RESTEK environmental

Applications note

GC/ECD Analysis of Haloacetic Acids in Water Samples Using Rtx®-CLPesticides and Rtx®-CLPesticides2 Columns

Haloacetic acids are a byproduct of chlorinated disinfection of drinking water. Recently, there has been some concern that these analytes may represent a chronic risk to human health, and toxicological evidence suggests that some of them are possible human carcinogens. Elevated levels of haloacetic acids in drinking water could pose acute human risk because of their corrosive natures. With the proper sample preparation technique and use of the Rtx®-CLPesticides and the Rtx®-CLPesticides2 columns, environmental chemists can achieve accurate analysis of these compounds. (Refer to US Environmental Protection Agency [EPA] Method 552).

Sample Extraction

Sample preparation requires a microextraction of a 40mL sample, methylation of the acids, and final neutralization of extract. The initial extraction of haloacetic acid compounds involves transferring 40mL of sample to a 60mL vial or separatory funnel, and adding the surrogate 2,3-dibromo-propionic acid.

The following steps are done in quick succession so that the heat generated from adding the acid to the sample helps dissolve the salts into the liquid phase: 1) Lower the sample pH to <0.5 using concentrated sulfuric acid. 2) Add two grams of copper II sulfate pentahydrate to the sample to color the water, making it is easy to distinguish the water phase from the organic phase. 3) Add 16gm of pre-cleaned sodium sulfate to the sample to increase the ionic strength of the aqueous phase. 4) Add 4mL of methyl *tert*-butyl ether (MTBE) to the sample and shake for two minutes.

Compound Methylation

To begin haloacetic acids methylation, transfer approximately 3mL of the MTBE extract to a 15mL graduated, conical centrifuge tube. Add 1mL of 10% sulfuric acid in methanol to the centrifuge tube. Cap the tube and heat at 50°C for two hours. After cooling, neutralize the extract with saturated sodium bicarbonate solution, adding it in 1mL increments. Continually vent the centrifuge tube because CO_2 will be generated during the neutralization process.

Transfer 1mL of the MTBE extract to an autosampler vial and spike 10uL of internal standard (25ppm 1,2,3-trichloropropane). Archive the remaining extract portion for later use if necessary.

Column Choice

The analysis of haloacetic acid compounds can be performed on a variety of GC column phases. An important criterion for column selection is the quality of resolution between the methylated haloacetic acid compounds and known interference compounds like bromoform. Bromoform may be present because of the partial decarboxylation of tribromoacetic acid in the methylation step using acidic methanol.

The Rtx®-CLPesticide and Rtx®-CLPesticide2 columns provide the necessary resolution for this analysis using GC/electron capture detection (ECD) (see chromatograms in **Figure 1**). These columns have historically been used for the analysis of chlorinated pesticides (US EPA Method 508), and chlorinated acids (Method 515), using the same analytical configuration.

Instrument Calibration

Analyze the laboratory performance check (LPC) solution to verify instrument performance. The LPC verifies three criteria: instrument sensitivity, chromatographic performance, and column performance. See **Table 1**, other side, for the results on the Rtx®-CLPesticide and Rtx®-CLPesticide2 columns. Monochloroacetic acid (MCAA) is used to verify instrument sensitivity. At a concentration of 6µg/L, MCAA must have a signal-to-noise ratio greater than three. Chromatographic performance is verified using a measure of peak symmetry called the Peak Gaussian Factor (PGF). The calculated PGF must be between 0.80 to 1.15 for optimum performance. The compound used for this is bromochloro- acetic acid (BCAA) at a concentration of 4µg/L (see below for calculation).

Peak Gausian Factor:

$PGF = (1.83 \times W_{1/2})/W_{1/10}$

where: $W_{1/2}$ = the peak width at half-height (in seconds)

$W_{1/10}$ = the peak width at one-tenth height (in seconds)

Peak Resolution:

Column performance is verified using the peak resolution between chlorodi-bromoacetic acid (CDBAA) and the surrogate (1,2,3-trichloropropane).

The criteria for resolution is greater than 0.5 using the following equation:

$R = t/W_{ave}$

where: t = the difference in elution time of the two peaks (in minutes)

W_{ave} = the average peak width of the two peaks measured at baseline (in minutes)

environmental

The GC is calibrated using standards that have been deriva- tized by the same procedure as the samples. This process helps reduce variability between extraction sets and laboratories. The low point of the curve should be near the detection limit and the high point should be 20 to 50 times higher. The last three standards should have concentrations evenly distributed between the low and high point in the curve.

Instrument stability is verified at every 10 sample injections by analyzing a mid-point calibration standard. All calculated compound concentrations in the standard must have a recovery of 70-130% of the theoretical value.

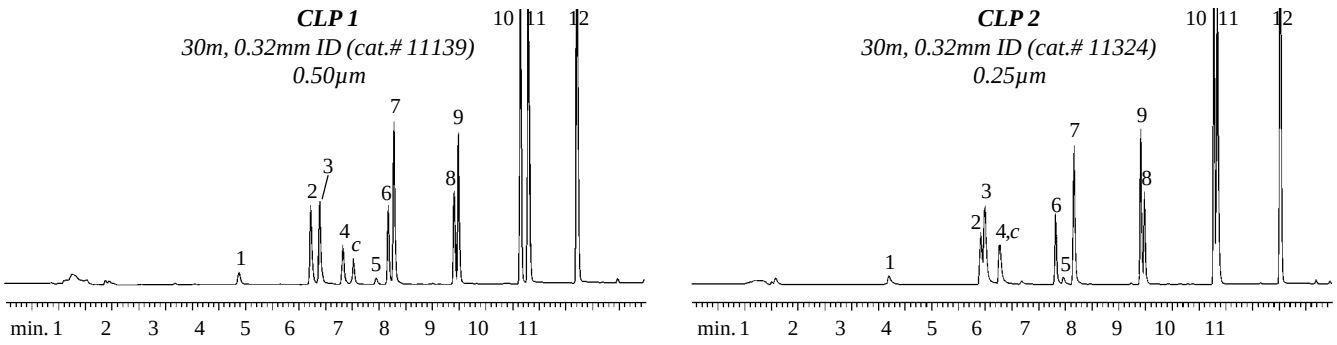
There are other quality controls that must be performed when analyzing samples by US EPA Method 552.2. They include laboratory duplicates, field duplicates, laboratory blanks, field blanks, laboratory fortified blank, laboratory fortified sample matrix spikes, and quality control samples. Read through the method and set-up a flowchart to determine when quality control samples should be performed. Doing so will reduce confusion and make the analysis straightforward.

Conclusion

The versatile Rtx®-CLPesticide and Rtx®-CLPesticide2 columns exhibit proper resolution of many compounds including haloacetic acids, chlorinated pesticides, chlorinated phenoxy herbicides, organophosphorus pesticides, and triazine herbicides. These columns help analysts reduce instrument downtime and increase sample throughput.

For more information, call Restek at 800-356-1688 or 814-353-1300, ext. 4, or your local Restek representative.

Figure 1: *The Rtx®-CLPesticide and Rtx®-CLPesticide2 columns provide the necessary resolution of haloacetic acids.*



c=solvent contaminant

1. monochloroacetic acid
2. monobromoacetic acid
3. dichloroacetic acid
4. dalapon
5. 1,2,3-trichloropropane
6. trichloroacetic acid
7. bromochloroacetic acid
8. dibromoacetic acid
9. bromodichloroacetic acid
10. chlorodibromoacetic acid
11. 2,3-dibromopropionic acid
12. tribromoacetic acid

Haloacetic acids, EPA Method 552.2 on Rtx-CLPesticides columns
Custom haloacetic acid methyl derivatives std. [20-200µg/mL] mix in MTBE.
Oven temp.: 40°C (hold 4 minutes) @ 14°C/min. to 200°C; **Inj. temp.:** 200°C, splitless, 2µL; **Carrier gas:** helium @ 46cm/sec.; **ECD Det.:** 300°C

Table 1: *Laboratory Performance Check Solution*

Parameter	Measurement	Analyte	Concentration	CLP Result	CLP2 Result	Acceptance Criteria
Instrument sensitivity	S/N	MCAA	0.006µg/mL	9	4	S/N>3
Chromatographic performance	PGF	BCAA	0.004µg/mL	0.92	1.05	PGF>0.08 and <1.15
Column performance	Resolution	CDBAA 2,3-DBPA	0.010µg/mL 0.010µg/mL	1.0	0.6	Resolution> 0.50

Product Listing

Rtx®-CLPesticides (Fused Silica) *Stable to 340°C*

ID	df (µm)	temp. limits	30-meter
0.32mm	0.50	-60 to 310/330°C	11139

Rtx®-CLPesticides2 (Fused Silica) *Stable to 340°C*

ID	df (µm)	temp. limits	30-meter
0.32mm	0.25	-60 to 310/330°C	11324

Restek Trademarks: Rtx.