

Ascorbic acid reduction of residual active chlorine in potable water prior to halocarboxylate determination†

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In studies on the formation of disinfection byproducts (DBPs), it is necessary to scavenge residual active (oxidizing) chlorine in order to fix the chlorination byproducts (such as haloethanoates) at a point in time. Such research projects often have distinct needs from requirements for regulatory compliance monitoring. Thus, methods designed for compliance monitoring are not always directly applicable, but must be adapted. This research describes an adaptation of EPA Method 552 in which ascorbic acid treatment is shown to be a satisfactory means for reducing residual oxidizing chlorine, *i.e.*, HOCl, ClO⁻, and Cl₂, prior to determining concentrations of halocarboxylates. Ascorbic acid rapidly reduces oxidizing chlorine compounds, and it has the advantage of producing inorganic halides and dehydroascorbic acid as opposed to halogenated organic molecules as byproducts. In deionized water and a sample of chlorinated tap water, systematic biases relative to strict adherence to Method 552 were precise and could be corrected for using similarly treated standards and analyte-fortified (spiked) samples. This was demonstrated for the quantitation of chloroethanoate, bromoethanoate, 2,2-dichloropropanoate (dalapon), trichloroethanoate, bromochloroethanoate, and bromodichloroethanoate when extracted, as the acids, into *tert*-butyl methyl ether (MTBE) and esterified with diazomethane prior to gas chromatography with electron capture detection (GC-ECD). Recoveries for chloroethanoate, bromoethanoate, dalapon, dichloroethanoate, trichloroethanoate, bromochloroethanoate, bromodichloroethanoate, dibromoethanoate, and 2-bromopropanoate at concentrations near the lower limit of detection were acceptable. Ascorbic acid reduction appears to be the best option presently available when there is a need to quench residual oxidants fast in a DBP formation study without generating other halospecies but must be implemented cautiously to ensure no untoward interactions in the matrix.

Aim of investigation

Issues surrounding the decision to reduce residual oxidizing disinfectants (*i.e.*, Cl₂, HOCl, and NaOCl) have been discussed previously as related to the analysis of halogenated disinfection byproducts.¹ The desirable characteristics of dechlorinating agents and the relevant chemical concerns have also been covered, including deficiencies of some reagents used in this manner.¹ In this report, we evaluate ascorbic acid as a dechlorinating agent in the determination of haloacetic acids containing bromine and chlorine. Previous work suggested that ascorbic acid (HAsc) might prove suitable for the haloacetic acids.^{1,2}

EPA's Environmental Monitoring Systems Laboratory (EMSL) established Method 552 for the quantitation of halocarboxylates (often referred to as the haloacetic acids or HAAs) in 1990.³ This version used diazomethane (CH₂N₂) to esterify the extracted carboxylic acids. In 1995, concerns over diazomethane led EPA's National Exposure Research Laboratory (NERL, previously EMSL) to change the esterification reagent to acidic methanol.⁴ However, many laboratories, including our own, have continued to safely use diazomethane

for methylation. In addition to changing the esterification, Revision 1.0 prescribes ammonium chloride to convert chlorine-based oxidants to chloramine.⁴ EPA's NERL demonstrated that ammonium ion is satisfactory within a specified limit of error and under a variety of drinking water conditions, using multiple laboratory testing. Nonetheless, the search for chlorine-oxidant scavengers that are generally useful for a wide variety of analytes continues. Following from previous work,¹ ascorbic acid was evaluated as a dechlorinating reagent prior to the quantitation of certain halocarboxylates in aqueous solution with particular interest in applying it to drinking water analysis.

Experimental section¶

Part I. Effects at high analyte concentrations (≥50 ng mL⁻¹)

Standards and test solutions. Halocarboxylic acid standards in *tert*-butyl methyl ether were obtained from Supelco (Bellefonte, PA, USA). Aliquots of the commercial solution were injected *via* gastight syringes into 20.0 mL portions of doubly deionized water in 40 mL EPA vials (polypropylene screw caps and PTFE septa) to produce standard test solutions. Twelve solutions at each concentration were prepared by injecting 0, 10, 20, or 50 µL of the stock standard. This gave the following concentrations: for chloroethanoic and dichloroethanoic acids, 0, 150, 300, 750 ng mL⁻¹; for bromoethanoic,

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2,2-dichloropropanoic, bromochloroethanoic, and bromodichloroethanoic acids, 0, 100, 200, 500 ng mL⁻¹; and for trichloroethanoic, dibromoethanoic, and 2-bromopropanoic acids, 0, 50, 100, 250 ng mL⁻¹.

These were acidified with 1.0 mL of 0.25 M sulfuric acid to minimize hydrolysis. Analyte concentrations for Part I are about 100 times greater than what would be found in most chlorinated potable water supplies. The concentrations were intentionally elevated with the aim of magnifying any adverse impacts as the concentrations of both the ascorbic acid and the analytes are very large relative to the lower limits of detection. A slow interaction, for example, might not be distinguishable from the normal imprecision of the method at low concentrations, but would be made more apparent if the concentrations were increased.

Ascorbic acid addition. Six of the standards at each concentration were reserved for the addition of ascorbic acid. A 2.00 mL aliquot of 1.1 M L-ascorbic acid solution was pipetted into each test standard, producing a post-mixing concentration of 0.10 M. This final concentration was chosen to ensure excess HAsc relative to typical residual chlorine concentrations found in tap water and to make any interactions more apparent.

Sample treatment. Half of each set (3 with HAsc and 3 without) of standards was analyzed immediately. The other half (3 with HAsc and 3 without) was retained for 16 d at 7 ± 2 °C. After addition of 2.0 mL of 98% w/w H₂SO₄, each standard was extracted with 4.0 mL of pesticide residue analysis grade *tert*-butyl methyl ether; dropwise addition of 0.25% w/w FD&C Blue No. 1 (Erioglaucine [3844-45-9] CI 42090) aqueous solution improved the visibility of the phase boundary. Extracts were drawn off from the aqueous phase and dried with anhydrous environmental analysis grade sodium sulfate. The carboxylic acid moieties were esterified with diazomethane using a method described elsewhere,⁵ then transferred to autosampler vials and stored in a freezer at -80 °C pending GC-ECD analysis.

GC-ECD analysis. Extracts were analyzed on a Hewlett-Packard (Palo Alto, CA, USA) 6890 GC-ECD system equipped with an HP 7673 autoinjector. Volumes of 2.5–5.0 µL (splitless) were injected onto a J&W Scientific (Folsom, CA, USA) DB-5MS column (30 m × 250 µm id × 0.25 µm film) at constant (high purity) helium flow of 1.0 mL min⁻¹; inlet and detector temperatures: 270 °C. Temperature program: hold 35 °C for 10.0 min; ramp 5.0 °C min⁻¹ to 75 °C, hold for 15.0 min; ramp 5.0 °C min⁻¹ to 100 °C, hold for 5.0 min; ramp 5.0 °C min⁻¹ to 135 °C; hold for 2.0 min. Analytes, chemical formulae, and related information are given in Table 1.

Recovery from fortified tap water. Cincinnati tap water (source: Ohio River) was collected from a laboratory faucet and represents a typical chlorinated municipal water supply. After 10 min of high flow to flush the pipes, water was collected in glass vessels and used within 1 h of collection. Ten replicates were fortified with 20.0 µL of the HAA standard and 1.00 mL of 0.25 M sulfuric acid. Five of each were treated with 2.0 mL of 1.1 M ascorbic acid, the same as the standards. After capping and mixing, samples were extracted and analyzed as described above. Unspiked samples were used to determine the background levels of chlorination byproduct analytes.

Determination of residual active chlorine in tap water.

Chlorine was determined titrimetrically with ferrous ammonium sulfate after reaction with *N,N*-diethyl-*p*-phenylenediamine (DPD). Commercial DPD #1 Powder reagent mix (LaMotte Co., Chestertown, MD, USA) was used. The method was essentially that in *Standard Methods*.⁶ Reduction of residual oxidant was demonstrated by the absence of color when DPD reagent was added to tap water pretreated with HAsc.

Part II. Effects at low analyte concentrations (2–10 ng mL⁻¹)

Standards and test solutions. Halocarboxylic acid standards in *tert*-butyl methyl ether were obtained from Supelco. Aliquots of the commercial solution were injected *via* gastight syringes into 30.0 mL portions of Cincinnati tap water in 40 mL EPA vials to produce standard test solutions. Three vials with 0.10 M HAsc (made by direct addition of the solid reagent) and three vials without were prepared at the analyte concentrations shown in Table 2. These concentrations reflect those likely to be encountered in chlorinated potable water supplies. The samples were analyzed immediately; therefore, no additional acid was added for preservation.

Sample treatment and analysis. Other than the ascorbic acid used to reduce the oxidizing chlorine, EPA Method 552 (microextraction)⁴ was used for these samples. The methylated extracts were analyzed on a Tremetrics 540 GC (Austin, TX, USA) with a J&W DB-1701 column (30 m × 322 µm id × 0.25 µm film) at constant He pressure of 101 kPa (15 psi). Injections of 2.0 µL were used. The temperature program was that of Method 552.

Results and discussion

Part I. Effects at high analyte concentrations (30–100 ng mL⁻¹)

Data treatment. Chromatographic peak areas were plotted against volume of standard used (µL) in 20 mL of water; see Table 1 for further explanation. Each line represents 3 replicates at each of 3 concentrations for each analyte.

Table 1 Halocarboxylate analytes examined in this work

Analyte anion	Formula of acid	CAS RN ^a	<i>t_r</i> /min ^b	Concentration/µg mL ⁻¹
Chloroethanoate	ClCH ₂ CO ₂ H	[79-11-8]	5.2	300 ^c
Bromoethanoate	BrCH ₂ CO ₂ H	[79-08-3]	8.4	200
2,2-Dichloropropanoate ^d	CH ₃ CCl ₂ CO ₂ H	[75-99-0]	8.8	200
Dichloroethanoate	Cl ₂ CHCO ₂ H	[79-43-6]	9.2	300
Trichloroethanoate	Cl ₃ CCO ₂ H	[76-03-9]	12.8	100
Bromochloroethanoate	BrClCHCO ₂ H	[55589-96-3]	14.8	200
Bromodichloroethanoate	BrCl ₂ CCO ₂ H	[7113-314-7]	17.4	200
Dibromoethanoate	Br ₂ CHCO ₂ H	[631-64-1]	17.9	100
2-Bromopropanoate	CH ₃ CBHCO ₂ H	[598-72-1]	18.3	100

^aRegistry numbers are for the acids, not the anions. ^bRetention times are for the methyl esters and were established using a methyl ester blend standard purchased from Supelco and refer to the DB-1701 column. ^cConcentrations refer to the concentration of each acid in the standard purchased from Supelco; thus, a 10 µL aliquot of standard diluted into 20 mL of water gives a chloroethanoate concentration of 150 ng mL⁻¹ (ppb), etc. ^dParent acid is also known as dalapon.

Table 2 Difference in analyte recovery near the detection limit for samples dechlorinated with ascorbic acid relative to untreated samples^a

Analyte	Concentration/ng mL ⁻¹	Relative recovery (%)	Concentration/ng mL ⁻¹	Relative recovery (%)
Chloroethanoate	5.0	-2 ± 10	10	-5 ± 6
Bromoethanoate	3.3	-17 ± 4	6.6	-11 ± 4
2,2-Dichloropropanoate	3.3	+8 ± 4	6.6	+3 ± 2
Dichloroethanoate	5.0	+1 ± 3	10	+3 ± 2
Trichloroethanoate	1.7	-16 ± 4	3.3	+10 ± 5
Bromochloroethanoate	3.3	+19 ± 5	6.6	+10 ± 5
Bromodichloroethanoate	3.3	-20 ± 20	6.6	-50 ± 10
Dibromoethanoate	1.7	+14 ± 6	3.3	+5 ± 5
2-Bromopropanoate	1.7	+6 ± 2	3.3	-9 ± 2

^aDifferences were calculated from the average of three fortified test solutions of Cincinnati tap water with HAsc and three without. Relative difference = $(A_{w/HAsc} - A_{w/o})/A_{w/o}$, expressed as a percent. Uncertainty was propagated from the estimated standard deviations of the means. No data were rejected as outliers. Other than the use of ascorbic acid, Method 552 (microextraction) was strictly followed.

Slopes and *y*-intercepts were determined by unweighted least squares linear regression; the *y*-intercepts were either statistically indistinct from zero based on the standard errors or less than 10% different from their standard errors. Propagated error was computed in the standard way.⁷

Initial effects. The effect of ascorbic acid on method performance is examined by computing the relative difference in the slopes of calibration curves made in deionized water with and without ascorbic acid treatment: $(m_{w/HAsc} - m_{w/o})/m_{w/o}$, where $m_{w/o}$ is the slope without ascorbic acid and $m_{w/HAsc}$ is the slope with ascorbic acid. Relative differences are shown in Table 3. Comparison of the slopes on day zero shows that ascorbic acid has minimal, but quantifiable impact directly on the analytical procedure in deionized water. Although the difference for 2,2-dichloropropanoate is of debatable meaning, bromochloroethanoate and bromodichloroethanoate are demonstrably affected, with signal reductions of 11% and 17%, respectively. It is unclear whether this is due to a loss of sensitivity or a loss of the analytes themselves. Regardless, the standard errors of the least squares parameters and the regression coefficients indicate that the effect is quantifiable and precise; therefore, it should represent a correctable bias in this instance. For bromochloroethanoate with HAsc: $m = 383 \pm 16$; $R^2 = 0.982$; for bromodichloroethanoate with HAsc: $m = 258 \pm 13$; $R^2 = 0.976$; *y*-intercepts were statistically indistinguishable from zero based on their standard errors.

Effects of extended exposure to HAsc. After 16 d of exposure to ascorbic acid, all analytes showed a signal reduction relative to samples stored without ascorbic acid except for trichloroethanoate, which showed a gain of questionable significance, $5 \pm 4\%$ (see Table 3). The greatest loss that was distinguishable from the propagated error was 6% for chloroethanoate. Consequently, we conclude that this reagent could be readily used for reducing residual chlorine, provided that suitable

Table 3 Relative differences in slopes of unweighted least squares calibration lines showing the effect of ascorbic acid treatment^a

	Day 0 ^b	Day 16 ^{b,c}
Chloroethanoate	+0.2 ± 2%	-6 ± 2%
Bromoethanoate	+4 ± 4	-3 ± 2
2,2-Dichloropropanoate	-4 ± 4	-4 ± 3
Trichloroethanoate	-3 ± 7	+5 ± 4
Bromochloroethanoate	-11 ± 4	-8 ± 8
Bromodichloroethanoate	-17 ± 5	-6 ± 9

^aCalibration lines were plots of peak area vs. volume of standard; each line was determined from duplicate test solutions prepared at five concentrations by diluting specific volumes of standard into 20.0 mL of water: 0 (blank), 10, 20, 50, 100 μL. ^bRelative difference = $(m_{w/HAsc} - m_{w/o})/m_{w/o}$, expressed as a percent; uncertainty was propagated from the standard errors of the least squares slopes. ^cSets with and without HAsc were stored for 16 d in a cold room at $7 \pm 2^\circ\text{C}$.

standards are prepared concurrently with sampling. It is not possible to state whether the effects on bromochloroethanoate and bromodichloroethanoate that are suggested by the day zero data are (1) mediated by other matrix elements over time, (2) rapidly brought about so that no additional effects are observable over 16 d, or (3) masked by the uncertainties of the experimental measurement. Any of these or some combination thereof is possible.

Recovery from fortified tap water. The concentration of residual active chlorine, $[\text{Cl}_2] + [\text{HOCl}] + [\text{ClO}^-]$, in the Cincinnati tap water samples found by DPD Fe^{II} titrimetry was $13 \mu\text{M} = 890 \mu\text{g L}^{-1} \text{Cl}_2$. Blank correction was made by determining background levels of chlorination byproduct analytes in unspiked tap water samples and these were subtracted prior to comparison of HAsc-treated and untreated samples. Fig. 1 shows the results for the HAAs. Analyte response in fortified tap water is actually increased a few percent after ascorbic acid treatment; however, this is certainly within acceptable limits. We note that EPA Method 552 allows for up to 20% variation in analyte recoveries for quality control test samples in deionized water, and up to 30% variation in analyte recoveries for fortified (spiked) tap water samples.

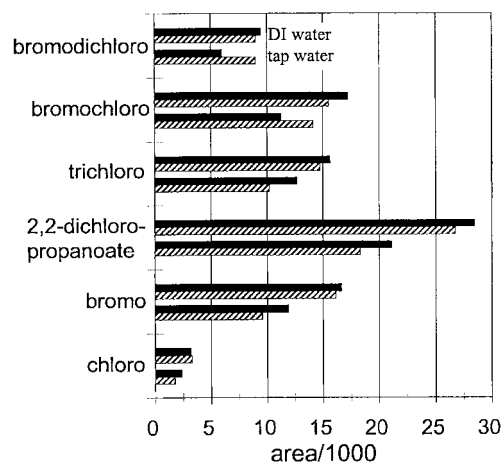


Fig. 1 Relative recoveries (average chromatographic peak areas) for several haloethanoates and 2,2-dichloropropanoate in deionized (DI) water and Cincinnati tap water. Areas are based on a concentration of 300 ng mL^{-1} relative to chloroethanoate (see Table 1 to determine other analytes) and are blank-corrected. Recovery in tap water falls within the permissible 30% window given in Method 552 relative to DI water when not treated with ascorbic acid (black bars). Hatched bars show effect of treatment with 0.10 M ascorbic acid. In general, ascorbic acid lowers the recovery in both DI water and tap water; however, bromochloro- and bromodichloroethanoate showed increased recovery in tap water. Although the allowable variation in recovery is 20% in DI water for Method 552, we infer that this concentration of ascorbic acid works well enough to allow quantitation, but probably influences conditions enough to warrant careful consideration before it is used in the matrix under study.

Based on the results obtained under our conditions, we found that ascorbic acid was suitable for the reduction of residual oxidizing chlorine, even when used in very large excess. We speculate that a more conservative addition of this reagent might result in even smaller effects. Because the data show precise biases, the effects we observed could be corrected for by the appropriate treatment of standards and spiked samples.

Part II. Effects at low analyte concentrations (2–10 ng mL⁻¹)

In order to determine the effect of ascorbic acid near the lower limit of detection, relative differences were computed using the average peak areas for the three treated and three untreated test solutions made by spiking Cincinnati tap water. Table 2 shows that there is a reproducible and quantifiable effect for all but the most highly oxidized species, specifically, bromodichloroethanoate and trichloroethanoate. Bromodichloroethanoate quantitation is intrinsically imprecise and this effect is somewhat magnified by the ascorbic acid, especially near the detection limit. At 6.6 ng mL⁻¹, the mean peak area for three replicates demonstrated a 16% RSD without HAsc, but the imprecision grew to 42% RSD for the HAsc-treated samples. Such effects were previously observed¹ for other analytes with a highly oxidized carbon atom (especially a trihalocarbon).

Bromochloroethanoate experiences a rather curious gain in response upon addition of ascorbic acid. As with the trihalocarbon effect, this has also been observed¹ for certain analytes. The mechanisms through which these effects occur remain unstudied. Based on these and previous results,¹ it is reasonable to speculate that ascorbic acid interacts with trihalogenated carbon atoms. The magnitude of the effect appears to vary with analyte concentration. This variability is especially noticeable for bromodichloroethanoate. Caution is therefore warranted when using ascorbic acid to dechlorinate water samples prior to the quantitative determination of chlorination byproducts containing trihalo (haloformyl) carbon atoms. In a DBP formation study, it would be necessary to carefully assess the side effects of ascorbic acid (used as a chlorine reductant) within a particular matrix. In routine monitoring of drinking water, ascorbic acid may be suboptimal for bromodichloroethanoate, but it has minimal or no effects on the monohalogenated species. It is worth pointing out, however, that Method 552 was never validated for bromodichloroethanoate, which we included in this study. Furthermore, we have found that methylation of brominated trihaloethanoates with diazomethane suffers from complicating side reactions;⁸ this implies that ascorbic acid treatment should be verified separately using acidic methanol (Method 552.2) for the brominated trihaloethanoates. The reaction chemistry of the dihalo- and trihalocarboxylates under drinking water conditions is not well-developed. Consequently, it is difficult to predict what conditions will promote decarboxylation, hydrolysis, reduction, or substitution and thereby complicate the analytical chemistry. Under the best conditions, the quantitation of these species is challenging; thus, careful attention must be paid to avoid introducing additional sources of error.

Concluding remarks

Our results suggest that, under some conditions, ascorbic acid can be used to reduce oxidizing chlorine compounds in order to fix the concentration of chlorination byproducts in time. Such quenching is particularly useful in studies on the formation of

chlorination byproducts where very substantial concentrations of oxidizing disinfectants are likely to be present. In these cases, the ammonium ion used in Method 552.2 would be inadequate as it reacts stoichiometrically with hypochlorite to give chloramine (except under breakpoint conditions). If samples are to be drawn as a function of time, it is clearly necessary to prevent subsequent chlorination of carbonaceous material. Obviously, any reductant chosen must not adversely interfere in the analysis. These preliminary experiments showed that ascorbic acid met the criteria¹ for the following analytes: chloroethanoate,|| bromoethanoate,|| 2,2-dichloropropanoate,|| dichloroethanoate,|| trichloroethanoate,|| bromochloroethanoate,|| dibromoethanoate,|| and 2-bromopropanoate in deionized water and a local chlorinated potable water supply. Nonetheless, care must be taken to evaluate any method modification in a particular matrix, as we pointed out previously when we used ascorbic acid in the Ames assay.⁹ In light of the other reductants that we have considered, ascorbic acid has been the most successful in meeting both the bioanalytical and chemoanalytical needs of disinfection byproduct formation studies. As always, there is a balance to be struck between the objectives of a particular study and the requisite levels of accuracy and precision in analytical measurements. We believe that judicious use of ascorbic acid can serve an important role in drinking water analytical chemistry and warrants further consideration in this capacity.

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||These analytes are often collectively referred to as HAA6 (six haloacetic acids included in EPA's Information Collection Rule).