METHOD 513. DETERMINATION OF 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN IN DRINKING WATER BY GAS CHROMATOGRAPHY WITH HIGH RESOLUTION MASS SPECTROMETRY

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This method is taken from the SW-846 Methods Manual, Method 8280, and adapted to drinking water.

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METHOD 513

DETERMINATION OF 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN IN DRINKING WATER BY GAS CHROMATOGRAPHY WITH HIGH-RESOLUTION MASS SPECTROMETRY

1. SCOPE AND APPLICATION

1.1 This method provides procedures for identification and measurement of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD, CASRN 1746-01-6) at concentrations of 20 pg/L to 2 ng/L in water sample extracts. The minimum measurable concentration will vary among samples, depending on the presence or absence of interfering compounds in a particular sample.

1.2 A water sample may contain floating, suspended, and settled particulate matter, which should not be removed by filtering before extraction. The estimated solubility of 2,3,7,8-TCDD in water is <50 ng/L (1), but larger measured concentrations can be caused by TCDD associated with particulates.

1.3 Because 2,3,7,8-TCDD may be extremely toxic, safety procedures described in Section 5 should be followed to prevent exposure of laboratory personnel to materials containing this compound.

2. SUMMARY OF METHOD

2.1 An entire 1-L water sample is transferred to a separatory funnel, and two isotopically-labeled analyte analogs, $^{37}Cl_4$-2,3,7,8-TCDD (surrogate compound, SC) and $^{13}C_{12}$-2,3,7,8-TCDD (internal standard, IS), are added to the water. The sample container is rinsed with methylene chloride, which is then added to the water sample. The water sample is extracted sequentially with three 60-mL portions of methylene chloride. AN optional liquid-solid extraction procedure using Empore disk technology is also described in this method. When using this option, all surrogate compounds and internal standards and other solutions are added just as in the liquid-liquid extraction procedure.The combined extract is subjected to column chromatographic procedures to remove sample components that may interfere with detection and measurement of TCDD. A 10-μL aliquot of a solution containing $^{13}C_{12}$-1,2,3,4-TCDD, which is used as a recovery standard (RS), is added to the extract before concentration and analysis. The sample extract is concentrated to 10 μL, and a 1-μL or 2-μL aliquot is injected into a gas chromatograph (GC) equipped with a fused silica capillary column and interfaced with a high resolution mass spectrometer (MS). Selected characteristic ions are monitored with high resolution MS (10,000 resolving power). Identification of a sample component as TCDD is based on detection of two characteristic ions (m/z 320 and 322) in the molecular ion cluster, measurement of acceptable relative abundance of those two ions, and

relative to the IS, $^{13}C_{12}$-2,3,7,8-TCDD. Because the IS is a labeled analog of the analyte, the procedure presumes that IS losses during method procedures are equal to unlabeled TCDD losses. Therefore, each calculated sample TCDD concentration has been compensated for losses during sample preparation.

3. DEFINITIONS

3.1 Calibration limits -- the minimum (20 pg/L) and maximum (2 ng/L) concentration of 2,3,7,8-TCDD in solutions used to calibrate detector response. In some samples, <20 pg/L of 2,3,7,8-TCDD may be detected but measured concentrations will only be estimated concentrations. In other samples, interferences may prevent identification and measurement of 20 pg/L.

3.2 Concentration calibration solution -- a solution containing known amounts of the analyte (unlabeled 2,3,7,8-TCDD), the IS ($^{13}C_{12}$-2,3,7,8-TCDD), the SC ($^{37}Cl_4$-2,3,7,8-TCDD), and the RS ($^{13}C_{12}$-1,2,3,4-TCDD); it is used to determine instrument response to the analyte, SC, and RS relative to response to the IS.

3.3 Field blank -- a portion of reagent water that has been shipped to the sampling site and exposed to conditions that samples have experienced.

3.4 Internal standard (IS) -- $^{13}C_{12}$-2,3,7,8-TCDD, which is added to every sample and is present at the same concentration in every blank, quality control sample, and concentration calibration solution. It is added to the water sample before extraction and is used to measure the concentration of unlabeled TCDD.

3.5 Laboratory reagent blank -- a blank prepared in the laboratory by performing all analytical procedures except a 1-L aliquot of reagent water is extracted rather than a sample.

3.6 Performance check solution -- a solution containing a mixture of known amounts of selected standard compound; it is used to demonstrate continued acceptable GC/MS system performance.

3.7 Recovery standard (RS) -- A compound ($^{13}C_{12}$-1,2,3,4-TCDD) that is present in every calibration solution and is added to each extract just before analysis. It is used to measure the recovery of the internal standard.

3.8 Response factor (RF) -- response of the mass spectrometer to a known amount of analyte relative to a known amount of internal standard.

3.9 Signal-to-noise ratio (S/N) -- the ratio of the area of the analyte signal to the area of the random background signal; it is determined by integrating the signal for a characteristic ion in a region of the selected ion current profile where only random noise is observed and relating that area to the area measured for a positive response

for the same ion. The same number of scans must be integrated for both areas. (The ratio of peak heights may be used instead of peak areas.)

3.10 Surrogate compound (SC) -- a compound ($^{37}Cl_4$-2,3,7,8-TCDD) that is present in each calibration solution and is added at a low concentration (20 pg/L) to each sample and blank before extraction. Successful detection and measurement of the SC in each sample provides some assurance that unlabeled 2,3,7,8-TCDD would be detectable if present in the sample at $\geq$20 pg/L.

4. INTERFERENCES

4.1 An organic compound that has approximately the same GC retention time 2,3,7,8-TCDD (within a few scans of the IS) and produces the ions that are monitored to detect 2,3,7,8-TCDD is a potential interference. Most frequently encountered interferences are other sample components that are extracted along with TCDD; some potential interferences are listed in Table 1. To minimize interference, high purity reagents and solvents must be used and all equipment must be meticulously cleaned. Laboratory reagent blanks must be analyzed to demonstrate lack of contamination that would interfere with 2,3,7,8-TCDD measurement. Column chromatographic procedures are used to remove some sample components; these procedures must be performed carefully to minimize loss of 2,3,7,8-TCDD during attempts to enrich its concentration relative to other sample components..

4.2 False positive identifications are produced only when an interfering compound elutes from the GC column within 3 sec of the IS and produces ions with exact masses and relative abundances very similar to those for 2,3,7,8-TCDD. The specified GC column separates 2,3,7,8-TCDD from all 21 other TCDD isomers.

5. SAFETY

5.1 Because 2,3,7,8-TCDD has been identified as an animal carcinogen and a possible human carcinogen, exposure to this compound and its isotopically labeled analogs must be minimized (2,3). The laboratory is responsible for maintaining a file of current OSHA regulations regarding the safe handling of chemicals specified in this method. A reference file of material data handling sheets should also be made available to all personnel involved in analyses.

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

5.2.1 Minimize laboratory contamination by conducting all manipulations in a hood.

5.2.2 Effluents of GC sample splitters and GC/MS vacuum pumps should pass through either a column of activated carbon or

be bubbled through a trap containing oil or high-boiling alcohols.

5.2.3 Liquid waste should be dissolved in methanol or ethanol and irradiated with ultraviolet light at a wavelength <290 nm for several days. Analyze the liquid wastes and dispose of the solutions when 2,3,7,8-TCDD can no longer be detected.

5.3 The following precautions for safe handling of 2,3,7,8-TCDD in the laboratory are presented as guidelines only. These precautions are necessarily general in nature, because detailed specific recommendations can be made only for the particular exposure and circumstances of each individual use. Assistance in evaluating the health hazards of particular conditions may be obtained from certain consulting laboratories or from state Departments of Health or of Labor, many of which have an industrial health service. Although 2,3,7,8-TCDD is extremely toxic to certain kinds of laboratory animals, it has been handled for years without injury in analytical and biological laboratories. Techniques used to handle radioactive and infectious materials are applicable to 2,3,7,8-TCDD.

5.3.1 Protective equipment: Laboratory hood adequate for radioactive work, safety glasses, and disposable plastic gloves, apron or lab coat.

5.3.2 Training: Workers must be trained in the proper method of removing contaminated gloves and clothing without contacting the exterior surfaces.

5.3.3 Person hygiene: Thorough washing of hands and forearms after each manipulation and before breaks (coffee, lunch, and shift).

5.3.4 Confinement: Isolated work area, posted with signs, segregated glassware and tools, plastic-backed absorbent paper on benchtops.

5.3.5 Waste: Good technique includes minimizing contaminated waste. Plastic liners should be used in waste cans.

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

5.3.7 Decontamination: Personnel - any mild soap with plenty of scrubbing action. Glassware, tools, and surfaces - rinse with 1,1,1-trichloroethane, then wash with any detergent and water. Dish water may be disposed to the sewer after percolation through a carbon filter. Solvent wastes should be minimized, because they require special disposal through commercial sources that are expensive.

5.3.8 Laundry: Clothing known to be contaminated should be disposed with the precautions described under "Disposal of Hazardous Wastes". Laboratory 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 washer without contact if the launderer knows the problem. The washer should be run through one full cycle before being used again for other clothing.

5.3.9 Wipe tests: A useful method to determine cleanliness of work surfaces and tools is to wipe a surface area of 2 in. X 1 ft. with an acetone-saturated laboratory wiper held in a pair of clean stainless steel forceps. Combine wipers to make one composite sample in an extraction jar containing 200 mL acetone. Place an equal number of unused wipers in 200 mL acetone and use as a control. Extract each jar with a wrist-action shaker for 20 min. Transfer extract to a Kuderna-Danish (K-D) apparatus fitted with a concentrator tube and a three-ball Snyder column. Add two boiling chips and concentrate the extract to an apparent volume of 1.0 mL with the same techniques used for sample extracts. Add 100 μL of the sample fortification solution that has not been diluted with acetone or 1.5 mL of the acetone-diluted solution (Section 7.14), and continue all extract preparation steps and analytical procedures described for samples. If any 2,3,7,8-TCDD is detected, report the result as a quantity (picograms) per wipe test. A lower limit of calibration of 20 pg/composite wipe test is expected. A positive response for the control sample is 8 pg/wipe test. When the sample contains $\geq$25 pg, steps must be taken to correct the contamination. First vacuum the working places (hoods, benches, sink) using a vacuum cleaner equipped with a high-efficiency particulate absorbent filter and then wash with a detergent. Analyze a new set of wipers before personnel are allowed in work in the previously contaminated area.

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

5.3.11 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.

6. APPARATUS AND EQUIPMENT

6.1 Computerized GC/MS System

6.1.1 The GC must be capable of temperature programming and be equipped with all required accessories, such as syringes, gases, and capillary columns. The GC injection port must be designed for capillary columns. Splitless or on-column injection technique is recommended. With this method, a 2-μL injection is used consistently. A 1-μL injection volume can be used, but the injection volume should be constant throughout analyses of calibration solutions and related blanks, sample extracts, and quality control samples.

6.1.2 GC/MS interface components should withstand temperatures up to 280°C. The interface should be designed so that separation of 2,3,7,8-TCDD from all other TCDD isomers achieved in the GC column is not appreciably degraded. Cold spots or active surfaces (adsorption sites) in the interface can cause peak tailing and broadening. The GC column should be inserted directly into the MS ion source without being exposed to the ionizing electron beam. Graphite ferrules should be avoided in the injection port because they may adsorb TCDD. Vespel or equivalent ferrules are recommended.

6.1.3 The static resolving power of the MS must be maintained at ≥10,000 (10% valley). The MS must be operated in a selected ion monitoring (SIM) mode, and data must be acquired for the ions listed in Table 2 during a total cycle time (including instrument overhead time) of ≤1 s. Selection of the lock-mass ion is left to the performing laboratory. Recommended MS tuning conditions are provided in Section 9.1. The ADC zero setting must allow peak-to-peak measurement of baseline noise for every monitored channel and allow good estimation of instrument resolving power.

6.1.4 A dedicated data system is used to control rapid SIM data collection. Quantitation data (peak areas or peak heights) must be acquired continuously and stored. The data system must be capable of producing selected ion current profiles (SICPs, which are displays of ion intensities as a function of time) for each monitored ion, including the lock-mass ion. Quantitation may be based on computer-generated peak areas or on measured peak heights. The data system must be capable of acquiring data for ≥ five ions and generating hard copies of SICPs for selected GC retention time intervals and permit measurement of baseline noise.

6.2 GC Column. Two narrow bore, fused silica capillary columns coated with phenyl cyanopropyl silicone are recommended; one is a 60-m SP-

2330 and the other is a 50-m CP-SIL 88. Any capillary column that separates 2,3,7,8-TCDD from all other TCDD isomers may be used, but this separation must be demonstrated. At the beginning of each 12-h period during which analyses are to be performed, column operating conditions must be demonstrated to achieve the required separation on the column to be used for samples. Operating conditions known to produce acceptable results with the recommended columns are shown in Table 3.

6.3 Miscellaneous Equipment.

6.3.1 Nitrogen evaporation apparatus with variable flow rate.

6.3.2 Balances capable of accurately weighing to 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 ±2°C.

6.3.5 Glove box.

6.3.6 Drying oven.

6.3.7 Minivials -- 1-mL amber borosilicate glass with conical-shaped reservoir and screw caps lined with Teflon-faced silicone disks.

6.3.8 Pipets, disposable, Pasteur, 150 mm X 5 mm i.d.

6.3.9 Separatory funnels, 2 L with Teflon stopcock.

6.3.10 Kuderna-Danish concentrator, 500 mL, fitted with 10-mL concentrator tube and three-ball Snyder column.

6.3.11 Teflon boiling chips washed with hexane before use.

6.3.12 Chromatography column, glass, 300 m X 10.5 mm i.d., fitted with Teflon stopcock.

6.3.13 Adapters for concentrator tubes.

6.3.14 Continuous liquid-liquid extractor (optional).

6.3.15 Glass funnels, appropriate size to accommodate filter paper used to filter extract (volume of approximately 170 mL).

6.3.16 Desiccator.

6.4 CAUTION: To avoid the risk of using contaminated glassware, all glassware that is reused must be meticulously cleaned as soon as

possible after use. Rinse glassware with the last solvent used in it. Wash with hot water containing detergent. Rinse with copious amounts of tap water and several portions of distilled. Drain dry and heat in a muffle furnace at 400°C for 15-30 min. Volumetric glassware must not be heated in a muffle furnace. Some thermally stable materials (such as PCBs) may not be removed by heating in a 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 it with hexane and store it inverted or capped with solvent-rinsed aluminum foil in a clean environment.

6.5 TCDD concentrations of concern in water are much lower than those of concern in many other sample types. Extreme care must be taken to prevent cross-contamination between water and other samples. The use of separate glassware for water samples is recommended.

6.6 Empore extraction disks, C-18, 47mm.

6.7 Millipore Standard Filter Apparatus (or equivalent) to hold disks, all glass

7. REAGENTS AND CONSUMABLE MATERIALS

7.1 Alumina, acidic (BioRad Lab. #132-1240 or equivalent). Extract in a Soxhlet apparatus with methylene chloride for 6 h (≥ 3 cycles/h) and activate it by heating in a foil-covered glass container for 24 h at 190°C.

7.2 Carbon, (Amoco PX-21 or equivalent).

7.3 Glass wool. Extract with methylene chloride and hexane and air-dry before use. Store in a clean glass jar.

7.4 Potassium hydroxide, ACS grade.

7.5 Potassium silicate. Slowly dissolve 56 g of reagent grade potassium hydroxide in 300 mL of anhydrous methanol in a 1-L round bottom flask. Add slowly with swirling 100 g silica gel (prewashed and activated). With a rotary evaporation apparatus with no vacuum applied, rotate the flask and heat to 55°C for 90 min. After the mixture cools to room temperature, pour it into a large glass column containing a plug of glass wool at the end. Wash the mixture into the column with methanol, and then add 200 mL of methanol. When the methanol level reaches the bed of sorbent, add 200 mL of methylene chloride to the column. Push the methylene chloride through the column of sorbent by applying nitrogen pressure to dry or partially dry the sorbent, which is then activated at 130°C overnight.

7.6 Silica gel, high purity grade, type 60, 70-230 mesh. Extract in a Soxhlet apparatus with methylene chloride for 6 h (≥3 cycles/h) and

activate by heating in a foil-covered glass container for 24 h at 130°C.

7.7 Silica gel impregnated with 40% (w/w) sulfuric acid. Add two parts (by weight) concentrated sulfuric acid to three parts (by weight) silica gel (extracted and activated), mix with a glass rod until free of lumps, and store in a screw-capped glass bottle.

7.8 Silica gel/Carbon. To a 20-g portion of silica gel add 500 mg carbon, and blend until the mixture is a uniform color.

7.9 Sodium sulfate, granular, anhydrous.

7.10 Solvents, high purity, distilled-in-glass, or highest available purity: methylene chloride, hexane, benzene, methanol, tridecane, isooctane, toluene, cyclohexane, and acetone.

7.11 Sulfuric acid, concentrated, ACS grade, specific gravity 1.84.

7.12 Concentration Calibration Solutions (Table 4) -- Five (or more) tridecane solutions (CAL 1-5) containing unlabeled 2,3,7,8-TCDD and isotopically labeled TCDDs. All five solutions contain unlabeled 2,3,7,8-TCDD at varying concentrations and the IS ($^{13}C_{12}$-2,3,7,8-TCDD, CASRN 80494-19-5) and the RS ($^{13}C_{12}$-1,2,3,4-TCDD) each at a constant concentration. Three of these solutions also contain the surrogate compound (SC, $^{37}Cl_4$-2,3,7,8-TCDD, CASRN 85508-50-5) at varying concentrations. All standards required for preparing CALs are commercially available but must be verified by comparison with the National Bureau of Standards certified solution SRM-1614, which contains 67.8 ng/mL of unlabeled 2,3,7,8-TCDD and 65.9 ng/mL of ^{13}C-labeled 2,3,7,8-TCDD at 23°C. Note: CALs can be prepared by diluting calibration solutions used in Contract Laboratory Program procedures for 2,3,7,8-TCDD determinations with low resolution MS; to obtain appropriate IS concentrations for CAL 4, however, solvent containing the IS must be used for dilution. Calibration solutions used for USEPA Method 8290 can also be used to determine RFs for 2,3,7,8-TCDD; with those solutions the lower calibration concentration may be higher (25 pg/L rather than 20 pg/L) or lower, depending on injected volume of calibration solution. Because Method 8290 solutions do not contain the SC, however, one or three additional solutions containing that compound will be necessary to measure its RF relative to the IS. Assuming adequate reproducibility of RF measurements, triplicate analyses of one solution (recommended SC concentration of 1.2 pg/μL) or single analysis of three solutions (0..6 to 1.8 pg/μL, Table 4) are acceptable.

7.12.1 Each of CALs 1-5 contains the IS at a concentration of 50 pg/μL; if 100% of the IS is extracted, 10 μL of this solution is equivalent to a 10-μL extract of a 1-L sample to which 500 pg of IS was added before extraction. If 100%

of the analyte is extracted, CALs 1-5 contain unlabeled 2,3,7,8-TCDD at concentrations that are equivalent to 10-μL extracts of 1-L samples containing 20 pg to 2 ng.

7.12.2 CALs 1-3 contain the SC (^{37}Cl-2,3,7,8-TCDD) at a concentration of 0.6 pg/μL, 1.2 pg/μL, and 1.8 pg/μL, respectively; 10 μL of those solutions are equivalent to 10 μL extracts containing 30%, 60%, and 90%, respectively, of the amount of SC added to each 1-L sample before extraction.

7.12.3 Store CALS in 1-mL amber minivials at room temperature in the dark.

7.13 Column Performance Check Solution -- contains a mixture of TCDDs including the IS, the SC, unlabeled 2,3,7,8-TCDD, 1,2,3,4-TCDD (CASRN 30746-58-8), 1,4,7,8-TCDD(CASRN 40581-94-0), 1,2,3,7,-TCDD (CASRN 67028-18-6), 1,2,3,8-TCDD (CASRN 53555-02-5), 1,2,7,8-TCDD (CASRN 34816-53-0), and 1,2,6,7-TCDD (CASRN 40581-90-6). Other TCDDs can be present. Except for the IS and SC, solution component concentrations are not critical. The IS concentration should be 10 $\pm$ 1 pg/μL and the SC concentration should be 0.6 $\pm$ 0.1 pg/L, because ions produced by these compounds will be used to check signal-to-noise ratios.

7.14 Sample Fortification Solution. A solution containing the IS at a concentration of 5 to 25 pg/μL and the SC at a concentration of 0.2 to 1 pg/μL, but with the ratio of IS to SC always 25:1. The solution solvent is not critical; mix 20 to 100 μL, as appropriate to produce needed IS and SC concentrations (50 pg/L and 2 pg/L, respectively) of this solution with 1.5 mL of acetone. Add the resulting solution to each sample and blank before extraction.

7.15 Recovery Standard Solution. A tridecane solution containing the recovery standard, $^{13}C_{12}$-1,2,3,4-TCDD at a concentration of 50 pg/μL. A 10-μL aliquot of this solution is added to each sample and blank extract before concentrating the extract to its final volume for analysis (Section 11.4.1).

8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Samples must be collected in glass containers. The container should not be rinsed with sample before collection.

8.2 Samples may be stored under ambient conditions as long as temperature extremes (below freezing or >90°F) are avoided. To prevent photo-decomposition, samples must be protected from light from the time of collection until extraction.

8.3 All samples must be extracted within 90 days after collection and completely analyzed within 40 days after extraction.

9. GC/MS SYSTEM CALIBRATION.

9.1 MS Performance.

9.1.1 The MS must be operated in the electron ionization mode, and a static resolving power of ≥10,000 (10% valley definition) at ≥m/z 334 must be demonstrated before any analysis is performed. The resolving power must be documented by recording the mass profile of the reference peak. The format of the peak profile representation must allow manual determination of resolution (i.e., the horizontal axis must be a calibrated mass scale (amu or ppm per division). The peak width at 5% peak height must appear on the hard copy and cannot exceed 100 ppm. Static resolving power must be checked at the beginning and end of each 12-h period of operation. A visual check of static resolution is recommended before and after each analysis.

9.1.2 Chromatography time may exceed the long-term mass stability of the high resolution MS, and mass drift of a few ppm can affect the accuracy of measured masses. Therefore, a mass drift correction is required. A lock mass ion from the reference compound (high boiling perfluorokerosene, PFK, is recommended) is used to calibrate the MS. An acceptable lock mass is an ion with mass larger than the lightest mass monitored but less than the heaviest ion monitored. The amount of PFK introduced into the ion chamber during analysis should be adjusted so that the amplitude of the lock mass ion is <10% full scale. Excessive PFK may cause noise problems and ion source contamination.

9.1.3 Using a PFK molecular leak, tune the MS to obtain resolving power of ≥10,000 (10% valley) at m/z 334. Using a reference peak near m/z 320, verify that the exact mass of the reference peak is within 5 ppm of the known mass. The low- and high-mass reference ions must be selected to provide the voltage jump required to detect ions from m/z 320 through m/z 334. (Note: With a qualitative confirmation option in Section 11.5.5, detected ion range will be m/z 257 to m/z 334.)

9.1.4 MS resolving power must be demonstrated by recording the mass peak profile of the high-mass reference signal obtained using the low-mass ion as a reference. The minimum resolving power of 10,000 must be demonstrated on the high-mass ion while it is transmitted at a lower accelerating voltage than the low-mass reference ion, which is transmitted at full sensitivity. The peak profile representation must allow manual determination of the resolution (i.e., the horizontal axis must be a calibrated mass scale in amu or ppm per division. The measured peak

width at 5% of the peak maximum must appear on the hard copy and cannot exceed 100 ppm at the high mass.

9.2 Initial Calibration

9.2.1 GC column performance. The laboratory must verify GC conditions necessary for required separation of 2,3,7,8-TCDD from other TCDD isomers. Inject 2 μL of the performance check solution and acquire SIM data for the five ions in Table 2 (nominal m/z 320, 322, 328, 332, and 334) within a total cycle time of ≤1 s. Acquire at least five scans for each ion across each GC peak and use the same data acquisition time for each ion monitored. The peak representing 2,3,7,8-TCDD and peaks representing any other TCDD isomers must be resolved with a valley of ≤25% (Figure 1), Valley % = 100 x/y, where y is peak height of 2,3,7,8-TCDD and x is measured as shown in Figure 1 between 2,3,7,8-TCDD and its closest eluting isomer. CAUTION: The same data acquisition parameters must be used to analyze all calibration and performance check solutions.

9.2.2 MS calibration and sensitivity check. Ratio of integrated ion current for m/z 320 to m/z 322 produced by unlabeled 2,3,7,8-TCDD and for m/z 332 and 334 produced by the IS (^{13}C-labeled 2,3,7,8-TCDD) must be ≥0.67 and ≤0.87. The S/N ratio for m/z 328 produced by the SC (^{13}C-labeled 1,2,3,4-TCDD) must be ≥2.5 and the S/N ratio for m/z 332 produced by the IS must be ≥10.

9.2.3 Using the same GC and MS conditions, analyze a 2-μL aliquot of the medium concentration CAL (CAL 3). Check ion ratios specified in Section 9.2.2. If criteria are met, analyze a 2-μL aliquot of each of the four (or more) remaining CALS.

9.2.4 For each CAL, ensure that ion ratios (Section 9.2.2) are acceptable. For CAL 1 (the lowest concentration CAL) data, ensure that each ion produces a signal-to-noise (S/N) ratio of >2.5. Display a SICP for a region of the chromatogram near the elution time of 2,3,7,8-TCDD but where no analyte or interference peak is present. The preferred width of the display is about 10 X full width at half height of the IS peak. The "noise" is the height (measured from the lowest point in the display window) of the largest signal not attributable to any eluting substance.

9.2.5 RF Measurements. Using data acquired for each CAL, calculate the RF for unlabeled 2,3,7,8-TCDD, the SC ($^{37}Cl_4$-2,3,7,8-TCDD), and the RS ($^{13}C_{12}$-2,3,7,8-TCDD) relative to the IS ($^{13}C_{12}$-2,3,7,8-TCDD) with the following equation:

$$RF = A_x Q_{is} / A_{is} Q_x$$

where A_x = the sum of integrated ion abundances of m/z 320 and 322 for unlabeled 2,3,7,8-TCDD, the abundance of m/z 328 for the SC, or the abundances of m/z 332 and 334 for the RS.

A_{is} = the sum of integrated ion abundances of m/z 332 and 334 for the IS,

Q_{is} = injected quantity of IS, and

Q_x = injected quantity of unlabeled 2,3,7,8-TCDD, the SC, or the RS.

RF is a unitless number; units used to express quantities must be equivalent.

9.2.6 For each compound (unlabeled 2,3,7,8-TCDD, the SC, and the RS), calculate a mean RF and the relative standard deviation (RSD) of the five measured RFs. When RSD exceeds 20%, analyze additional aliquots of appropriate CALs to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance.

9.3 Routine Calibration. If a laboratory operates during only one ≤12-h period (shift) each day, routine calibration procedures must be performed at the beginning (after mass calibration and successful analysis of the performance check solution to ensure adequate sensitivity and acceptable ion ratios) of that shift, and the performance check solution must be analyzed again at the end of that shift to validate data acquired during the shift. If the laboratory operates during consecutive shifts, routine calibration procedures must be performed at the beginning of each shift, but analysis of the performance check solution at the beginning of each shift and at the end of the final 12-h period is sufficient.

9.3.1 Inject a 2-μL aliquot of CAL 3, and analyze with the same conditions used during Initial Calibration.

9.3.2 Demonstrate acceptable performance for ions abundance ratios, and demonstrate that each measured RF for unlabeled 2,3,7,8-TCDD, the SC, and the RS is within 20% of the appropriate mean RF measured during initial calibration. If one or more of these criteria are not met, up to two additional attempts can be made before remedial action is necessary and the entire initial calibration process is repeated. Corrective action may include increasing the detector sensitivity, baking the GC column, clipping a short length (about 0.3-0.5 m) of the injector side of the GC column, washing or replacing the GC column, and cleaning the

ion source. If degradation of the standards in CALs is suspected, a fresh set of CALs should be used for repeating initial calibration procedures.

10. QUALITY CONTROL

10.1 Laboratory Reagent Blank. Perform all steps in the analytical procedure using all reagents, standards, equipment, apparatus, glassware, and solvents that would be used for a sample analysis, but omit a water sample, and substitute 1 L of reagent water.

10.1.1 Analyze two laboratory reagent blanks (LRBs) before sample analyses begin and when a new batch of solvents or reagents is used for sample extraction. Do not add any IS, SC or RS to one blank; this will allow demonstration that reagents contain no impurities producing any ion current above the level of background noise for monitored ions.

10.1.2 Criteria for acceptable LRBs.

10.1.2.1 When no IS, SC, or RS is present, no ion current above the level of background S/N is detected for any monitored ion within 20 s of the retention times previously measured for labeled 1,2,3,4-TCDD or for unlabeled and labeled 2,3,7,8-TCDD.

10.1.2.2 When the IS is present, no ion current for m/z 259, 320, or 322 is observed that is >2% of the abundance of m/z 332 within 5 scans of the IS peak maximum.

10.1.3 Corrective action for unacceptable LRB. Check solvents, reagents, apparatus, and glassware to locate and eliminate the source of contamination before any samples are extracted and analyzed. Purify or discard contaminated reagents and solvents.

10.2 Field Blanks. An acceptable field blank must meet criteria in Section 10.1.2.2. When results for a field blank are acceptable, analysis of an LRB is not needed with that sample batch. When field blank results are not acceptable, analysis of an LRB is needed; if LRB results are acceptable, data for samples associated with the field blank must be accompanied by pertinent information about the nature and amount of contamination observed in the field blank.

10.3 Corrective action for unacceptable performance check solution data. When the MS sensitivity requirement (Section 9.2.2) is not met at the end of a 12-h period in which sample extracts were analyzed, all related sample extracts must be reanalyzed after criteria have been met. When other criteria (ion ratios or GC resolution) are not met, all sample extracts that produced positive results or potential

positive results must be reanalyzed after calibration criteria have been met.

11. PROCEDURE

11.1 Sample Extraction -- Liquid-Liquid Extraction

11.1.1 Mark the water meniscus on the side of the 1-L sample bottle for later determination of the exact sample volume. Pour the entire sample (approximately 1 L) into a 2-L separatory funnel. A continuous liquid-liquid extractor may be used instead of a separatory funnel.

11.1.2 Add 1.5 mL of the sample fortification solution (Section 7.14) to the sample in the separatory funnel.

11.1.3 Add 60 mL of methylene chloride to the sample bottle, seal and shake 30 s to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 min with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 min. If an emulsion interface between layers exists, the analyst may use mechanical techniques to complete the phase separation. Collect the methylene chloride layer directly into a 500-mL Kuderna Danish (K-D) concentrator (mounted with a 10-mL concentrator tube) by passing the sample extract through a filter funnel packed with a glass wool plug and 5-g of anhydrous sodium sulfate. Repeat the extraction with two additional 60-mL portions of methylene chloride, filtering each extract before adding it to the K-D concentrator. After the third extraction, rinse the sodium sulfate with an additional 30 mL of methylene chloride to ensure quantitative transfer, and add rinse to composite extract.

11.1.4 Add one or two clean boiling chips to the evaporative flask and attach a Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top. Place the K-D apparatus on a hot water bath (60-65°C) so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Concentrate the extract until the apparent volume of the liquid reaches 1 mL. Remove the K-D apparatus and allow it to drain and cool for at least 10 min. Remove the Snyder column, add 50 mL of hexane and a new boiling chip and reattach the Snyder column. Increase the water bath temperature to 85-90°C and concentrate the extract to approximately 1 mL. Rinse the flask and the lower joint with 1-2 mL hexane. Concentrate the extract to 1 mL under a gentle stream of nitrogen. If further extract processing is to be delayed, the extract should be quantitatively

transferred to a Teflon-sealed, amber, screw-cap vial and stored refrigerated and protected from light.

11.1.5 Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.2 Sample Extraction -- Liquid-Solid Extraction

11.2.1 Preparation of disks

11.2.1.1 Insert the disk into the 47mm filter apparatus. Wash the disk with about 10 mL of benzene by adding the solvent to the disk, pulling about half through the disk and allowing it to soak the disk for about a minute, then pulling the remaining rinse solvent through the disk. With the vacuum on, pull air through the disk for about one minute.

11.2.1.2 Pre-wet the disk with 10 mL methanol (MeOH) by adding the MeOH to the disk, pulling about half through the disk and allowing it to soak for about a minute, then pulling MOST of the MeOH through. A layer of MeOH should be left on the surface of the disk, which should not be allowed to go dry from this point until the end of the sample extraction. This is an important step to ensure uniform flow and good analyte recoveries.

11.2.1.3 Rinse the disk with 10 mL reagent water by adding the water to the disk and pulling most through, again leaving a layer on the surface of the disk.

11.2.2 Mark the water miniscus on the side of the 1-L sample bottle for later determination of the exact sample volume.

11.2.3 Add the water sample, to which all necessary surrogate compounds and internal standards have been added according to Section 11.1.2, to the reservoir and turn on the vacuum to begin the extraction. Aspirator vacuum should be adjusted to allow the sample to pass through the disk in approximately 20 minutes. Extract the entire sample, draining as much water as possible from the sample container. After all the sample has passed through, draw air through the disk for about 10 minutes to remove some of the residual water.

11.2.4 Remove the filtration top from the apparatus, but do not disassemble the reservoir and fritted base. Empty the

water from the flask and insert a suitable sample tube to contain the eluate. The only constraint on the sample tube is that it fit around the drip tip of the fritted base. Reassemble the apparatus.

11.2.5 Add 5 mL benzene to the sample bottle and rinse the inside of the container. Transfer this benzene to the disk with a dispo- pipet or other suitable vessel, rinsing the sides of the filtration reservoir in the process. Pull about half of the benzene through the disk, release the vacuum, and allow the disk to soak for about a minute. Pull the remaining benzene through the disk.

11.2.6 Repeat the above step twice. Pour the combined eluates through a small funnel containing about 3 grams of anhydrous sodium sulfate. The sodium sulfate may be contained in a prerinsed filter paper, or by a plug of prerinsed glass wool in the stem of the funnel. Rinse the sodium sulfate with a 5 mL aliquot of benzene.

11.2.7 Quantitatively transfer the combined eluate to a suitable graduated concentrator tube, and rinse the test tube with benzene. Using micro-Kuderna-Danish or nitrogen blowdown, concentrate the eluate almost to dryness, then add hexane to bring the volume to 1 mL for sample extract cleanup.

11.2.8 Determine the original sample volume by refilling the sample bottle to the mark, and transferring the liquid to a 1000 mL graduated cylinder. Record the sample volume to the nearest 5 mL.

11.3 Sample Extract Cleanup

11.3.1 Chromatography columns 1 and 2, described below, are recommended for every sample extract. A third column containing silica gel and carbon may be useful for removal of interferences from some sample extracts and may be used at the analyst's discretion. Because each cleanup procedure increases the chances of analyte loss, such procedures should be minimized. Criteria for predicting when the carbon column will be needed are not available, but that column is probably not needed for finished drinking water samples that have been filtered through granular activated carbon.

11.3.2 Column Preparation

11.3.2.1 Column 1. Place 1.0 g of silica gel (See NOTE) into a 1.0 cm X 20 cm column and tap the column gently to settle the silica gel. Add 2 g potassium hydroxide impregnated silica gel, 1 g silica gel, 4.0 g of sulfuric acid impregnated

silica gel, and 2 g silica gel. Tap column gently after each addition. NOTE: The silica gel for this application is partially deactivated with 1% water immediately before packing the column.

11.3.2.2 Column 2. Place 6.0 g of alumina into a 1.0 cm X 30 cm column and tap the column gently to settle the alumina. Add a 1-cm layer of purified sodium sulfate to the top of the alumina.

11.3.2.3 Add hexane to each column until the packing is free of channels and air bubbles. A small positive pressure (5 psi) of clean nitrogen can be used if needed.

11.3.3 Quantitatively transfer the sample extract to the top of the silica gel in column 1. Rinse the concentrator tube with two 0.5 mL portions of hexane; transfer rinses to Column 1. With 90 mL of hexane, elute the extract from Column 1 directly into Column 2.

11.3.4 Add an additional 20 mL of hexane to Column 2 and elute until the hexane level is just below the top of the sodium sulfate; discard the eluted hexane.

11.3.5 Add 20 ml of 20% methylene chloride/80% hexane (v/v) to Column 2 and collect the eluate.

11.3.6 If carbon column cleanup is selected, proceed with Section 11.3.7. If not, proceed with Section 11.3.8.

11.3.7 Optional cleanup with Column 3. Reduce the volume of eluate from Column 2 to about 1 mL in a K-D apparatus. Transfer the concentrated eluate from Column 2 to a 4 mm X 200 mm column (2 mL disposable pipette) containing 200 mg silica gel/carbon. Elute with 15 mL methylene chloride and 15 mL 80% methylene chloride/20% benzene (v/v) in forward direction of flow. Discard these fractions. Elute TCDD with 15 mL toluene in a reverse direction flow. Collect this eluate.

11.3.8 Concentrate the eluate (either the toluene fraction from Section 11.3.7 or the methylene chloride/hexane fraction from Section 11.3.5) to a small volume (<0.5 mL) and transfer to a 1-mL minivial. Store the extract in the dark at 4°C until just before analysis. Note: The final volume is adjusted to 10 μL immediately before GC/MS analysis.

11.4 GC/MS Analysis of Extracts

11.4.1 Remove the sample or blank extract from storage and allow it to warm to ambient laboratory temperature. Add a 10-μL aliquot of the RS solution (Section 7.15) to the extract and reduce the extract volume to 10 μL with a stream of dry, purified nitrogen.

11.4.2 Inject a 2-μL aliquot of the extract into the GC, operated under conditions previously used to produce acceptable results with the performance check solution.

11.4.3 Acquire SIM data using the same analytical conditions previously used to determine RFs.

11.5 Identification Criteria

11.5.1 Obtain SICPs for each ion monitored.

11.5.2 The abundance of m/z 332 relative to m/z 334 produced by the IS must be $\geq$0.67 and $\leq$0.87, and these ions must maximize within 1 scan of each other. Retention time should be within $\pm$5 scans of that observed during the most recent acceptable calibration. For good performance, the retention time of the IS must be reproducible to $\pm$5 scans from one injection to the next. Over the course of a 12-h work period, the IS retention time should be reproducible within $\pm$10 scans. Less reproducible IS retention times indicate serious chromatography problems that should be corrected before further sample analyses.

11.5.3 The sample component must produce a signal for both ions monitored to detect and measure unlabeled 2,3,7,8-TCDD, and the abundance of m/z 320 relative to m/z 322 must be $\geq$0.67 and $\leq$0.87. All ions must maximize within 1 scan of each other and within 3 sec of the IS.

11.5.4 The S/N ratio for each unlabeled TCDD and SC ion must be >2.5 and must not have saturated the detector; the S/N ratio for each IS and RS ion must be $\geq$10 and must not have saturated the detector.

11.5.5 Additional qualitative confirmation can be obtained by monitoring m/z 257 and 259 (fragment ions produced by loss of COCl from the analyte) along with ions previously specified or by reanalysis of an aliquot of the extract to monitor m/z 257 and 259 along with m/z 268 and 270, fragment ions produced by loss of COCl from the IS. The relative abundance of m/z 257 to 259 and m/z 268 to 270 should be 0.9 to 1.1, and the abundance of 259 to 270 should be the same as the ratio of 322 to 334 measured in the previous injection. Although variable with instrumental conditions, the abundance of fragment ions relative to molecular ions

is approximately 30-45% for each compound; therefore, the detection limit for these ions will be greater than for molecular ions.

12. CALCULATIONS

12.1 From appropriate SICPs of nominal m/z 259, 320 and 322, obtain and record the spectrum number of the apex of the chromatographic peak produced by unlabeled TCDD and the area of the entire chromatographic peak.

12.2 Calculate the concentration using the formula:

$$C_x = (A_x \cdot Q_{is})/(A_{is} \cdot RF \cdot V)$$

where C_x = concentration (picograms per liter),

A_x = sum of areas for m/z 320 and m/z 322 produced by the sample component,

A_{is} = sum of areas for m/z 332 and m/z 334 produced by the IS,

Q_{is} = quantity (picograms) of IS added to the sample,

RF = mean RF measured for unlabeled 2,3,7,8-TCDD during initial calibration, and

V = Volume (liters) of water extracted.

12.3 When fortified samples of known composition are analyzed, calculate the percent method bias using the equation:

$$B = 100\ (C_s - C_t)/\ C_t$$

where C_s = measured concentration (in picograms per liter),

C_t = theoretical concentration (i.e., the concentration resulting from fortification plus any concentration measured in the sample when an unfortified sample extract was analyzed).

NOTE: The bias value retains a positive or negative sign.

12.4 Calculate the IS concentration using the formula:

$$C_{is} = (A_{is} \cdot RF \cdot Q_{rs})/(A_{rs} \cdot V)$$

where C_{is} = concentration (picograms per liter),

A_{is} = sum of areas for nominal m/z 332 and 334 produced by the IS,

A_{rs} = sum of areas for m/z 332 and m/z 334 produced by the RS,

Q_{rs} = quantity (picograms) of RS added to the sample,

RF = mean RF measured for the RS relative to the IS during initial calibration, and

V = Volume (liters) of water extracted.

12.5 Report calculated concentrations with three significant figures when measured concentration is >100 pg/L and with two significant figure when value is <100 pg/L. The recovery of the IS should be $\geq$40% and $\leq$120%.

12.6 Estimated Maximum Possible Concentration (EMPC) -- For samples in which no unlabeled 2,3,7,8-TCDD is detected, calculate the EMPC, which is the concentration required to produce a signal with S/N ratio of 2.5. The background signal level (area or height) within $\pm$5 scans of the IS peak is determined as previously described and is multiplied by 2.5. With the following formula, the product is related to the estimated unlabeled TCDD concentration required to produce a signal equivalent of 2.5 S/N.

$$EMPC = 2.5 \cdot B_x \cdot Q_{is} / A_{is} \cdot RF \cdot V$$

B_x = background (height or area) for either nominal m/z 320 or 322 within $\pm$5 scans of the IS peak,

A_{is} = peak height or area (depending on selection for B_x) for nominal m/z 332 when m/z 320 is used to determine B_x or nominal m/z 334 when m/z 322 is used to determine B_x, and

Q_{is}, RF, and V retain previous definitions.

12.7 An interference results when sample a component elutes in the retention time window for 2,3,7,8-TCDD and produces both monitored TCDD ions but measured relative abundances do not meet identification criteria. Any ion with S/N of <2.5 should be ignored. Ions producing S/N of >2.5 but with unacceptable relative abundance should be treated as an interference, and a quantitative estimate of that interference should be calculated using the equation in Section 12.2. Interferences observed in blanks and also present in samples should not be reported as a sample interference but should be reported as a blank interference.

12.8 Table 5 lists results of analyses of fortified reagent water samples carried out using the Empore disk extraction method according to the procedure detailed in Section 11.2. Even though this method was developed for only 2,3,7,8-TCDD, since the other dioxins and furans

had been studied, the results were included. The fortifying levels were 0.16 ng/L for the tetra isomers, 0.8 ng/L for the penta, hexa, and hepta isomers, and 1.6 ng/L for the octa isomers. The average recovery for all isomers in all replicate analyses is 80% with an 11% relative standard deviation. No clean up was done on these samples.

13. REFERENCES

1. "Water Solubility of 2,3,7,8-Tetrachlorodibenzo-p-dioxin," L. Marple, R. Brunck, and L. Throop, Environ. Sci. and Technol. 1986, 20(2), 180-182.

2. "Carcinogens -- Working with Carcinogens," Department of Health, Education, and Welfare, Public Health Service, Centers for Disease Control, NIOSH, Pub. #77-206, August 1977.

3. "Safety in Academic Chemistry Laboratories," American Chemical Society Publication, Committee on Chemical Safety, 3rd Ed., 1979.

4. Statement of Work, Dixoin Analysis, Soil/Sediment and Water Matrices, IFB WA86-K357, September 1986.

TABLE 1. POTENTIAL INTERFERENCES

Compound	Interfering Ion		Required Resolution
	Formula	m/z	
Heptachlorobiphenyl	$M^+ - 2\ ^{35}Cl$	321.867	12,476
Nonachlorobiphenyl	$M^+ - 4\ ^{35}Cl$	319.8521	7,189
	$M^+ - 3\ ^{35}Cl^{37}Cl$	321.8491	7,233
Tetrachloromethoxy-biphenyl	M^+	319.9329	8,805
	M^+	321.9299	8,848
Tetrachlorobenzyl-phenyl ether	M^+	319.9329	8,813
	M^+	321.9300	8,843
DDT	$M+ - H^{35}Cl$	319.9321	9,006
	$M^+ - H^{35}Cl$	321.9292	9,050
DDE	M^+	319.9321	9,011
	M^+	321.9292	9,050
Pentachlorobenzyl-phenyl ether	$M^+ - H^{35}Cl$	319.9143	18,043
	$M^+ - H^{35}Cl$	321.9114	18,104
Tetrachloroxanthene	M^+	319.9143	18,043
	M^+	321.9114	18,104
Hydroxytetrachloro-dibenzofuran	M^+	319.8966	-
	M^+	321.8936	-
Tetrachlorophenyl-benzoquinone	M^+	319.8966	-
	M^+	321.8936	-

TABLE 2. IONS TO BE MONITORED

Accurate Mass	Elemental Composition	Compound
258.9298	$C_{11}H_4{}^{35}Cl_2{}^{37}ClO$	Unlabeled 2,3,7,8-TCDD
319.8965	$C_{12}H_4{}^{35}Cl_4O_2$	Unlabeled 2,3,7,8-TCDD
321.8936	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	Unlabeled 2,3,7,8-TCDD
327.8847	$C_{12}H_4{}^{37}Cl_4O_2$	$^{37}Cl_4$-2,3,7,8-TCDD (SC)
331.9368 and	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	$^{13}C_{12}$-2,3,7,8-TCDD (IS)
		$^{13}C_{12}$-1,2,3,4-TCDD (RS)
333.9339 and	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	$^{13}C_{12}$-2,3,7,8-TCDD (IS)
		$^{13}C_{12}$-1,2,3,4-TCDD (RS)

TABLE 3. GC OPERATING CONDITION GUIDELINES

Column coating	SP-2330	CP-SIL 88
Film thickness	0.2 um	0.22 um
Column dimensions	60 m X 0.24 mm	50 m X 0.22 mm
Helium* linear velocity	28-29 cm/sec at 240°C	28-29 cm/sec at 240°C
Initial temperature	70°C	45°C
Initial time	4 min	3 min
Temperature program	Rapid increase to 200°C; 200°C to 240°C at 4°C/min	Rapid increase to 190°C; 190°C to 240°C at 5°C/min
Retention time of 2,3,7,8-TCDD	24 min	26 min

*Hydrogen is an acceptable carrier gas.

TABLE 4. COMPOSITION OF CONCENTRATION CALIBRATION SOLUTIONS

	Analyte	Surrogate Cmpd.	Internal Std.	Recovery Std.
CAL #	Unlabeled 2,3,7,8-TCDD	$^{37}Cl_4$-2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	$^{13}C_{12}$-1,2,3,4-TCDD
1	2 pg/μL	0.6 pg/μL	50 pg/μL	30 pg/μL
2	10	1.2	50	30
3	50	1.8	50	30
4	100	0	50	30
5	200	0	50	30

TABLE 5. RECOVERY OF CHLORINATED DIOXINS AND FURANS FROM FORTIFIED* REAGENT WATER USING EMPORE DISK EXTRACTION

Compound	No. Samples	% Recovery	% RSD
TCDF	2	72	6
TCDD	2	75	0
PCDF	4	78	11
PCDD	2	86	5
HxCDF	8	83	16
HxCDD	6	80	11
HpCDF	4	77	23
HpCDD	2	80	10
OCDF	2	91	15
OCDD	2	82	11

* Fortifying levels were 0.16 ng/L for the tetra isomers, 0.8 ng/L for the penta and hexa isomers, and 1.6 ng/L for the octa isomers. Analyses were carried out using the procedure described in Section 11.2 of this method.

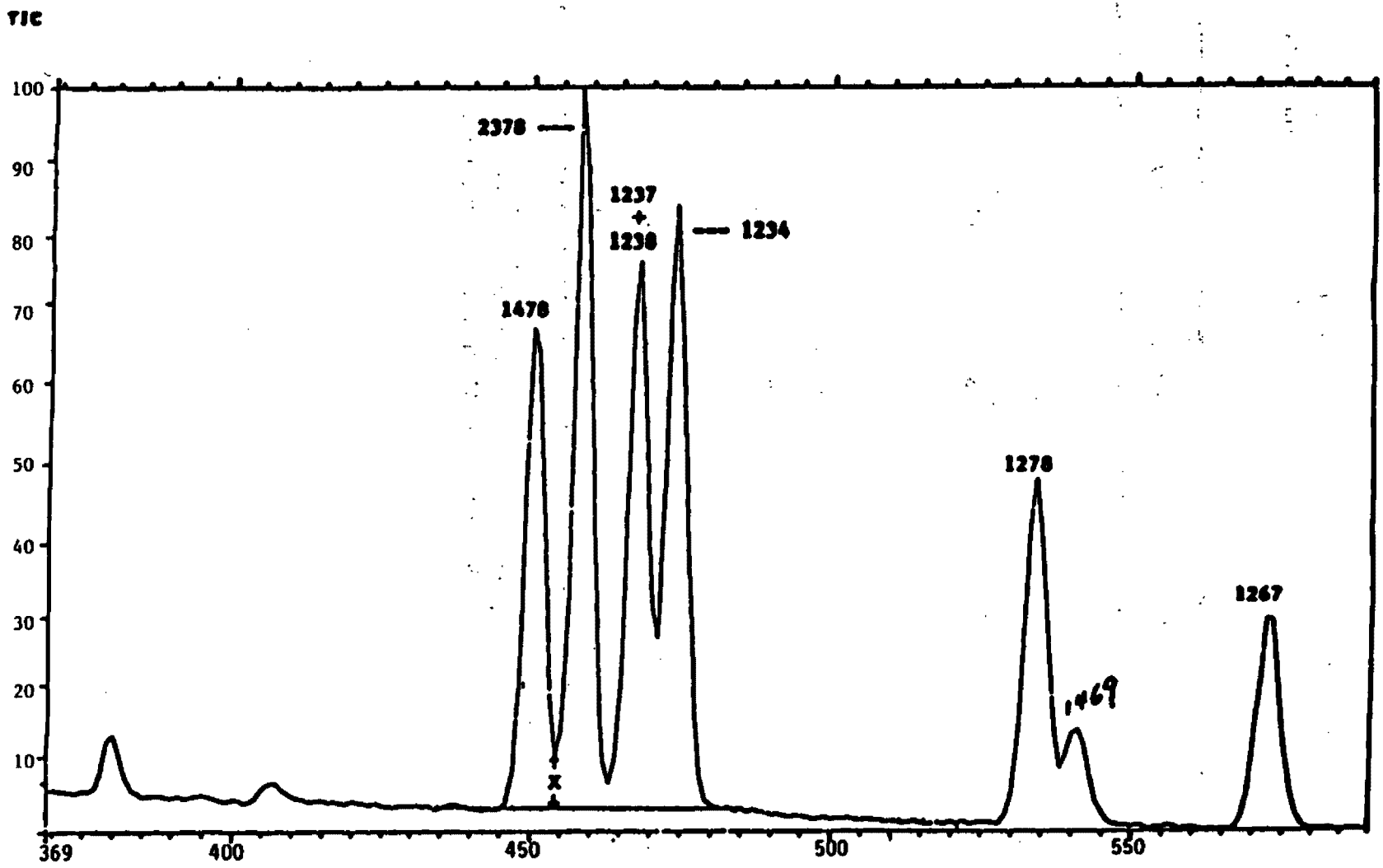

Figure 1. Ion current profile for m/z 210 and 322 produced by analysis of performance check solution using a 50-m CP-SIL 88 fused silica capillary column and conditions listed in Table 3. Percent relative abundance versus scan number.