

METHOD 9021

PURGEABLE ORGANIC HALIDES (POX)

1.0 SCOPE AND APPLICATION

1.1 Method 9021 determines organically bound halides (chloride, bromide, and iodide) purged from a sample of drinking water or ground water. They are reported as chloride. This method is a quick screening procedure requiring about 10 minutes. The method uses a sparging device, a pyrolysis furnace, and a microcoulometric-titration detector.

1.2 Method 9021 detects purgeable organically bound chlorine, bromine, and iodine. Fluorine containing species are not determined by this method. Method 9021 measures POX concentrations ranging from 5 to 1,000 µg/L.

1.3 Method 9021 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.

2.0 SUMMARY OF METHOD

2.1 A sample of water, protected against the loss of volatiles by the elimination of headspace in the sampling container, is transferred to a purging vessel. The volatile organic halides are purged into a pyrolysis furnace using a stream of CO₂ and the hydrogen halide (HX) pyrolysis product is trapped and titrated electrolytically using a microcoulometric detector.

3.0 INTERFERENCES

3.1 Contaminants, reagents, glassware, and other sample processing hardware may cause interferences. Method blanks must be routinely run to demonstrate freedom from interferences under the conditions of the analysis.

3.1.1 Glassware must be scrupulously clean. 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 reagent water and dry at 105°C for 1 hour or until dry. Glassware which is not volumetric should, in addition, be heated in a muffle furnace at 300°C for 15 to 30 minutes (Class A 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 Use high purity reagents and gases to minimize interference problems.

3.1.3 Avoid using non-PTFE (polytetrafluoroethylene) plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purge gas stream.

3.2 Samples can be contaminated by diffusion of volatile organics (methylene chloride) through the septum seal into the sample during shipment and especially during storage. A trip blank prepared from water and carried through the sampling and handling protocol serves as a check on such contamination. A trip blank should be run with each analytical batch.

3.3 Contamination by carry-over occurs whenever high level and low level samples are sequentially analyzed. To reduce carryover, the purging device and sample syringe must be rinsed with water between sample analyses. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of water to check for cross contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds or high organohalide levels, wash out the purging device with a detergent solution, rinse it with water, and then dry it in a 105°C oven between analyses.

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

3.5 Residual free chlorine interferes in the method. Free chlorine must be destroyed by adding sodium sulfite when the sample is collected.

4.0 APPARATUS AND MATERIALS

4.1 Sampling equipment (for discrete sampling)

4.1.1 Vial - 25-mL capacity or larger, equipped with a screw-cap with hole in center (Pierce #13075 or equivalent).

4.1.2 Septum - Teflon lined silicone (Pierce #12722 or equivalent). Detergent wash, rinse with tap and reagent water, and dry at 105°C for 1 hour before use.

4.2 Analytical system

4.2.1 Microcoulometric-titration system containing the following components (a schematic diagram of the microcoulometric-titration system is shown in Figure 1).

4.2.1.1 Purging device.

4.2.1.2 Pyrolysis furnace.

4.2.1.3 Titration cell.

4.2.2 Strip chart recorder (optional) - The recorder is recommended to make sure the peak is down to baselines before stopping integration.

4.2.3 Microsyringes - 10- μ L and 25- μ L with 0.006 in i.d. needle (Hamilton 702N or equivalent).

4.2.4 Syringe valve - 2 way, with Luer ends.

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 Sodium sulfide, Na_2S . Granular, anhydrous.

5.4 Acetic acid in water (70%), CH_3COOH . Dilute 7 volumes of glacial acetic acid with 3 volumes of water.

5.5 Sodium chloride calibration standard ($1 \mu\text{g Cl}^-/\mu\text{L}$). Dissolve 1.648 g NaCl in water and dilute to 1 liter.

5.6 Carbon dioxide.

5.7 Methanol, CH_3OH . Store away from other solvents.

5.8 Chloroform, CHCl_3 .

5.9 Chloroform (stock) solution ($1 \mu\text{L} = 11.2 \mu\text{g}$ of CHCl_3 or $10 \mu\text{g Cl}^-$). Prepare a stock solution by delivering accurately 760 μL (1120 mg) of chloroform into a 100-mL Class A volumetric flask containing approximately 90 mL of methanol. Dilute to volume with methanol (10,000 mg of chlorine/L).

5.10 Chloroform (calibration) solution ($1 \mu\text{L} = 0.1 \mu\text{g Cl}^-$). Dilute 1 mL of the chloroform stock solution to 100 mL with methanol (100 mg of chlorine/L).

5.11 Chloroform Quality Control (QC) reference sample ($100 \mu\text{g/L}$). Prepare an aqueous standard by injecting 100 μL of the chloroform calibration standard ($100 \text{ mg of Cl}^-/\text{L}$) into a Class A volumetric flask containing 100 mL of water. Mix and store in a bottle with zero headspace. Analyze within two hours after preparation.

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 of this manual.

6.2 All samples should be collected in bottles with Teflon lined silicone septa (e.g., Pierce #12722 or equivalent) and be protected from light. If this is not possible, use amber glass 250-mL bottles fitted with Teflon lined caps.

6.3 All glassware must be cleaned prior to use according to the process described in Step 3.1.1.

6.4 Special care should be taken in handling the sample in order to minimize the loss of volatile organohalides. This is accomplished through elimination of headspace and by minimizing the number of transfers.

6.5 Reduce residual chlorine, if present, by adding sodium sulfite (5 mg of sodium sulfite crystals per liter of sample). Sodium sulfite should be added to empty sample bottles at the time of sampling. Shake vigorously for 1 minute after bottle has been filled with sample and properly sealed. Samples should be stored at 4°C without headspace. POX may increase during storage of the sample.

6.6 All samples must be analyzed within 14 days of collection.

7.0 PROCEDURE

7.1 Calibration.

7.1.1 Assemble the sparging/pyrolysis/microcoulometric-titration apparatus shown in Figure 1 in accordance with the manufacturer's specifications. Typically a CO₂ flow of 150 mL/min and a sparger temperature of 45 ± 5°C are employed. 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). Flow rate and temperature changes will affect the compounds that are purged and change the percent recovery of marginal compounds. Therefore, these parameters should not be varied. Adjust gas flow rate according to manufacturer's directions.

7.1.2 Turn on the instrument and allow the gas flow 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⁻ equivalents by injecting various amounts (1 to 80 µL) of the sodium chloride calibration standard directly into the titration cell and integrating the response using the POX integration mode. If desired, the analog output of the titration cell can be displayed on a strip chart recorder. The range of sodium chloride amounts should cover the range of expected sample concentrations and should always be less than 80 µg of Cl⁻. The integrated response should read within 2% or 0.05 µg of the quantity injected (whichever is larger) over the range 1-80 µg Cl⁻. If this calibration requirement is not met, then the instrument sensitivity parameters should be adjusted according to the manufacturer's specifications to achieve an accurate response.

7.1.4 Check the performance of the analytical system daily by analyzing three 5-mL aliquots of a freshly prepared 100 µg/L chloroform check standard. The mean of these three analyses should be between 0.4-0.55 µg of 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.

NOTE: Low chloroform recovery can often be traced to a vitrified inlet tube. The tube should be checked regularly and the analyst should be able to determine, based on chloroform recoveries, when the tube should be replaced.

7.1.5 Determine an instrument blank daily by running an analysis with the purge vessel empty. The instrument blank should be 0.00 ± 0.05 μg of Cl^- . Analyze a calibration blank sample daily. The calibration blank should be within 0.02 μg of Cl^- of the reagent blank.

7.2 Sample analysis

7.2.1 Select a chloroform spike concentration representative of the expected levels in the samples. Using the chloroform stock solution, prepare a spiking solution in methanol which is 500 times more concentrated than the selected spike concentration. Add 10 μL of the spiking solution to 5 -mL aliquots of the samples chosen for spiking (refer to Section 8.0, Quality Control, for guidance in selecting the appropriate number of samples to be spiked).

7.2.2 Allow sample to come to ambient temperature prior to drawing it into the syringe. Remove the plunger from a 5 -mL or 10 -mL syringe and attach a closed syringe valve. If maximum sensitivity is desired and the sample does not foam excessively, a 10 -mL sample aliquot may be analyzed. Otherwise 5 -mL aliquots should be used. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5 mL. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data (e.g., accidental spill), or for duplicate analysis.

7.2.3 Attach the syringe valve assembly to the syringe valve on the purging device. Place the pyrolysis/microcoulometer system in the POX integration mode to activate the integration system. Immediately open the syringe valves and inject the sample into the purging chamber.

7.2.4 Close both valves and purge the sample for 10 minutes.

7.2.5 After integration is complete, open the syringe valves and withdraw the purged sample. Flush the syringe and purging device with water prior to analyzing other samples.

7.2.6 If the integrated response exceeds the working range of the instrument, prepare a dilution of the sample from the aliquot in the second syringe with water and reanalyze. The water must meet the criteria of Step 7.1.5. It may be necessary to heat and purge dilution waters.

7.3 Pyrolysis procedure

7.3.1 Pyrolysis of the purged organic component of the sample is accomplished by pyrolyzing in a CO_2 -rich atmosphere at a low temperature

to ensure the conversion of brominated trihalomethanes to a titratable species.

7.4 Directly analyze the effluent gases in the microcoulometric-titration cell. Carefully follow instrument manual instructions for optimizing cell performance.

7.5 Calculations - POX as Cl^- is calculated using the following formula:

$$\frac{Q_s}{V} \times 1000 = \mu\text{g/L Purgeable Organic Halide}$$

where:

Q_s = Quantity of POX as μg of Cl^- in the sample aliquot.
 V = Volume of sample aliquot in mL.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection for 3 years. This method is restricted to use by or under supervision of experienced analysts. Refer to the appropriate section of Chapter One for additional quality control guidelines.

8.2 Analyze a minimum of one reagent blank every 20 samples or per analytical batch, whichever is more frequent, to determine if contamination or any memory effects are occurring.

8.3 In addition to the performance check mentioned in Step 7.1.4, verify calibration with an independently prepared chloroform QC reference sample every 15 samples.

8.4 Analyze matrix spiked samples for every 10 samples or analytical batch, whichever is more frequent. The spiked sample is carried through the whole sample preparation process and analytical process.

8.5 Analyze all samples in replicate.

9.0 METHOD PERFORMANCE

9.1 Under conditions of duplicate analysis, the reliable limit of detection is 5 $\mu\text{g/L}$.

9.2 Analyses of distilled water, uncontaminated ground water, and ground water from RCRA waste management facilities spiked with volatile chlorinated organics generally give recoveries of 44-128% over the concentration range of 29-4500 $\mu\text{g/L}$. Relative standard deviations are generally less than 20% at concentrations greater than 25 $\mu\text{g/L}$. These data are shown in Tables 1 and 2.

10.0 REFERENCES

1. Takahashi, Y.; Moore, R.T.; Joyce, R.J. "Measurement of Total Organic Halides (TOX) and Purgeable Organic Halides (POX) in Water Using Carbon Adsorption and Microcoulometric Determination"; Proceedings from Division

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3. Fed. Regist. 1979, 45, 69468-69473; December 3.
4. Rohrbough, W.G.; et al. Reagent Chemicals, American Chemical Society Specifications, 7th ed.; American Chemical Society: Washington, DC, 1986.
5. "Development and Evaluation of Methods for Total Organic Halide and Purgeable Organic Halide in Wastewater"; U.S. Environmental Protection Agency. Environmental Monitoring and Support Laboratory. Cincinnati, OH, 1984; EPA-600/4-84-008; NTIS-PB-84-134-337.
6. 1985 Annual Book of ASTM Standards, Vol. 11.01; "Standard Specification for Reagent Water"; ATSM: Philadelphia, PA, 1985; D1193-77.
7. Dohrmann. Rosemount Analytical Division. Santa Clara, CA 95052-8007.
8. Cosa Instruments. Norwood, NJ 21942.

TABLE 1.
PRECISION AND ACCURACY DATA FOR SELECTED PURGEABLE ORGANIC HALIDES
(Reference 5)

Compound	Dose ¹ (µg/L as Cl ⁻)	Average Recover (µg/L as Cl ⁻)	Average Percent Recovery	Standard Deviation	MDL ² (µg/L)	Number of Replicates
Chloroform	11	11	100	1.4	4.5	7
Trichloroethene	10	6	60	0.7	2.2	7
Tetrachloroethene	10	5	50	0.8	3.2	7
Chlorobenzene	8	3	38	0.6	2.0 ³	7

¹Ten milliliter aliquot of spiked reagent water analyzed.

²The 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.

³Practical MDL probably greater (approximately 5 to 6 µg/L) due to low recovery.

TABLE 2.
PRECISION AND ACCURACY DATA FOR VARIOUS WATER SAMPLES
(Reference 5)

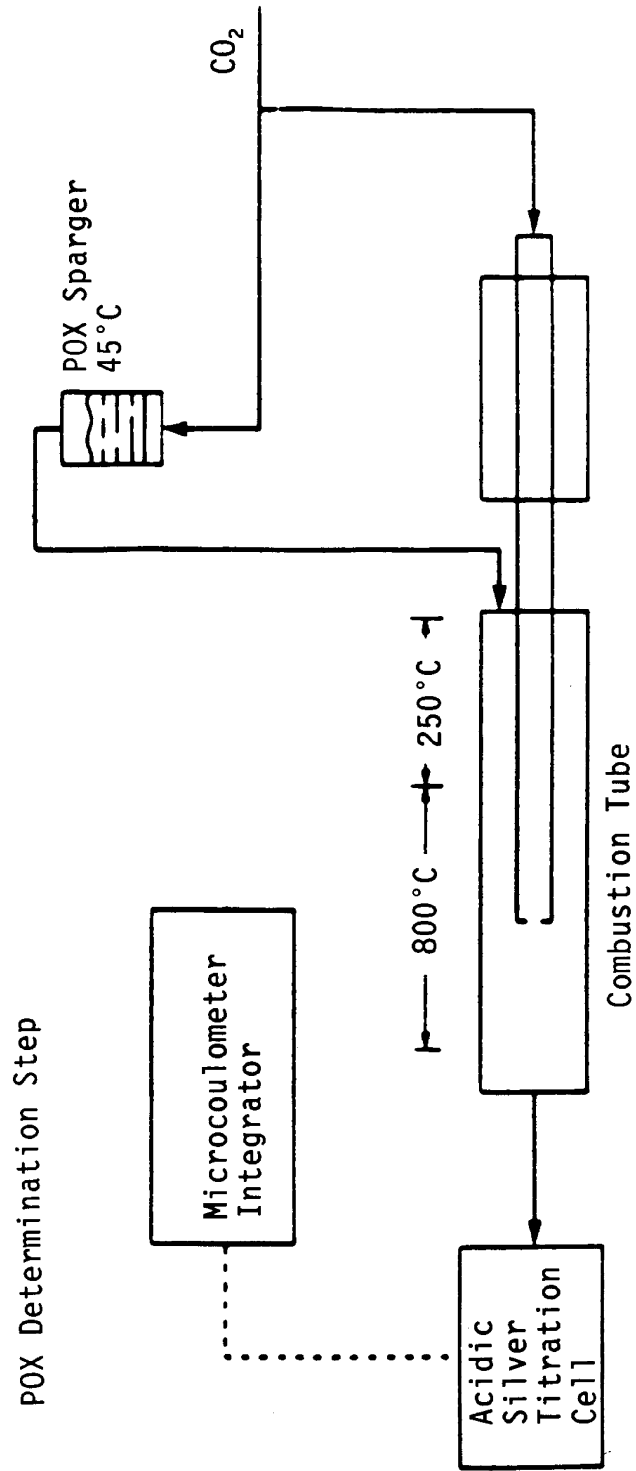
Sample ¹	Background Spike Component	Level (µg/L as Cl ⁻)	Spike Level (µg/L as Cl ⁻)	Average Percent Recovery	Standard Deviation	Number of Replicates
Tap Water	---	---	0	---	2	3
POTW Sewage	Chloroform	68	29	128	5	3
Chlorinated Hydrocarbon Plant Wastewater	Chloroform	114	460	77	36	3
Chlorinated Hydrocarbon Plant Wastewater	Chloroform	32	1,500	50	32	3
Chlorinated Hydrocarbon Plant Wastewater	Chloroform	32	4,500	87	470	3
Solid Waste ² Leachate	1,1-Dichloro-ethane	171	800	41	17	3
Industrial Wastewater	Methylene chloride	510	800	65	120	3
Aniline ³ Wastewater	Chloroform	15,700	15,000	150	58	3
Aniline ³ Wastewater	Chloroform	15,700	45,000	91	400	3

¹Five milliliter sample aliquots analyzed.

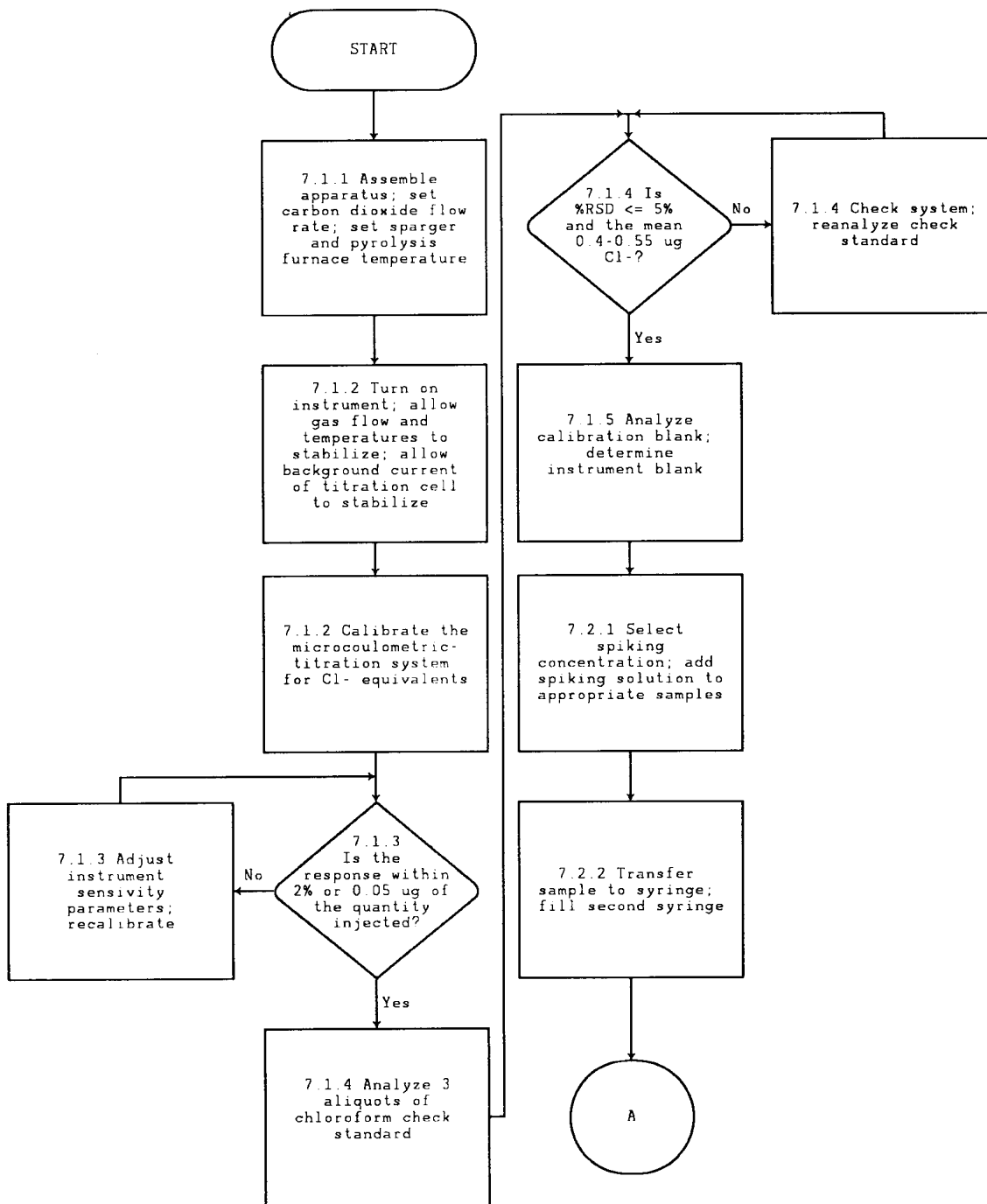
²Diluted 200:1 prior to analysis. Values for this sample are in mg/L for original sample.

³Diluted 10:1 prior to analysis. Values are for undiluted sample.

FIGURE 1.
MICROCOULOMETRIC - TITRATION SYSTEM



METHOD 9021
PURGEABLE ORGANIC HALIDES (POX)



METHOD 9021
(Continued)

