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ORIGINAL PAPER

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Determination of TOCl, TOBr and TOI in drinking water by pyrolysis and off-line ion chromatography

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Abstract The objective of this research was to determine the optimum total organic halogen (TOX) protocol for use with ion chromatographic (IC) detection to analyze total organic chlorine (TOCl), bromine (TOBr), and iodine (TOI) in drinking water simultaneously. Two commercial analyzers (one using a pure O_2 carrier and one using O_2/CO_2 mixture) and three commercially available activated carbons (two coconut-based and one bituminous coal-based) were examined in this study. Results showed that the pyrolytic analyzer using pure O_2 and off-line IC combined with a standard TOX carbon (coconut-based) achieved the most complete recovery of TOCl, TOBr and TOI for both model compounds and real samples. There was no obvious difference between the two analyzers when used in microcoulometric detection mode. The TOX method is moderately sensitive to nitrate rinse volume. The monohaloacetic acids were partly washed out during sample preparation. This problem was solved by a modified nitrate rinsing solution.

Keywords TOX · TOCl · TOBr · TOI · Pyrolysis · Ion chromatography

Introduction

Total organic halogen (TOX) analysis plays an important role in environmental analysis as a measure of the total amount of organic bound halogen in waters [1–3]. In drinking water, TOX is used as a surrogate measurement for the total halogenated disinfection by-products (DBPs) formed from the reaction between chemical disinfectants and natural organic matter (NOM) [4, 5]. Conventional TOX analysis combines carbon adsorption, pyrolysis, and measurement of hydrogen halides by microcoulometry. However, the silver-based microcoulometric titration used in conventional TOX measurement is incapable of differentiating between the halides, and therefore the method cannot distinguish total organic chlorine (TOCl) from total organic bromine (TOBr) and total organic iodine (TOI). By convention, TOX is calculated as the molar mass of organic halides, expressed as chlorine. However, brominated and iodinated DBPs are produced from the disinfection of water in the presence of bromide and iodide [6–8]. The nonspecific TOX analysis might be a biased estimator of toxicity since brominated and iodinated DBPs are thought to present higher adverse health effects than their chlorinated analogues [9].

Neutron activation [10] and ion chromatography (IC) [11–13] have been used for the differential analysis of TOCl, TOBr, or TOI. Although the neutron activation method can successfully differentiate between halogens of TOX, this technology cannot be applied for routine analysis due to its high cost. The idea of applying ion chromatography to TOX analysis has existed for a long time [4], and major advances have been made by several research groups. Brandt and Kettrup [11] developed a system to measure organic chlorine, bromine and sulfur compounds; the system involved carbon combustion under a pure oxygen environment, reaction gas collection by hydrogen peroxide solution, and halide detection by ion chromatography. The recovery of model chlorine and bromine compounds ranged from 6.6–109.0%. Oleksy-Frenzel and colleagues [12] developed another pyrolysis and absorption system. Sulfuric acid absorber was employed to remove water vapor before reaction gas collection by Na_2S solution. The recovery of model compounds ranged from 35–103%, yet the analysis of two wastewater samples by this method showed good agreement between IC detection and conventional microcoulometry detection. Low recovery of monochloroacetic acid was reported by the two groups. Echigo and colleagues [13] used oxygen as a carrier gas and carbon dioxide as an auxiliary gas during combustion. The exit gas from the combustion tube was collected directly into water. A 75% recovery was obtained

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Table 1 Three activated carbons selected for TOX analysis

Characteristics[a]	Carbon identification		
	CPI-002 (standard)	CPI-001	F-600
Supplier	CPI	CPI	Calgon
P/N	475-002	475-001	F-600
Source	Coconut	Coconut	Coal
Particle size	100–200 mesh	100–200 mesh	Granular
Background	0.4 µg Cl/40 mg	≤1.0 µg Cl/40 mg	Unknown

[a] Information provided by manufacturer

for the full process by model compounds. The use of CO_2 as an auxiliary gas resulted in interference in IC analysis. A nitrogen gas purge step was added before IC analysis to remove this interference. It is clear that more experiments are necessary to optimize this method and improve the overall recovery.

The objective of this research was to determine the optimum TOX protocol for use with IC detection. The experimental work of this study was divided into three parts. First, various factors that might affect TOX recovery when combined with IC detection were studied. Secondly, model compounds containing chlorine, bromine and iodine were tested for TOX recovery. Finally, two natural waters were chlorinated to produce a certain amount of unknown TOX to test the methodologies.

Experimental

Materials

All tests were conducted on two TOX analyzers and three commercially available carbons. A Dohrmann DX20 TOX analyzer (Dohrmann Division, Xertex, Santa Clara, CA) and a Euroglas ECS1200 TOX analyzer (Euroglas B.V., Delft, Netherlands) were selected for this study. The three commercially available granular activated carbons (GAC) tested are listed in Table 1. CPI-002 and CPI-001 carbons were prepacked by CPI International (Santa Rosa, CA) and supplied as microcolumns. CPI-002 is the standard carbon for the Euroglas TOX analyzer. F-600 GAC was obtained from Calgon Carbon (Pittsburgh, PA) and was ground and sieved to 100–200 mesh at the University of Massachusetts, Amherst. Ceramic wool and empty columns supplied by CPI were used to pack F-600 carbon columns. All reagents used in this work were of ACS grade or higher and purchased from Aldrich Chemical Company (Milwaukee, WI) unless otherwise noted. Trace metal grade acetic acid (Fisher Scientific, Fairlawn, NJ) was used to prepare the TOX titration solution. ACS grade nitric acid and sulfuric acid were purchased from Fisher. Potassium nitrate of ACS grade (Fisher) was used to prepare the nitrate washing solution. High-purity potassium chloride (99.99%), potassium bromide (99.95%) and potassium iodide (99.99%) were purchased from Aldrich to prepare IC calibration standards. The water used in this study was 18 MΩ·cm quality, generated from a D4700 NANOpure Deionization System (Barnstead, Dubuque, IA).

Procedure

The method for differentiating TOCl, TOBr and TOI by coupling a TOX analyzer with IC detection consists of three major steps. First, organic halogen compounds are adsorbed onto GAC followed by inorganic halide removal with a nitrate solution wash. Since only adsorbable organic compounds can be analyzed by this method, TOX is sometimes referred to as AOX (adsorbable organic halogen) in the literature [12]. Then, GAC is combusted under high temperature while the off-gas containing hydrogen halides is collected into water. Finally, chloride, bromide, and iodide ions are determined by ion chromatography. The details about these steps are given below.

Sample adsorption

All samples were adjusted to pH 2 with nitric acid and then passed through two consecutive microcolumns by a Euroglas EFU 1700 Filtration Unit (Euroglas B.V., Delft, Netherlands). The flow rate of the filtration was 3 ml/min. After adsorption, a nitrate solution rinse was used to remove the interfering inorganic halides. The flow rate of the nitrate rinse was 3 ml/min.

Pyrolysis and off-gas collection

Schematic diagrams of Euroglas and Dohrmann pyrolysis systems are presented in Figs. 1 and 2 respectively. For the

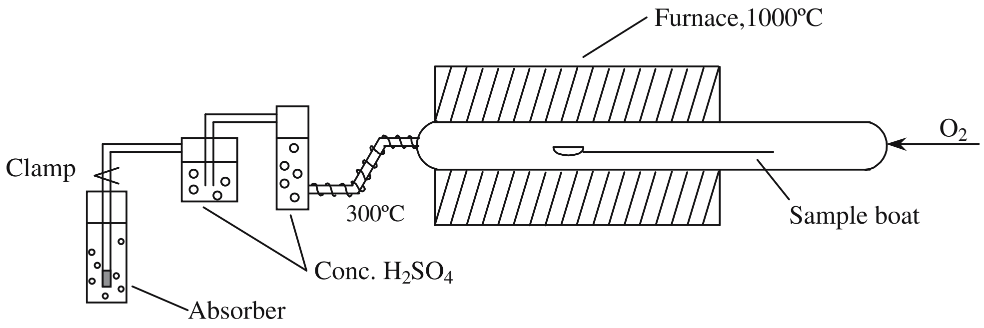


Fig. 1 Schematic diagram of the Euroglas pyrolysis and absorption system

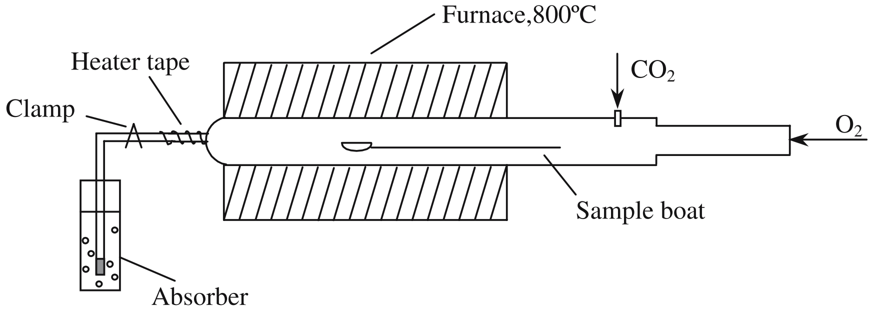


Fig. 2 Schematic diagram of the Dohrmann pyrolysis and absorption system

Euroglas system, oxygen was the only carrier gas. The temperature of the furnace was kept at 1,000°C. The sample quartz boat loaded with GAC was introduced into a combustion tube automatically. The sample was dried in the front compartment of the furnace for 1.5 min before combustion. The temperature of the exit tube of the pyrolysis assembly was kept at 300°C by heater tape. Two concentrated sulfuric acid absorbers were connected to the exit tube to remove the water vapor in the off-gas. Dry gas containing hydrogen halides was then collected into a 15-ml volume of deionized water using a specially fabricated off-gas collector. After absorption, 5 ml of deionized water was used to rinse the transfer line. The final sample volume for IC detection was adjusted to 20 ml.

For the Dohrmann system, oxygen was used as carrier gas while carbon dioxide was used as auxiliary gas. The temperature of the furnace was kept at 800°C. The sample quartz boat loaded with GAC was initially dried in a vaporization zone (about 250°C) in the front compartment of the furnace and swept with CO_2 only. After 2 min, the boat with the GAC was introduced into the pyrolysis tube. Simultaneously, the gas was switched to O_2 only. The exit tube from the pyrolysis tube was kept warm with heater tape. Reaction gas containing hydrogen halides was then collected into 15 ml of deionized water by a specially made off-gas collector. After absorption, 5 ml of deionized water was used to rinse the transfer line. The final sample volume for IC detection was adjusted to 20 ml. It has been a concern that some other halogen species, such as Br_2 and I_2, might be produced during combustion [12, 14]. Because of this concern, the Dohrmann analyzer uses carbon dioxide during the first stage of pyrolysis to avoid the formation of other halogen species; Oleksy-Frenzel and colleagues [12] used Na_2S as a reducing agent to convert those halogen species to halide ions during absorption. However, the results of this study suggest that, at least for drinking water samples, the formation of other halogen species during combustion may be insignificant.

Ion chromatography

A DX-500 ion chromatography system (Dionex, Sunnyvale, CA) equipped with a conductivity detector (CD-20, Dionex) was employed to measure halide ion concentration. For the determination of chloride and bromide ions, the IonPac AS14A analytical column with AG14A guard column (Dionex) was used. The eluent was 8.0 mM Na_2CO_3 and 1.0 mM $NaHCO_3$. For the analysis of iodide ion, the IonPac AS16 analytical column with AG16 guard column (Dionex) was selected. The eluent was 35 mM NaOH. An ASRS-Ultra anion suppressor (Dionex) used with AutoSuppression Recycle Mode was employed for the suppression for both cases. The flow rate of eluent was kept at 1 ml/min for all analyses. The sample was delivered by an AS3500 autosampler (Dionex) and was injected with a volume of 100µl. PeakNet software (Dionex) was used for automatic control and data processes.

Conventional TOX detection

Conventional TOX detection was performed on both analyzers to compare the results of microcoulometric detection and IC detection. The microcoulometric detection was carried out based on the standard method [15] and operational manuals from the manufacturers.

Sample preparation

Several organic compounds containing chlorine, bromine and iodine were selected to test the recovery. These included trihalomethanes (THMs), haloacetic acids (HAAs) and nitrogenous compounds. THM compounds were dissolved into acetone to make stock solutions. Other compounds were directly dissolved into deionized water. Standard solutions with concentrations of 100, 300 and 500 µg Cl/l were prepared freshly prior to analysis by diluting stock solution with water. Nitric acid was added to acidify the samples to pH 2. To test the method with a broad spectrum of organic halides, two raw waters (collected from Winnipeg, Manitoba and from Tulsa, OK) were chlorinated after being dosed with various bromide and iodide concentrations (0, 2, 10 and 30 µmol/l). The applied chlorine dose was 6.2 mg Cl_2/l for Winnipeg water and 5.0 mg Cl_2/l for Tulsa water, respectively. These conditions resulted in different levels of TOCl, TOBr and TOI to be used for testing the method. Chlorination was conducted in 1-l, chlorine demand-free, glass-stoppered bottles, and samples were buffered with 1mM phosphate at pH 7. Samples were stored for 48 h at 20°C in the dark after adding chlorine. Then all samples were quenched with sodium sulfite and acidified to pH 2 by nitric acid and

Table 2 Comparison of nitrate washing methods

Method	Working solution concentration	Rinsing volume	Nitrate loading^a
Euroglas	1,240 mg NO_3^-/l^a	25 ml	31 mg NO_3^-/sample
Dohrmann	5,000 mg NO_3^-/l	2 ml	10 mg NO_3^-/sample
Standard method	5,000 mg NO_3^-/l	2–5 ml	10–25 mg NO_3^-/sample

[a] Values were calculated based on information from operational manual and standard method

stored at 4°C before analysis. The addition of sodium sulfite is necessary to reduce chlorine, bromine, iodine and haloamines. Nitric acid is used to preserve the samples and avoid the adsorption of inorganic halides. All samples were tested on the Euroglas TOX analyzer and CPI-002 carbon with microcoulometric detection and IC detection. Selected samples were also tested on the Dohrmann TOX analyzer and the other two carbons.

Results and discussions

Development of the differential TOX analysis method

Effect of nitrate washing solution on TOX recovery

The purpose of the nitrate washing step is to remove interference from inorganic halides. Table 2 lists the nitrate rinsing methods for the Euroglas, Dohrmann and standard methods [15]. From Table 2, it can be seen that the three methods are quite different when comparing the concentration of working solution and rinsing volume. Experiments were performed to test the possible impact of nitrate washing solution on TOX recovery. Preliminary recovery tests were conducted on several solutions of HAAs (100, 300 and 500 µg Cl/l) using the Euroglas TOX analyzer with CPI-002 carbon and microcoulometric detection. For these tests, a sample volume of 50 ml was used, and columns were rinsed with 30 ml of the Euroglas nitrate wash solution. The results are shown in Fig. 3. It can be seen that the recoveries of the HAAs were species specific. The monohaloacetic acids were poorly recovered: 41–60% for chloroacetic acid (MCAA) and 60–76% for bromoacetic acid (MBAA). Low recovery of MCAA and MBAA was also reported previously [11, 12, 14]. Dichloroacetic acid (DCAA) recoveries ranged from 78–87%. Dibromoacetic acid (DBAA) and trichloroacetic acid (TCAA) showed nearly complete recoveries. Compounds with higher molecular weight and higher degree of halogenation exhibited higher recoveries. The increased recoveries were also accompanied by deceased ratios of second column to total. After comparing the TOX results of the

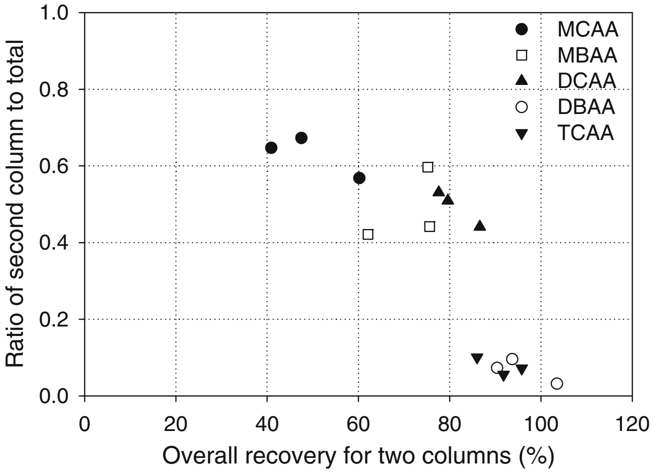


Fig. 3 Relationship between HAA recovery and carry-over to 2nd column (standards: 100, 300, 500 µgCl/l)

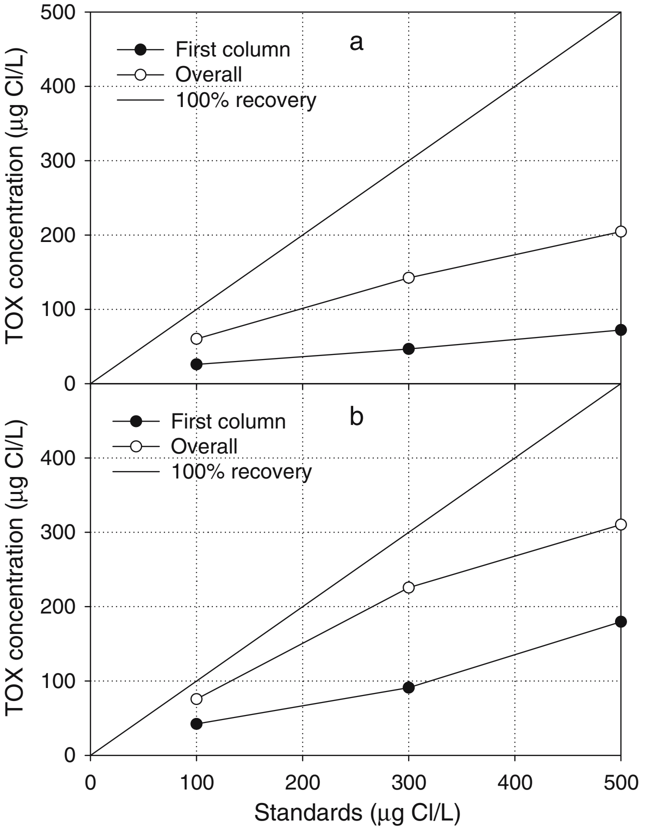


Fig. 4 **a, b** Recovery of monohaloacetic acid standards. **a** Chloroacetic acid. **b** Bromoacetic acid

Table 3 Test of DCAA recovery with different Euroglas nitrate washing volumes

Standards	Washing volume	1st column (µg Cl/l)	2nd column (µg Cl/l)	Total (µg Cl/l)	Recovery
DCAA 300 µg Cl/l	30 ml	108	125	233	78%
	25 ml	141	112	253	85%
	13 ml	208	77	285	95%

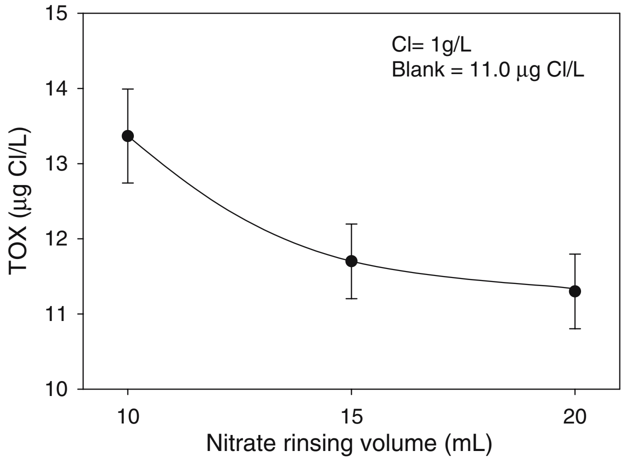


Fig. 5 Effect of nitrate rinsing volume on inorganic chloride removal

first and second columns, it was clear that some HAAs, especially MCAA and MBAA were partly washed out during the nitrate rinsing step, as shown in Fig. 4. The TOX washed onto the second column for monohaloacetic acids was significant compared to overall TOX recovery. It is also shown in Fig. 4 that the percent recovery increased with decreasing standard concentrations since highly concentrated standards would suffer more from the nitrate rinsing step.

Recovery tests using dichloroacetic acid standards were conducted with different Euroglas nitrate wash volumes. From Table 3, the recovery of DCAA increased to 95% from 78% when reducing the nitrate rinse volume to 13 ml from 30 ml. By comparing the TOX of the first and second columns, it becomes clear that the problem of analyte wash-out is greatly ameliorated by reducing the nitrate rinse volume. However, the reduced nitrate rinse volume must also ensure adequate removal of inorganic halides to guarantee unbiased TOX measurement. Tests were conducted to determine the impact of nitrate rinse volume on inorganic chloride removal by the Euroglas analyzer and CPI-002 carbon. New nitrate washing solution was prepared by dissolving 1.63 g KNO_3 in 1 l deionized water (1,000 mg NO$_3^-$/l), and pH was adjusted to 2 with nitric acid. Chloride solutions of 1.0 g Cl/l were also prepared and pH was again adjusted to 2 with nitric acid. A sample volume of 100 ml was used. The TOX results of the sum of the two columns resulting from different nitrate rinse volumes are shown in Fig. 5. When increasing nitrate rinse volume to 15 ml from 10 ml, the TOX could be brought back to the blank value. From this test, it is concluded that 15 ml of 1,000 mg NO$_3^-$/l rinse solution can achieve adequate removal of inorganic chloride when the influent level is 1 g Cl/l or lower. Larger amounts of rinse would not be necessary and could result in unwanted washout of weakly adsorbed organic halides. Therefore, it was decided that 15 ml of the 1,000 mg NO$_3^-$/l rinse solution should be used for subsequent TOX analyses.

Inorganic halide rejection

Inorganic halide rejection is important to TOX analysis since the interference from inorganic halides would result in biased TOX results. The three carbons selected for this research were tested on halide rejection by Euroglas TOX analyzer and modified nitrate rinse solution. A volume of 100 ml was used for each halide standard prepared with deionized water. The results are shown in Table 4. The rejection ratio is the inorganic halide concentration divided by the measured TOX value for solutions containing only inorganic halide. CPI-002 and CPI-001 exhibited excellent chloride and bromide rejection. F-600 showed lower rejection ratios for chloride and bromide ions, but it can still meet the requirement of the analysis of most water samples. No retention was found for CPI-002 and CPI-001 when the iodide concentration was 1 mg/l. CPI-002 showed some iodide retention when the iodide level was elevated to 5 mg/l, while no retention was found for CPI-001 at this level. In contrast, F-600 showed low iodide rejection ratios at both levels. Considering the low levels of iodide in natural water sources, both CPI-002 and CPI-001 carbons can be used for TOI analysis without interference from inorganic iodide ions. However, F-600 carbon might experience unacceptable levels of interference from inorganic iodide ions and result in biased TOI analysis.

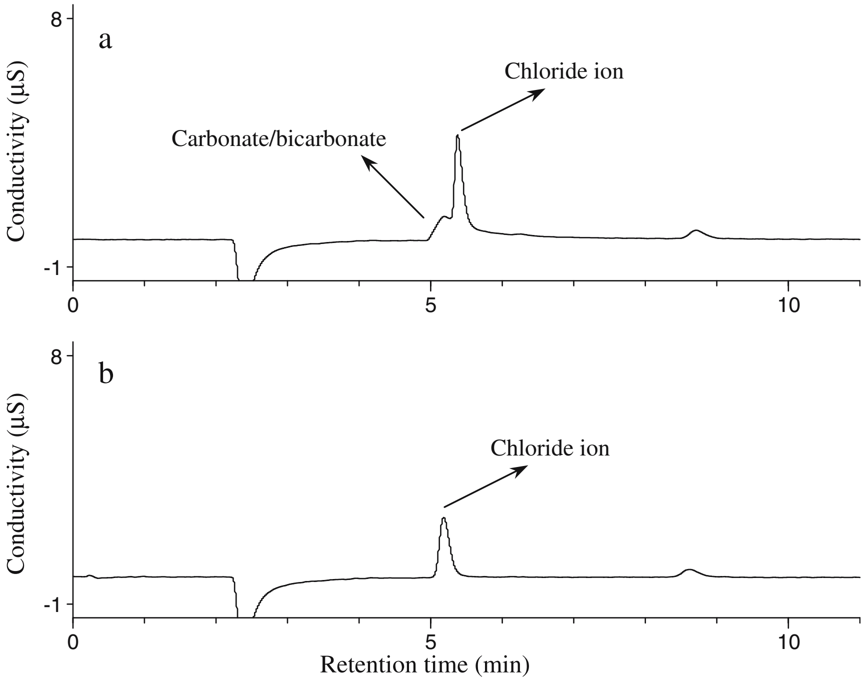
Factors affecting performance of TOX analyzer with IC detection

A large number of experiments were conducted to test various factors that might affect the TOX recovery when combining the TOX analyzer and IC detection. These included tests of absorber type (Frit and Fine bubbler), oxygen flow rate (200 and 150 ml/min) and absorption time. In summary, the conditions determined for future

Table 4 Inorganic halide rejection by three carbons

Halide	Concentration (mg/l)	CPI-002		CPI-001		F-600	
		TOX (µg /l)	Rejection ratios	TOX (µg /l)	Rejection ratios	TOX (µg /l)	Rejection ratios
Cl^-	1,000	<1	1,000,000	<1	1,000,000	3.9	250,000
Br^-	500	1.9	250,000	2.0	250,000	26.8	20,000
I^-	1	<1	>100	<1	>100	84.9	12
	5	164	30	<1	>100	2,760	2

Fig. 6 **a, b** IC interference from CO_2. **a** Unsparged sample from Dohrmann analyzer. **b** Sparged sample from Dohrmann analyzer (Cl^-=614 µg/l)



tests were an absorption time of 15 min, an oxygen flow rate of 150 ml/min, and use of the fritted absorber. It has been reported that the use of CO_2 as an auxiliary gas with Dohrmann analyzers results in interference during IC analysis [13]. This was confirmed when combining the Dohrmann analyzer with IC detection as shown in Fig. 6. The interference of carbonate and bicarbonate on chloride ion analysis could be avoided by sparging samples for 3 min with nitrogen gas before IC analysis. The sparge step was applied to all IC samples from the Dohrmann analyzer for subsequent experiments. No such interference was found for samples from the Euroglas pyrolysis and absorption system, as this system does not use carbon dioxide as an auxiliary gas.

Transfer-line flush was found to have significant impact on the TOX recovery for samples from the Dohrmann analyzer. Recovery test using TCAA solutions of 500 µg Cl/l showed that only 22–26% of TCAA was recovered without transfer-line flush, while the recovery was increased to 93–96% with careful transfer line flush (Fig. 7). The two oxygen flow rates did not significantly affect the recovery. A lower flow rate (150 ml/min) was selected for subsequent tests since that might help reduce the water splash. From Fig. 2, it can be seen that the exit gas from the combustion tube is directly collected into the absorber. The water vapor, as well as halide ions, would condense on the inner wall of the transfer line. The overall recovery depends on thorough flushing of the transfer line. However, complete flushing may not happen each time since only a small volume (about 5 ml) can be used. Condensation is not a problem for the Euroglas analyzer since concentrated sulfuric acid absorbers are quite effective at drying the off-gas before the collection by deionized water.

Ion chromatography method development

The objective of the IC method development was to identify a set of conditions that allows the analysis of all halides of interest (chloride, bromide and iodide) with appropriate low-level detection and without substantial interference from other ions contained in the pyrolysate. Chloride and bromide are common anions and can be easily resolved and quantified by common anion columns and a conductivity detector. The IonPac AS14A analytical column with AG14A guard column (Dionex) was selected for the analysis of chloride and bromide. The chromatogram of the carbon blank analyzed by an AS14A column is shown in Fig. 8a. The carbon blank was treated by the same

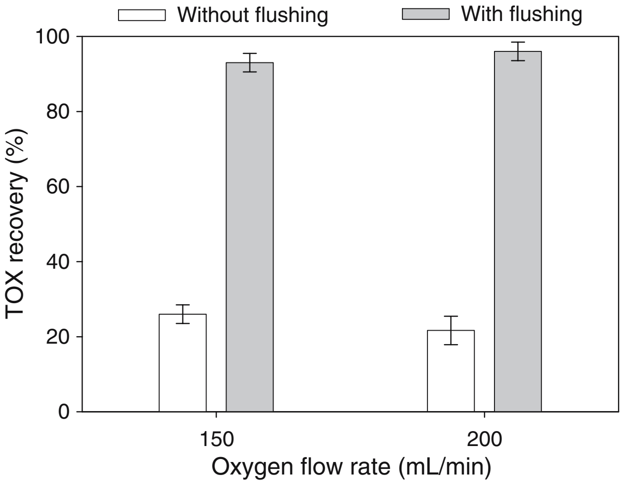
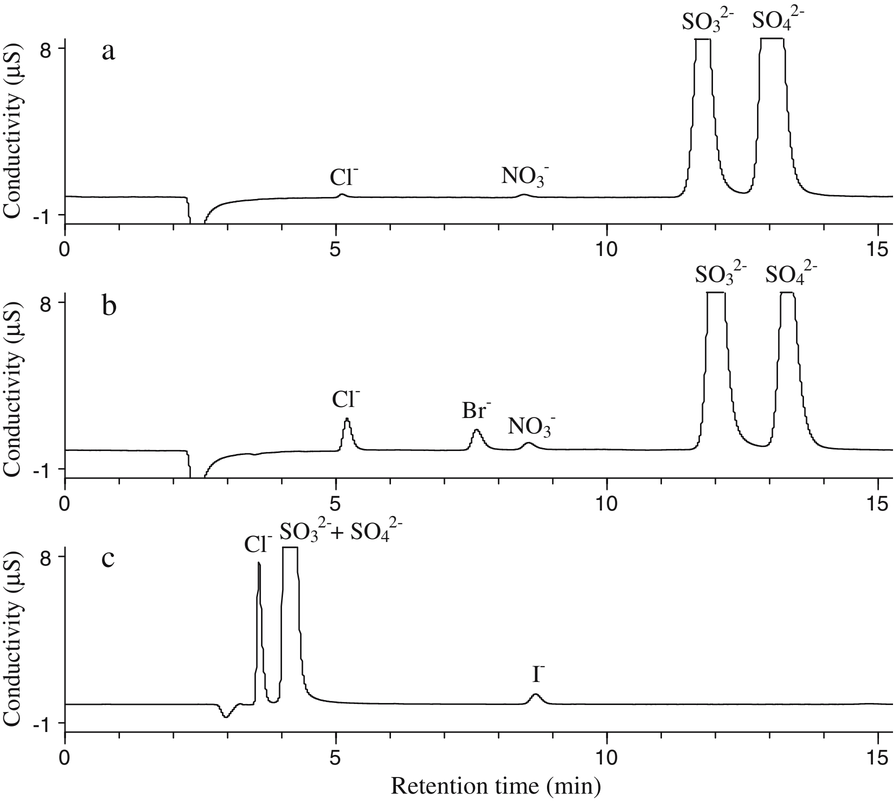


Fig. 7 Effect of transfer-line flushing on TCAA recovery from Dohrmann IC samples

Fig. 8 **a–c** Ion chromatograms. **a** Blank analyzed by an AS14A column (Cl^-=37 µg/l). **b** Chloride (510 µg/l) and bromide (986 µg/l) ions on an AS14A column. **c** Iodide ion (551 µg/l) on an AS16 column



procedure as samples, using the Euroglas pyrolysis absorption unit. The background ions in the activated carbon and nitrate rinse solution resulted in a small quantity of chloride and nitrate ions in the pyrolysate. The concentrated sulfate and sulfite ions indicated a large amount of sulfur contained in the carbon. The chromatogram of a sample containing TOCl and TOBr treated by Euroglas pyrolysis and absorption unit and measured by the AS14A column is shown in Fig. 8b. It is evident that the nitrate, sulfite and sulfate ions resulting from the carbon blank do not seriously interfere with the analysis of chloride and bromide ions. The low level of chloride ions from the carbon blank can be subtracted from the gross TOCl measured in the samples. Due to its much larger atomic mass, iodide places certain constraints on the ion chromatography system. The AS14A column does not produce chromatograms with clear and quantifiable iodide peaks using conductivity detection at low levels. Another column (AS16), which is designed for the determination of polarizable anions, does allow the analysis of low-level iodide with conductivity detector. Fig. 8c shows the chromatogram of a real sample treated by the Euroglas pyrolysis and absorption unit and analyzed by an AS16 column. Iodide ions were well resolved within a comparatively short retention time. However, this column does not resolve bromide and nitrate. Furthermore, the analysis of the real samples showed that the peak of concentrated sulfate and sulfite covered the bromide and nitrate peaks (Fig. 8c). The final decision was to use two separate columns for IC analysis, IonPac AS14A for chloride and bromide, and IonPac AS16 for iodide. In addition to conductivity detection, UV/visible detection following AS9-SC analytical column has been used for the analysis of iodide ions at low levels, and conductivity and UV/visible double-channel detection has been used for the analysis of chloride, bromide and iodide simultaneously [12].

Table 5 summarizes the working concentrations of the calibration, the linear regression coefficients (R^2) and detection limits that resulted from the two columns and conditions described previously. The detection limits were determined from seven replicates of low-level samples, from which 99% confidence limits were calculated from the standard deviations. Chromatograms in Fig. 8 represented a 50-ml sample volume and a 20-ml trap volume. The resulting concentration factor was 2.5. These conditions were applied to the following model compound recovery tests and chlorinated natural waters. The sensitivity of the method (especially for bromide and iodide) can be further increased by using larger concentration factors. However, lower trap volume would also lead to higher levels of concentrated sulfite and sulfate ions, which may accelerate column aging.

Table 5 Detection limits of three anions by IC

Anion	Analytical column	Working range (mg/l)	R^2	Detection limits (µg/l)
Chloride	AS14A	0.03–1.5	0.9996	3.1
Bromide	AS14A	0.05–3.0	0.9996	5.3
Iodide	AS16	0.10–4.0	0.9986	10.3

Table 6 Recoveries of model compounds by Euroglas analyzer and standard carbon

Compound	Recovery (%)	
	Microcoulometric detection	IC detection
Dichlorobromomethane	102±1	101±4
Dibromochloromethane	103±3	104±2
Bromoform	98±5	98±4
Tribromoacetic acid	98±3	98±5
Trichloroacetic acid	100±2	97±4
Dibromoacetic acid	102±3	101±4
Dichloroacetic acid	98±4	101±5
Bromochloroacetic acid	97±5	100±5
Monoiodoacetic acid	99±3	94±5
Monobromoacetic acid	96±2	95±1
Monochloroacetic acid	91±3	92±4
(6-Bromo-pyridin-2-yl) methanol	101±2	99±4
3,5-Dichloroisonicotinic acid	100±2	101±3

Model compound recovery test

Chlorine, bromine and iodine containing THMs, HAAs and nitrogenous compounds were tested as to their recoveries by the two detection modes. Table 6 shows the average recoveries and 95% confidence intervals that resulted from three standards (100, 300 and 500 μg Cl/l). The Euroglas analyzer and standard carbon (CPI-002) were used in this test. Nearly complete recoveries were obtained for all selected model compounds by both microcoulometic detection and ion chromatography. The two analytical modes showed almost identical model compound recoveries.

Analysis of natural water samples

Raw waters collected from Winnipeg and Tulsa were chlorinated after being dosed with various levels of bromide and iodide ions (0–30μM). Table 7 shows the results of TOCl, TOBr, TOI and TOX using the Euroglas analyzer and standard carbon (CPI-002). The concentration of TOBr or TOI increased substantially and TOCl decreased significantly with increasing initial halide concentrations. A good agreement was obtained between TOX determined by ion chromatography (the sum of TOCl, TOBr and TOI) and TOX determined by microcoulometric detection. These water samples were also analyzed using CPI-001 and F-600 carbons with the Euroglas analyzer and IC detection. A comparison of the sum of TOCl, TOBr and TOI using the three different carbons is illustrated in Fig. 9. The CPI-002 carbon showed slightly higher levels of TOX than the CPI-001, while F-600 gave slightly lower levels than CPI-002, except for the highest iodide level. F-600 carbon exhibited consistently higher TOI concentrations, but lower TOCl concentrations than the other two carbons for various iodide levels. It is concluded that part of inorganic iodide was retained by F-600, which resulted in a positive bias for TOI analysis. This is consistent with the results of the inorganic halide rejection test.

The final comparison of the two analyzers with the two detection modes is demonstrated in Fig. 10, which summarizes all the data from model compound tests and natural waters. The Euroglas instrument gave nearly identical results when comparing the standard mode (microcoulometric detection) with IC mode. This was not the case for the Dohrmann instrument. The transfer and trapping of inorganic halides was not as efficient when applied to the Dohrmann instrument design as compared to Euroglas, due to condensation of halide ions and

Table 7 Real water sample analysis by Euroglas analyzer and standard carbon

Sample	TOCl (μg Cl/l)	TOBr (μg Cl/l)	TOI (μg Cl/l)	TOX $_{ic}$[a] (μg Cl/l)	TOX $_{mc}$[b] (μg Cl/l)
Winnipeg, chlorinated water	575	4	0	579	582
Winnipeg+Br (2 μM)	520	54	0	574	561
Winnipeg+Br (10 μM)	278	259	0	537	525
Winnipeg+Br (30 μM)	87	514	0	601	609
Winnipeg+I (2 μM)	590	6	6	602	587
Winnipeg+I (10 μM)	438	4	88	530	533
Winnipeg+I (30 μM)	161	0	247	408	403
Tulsa, chlorinated water	504	19	0	523	523
Tulsa+Br (2 μM)	425	67	0	492	479
Tulsa+Br (10 μM)	193	275	0	468	481
Tulsa+Br (30 μM)	64	472	0	536	537
Tulsa+I (2 μM)	501	19	7	527	515
Tulsa+I (10 μM)	310	17	27	354	362
Tulsa+I (30 μM)	113	13	197	323	340

[a] The sum of TOCl, TOBr and TOI determined by ion chromatography
[b] TOX determined by microcoulometry

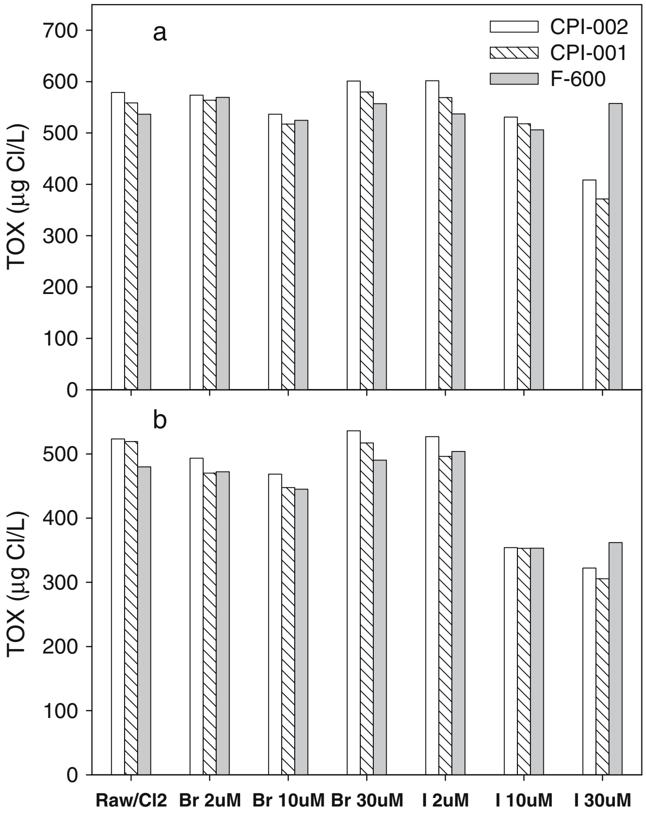


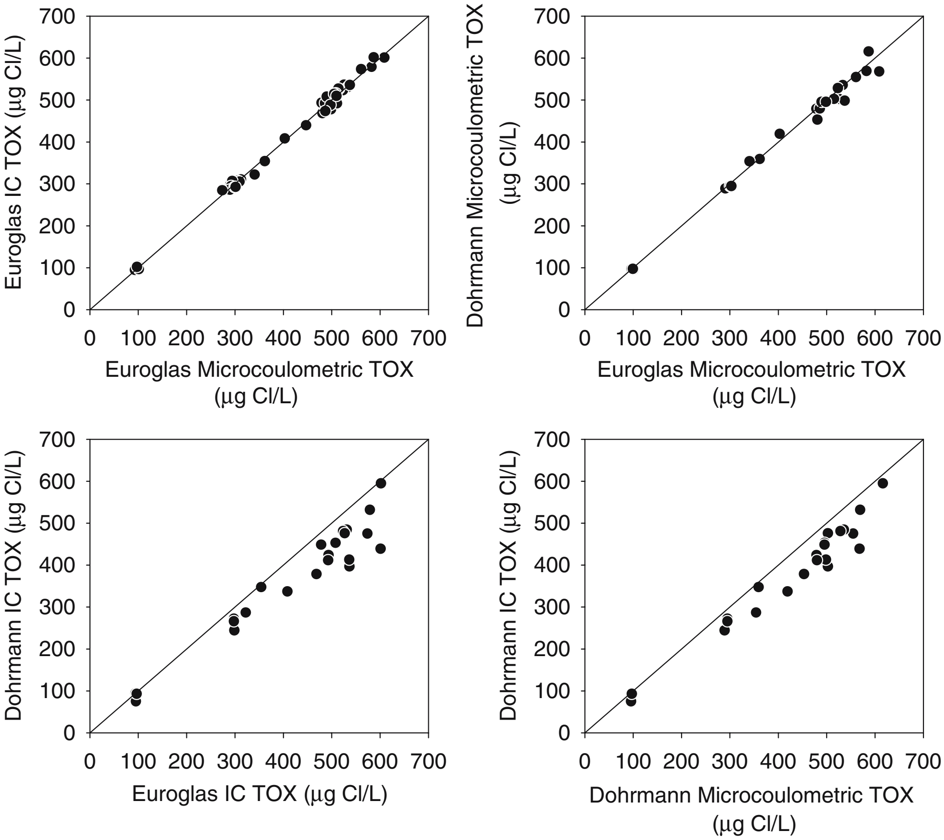
Fig. 9 **a, b** TOX analysis of natural water samples by three carbons. **a** Winnipeg. **b** Tulsa

incomplete transfer-line flush. It is an advantage of the Euroglas absorption system to remove the water vapor by the concentrated sulfuric acid absorbers before trapping of halide ions. No obvious difference was found for the two instruments when used in standard microcoulometry mode.

Conclusions

The pyrolytic analyzer using pure O_2 and off-line IC combined with a standard TOX carbon (coconut-based) achieved complete recovery of TOCl, TOBr and TOI from model compounds. The O_2/CO_2 pyrolytic system and off-line IC showed incomplete recovery for some samples due to condensation of halide ions and the difficulty in flushing these halide ions. The use of CO_2 as an auxiliary gas resulted in interference in IC analysis, which made it necessary to purge dissolved CO_2 before IC analysis. There was no obvious difference between the two analyzers when used in microcoulometric detection mode. The TOX method is moderately sensitive to nitrate rinse volume. The monohaloacetic acids were partly washed out during sample preparation. This problem was solved by modifying the nitrate rinsing procedure. Complete recovery was achieved for all selected model compounds by this modified TOX protocol. The two coconut-based carbons (CPI-001 and CPI-002) gave nearly identical results for natural water samples. The bituminous coal-based carbon (F-600) suffered from excessive inorganic iodide retention.

Fig. 10 Comparison of two analyzers with two detection modes



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