

**Originator: Kenyon C. Carlson, Manager
ADEQ QA Unit**

**Contact For
Information: Kenyon C. Carlson, Manager
ADEQ QA Unit**

METHOD 551

I. SCOPE AND APPLICATION:

This method is applicable to the determination of the following analytes in finished drinking water, drinking water during intermediate stages of treatment, and raw source water:

<u>Analyte</u>	<u>Chemical Abstract Services Registry Number (CASRN)</u>
Bromochloroacetonitrile *	83463-62-1
Bromodichloromethane E	75-27-4
Bromoform E	75-25-2
Carbon tetrachloride •	56-23-5
Chloral hydrate *	75-87-6
Chloroform E	67-66-3
Chloropicrin *	76-06-2
Dibromoacetonitrile *	3252-43-5
Dibromchloromethane E	124-48-1
1,2-Dibromo-3-chloropropane (DBCP) •	96-12-8
1,2-Dibromoethane (EDB) •	106-93-4
Dichloroacetonitrile *	3018-12-0
Trichloroacetonitrile *	545-06-2
Tetrachloroethylene (PCE) •	127-18-4
1,1,1-Trichloroethane (TCA) •	71-55-6
Trichloroethylene (TCE) •	79-01-6
1,1,1-Trichloro-2-propanone *	918-00-3
1,1-Dichloro-2-propanone *	513-88-2

E THMs

• Halogenated solvents

*Organic disinfection by-products

II. REAGENTS:

- Ammonium chloride solution -(dechlorinating preservative used for analysis of total analyte list)
- Sodium thiosulfate solution -(dechlorinating preservative used for THMs)
- Sodium sulfite solution -(dechlorinating preservative used for THMs)
- Ascorbic acid solution -(dechlorinating preservative used for THMs)
- Ammonium chloride -(dechlorinating preservative used for THMs)
- 0.2 N HCl solution

III. MATERIALS:

- & 40 ml amber VOA vial
- & Kim Wipe napkins
- & Glass pipettes with rubber bulbs
- & 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

III. DECHLORINATION:

The analyte list of for this method may be conveniently divided into three classes: the four THMs, the six halogenated solvents, and the remaining eight organic disinfectant by-products. The halogenated solvents are quite stable compounds by design and the stability upon storage after collection is not an issue. Likewise, the THMs can be preserved by any of the following dechlorinating reagent: sodium thiosulfate, sodium sulfite, ascorbic acid, or ammonium chloride.

If the sample assay is only for the THMs and/or solvents, the acidification step should be omitted and only the dechlorination reagent should be employed. Thiosulfate, sulfite, and ascorbic acid promote the decomposition of some members of the organic disinfection by-products (e.g. the dihaloacetonitriles and chloropicrin) and may not be used as a dechlorination reagent in their analysis. Also, most of the organic disinfection by-products require the acidification step for storage stability. Therefore, analysis for the total analyte list requires the use of ammonium chloride for dechlorination as well as sample acidification.

There is an, however, a possible exception of a separate sampling requirement for chloral hydrate. In some matrices dechlorinated with ammonium chloride, the fortified matrix recoveries (spikes) have been lower than expected by 50% or greater, when compared to the same sample dechlorinated with ascorbic acid, or sodium sulfite. In other matrices, recoveries have been normal and the reasons for these differences has not been determined. To avoid problems and a resampling event, a separate sample, dechlorinated with ascorbic acid or sodium sulfite must be collected for the analysis of chloral hydrate.

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 low 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.
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 ($\text{Na}_2\text{S}_2\text{O}_3$), ascorbic acid, sodium sulfite, or ammonium chloride (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 551 may use any of the four preservatives, depending on what target compounds are being analyzed**
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 whatever preservative was used initially, recapping, inverting, uncapping, and retesting until no chlorine is detected. Remember to annotate in the field notebook the final amount of $\text{Na}_2\text{S}_2\text{O}_3$ or ascorbic acid added. When the *regulatory* voa sample is obtained, preserve that sample using the same amount of $\text{Na}_2\text{S}_2\text{O}_3$ (or ascorbic acid) as determined by the *experimental* sample.

IV. PROCEDURE (CONTINUED):

11. 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 4.5-5.0 using 0.2 N HCL. 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.
14. 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.
15. After establishing the number of drops of $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{Na}_2\text{S}_2\text{O}_3$ 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, 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 4°C and maintained at that temperature until analysis. Always use chopped, grated, or dry ice when chilling the voa samples for transportation. Never use blue 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 4°C 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 (Cl₂), 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 METHOD:

A 35 ml sample aliquot is extracted with 2 ml of methyl-tert-butyl ether (MTBE). After the two phases separate, the top phase (MTBE solvent containing the target compounds) is removed and placed in a hermetically sealed container. Two μl of the extract is then injected into a gas chromatograph (GC) equipped with a fused silica capillary column and linearized electron capture detector for separation and analysis. Aqueous calibration standards are also extracted and analyzed in order to compensate for any extraction losses. A typical sample can be extracted and analyzed in 40 to 50 min using the primary column chosen for this method. Confirmation of the eluted compounds may be obtained using a dissimilar column or by the use of gas chromatography-mass spectroscopy (GCMS).