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METHODS 502.2 & 524.2

I. SCOPE AND APPLICATION:

This is a general purpose procedure for the collection of volatile organic compounds in finished drinking water, raw source water, or drinking water in any treatment stage. This collection procedure is applicable to a wide range of organic compounds, including the four trihalomethane disinfection byproducts, that have sufficiently high volatility and low water solubility to be efficiently removed from water samples with purge and trap procedures. This sampling procedure is used to obtain water samples for the analysis of the following 60 different volatile organic compounds. Of these, EPA requires that 23 regulated and 20 unregulated compounds be reported for compliance purposes.

Analyte	Chemical Abstract Services Registry Number (CASRN)
Benzene*****	71-43-2
Bromobenzene °	108-86-1
Bromochloromethane	74-97-5
Bromodichloromethane °	75-27-4
Bromoform °	75-25-2
Bromomethane °	74-83-9
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
Carbon tetrachloride*****	56-23-5
Chlorobenzene*****	108-90-7
Chloroethane °	75-00-3
Chloroform °	67-66-3
Chloromethane °	74-87-3
2-Chlorotoluene °	95-49-8
4-Chlorotoluene °	106-43-4
Dibromochloromethane °	124-48-1

Analyte	Chemical Abstract Services Registry Number (CASRN)
1,2-Dibromo-3-chloropropane	96-12-8
1,2-Dibromoethane	106-93-4
Dibromomethane °	106-93-4
1,2-Dichlorobenzene*****	95-50-1
1,3-Dichlorobenzene °	541-73-1
1,4-Dichlorobenzene*****	106-46-7
Dichlorodifluoromethane	75-71-8
1,1-Dichloroethane °	75-34-3
1,2-Dichloroethane*****	107-06-2
1,1-Dichloroethene*****	75-34-4
cis-1,2-Dichloroethene*****	156-59-4
trans-1,2-Dichloroethene*****	156-60-5
1,2-Dichloropropane*****	78-87-5
1,3-Dichloropropane °	142-28-9
2,2-Dichloropropane °	590-20-7
1,1-Dichloropropene °	563-58-6
cis-1,3-Dichloropropene °	10061-01-5
trans-1,3-Dichloropropene °	10061-02-6
Ethylbenzene*****	100-41-4
Hexachlorobutadiene	87-68-3
Isopropylbenzene	98-82-8
4-Isopropyltoluene	99-87-6
Methylene chloride*****	75-09-2
Naphthalene	91-20-3
Propylbenzene	103-65-1
Styrene*****	100-42-5
1,1,1,2-Tetrachloroethane °	630-20-6
1,1,2,2-Tetrachloroethane °	79-34-5
Tetrachloroethene*****	127-18-4
Toluene*****	108-88-3
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trichlorobenzene*****	120-82-1
1,1,1-Trichloroethane*****	71-55-6
1,1,2-Trichloroethane*****	79-00-5
Trichloroethene*****	79-01-6
Trichlorofluoromethane	75-69-4
1,2,3-Trichloropropane °	96-18-4
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8
Vinyl chloride*****	75-01-4
o-Xylene*****	95-47-6

Analyte	Chemical Abstract Services Registry Number (CASRN)
m-Xylene*****	108-38-3
p-Xylene*****	106-42-3

***** Regulated compounds
°Unregulated compounds

II. REAGENTS :

- Ascorbic acid- ACS Reagent grade
- Sodium Thiosulfate ($Na_2S_2O_3$)- ACS Reagent grade
- Hydrochloric acid 18% (1:1) 0.5 ml per 40 ml voa vial
- Reagent water- free of analytes (used for travel blanks)

III. MATERIALS:

& 40 ml voa vials.
& Glass pipettes with rubber bulbs
& Paper towels & Kim Wipe napkins
& 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. Open the tap and allow the system to flush until the water temperature has stabilized (usually about 10 minutes.)

2. Adjust the flow to about 500 ml/min and collect the ***experimental*** voa 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.

3. 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.

IV. PROCEDURE (continued):

4. If chlorine is present, cap the sample ensuring there is little to no headspace and invert the vial three times.

5. Uncap the vial and retest using a fresh test strip.

6. If no chlorine is detected, annotate results in the field notebook and proceed with the acidification procedure in step #11.

7. If chlorine persists, add two drops of either liquid sodium thiosulfate ($Na_2S_2O_3$) or ascorbic acid (whichever preservative is present in the voa vial originally) using a clean glass pipette, recap ensuring little to no head space and invert the vial three times. ***Remember: Method 502.2 may use either preservative while Method 524.2 requires ascorbic acid only!***

8. Uncap the vial and retest using a fresh test strip.

9. If no chlorine is detected, annotate results in the field notebook and proceed with the acidification procedure in step #11.

10. If chlorine persists, continue the cycle of adding two drops of $Na_2S_2O_3$ (or ascorbic acid) 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 $Na_2S_2O_3$ or ascorbic acid added. When the ***regulatory*** voa sample is obtained, preserve that sample using the same amount of $Na_2S_2O_3$ (or ascorbic acid) as determined by the ***experimental*** sample.

11. The ***experimental*** sample must now be tested for pH concentration. Begin by adding 5 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.

12. 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.

13. Uncap the vial and retest using a fresh pH test strip.

IV. PROCEDURE (continued):

14. If the pH is $\leq$ 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 $\leq$ 2 in the field notebook.

15. After establishing the number of drops of $Na_2S_2O_3$ and HCl required by the ***experimental*** voa 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 $Na_2S_2O_3$ 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, attach the completed sample label to the voa vial and the chain of custody seal around the plastic cap of each voa vial. Information to document on the label includes, field sampling number, sampler=s initials, date and time, type of analysis requested and any chemical preservatives. Place each pair of vials into a ziplock baggie and seal. The samples must be placed in the ice chest and chilled to 4EC and maintained at that temperature until analysis. Always use chopped, grated, or dry ice when chilling the voa samples for transportation. Never use Ablue ice@ as the voa samples may not chill adequately. 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 4EC upon arrival at the laboratory.

VI. SAMPLE STORAGE:

Store samples at 4EC until analysis. The sample storage area must be free of organic solvent vapors.

All samples must be analyzed within 14 days of collection. Any samples not analyzed within this period must be discarded and replaced.

VII. DEFINITIONS:

A. *Experimental Voa 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 Voa Vial*-- The actual voa sampling vial to be submitted to the laboratory for analysis. The regulatory voa vial shall contain the same amount of chlorine reducing agent and acid as was determined with the experimental voa vial.

C. *Preservative*-- As used in this procedure refers to any chemical additive used to reduce chlorine or acidify the sample. Method 502.2 requires sodium thiosulfate or ascorbic acid to dechlorinate treated water. Method 524.2 requires ascorbic acid only to dechlorinate treated waters.

D. *VOA*-- Volatile organic compound

E. *Free Chlorine Residual*-- Chlorine (Cl_2), hypochlorous acid (HOCl), or hypochlorite ion (OCl^-).

F. *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 502.2--Highly volatile organic compounds with low water solubility are extracted (purged) from the sample matrix by bubbling an inert gas through a 5 ml aqueous sample The purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and back flushed with helium to desorb the trapped sample components onto a capillary gas chromatography (GC) column. The column is temperature programmed to separate the method analytes that are then detected with a photoionization detector (PID) and a halogen specific detector such as an electrolytic conductivity detector (ELCD) which are placed in series. The elution time and size of the peak help identify the contaminant and its concentration in the sample.

IX. SUMMARY OF METHODS (continued):

METHOD 524.2--This method is identical to the 502.2 method up through the desorption of the trapped sample components onto the capillary column. As the column separates the sample into its various components the method analytes are detected with a mass spectrometer (as opposed to a PID and ELCD detector). The compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times in a library database. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples. The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.