METHOD 9023

EXTRACTABLE ORGANIC HALIDES (EOX) IN SOLIDS

1.0 SCOPE AND APPLICATION

1.1 This method is to be used for the determination of total extractable organic halides (EOX) as Cl^- in solids. EOX is defined as the sum of those organic halides which are extracted and detected by pyrolysis/microcoulometry under the conditions specified in this method. Extractable organic halides containing chlorine, bromine, or iodine are detected. However, fluorine containing species are not detected by this method.

1.2 This method has been evaluated for solid wastes, soils, and suspended solids isolated from industrial wastewater.

1.3 This method is recommended for use in the concentration range from the MDL up to 1000 x MDL (see Section 9.1).

1.4 This method is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis microcoulometer and in the interpretation of the results.

1.5 Since this method does not identify individual components, it is advisable that compound specific techniques be employed to determine the individual components present in samples exhibiting significant EOX levels, unless the nature of the sample is already known.

2.0 SUMMARY OF METHOD

2.1 A 1-gram aliquot of solid sample is extracted with ethyl acetate by sonification to isolate organic halides. A 25 µL aliquot of the extract is either injected or delivered by boat inlet into a pyrolysis furnace using a stream of CO_2/O_2 (or appropriate alternate gas mixture) and the hydrogen halide (HX) pyrolysis product is determined by microcoulometric titration.

3.0 INTERFERENCES

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400°C for 15 to 30 minutes. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases helps to minimize interference problems.

3.1.3 The use of non-PTFE (polytetrafluoroethylene) plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purge gas stream should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly solvents such as methylene chloride) through the septum seal into the sample during shipment and storage.

3.3 All operations should be carried out in an area where halogenated solvents, such as methylene chloride, are not being used.

3.4 Certain inorganic halide salts (e.g., mercuric chloride) will be extracted, and therefore interfere to some extent.

4.0 APPARATUS AND MATERIALS

4.1 Modified Dohrmann microcoulometric-titration system DX-20, or equivalent, containing the following components:

4.1.1 Solvent injection system.

4.1.2 Pyrolysis furnace.

4.1.3 Titration cell.

4.2 Boat inlet or Microsyringes - 10, 25 µL with 26 gauge 4-inch-long needle.

4.3 Laboratory centrifuge to hold 15 mL conical centrifuge tubes.

4.4 Sonic bath or sonic probe to fit 10 mL vial. A power level of at least 200 watts is required.

4.5 Centrifuge Tubes - 15 mL, conical, with PTFE-lined screw caps.

4.6 Vials - 10 mL, with PTFE-lined screw caps.

4.7 Metal spatula

4.8 Disposable Pasteur pipettes and bulbs.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Carbon dioxide gas (CO_2)or appropriate alternate gas mixture. 99.9 percent purity.

5.4 Oxygen (O_2)or appropriate alternate gas mixture. 99.9 percent purity.

5.5 Ethyl acetate ($C_4H_8O_2$). Pesticide quality or equivalent.

5.6 1,2,4-Trichlorobenzene ($C_6H_3Cl_3$). 99 percent.

5.7 Acetic acid ($C_2H_4O_2$), 70% in water. Dilute 7 volumes of acetic acid with 3 volumes of water.

5.8 Trichlorobenzene solution ($C_6H_3Cl_3$), stock (1 µL = µg Cl^-). Prepare a stock solution by accurately delivering 117 µL (170 mg) of trichlorobenzene into a 100-mL volumetric flask and dilute to volume with ethyl acetate.

5.9 Trichlorobenzene solution ($C_6H_3Cl_3$), calibration (1 µL = 100 ng Cl^-). Dilute 10 mL of the trichlorobenzene stock solution to 100 mL with ethyl acetate.

5.10 Sodium chloride (NaCl) calibration standard, (1 µg Cl^-/µL). Accurately weigh 0.1648 g of sodium chloride into a 100-mL volumetric flask. Dilute to volume with reagent water.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 All samples must be iced or refrigerated from the time of collection until analysis.

6.3 All samples should be collected in bottles (at least 25 mL) with PTFE septa and be protected from light. If this is not possible, use amber glass 250-mL bottles fitted with PTFE-lined caps. Foil may be substituted for PTFE if the sample is not corrosive. Fill the sample bottle as completely as possible to minimize headspace until time of analysis. Samples must be stored at 4°C, and protected against loss of volatiles by eliminating as much headspace as possible in the container. Samples should be analyzed within 28 days. The container must be washed and muffled at 400°C before use, to minimize contamination.

6.4 If the analysis is to be conducted on suspended solids from a wastewater sample, isolate the solids by centrifugation, weigh the wet solids, and analyze immediately. Determine the dry weight of a separate portion of the wet solids by heating overnight at 110°C.

6.5 All glassware must be dried prior to use according to the protocols discussed in Sec 3.1.1.

7.0 PROCEDURE

7.1 Calibration: Following is one type of instrument's calibration parameters. Follow your instrument manufacturer's direction if the calibration set-up precludes your instrument.

7.1.1 Assemble the solvent injection or boat-inlet/pyrolysis/microcoulometric titration apparatus shown in accordance with the manufacturer's specifications. Adjust the CO_2 flow (or appropriate alternate gas mixture) to 300 mL/minute and the O_2 flow to 100 mL/minute using the auxiliary flow controllers (bypass the flow controllers). The pyrolysis furnace should be set at 800 ± 10°C. Attach the titration cell to the pyrolysis tube outlet and fill with electrolyte (70% acetic acid).

7.1.2 Turn on the instrument and allow the gas flows and temperatures to stabilize. When the background current of the titration cell has stabilized, the instrument is ready for use.

7.1.3 Calibrate the microcoulometric titration system for Cl^- detection by injecting various amounts of the sodium chloride calibration standards directly into the titration cell and integrating the response using the POX integration mode. The range of sodium chloride amounts should cover the range of expected sample concentrations and should always be less than 80 µg Cl^-. Over the range 1 - 80 µg Cl^- the integrated response should read within 5% or 0.05 µg (whichever is larger) of the quantity injected. If this calibration requirement is not met then the instrument sensitivity parameters should be adjusted according to the manufacturer's specifications to achieve accurate response.

7.1.4 Check the performance of the entire analytical system by delivering three 25-µL aliquots of the trichlorobenzene calibrate standard into the furnace at a rate of 1 µL/second. The mean of these three analyses should be 2.2 - 2.8 µg Cl^- and the percent relative standard deviation should be 5% or less. If these criteria are not met the system should be checked as described in the instrument maintenance manual in order to isolate the problem.

7.1.5 Perform a blank ethyl acetate standard (25-µL) each day. If the integrated response is greater than 0.1 µg Cl^-, then the system should be checked for sources of contamination.

7.2 Transfer a 1-gram aliquot of the solid sample to a 10 mL vial using a metal spatula. Add 1 mL of reagent water and 5 mL of ethyl acetate to the sample and cap tightly.

7.3 Shake the sample vigorously for thirty seconds and then place the vial in a sonic bath filled with water to a level of ~1 inch, or agitate the suspension directly using a sonic probe, if available. Sonify the sample for 15 minutes if using a sonic bath or 5 minutes if using a sonic probe.

7.4 Allow the suspension to settle for 10 minutes and then transfer the upper layer (ethyl acetate) to a 15-mL conical centrifuge tube. Cap the tube and centrifuge at approximately 1000 x g for five minutes.

7.5 Transfer the ethyl acetate layer to a clean 10 mL vial, cap, and store refrigerated until analyzed.

7.6 For analysis, withdraw a 5 to 25 µL aliquot of the ethyl acetate into a microsyringe having a 4-inch long needle. Place the pyrolysis/microcoulometer system into the POX integration mode and immediately pierce the septum and if using an injection instrument, position the tip of the microsyringe into the furnace. Deliver the sample at a rate of approximately 1 µL/second and

withdraw the needle when sample delivery is complete. If using a boat-inlet instrument, inject or place the sample into the boat and follow the manufacturer's recommended run time or program.

7.7 After the integration cycle is complete record the integrated response. If the response exceeds the working range of the instrument, repeat the analysis after dilution of the extract with reagent grade ethyl acetate. Follow manufacturer's instructions on integrating response.

7.8 Determine the EOX concentration in the sample as follows:

where:

$$EOX\ Concentration,\ \mu g/g\ as\ Cl^- = \frac{Q_S \times V_E}{W_S \times V_I} \times 1000$$

Q_S = Quantity of EOX as µg of Cl^- in the aliquot injected.

V_I = Volume of aliquot injected in µL.

V_E = Total volume of extract in mL.

W_S = Weight of sample extracted in grams.

7.9 Report results in micrograms per gram. When duplicate and spiked samples are analyzed, report all data obtained with the sample results.

7.10 For samples processed as part of a set where the spiked sample recovery falls outside of the historically derived control limits, data for the affected parameters must be labeled as suspect.

7.11 If the aqueous portion of a water sample, from which the suspended solids are being analyzed, is expected to contain high levels of organic halide, a 1-mL aliquot of the centrifuged sample should be reanalyzed starting with Section 7.2. The solids data must then be corrected using the following equation:

where:

$$EOX\ (corrected) = EOX_S - EOX_W \times \frac{W_S}{W_D}$$

EOX_S = EOX in wet solids, µg/g as Cl^-

EOX_W = EOX in water sample, µg/g as Cl^-

W_S = Wet weight of solids, grams

W_D = Dry weight of solids, grams

8.0 QUALITY CONTROL

8.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of spiked samples as a continuing check on performance. The laboratory is required to maintain performance records to define the quality of data that is generated.

8.2 Before performing any analyses, the analyst must demonstrate the ability to generate acceptable accuracy and precision with this method.

8.2.1 Select a trichlorobenzene spike concentration representative of the expected levels in the samples. Using stock standards, prepare a quality control check sample concentrate in ethyl acetate 100 times more concentrated than the selected concentration.

8.2.2 Place a minimum of six 1-gram aliquots of an uncontaminated soil sample in 10 mL vials. Spike four of the samples with 10 µL of the check sample, cap the vials, shake vigorously, and allow the spike to equilibrate with the sample by standing overnight. Analyze the aliquots according to the procedure beginning in Section 7.2.

8.2.3 Calculate the average percent recovery, (R), and the standard deviation of the percent recovery (S), for the results. Soil background corrections must be made before R and S calculations are performed.

8.2.4 Acceptance limits for recovery and precision must be derived from repeated analyses of the standard discussed in Section 8.2.1. Base the accuracy acceptance criteria on +/- 3 standard deviations from the mean recovery and the precision acceptance criteria on the relative standard deviation. If the recovery for a particular parameter does not fall within the control limits for method performance, the results reported for that parameter in all samples processed as part of the same set must be qualified as described in Section 7.10.

8.3 The laboratory must spike in duplicate and analyze a minimum of 5% of all samples to monitor continuing laboratory performance. All spikes and spike duplicates must be treated in the same manner as the samples.

8.4 Each day, the analyst must demonstrate, through the analysis of uncontaminated soil, that interferences from the analytical system are under control.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. An MDL of 10 µg/g was obtained using ethyl acetate standards. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 In a single laboratory, using solid spiked at various levels, the average recoveries presented in Table 1 were obtained.

10.0 REFERENCES

10.1 "Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater". EPA-600/4-84-008, PB84-134337 (NTIS). U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory - Cincinnati, Ohio 45268, January 1984.

TABLE 1. METHOD PERFORMANCE DATA FOR VARIOUS SOLID SAMPLES

Sample	Spike Compound	Spike Level µg/g	Spike Level µg/g as Cl^-	Average Percent Recovery	Standard Deviation of Recovery	Number of Replicates
"Clean Soil"	1,2,4-Trichlorobenzene	10	6	69	11	3
"Clean Soil"	1,2,4-Trichlorobenzene	49	29	103	20	3
"Clean Soil"	2,4,6-Trichloroaniline	47	26	58	15	3
"Clean Soil"	2,4,6-Trichlorophenol	46	25	48	11	3
Suspended Solids from Industrial Effluent	1,2,4-Trichlorobenzene	850	500	104	3	3
Solid Waste from Landfill	1,2,4-Trichlorobenzene	51	30	83	8	3
"Drying Bed" Solid Waste from Chloroethylene Manufacturing	1,2,4-Trichlorobenzene	290	170	94	10	3

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