

Jessin Mathai, Anant Lohar, Jenishia, Menezes and Shailesh Damale. Shimadzu Middle East and Africa FZE, Dubai, United Arab Emirates.

1. Introduction

Halo ethers are organic compounds which contains ether molecules with halogen substituents in the carbon framework. These chemicals are commonly used in manufacturing industries especially for polymers and resins.

Many of these Halo ethers are partially soluble in water and are highly soluble in various organic solvents. Some of these compounds are biodegradable at specific conditions whereas some others are not. Halo ethers are reported to be harmful to marine species as well as humans, if ingested orally¹.

This article presents the use of the Shimadzu GCMS-QP2050 along with Brevis[™] GC-2050 (Fig. 1) for both quantification and qualification of 23 halo ethers listed in United States Environmental Protection Agency (USEPA) 8111 method². Out of these 23 compounds, 4 are categorized as Resource Conservation and Recovery Act (RCRA) analytes and the rest as non-RCRA analytes.



Fig. 1 Brevis[™] GC-2050 + GCMS-QP2050.

2. Materials and Methods

The certified 23-halo ether standards in isooctane is sourced from AccuStandard (Cat. M-8111 & M-8111-X1). Surrogate analytes (2,4-Dichlorodiphenyl ether, Phenyl 2,3,4-trichlorophenyl ether) and the internal standard compound (4,4'-Dibromobiphenyl) in acetone are also sourced from AccuStandard (Cat. M-8111-SS-50X, M-8111-IS-20X respectively). MTBE (≥99.5%) is used as the extraction solvent. Reagent grade Na₂HPO₄, KH₂PO₄, and NaCl are used for buffering and salting out. Tap water is used as the test matrix and for recovery analysis. A 500 ppb mixed halo ether stock is prepared in MTBE, with separate 1 ppm surrogate and internal standard. Six level calibration standards with concentrations ranging from 5-100 ppb are prepared

from this stock. Standards #2 and #5 are spiked with surrogates to achieve concentrations of 10 ppb and 75 ppb, respectively. Then, 200 µL of each level standard is transferred to vial inserts, which is then added with 20 µL of 1 ppm internal standard to assess instrument performance. The prepared standards are injected into the GCMS.

Tap water sample is first buffered to attain a pH range of 4.8–5.5 with 1 g of phosphate buffer (1% Na₂HPO₄, 99% KH₂PO₄) per 50 mL sample. Extraction steps are illustrated in fig. 2. Spike recovery tests at 1 and 7.5 ppb analyte concentrations are conducted using the same procedure outlaid below, with surrogates added to reach a concentration of 7.5 ppb. This recovery results are used to validate method accuracy and corrections in sample results.



Fig. 2 Sample extraction flow process.

The analytical method is established as per the instrument parameters listed in table 1. A 500 ppb standard containing target analytes, surrogates, and internal standard is first injected in full scan mode to determine retention times. All the peaks are then identified using the NIST GC/MS library. The quantifier and qualifier ions for the individual analytes are selected to build a compound table. The "Smart SIM" feature of GCMS-QP2050 is utilized to generate a time segmented SIM acquisition method for all the chosen ions, from the scan data. The ultra-fast scanning speed of 30,000 u/s on the GCMS-QP2050 enables the creation of a simultaneous Scan/SIM acquisition method, which can collect data in both scan and SIM modes, ensuring comprehensive qualitative and quantitative analysis.

Table. 1 Instrument parameters

Column Carrier gas Flow contro Column flow Purge flow Injection vo Injection po Ion Source Interface ter

3. Results

The correlation coefficient for all the analytes \geq 0.99. The accuracy results for all analytes fall between 80-120%. The representative chromatograms with the respective linearity plots for three halo ether analytes are presented in fig. 3.

In the tap water sample, four halo ether compounds are observed at a concentration less than 5 ppb. The results of the analysis are presented in table 2.

Two pairs of halo ether compounds are found to be coeluting, hence their combined concentrations are reported. Recovery for most of the analytes in both spike samples fall within the range of 80-120%.



	SH-I-5Sil MS (30 m x 0.25 mm; df: 0.25 µm)				
	Helium				
l mode	Linear-Velocity (41.2 cm/s)				
N	1.26 mL/min				
	3.0 mL/min				
lume	2.0 μL				
rt temperature	200 °C				
temperature	220 °C				
mperature	250 °C				

Table. 2 Analytical results

Name

Bis(2-chloroethyl) ether Bis(2-chloro-1-methylethy Bis(2-Chloroethoxy)Metha 4-Chlorophenyl phenyl eth 4-Bromophenyl-phenyl etl 2,4-Dichlorodiphenyl ether Phenyl 4-nitrophenyl ether Phenyl 2,3,4-trichloropher 2-Chlorophenyl 4-nitrophe 3-Chlorophenyl 4-nitrophe 4-Chlorophenyl 4-nitrophe 2,6-Dichlorophenyl 4-nitro 2,5-Dichlorophenyl 4-nitro 3,5-Dichlorophenyl 4-nitro 2,4-Dichlorophenyl 4-nitro 2,3-Dichlorophenyl 4-nitro 3,4-Dichlorophenyl 4-nitro 2,4,6-Trichlorophenyl 4-nit 2,3,6-Trichlorophenyl 4-nit 2,3,5-Trichlorophenyl 4-ni 2,4,5-Trichlorophenyl 4-n 2,4-Dibromophenyl 4-nitr

3,4,5-Trichlorophenyl 4-n & 2,4-Dichlorophenyl 3-m nitrophenyl ether

2,3,4-Trichlorophenyl 4-n

4. Conclusion

- the established procedure.

Reference

(RUO). Not for use in diagnostic procedures. and/or other countries.

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		m/z	Accuracy (%)	Water sample (ppb)	Recovery%	
	RT				(1.0 ppb)	(7.5 ppb)
	4.26	93	95.2	ND	101	86
) ether	5.82	45	94.3	ND	105	90
ne	8.63	63	103.4	ND	113	92
er	20.20	204	96.8	ND	106	92
ner	22.50	248	98.2	ND	104	92
⁻ (SS-1)	23.45	168		80.6	101	91
	26.85	215	105.5	ND	106	88
yl ether (SS-2)	28.79	202		85.6	106	94
nyl ether	30.94	168	100.9	ND	112	91
nyl ether	31.37	219	107.4	2.6	89	97
nyl ether	31.92	168	109.8	2.4	85	85
phenyl ether	34.05	202	105.7	2.3	88	87
phenyl ether & phenyl ether	34.59	202	106.5	2.9	79	86
phenyl ether	34.92	202	109.2	ND	105	89
phenyl ether	35.66	283	115.2	ND	106	88
phenyl ether	36.14	283	113.4	ND	103	87
rophenyl ether	36.90	317	115.2	ND	105	88
rophenyl ether	37.96	236	112.3	ND	105	89
itrophenyl ether	38.18	238	112.4	ND	104	88
itrophenyl ether	38.40	236	117.5	ND	104	88
ophenyl ether	39.46	139	114.4	ND	128	92
itrophenyl ether nethyl-4-	39.59	319	116.1	ND	102	85
itrophenyl ether	39.80	236	114.5	ND	99	87

◆ A comprehensive and highly sensitive GCMS method for RCRA and non RCRA compounds using Shimadzu GCMS-QP2050 is developed and shows excellent accuracy and precision.

◆ A simple and cost-effective sample extraction method demonstrates excellent recovery, proving the high efficiency of

^{1) &}lt;u>https://nepis.epa.gov/Exe/ZyPDF.cgi/9100RGJQ.PDF?Dockey=9100RGJQ.PDF</u> 2) <u>https://www.epa.gov/sites/default/files/2015-12/documents/8111.pdf</u>

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