Improved Extraction and Analysis of Haloacetic Acids from Water Samples

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The extraction and analysis of haloacetic acids, specifically those specified in EPA Method 552.1, are effectively extracted and concentrated from water samples by a new high capacity polymeric strong anion exchange SPE sorbent, which provides benefits such as dry-out resistance and reduced solvent consumption. When combined with a sensitive dual column GC application on a Zebron™ ZB-XLB-HT Inferno™ and a ZB-MR2, the improved extraction procedure provides reliable and reproducible chromatographic results.

Introduction

Drinking water is often chlorinated in an effort to disinfect the water prior to human consumption. While this step is helpful in preventing bacteria and other unwanted substances from tainting water supplies, it can also introduce haloacetic acids. These by-products of the drinking water chlorination process have been associated with a number of health concerns including spontaneous abortions and an increased risk of cancer. Due to these potential health risks, the EPA regulates the levels of haloacetic acids present in drinking water under EPA Method 552.1. This method is traditionally done by extracting the haloacetic acids using Solid Phase Extraction (SPE) and analyzing by Gas Chromatography (GC).

Although EPA Method 552.1 includes a detailed extraction method, it has been recognized that several portions of the method could be improved. The extraction method outlined by EPA 552.1 utilizes loose strong anion exchange sorbent which must be hand packed into an SPE tube – this significantly slows down total processing time per sample. The method also requires an equilibration of 60 mL of solvent and a wash of 10 mL of solvent, followed by an elution of 4 mL of solvent. This large amount of solvent usage increases the cost per sample while also increasing solvent disposal fees. One last downfall to the specified extraction method is that the sorbent should not be allowed to dry out, meaning that technicians must be properly trained to tend to the sorbent at all times in order to prevent dry-out. Because the EPA allows for alternative extraction procedures, the objective of this work was to develop an easy-to-use extraction method on a dry-out resistant SPE sorbent to provide benefits such as a reduction in solvent consumption, which in turn provides monetary savings for solvent and waste disposal without sacrificing recovery or performance.

Experimental Conditions

100 mL of water was spiked with haloacetic acids (as specified under EPA 552.1) ranging in concentration from 10 µg/L to 100 µg/L. The prepared samples were then extracted using a novel polymeric strong anion exchange SPE sorbent, Strata™-X-A (**Table 1**). A blank sample was also run through the Strata-X-A sorbent and spiked after elution as an extracted reference sample (EREF) to calculate absolute recovery of the haloacetic acids.

Table 1.
SPE Protocols

Strata-X-A Polymeric Strong Anion Exchange SPE Sorbent (100 mg/3 mL, Part Number 8B-S123-EBJ)	Bio-Rad® AG® 1-X8 Strong Anion Exchange Resin (10 mm bed height)*
1. Condition - 2 mL of Methanol - 2 mL Water	**1. Condition** - 10 mL Methanol - 10 mL Water - 10 mL 1 M Hydrochloric acid/ Methanol - 10 mL Water - 10 mL 1 M Sodium hydroxide - 10 mL Water
2. Load - 100 mL Water containing haloacetic acids ranging in concentration from 10 µg/L to 100 µg/L	**2. Load** - 100 mL Water containing spiked analytes, pH adjusted to 5 with 1:2 Sulfuric acid:Water
3. Wash - 1 mL Methanol	**3. Wash** - 10 mL Methanol
4. Elute - 1 mL 10 % Sulfuric acid in Methanol	**4. Elute** - 4 mL 10 % Sulfuric acid in Methanol

* EPA Method 552.1, August 1992, Jimmie W. Hodgeson and David Becker

The extracted eluent was then prepared for GC/ECD analysis by performing a derivatization procedure. 2 mL of MTBE was added to the eluent in a screw cap vial. The sample was then heated at 50 °C for 1.5 hours, after which it was allowed to cool to room temperature. 10 mL of sodium bicarbonate was added to the cooled sample, which was then inverted several times while carbon dioxide was frequently released in between inversions. 100 µL of the organic layer was aspirated and transferred to a 2 mL vial with insert.

To the transferred sample, 10 µL of internal standard (1,2,3-Trichloropropane) was added and the sample was injected onto a GC/ECD system that consisted of a Zebron™ ZB-XLB-HT Inferno™ GC column (30 x 0.32 x 0.25) and a Zebron ZB-MR2 GC column (30 x 0.32 x 0.25) which were fitted in parallel dual column configuration. The oven program was set as specified in **Table 2**.

Table 2.
GC Oven Program

Columns:	Zebron ZB-XLB-HT Inferno Zebron ZB-MR2
Dimensions:	30 m x 0.32 mm x 0.25 µm (for both columns)
Flow Rate:	2.3 mL/min
Injection:	Pulsed 1 µL @ 250 °C
Carrier Gas:	Constant Flow Helium, @ 2.3 mL/min

Oven Program:

Oven Ramp	°C/min	Next °C	Hold Min
Initial		30	4.00
Ramp 1	30.00	50	1.00
Ramp 2	15.00	70	1.00
Ramp 3	20.00	115	2.00
Ramp 4	30.00	150	1.00

Detector:	Electron Capture (ECD) (340 °C)

Results and Discussion

The Strata™-X-A protocol has been optimized to target and concentrate all 7 compounds that are regulated under EPA 552.1. Due to the high loading capacity of the novel Strata-X-A SPE sorbent, the use of a 100 mg sorbent bedmass significantly reduced the amount of conditioning, wash, and elution solvent required for the extraction as compared to the traditional extraction outlined in EPA 552.1 (**Table 3**).

Table 3.
Reduced Solvent Consumption and Disposal Benefits of Strata-X-A

Solvent	Strata-X-A Volume Required (mL)	BioRad® AG® 1-X8 Strong Anion Exchange Resin Volume Required$^{\Delta}$ (mL)	Solvent Saved by Using Strata-X-A
Methanol	3.9	33	29.1
Water	2.1	30	27.9
1 M Hydrochloric acid	0	0.8	0.8
1 M Sodium hydroxide	0	10	10
Sulfuric acid	0.1	0.4	0.3
$^{\Delta}$ estimated volumes			TOTAL: 68.1 mL

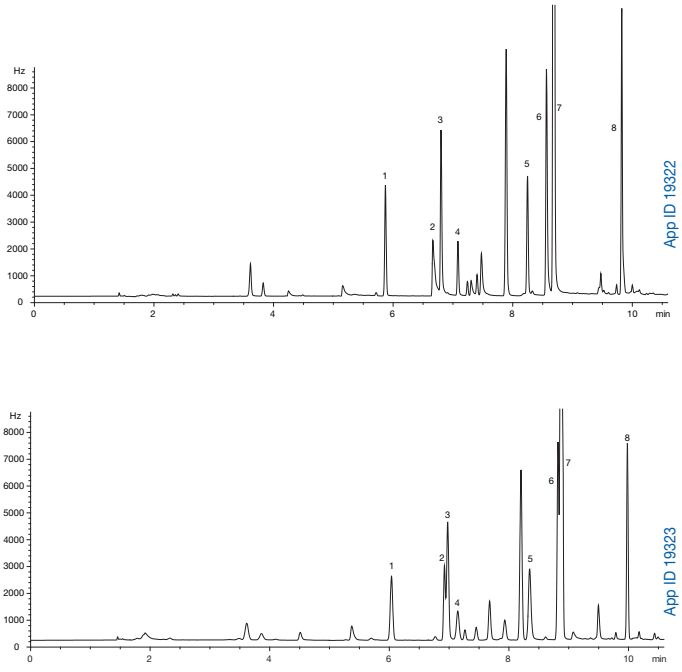
The Strata-X-A sorbent not only saved costs by reducing solvent consumption and disposal costs, but it also maintained consistent, high recoveries of haloacetic acids. Because haloacetic acids are retained on the Strata-X-A sorbent by both reversed phase and ion-exchange interactions, a strong interaction between sorbent and analyte is created. The strong analyte-sorbent interaction allows for a strong organic wash to be applied without sacrificing recovery, resulting in an ultra-clean eluent (**Table 4**).

Table 4.
Absolute Recoveries of Haloacetic Acids on Strata-X-A

	Analyte	% Absolute Recovery	% RSD (N=5)
1.	Chloroacetic acid	93	4.3
2.	Bromoacetic acid	92	9.5
3.	Dichloroacetic acid	90	5.1
4.	Dalapon	97	1.3
5.	Trichloroacetic acid	93	3.3
6.	Bromochloroacetic acid	93	5.9
7.	1,2,3-Trichloropropane	IS	IS
8.	Dibromoacetic acid	89	4.1

After extraction and concentration by SPE, haloacetic acids were effectively separated and confirmed by GC analysis using a dual column configuration that included a Zebron™ ZB-XLB-HT Inferno™ and a Zebron ZB-MR2 GC column (**Figure 1**).

Figure 1.
Haloacetic Acids Separated and Confirmed on ZB-XLB Inferno (Top) and ZB-MR2 (Bottom)



Conclusion

The extraction procedure specified under EPA 552.1 was dramatically improved upon by developing a protocol using Strata™-X-A polymeric strong anion exchange SPE sorbent. Strata-X-A was able to effectively clean and concentrate the analytes of interest while providing additional benefits such as dry-out resistance and reduced solvent consumption. Cost per sample was also significantly decreased by reducing solvent consumption and disposal by almost 70 mL per sample.

APPLICATIONS

Ordering Information

Strata™-X-A

Sorbent Mass	Part No.	Unit
Tube		
30 mg	8B-S123-TAK	1 mL (100/box)
30 mg	8B-S123-TBJ	3 mL (50/box)
60 mg	8B-S123-UBJ	3 mL (50/box)
100 mg	8B-S123-EBJ	3 mL (50/box)
100 mg	8B-S123-ECH	6 mL (30/box)
200 mg	8B-S123-FBJ	3 mL (50/box)
200 mg	8B-S123-FCH	6 mL (30/box)
500 mg	8B-S123-HBJ	3 mL (50/box)
500 mg	8B-S123-HCH	6 mL (30/box)
Giga™ Tube		
500 mg	8B-S123-HDG	12 mL (20/box)
1 g	8B-S123-JDG	12 mL (20/box)
1 g	8B-S123-JEG	20 mL (20/box)
2 g	8B-S123-KEG	20 mL (20/box)
5 g	8B-S123-LFF	60 mL (16/box)
96-Well Plate		
10 mg	8E-S123-AGB	2 Plates/Box
30 mg	8E-S123-TGB	2 Plates/Box
60 mg	8E-S123-UGB	2 Plates/Box

Zebron™

Part No.	Description	Dimensions	Unit
7HM-G024-11	Zebron ZB-XLB-HT Inferno™	30 m x 0.32 mm x 0.25 µm	ea
7HM-G017-11	Zebron ZB-MR2	30 m x 0.32 mm x 0.25 µm	ea

guarantee

If Phenomenex products in this technical note do not provide at least an equivalent separation as compared to other products of the same phase and dimensions, return the product with comparative data within 45 days for a FULL REFUND.

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