## The Determination of Total Organic Halide in Water: A Comparative Study of Two Instruments

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# THE DETERMINATION OF TOTAL ORGANIC HALIDE IN WATER: A COMPARATIVE STUDY OF TWO INSTRUMENTS

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Total organic halide (TOX) analyzers are commonly used to measure the amount of dissolved halogenated organic byproducts in disinfected waters. Because of the lack of information on the identity of disinfection byproducts, rigorous testing of the dissolved organic halide (DOX) procedure for method bias is not always possible. This note presents the results of a brief study comparing two commercial TOX analyzers with neutron activation. The purpose was to determine if differential bias exists between the two analyzers, and to determine analyte recovery of adsorbed disinfection byproducts. Disinfection byproducts of aquatic fulvic acid were prepared using the following disinfectants: chlorine, bromine, and monochloramine. Analysis of these samples indicated that the two commercial TOX analyzers gave similar results. Neutron activation analysis suggested that organic chlorine recovery from the activated carbon adsorbent was complete, however results with organic bromine recovery were inconclusive. Additional tests indicated that one of the TOX analyzers is subject to significant interferences from inorganic iodide.

KEY WORDS: TOX, DOX, organic halide, drinking water, trihalomethanes, chlorination byproducts.

## INTRODUCTION

Dissolved organic halide (DOX) is a group parameter that is intended to reflect the amount of organically bound chlorine, bromine and iodine in a water sample. In general, it is used as a surrogate measurement for the contamination of water

by anthropogenic compounds, however, DOX is most often associated with the analysis of drinking water for the presence of chlorination byproducts.[1] Total organic halide may also be employed as a screening tool for detecting chlorinated solvents in groundwater and leachate waters. It has the advantages of relative simplicity and low cost over other techniques (e.g., GC/MS). Furthermore, organo-halide recovery by this method is not as sensitive to differences in the chemical properties of the individual compounds (e.g., volatility, polarity, heat-lability). About half of the DOX, as well as the majority of the mutagenic compounds found in chlorinated drinking waters have not yet shown themselves to be amenable to the more specific methods.

Kuhn and Sontheimer,[2,3] and Kuhn and Fuchs[4] laid most of the groundwork for the activated carbon adsorption-pyrolysis-halide detection method that is widely used today. Additional modifications and improvements led to the adoption of a standard method for DOX.[5,6] Following the early work, a commercial analyzer was developed with the assistance of the US EPA.[7,8] This instrument (manufactured by Dohrmann Division of Rosemont Analytical Corporation) was the subject of an intralaboratory comparative test[8] and a full interlaboratory collaborative study.[9]

Several years later, a second analyzer was introduced into the U.S. market (manufactured by Mitsubishi Chemical Industries Ltd.). This instrument differs from the Dohrmann product in several ways. The sample reservoir employs a headspace-free piston design as opposed to the Dohrmann pressurized headspace system. The adsorption cartridges contain 150/200 mesh coal-based activated carbon whereas Dohrmann supplies 100/200 mesh Calgon APC activated carbon for their mini-columns. Volatile organics are driven off the adsorbent at 800 °C in an argon atmosphere (carrier gas), and they are swept into a 900 °C zone of the furnace where oxygen is added for combustion. After a chosen delay, the carrier gas is switched to pure oxygen so combustion of the remaining material can take place. In contrast, the Dohrmann analyzer employs a low temperature (400 °C) first stage where both volatilization and combustion occur in an atmosphere of carbon dioxide. Then, after a pre-set time period, the adsorbent is introduced into the high temperature zone (800 °C) and the carrier/combustion gas is switched to pure oxygen.

Because the identity of many of the compounds detected by DOX analysis is not known (e.g., disinfection byproducts), rigorous testing of DOX methods for bias is not always possible. In an effort to infer an overall method bias, a small number of commercially-available halogenated compounds have been tested for recovery. Most of these have been determined using the Dohrmann instrument/method. Biases from $-38\%$ to $+4\%$ have been found for compounds that are neither desorbed in the nitrate wash nor poorly adsorbed on the GAC (Table 1). If the highly volatile chloroethylenes are excluded (they may be lost to a significant extent due to volatilization in the sample reservoir), the range of biases becomes $-14\%$ to $+4\%$. Many classes of compounds have not been tested, however, especially those representing the high molecular weight and unstable products formed upon water disinfection. In order to render the DOX parameter more useful, determining the method bias for some of these other compounds is

**Table 1** Single compound bias using the Dohrmann system

| Compound | Avg. % Recovery[c] | References |
|---|---|---|
| Chloroform | 89, 94, 79 | (7, 8, 14) |
| Bromodichloromethane | 98 | (8) |
| Chlorodibromomethane | 86 | (8) |
| Bromoform | 111, 101, 93 | (7, 8, 14) |
| 1-Chloro-2-Bromoethane | 106 | (7) |
| Dichloroethylene | 62 | (14) |
| Tetrachloroethylene | 77 | (14) |
| Chloroethanol | 20[a] | (7) |
| Chloroacetone | 90 | (7) |
| bis(2-chloroethyl)ether | 92 | (8) |
| Monochloroacetic Acid | 0[b] | (7) |
| Dichloroacetic Acid | 94 | (15) |
| Trichloroacetic Acid | 97 | (15) |
| Bromobenzene | 95 | (7) |
| m-Dichlorobenzene | 107 | (7) |
| 3-Bromobenzoic Acid | 104 | (7) |
| 2,4,6-Trichlorophenol | 101 | (7) |
| 2,4,6-Tribromophenol | 102 | (7) |
| Pentachlorophenol | 93 | (8) |

[a]Desorbed by nitrate wash
[b]Weakly adsorbed on GAC
[c]Standard concentrations generally in the range of 20–200 ug/L as Cl

important. Also important is determining if the differences in the various commercially-available analyzers cause significant differences in this bias. For example, the redox potential of the carrier/combustion gas (i.e., oxygen versus carbon dioxide) may affect analyte recovery. Pyrolysis of brominated organics in an atmosphere of oxygen has been reported to lead to bromine-containing combustion products (perhaps $Br_2$) that are not entirely titratable in the silver microcoulometric cell.[7,10] During the first phase of pyrolysis in the Dohrmann instrument (low temp) an atmosphere of carbon dioxide is necessary to avoid oxidation of bromine to $Br_2$ and incomplete recovery. During high-temperature combustion, however, rapid oxidation of the carbon depresses the partial pressure of oxygen and avoids $Br_2$ formation even though oxygen is used as the carrier gas. Differences in the adsorption system may also be important, because the adsorption of large molecules to activated carbon may be sterically and kinetically hindered to varying degrees. Accordingly, the objective of this study was to evaluate the Dohrmann and Mitsubishi TOX analysis systems with respect to their recovery of halogenated disinfection byproducts including those of high molecular weight.

*Experimental Section*

A series of identical aquatic fulvic acid solutions were prepared and halogenated at the University of Massachusetts (UMass). Both chlorinating and brominating agents were used. This was done to ensure that problems of incomplete recovery with only one of the halogens could be readily identified. Also, inorganic

chloramine (i.e., principally monochloramine) was used as well as the hypohalous acids. The inorganic chloramine is thought to be a less powerful oxidant, and less apt to fragment the large fulvic molecules into smaller compounds. The chloramine may, therefore, serve to better test high molecular weight DOX recovery.

The participating DOX laboratories were at the University of Massachusetts (Environmental Engineering Laboratories, Dohrmann instrument), the University of Houston (Environmental Engineering Laboratories, Mitsubishi instrument) and the US Environmental Protection Agency (WERL, Cincinnati, Dohrmann instrument). Total organic halide analyses were performed in accordance with Standard Methods,[6] method no. 506. Samples were directly adsorbed without a prior purging step. At UMass and the US Environmental Protection Agnecy (USEPA) all samples were run in triplicate at varying dilutions (e.g., 80%, 60% and 40%). The samples tested at the University of Houston (U of H) were not diluted, but were measured in duplicate. The USEPA's instruments and procedures are not substantially different from those of UMass, except that EPA grinds and sieves their own activated carbon (Filtrasorb 400) rather than using the activated carbon prepared by Dohrmann.

After halogenation, in addition to DOX analysis, samples were adsorbed to activated carbon microcolumns (activated carbon supplied by Dohrmann) and subjected to Neutron Activation Analysis (NAA). NAA was used as a referee method, permitting the calculation of recoveries of adsorbed DOX by the TOX analyzers. Neutron activation analyses were performed at the Neutron Activation Laboratory at Massachusetts Institute of Technology (MIT), in accordance with EPA method no. 9022.[11]

Chlorine stock solutions of 50 mM were prepared by diluting 5% sodium hypochlorite with Milli-Q water. Bromine stock solutions of 50 mM were prepared by adding 5% sodium hypochlorite to a 10 g/L KBr stock. Chloramine stock solutions (10 mM) were prepared by adding equal volumes of 20 mM chlorine to 60 mM ammonium chloride buffered at pH 8.5.[12] The DPD-ferrous titrimetric method[6] was used to standardize halogen stock solutions and to verify the presence of a halogen residual at the end of each reaction. Fulvic acid was extracted and concentrated to 400 mg/L DOC[13] using water from the Thousand Acre Reservoir that serves as an emergency water supply for Athol, MA. Dilute (5 mg/L DOC) fulvic acid solutions used in this study were prepared from this concentrated stock and buffered with 0.14 mM phosphate at pH 7. All glassware was washed in acid dichromate and rinsed a dozen times with distilled water prior to use.

*Phase* 1   The first test was conducted in the summer of 1986. At UMass, a series of fulvic acid solutions that had been previously spiked with inorganic bromide (0–20 mg/L) were chlorinated with 0.282 mM/L (20 mg/L) hypochlorite. They were allowed to react for 24 hours at 20 °C and quenched with a near stoichiometric quantity of sodium sulfite. Samples were then stored at 20 °C and for 48 hours to allow the decomposition of some of the more unstable halogenated products. After this time, the pH of each sample was dropped to 2 with nitric acid in order to inhibit further DOX decomposition. Samples were then homogenized and split into 3–6 identical aliquots and sealed in crimp-top vials.

**Table 2** Phase 1: Comparison of DOX and NAA results[a]. Chlorination of Thousand Acre fulvic acid with and without added bromide

| Bromide Conc (mg/L) | Dohrmann DOX | Mitsubishi DOX | Neutron Activation DOCl+DOBr | DOCl | DOBr |
|---|---|---|---|---|---|
| 0 | $860 \pm 50$ | $820 \pm 20$ | $850 \pm 70$ | $850 \pm 70$ | $1 \pm 1$ |
| 5 | $780 \pm 45$ | $760 \pm 35$ | [b] | [b] | [b] |
| 10 | $880 \pm 5$ | $790 \pm 15$ | [b] | [b] | [b] |
| 20 | $910 \pm 30$ | $870 \pm 10$ | $1,520 \pm 230$ | $260 \pm 150$ | $2,840 \pm 380$ |
| *Standards (average % recovery)* | | | | | |
| Chloroform | 83.8 | 93.0 | | | |
| Trichlorophenol | 96.8 | 96.8 | | | |
| Bromoform | 97.7 | 95.3 | | | |
| Tribromophenol | 90.6 | [b] | | | |

[a]All values in ug/L as chloride, except DOBr which is expressed in ug/L as bromide.
[b]Not tested

Each set of samples was either hand delivered or sent via overnight express to the appropriate laboratory. Samples were refrigerated upon receipt and analyzed simultaneously for DOX at the participating laboratories 1 week from the day they were originally halogenated. Note that the USEPA laboratory did not participate in phase 1.

*Phase 2* The second test, conducted during the summer of 1987, followed the same procedure as the first with a few exceptions. Instead of bromide addition, some samples were treated directly with bromine. Also, chloramine treatment was included. As before, total halogen doses were 0.282 mM/L (20 mg/L as chlorine) for all samples. Samples receiving a mixture of halogenating agents were dosed with 0.141 mM/L of each.

## RESULTS AND DISCUSSION

*Phase 1* Results from the two TOX analyzers showed little change in DOX with increasing bromide (Table 2). Futhermore, Table 2 shows that the two analyzers are in excellent agreement. This was true even though some samples were dominated by dissolved organic chlorine (DOCl) and some were dominated by dissolved organic bromine (DOBr; as indicated by NAA and suggested by THM analyses, the latter not shown). The values in Table 2 represent averages ± one standard deviation of the population of single DOX determinations as estimated from the individual results. Note that all Mitsubishi measurements and the third (10 mg/l bromide) Dohrmann measurement were made in duplicate. All remaining Dohrmann measurements were made in triplicate. Only the third sample showed significantly different mean DOX values between laboratories at the 95% confidence level. Except for the low value for chloroform on the Dohrmann instrument, only small negative biases were found for the standards.

Neutron Activation results are generally reported as total elemental concentration (e.g., total chlorine and total bromine). Since the NAA samples for this study were all prefiltered, adsorbed and nitrate washed, the terms DOCl and

**Table 3**  Phase 2: Comparison of DOX and NAA results[a]. Halogenation of Thousand Acre fulvic acid

| Halogen | DOX | | | Neutron Activation | | |
|---|---|---|---|---|---|---|
| | Dohrmann | | Mitsubishi | DOCl + DOBr | DOCl | DOBr |
| | UMass | EPA | U of H | | | |
| HOCl | $822 \pm 33$ | $735 \pm 29$ | $797 \pm 23$ | $780 \pm 80$ | $780 \pm 80$ | 0 |
| HOCl/HOBr | $1018 \pm 21$ | $890 \pm 62$ | $955 \pm 18$ | $1430 \pm 400$ | $98 \pm 28$ | $3000 \pm 920$ |
| HOBr | $1129 \pm 19$ | $948 \pm 5$ | $991 \pm 10$ | $1690 \pm 530$ | 0 | $3800 \pm 1200$ |
| $NH_2Cl$ | $103 \pm 5$ | $92 \pm 8$ | $89 \pm 1$ | $134 \pm 30$ | $134 \pm 30$ | 0 |
| Standards (average % recovery) | | | | | | |
| Chloroform | [b] | [b] | 93 | | | |
| Trichlorophenol | 96.5 | $98 \pm 4$ | 97 | | | |
| Bromoform | [b] | [b] | 93 | | | |
| Tribromophenol | [b] | [b] | 95 | | | |

[a]All concentrations are in ug/L as Cl, except DOBr which is in ug/L as Br.
[b]Not tested.

**Table 4**  Inorganic halide rejection

| Halide | Dohrmann (UMass)[a] | | Mitsubishi (U of H)[a] | |
|---|---|---|---|---|
| | Ratio[b] | Conc tested (mg/L) | Ratio[b] | Conc tested (mg/L) |
| Chloride | 10,000 | 750   −1,000 | 500,000 | 0–10,000 |
| Bromide | 10,000 | 750   −1,000 | 100,000 | 500–1,000 |
| Iodide | 3 | 0.25–5 | 50,000 | 5–1,000 |

[a]Activated carbon: UMass – Calgon APC; U of H – coal based.
[b]Rejection ratios are the reciprocal of theoretical recoveries for a single column. Inorganic halide solutions are treated exactly as an ordinary DOX sample, including acidification and nitrate washing.

DOBr will be used. The calculated sum of the two (DOCl + DOBr) is the appropriate parameter to use in assessing analyte recovery of the TOX analyzers. Thus, the NAA results for the sample that was not spiked with inorganic bromide prior to chlorination gave excellent agreement with both TOX analyzers. However, the samples previously spiked with (20 mg/L) inorganic bromide gave a much higher DOX (i.e., DOCl + DOBr) from NAA than from the TOX analyzers. Note that low molecular weight standards (bromoform & tribromophenol) gave near 100% recovery.

*Phase* 2  Once again, the TOX analyzers agreed quite well (Table 3), whereas the neutron activation analysis indicated higher concentrations when DOBr predominates. Only the brominated sample showed a significant difference among the three laboratories. Even so, the Mitsubishi determination fell between the concentrations given by the two Dohrmann instruments. In addition to the analysis of DOX standards, both instruments were tested for inorganic halide rejection. The Mitsubishi system generally showed higher rejection ratios than the Dohrmann system (Table 4). These differences may reflect differences in the activated carbon rather than the instruments. Takahashi and co-workers[7] reported chloride rejection ratios of 50,000 for the Dohrmann instrument. The UMass values were lower, although still acceptable for all but the most saline samples. However, the Dohrmann system showed very poor iodide rejection. The reasons

for the high iodide interference are not clear. This may not pose a problem with most environmental samples, however, polluted samples containing high levels of iodide may show significant positive bias with the Dohrmann system. As before, only a slight and consistent negative bias was found in the analysis of standards.

## CONCLUSION

1.  Both TOX systems (Dohrmann & Mitsubishi) gave similar results for disinfection byproducts.
2.  Both TOX systems gave complete recovery of chlorinated disinfection byproducts once adsorbed to activated carbon, however, the recovery of brominated disinfection byproducts may have been less than complete as compared to Neutron Activation Analysis.
3.  The Dohrmann TOX system may suffer from significant positive bias with samples high in inorganic iodide.

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