ Batch #: _____
 Targets compounds: _____ Glassware: HL or LL

LIMS CODE(S): _____

SPIKE (Surrogate(s)-Volume-Date-Initials)

Pipette ID: _____

<u>SEQUENCE</u>	<u>COMPLETE</u>	
_____	_____	Extraction (Type-Solvent-Date-Initials)
_____	_____	
_____	_____	Pass through Na2SO4
_____	_____	Rotavap Exchange to Cyclohexane
_____	_____	Split for PAH analysis Organic lab
_____	_____	Update LIMS (Extract & PAHEXT)-Print Tracking Sheet
_____	_____	Deliver PAH Split to Organic Lab (Date-Time-Initials)
_____	_____	Acid/Base Column
_____	_____	Rotavap Exchange to Hexane
_____	_____	Alumina Column
_____	_____	2nd Clean-Up
_____	_____	F2
_____	_____	Archive
_____	_____	F3 (PCDD/F)
_____	_____	Concentrate to dryness in Reacti-vials
_____	_____	Add recovery standard
_____	_____	Update LIMS (DIOEXT)-Print Tracking Sheet

SUBMISSION DATE: _____

Remarks: _____