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METHOD 504.1

I. SCOPE AND APPLICATION:

This method is applicable to the determination of the following compounds in finished drinking water and groundwater.

<u>Analyte</u>	<u>Chemical Abstract Services Analyte Registry Number (CASRN)</u>
1,2-Dibromoethane (EDB)	106-93-4
1,2-Dibromo-3-chloropropane (DBCP)	96-12-8

II. REAGENTS :

- Sodium Thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$)- ACS Reagent grade
- Hydrochloric acid 18% (1:1) 0.5 ml per 40 ml vial
- Reagent water- free of analytes (used for travel blanks)

III. MATERIALS:

- 40 ml amber vial vials.
- Glass pipettes with rubber bulbs
- Kim Wipe napkins
- Paper towels
- Pool and Spa 3-Way Test Strips (Chem Lab Products, Inc.)
- pH indicator test strips (low end)
- Laboratory grade latex gloves
- Protective eyewear
- Pliers

IV. PROCEDURE:

1. Remove any attachments such as hoses, screens or aeration devices on the faucet. Inspect the faucet for anything that may fall into the sample container.
2. Open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 minutes).
3. Adjust the flow to about 500 ml/min and collect the *experimental* semi-volatile vial sample ensuring not to overflow the vial. Allow a meniscus to form at the mouth of the vial. The flow should be slow enough as to prevent tiny air bubbles from purging the sample during collection. Avoid trapping air bubbles in the sample.
4. Test the sample for free and combined chlorine by dipping a test strip into the sample and remove, giving the test strip a quick flick of the wrist to shake off excess water. Compare the color of the test patch with the reference chart on the bottle. This determination should be ascertained within the first 30 seconds.
5. If chlorine is present, cap the sample ensuring there is little to no headspace and invert the vial three times.
6. Uncap the vial and retest using a fresh test strip.
7. If no chlorine is detected, annotate results in the field notebook and proceed with the acidification procedure in step #11.
8. If chlorine persists, add two drops of liquid sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) using a clean glass pipette, recap ensuring little to no head space and invert the vial three times.
9. Uncap the vial and retest using a fresh test strip.
10. If no chlorine is detected, annotate results in the field notebook and proceed with the acidification procedure in step #11.
11. If chlorine persists, continue the cycle of adding two drops of $\text{Na}_2\text{S}_2\text{O}_3$ using to the vial, recapping, inverting, uncapping, and retesting until no chlorine is detected. Remember to annotate in the field notebook the final amount of $\text{Na}_2\text{S}_2\text{O}_3$ added. When the *regulatory* semi-volatile sample is obtained, preserve that sample using the same amount of $\text{Na}_2\text{S}_2\text{O}_3$ as determined by the *experimental* sample.

IV. PROCEDURE (continued):

12. The *experimental* sample must now be tested for pH concentration. Begin by adding 10 drops of 1:1 HCl (0.5 ml) to the sample and capping. Invert three times and uncap. Dip a strip of pH test paper indicator into the experimental sample and remove, giving the test strip a quick flick of the wrist to shake off excess water. Compare the color change to the reference chart. Determining the pH must be accomplished within a 30 second period. The sample must be acidified to a pH of ≤ 2 . If the sample is adequately preserved, then annotate the results in the field notebook and store the *experimental* sample in its rack until it can be disposed of back at ADEQ.
13. If the pH is higher than 2, add 5 drops of 1:1 HCl using a clean glass pipette to the sample, recap, and invert three times.
14. Uncap the vial and retest using a fresh pH test strip.
15. If the pH is ≤ 2 , then record in the field notebook the number of drops needed to adequately acidify the sample. If the pH is > 2 , continue the cyclic procedure of adding 5 drops of HCl, capping, inverting three times, uncapping and retesting using a fresh pH strip until the sample is adequately preserved. Record the final number of drops required by the sample to acidify to a pH ≤ 2 in the field notebook.
16. After establishing the number of drops of $\text{Na}_2\text{S}_2\text{O}_3$ and HCl required by the *experimental* semi-volatile sample for proper preservation, obtain the *regulatory* sample in precisely the same fashion ensuring not to trap any air in the vial. Add the same number of drops of $\text{Na}_2\text{S}_2\text{O}_3$ and HCl as determined by the previous *experimental* sample, cap, invert the sample three times and place in the ice chest for transportation.

V. SAMPLE TRANSPORT:

After obtaining the water samples in duplicate, dry the bottle and attach the preprinted label to it as well as securing the completed chain of custody seal around the plastic cap of each semi-volatile vial. Place each pair of vials into a ziplock baggie and seal. The samples must be placed in the ice chest and chilled to 4°C and maintained at that temperature until analysis. Always use chopped, grated, or dry ice when chilling the samples for transportation. Never use “blue ice” as the samples may not chill adequately.

VI. SAMPLE STORAGE:

Field samples that will not be received at the laboratory on the day of collection must be packaged for shipment with sufficient ice to ensure they will be at 4°C upon arrival at the laboratory. Store samples and field reagent blanks together at 4°C until analysis. The sample storage area must be free of organic solvent vapors. All samples must be analyzed within 28 days of collection. Any samples not analyzed within this period must be discarded and replaced.

VII. DEFINITIONS:

- A. *Experimental Semi-Volatile Vial*-- The preliminary sampling vial used to determine the amount of sodium thiosulfate or ascorbic acid required to reduce the free and combined chlorine in the water sample as well as the amount of acid necessary to bring the sample to a pH of 2 or below.
- B. *Regulatory Semi-Volatile Vial*-- The actual semi-volatile sampling vial to be submitted to the laboratory for analysis. The regulatory semi-volatile vial shall contain the same amount of chlorine reducing agent and acid as was determined with the experimental semi-volatile vial.
- C. *Preservative*-- As used in this procedure refers to any chemical additive used to reduce chlorine or acidify the sample.
- D. *Free Chlorine Residual*-- Chlorine (Cl₂), hypochlorous acid (HOCl), or hypochlorite ion (OCl⁻).
- E. *Combined Chlorine Residual*-- synonymous with the chloramine class consisting of monochloramine, dichloramine, and trichloramine.

VIII. SAFETY:

The use of protective eyewear and laboratory quality latex gloves is highly recommended when collecting and preserving samples.

IX. SUMMARY OF METHODS:

Method 504.1: In the 40 ml vial which contains the sample, 5 ml of sample are removed from the vial and discarded. The sample is spiked with a surrogate and any other target compounds for quality control purposes. The spikes containing surrogate or target compounds are in either acetone or an alcohol matrix that forms an azeotroph with the water in the sample. The sample is “salted” out by adding 6 grams of sodium chloride and then 2 ml of hexane extraction solvent is added to the sample. Because water is a denser, polar substance and hexane is a lighter, nonpolar substance, the two immiscible liquids form a bilayer with hexane at the top. The sample is then recapped and mixed vigorously to complete the extraction process. The overall effect of this “salting” out procedure acts to “partition” or push the nonpolar EDP and DBCP analytes out of the water sample and into the nonpolar hexane extraction solvent. The hexane layer is removed from the sample and placed into a micro-vial.

Two μ l of the hexane extract is then injected into onto the column of a gas chromatograph for separation which is equipped with a linearized electron capture detector (ECD) for analysis and quantitation. Aqueous calibration standards are extracted and analyzed in an identical manner as the samples in order to compensate for extraction losses. The extraction time is 30 to 50 minutes per sample depending upon the analytical conditions selected. Confirmatory evidence can be obtained using a dissimilar column. When component concentrations are sufficiently high, Method 524.2 may be employed for improved specificity.