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GC-MS DETERMINATION OF HALOGEN DERIVATIVES OF ACETIC ACID

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Abstract

The number of haloacetic acids exhibit carcinogenic properties so their occurrence in drinking water makes them hazardous to human health. Both Polish and international regulations impose certain limitations on their levels in water. This study addresses determination of haloacetic acids by liquid-liquid extraction, derivatization and GC-MS. The inclusion of GC-MS is a modification of standard techniques for assaying haloacetic acids. The procedure used herein enabled the separation of a 5-component mixture of haloacetic acids and their quantitative analysis in water at a concentration range of 15-30 μg/dm^3, depending on a compound. The repeatability of the technique did not exceed 16%.

Streszczenie

Szereg kwasów halogenooctowych jest rakotwórcza, co sprawia, że ich obecność w wodzie do picia stanowi zagrożenie dla zdrowia. Przepisy krajowe jak i międzynarodowe ograniczają zawartość wybranych kwasów w wodzie. Niniejsza praca opisuje metodę oznaczania kwasów halogenooctowych przy pomocy ekstrakcji ciecz-ciecz, upochodnienia oraz GC-MS. Włączenie analizy GC-MS w szlak oznaczania kwasów halogenooctowych stanowi modyfikację standardowo wykorzystywanych metod. Przedstawiona procedura umożliwia rozdział 5 składnikowej mieszaniny kwasów halogenooctowych i ich oznaczenie ilościowe w wodach na poziomie stężeń od 15 do 30 μg/dm^3 w zależności od związku. Powtarzalność metody nie przekraczała 16%.

Keywords: **Haloacetic acid; GC-MS; Liquid-liquid extraction; Derivatization; Water analysis.**

1. INTRODUCTION

After trihalomethanes (THMs), haloacetic acids (HAAs) are the second group of by-products of water disinfection, significant in terms of its health advantages. They form as a result of HAA precursors (mainly humus matter) transformation caused by chlorine [1-4]. The haloacetic acids formed during water disinfection include: monochloroacetic acid $CH_2ClCOOH$ (MCAA), monobromoacetic acid $CH_2BrCOOH$ (MBAA), dichloroacetic acid $CHCl_2COOH$ (DCAA), trichloroacetic acid CCl_3COOH (TCAA), dibromoacetic acid $CHBr_2COOH$ (DBAA) and others.

Haloacetic acids occurring in drinking water are harmful to people and animals. Some of them, such as dichloroacetic and trichloroacetic acids, have been classified as carcinogenic [5-6]. Dichloroacetic acid causes neuropathy, weight loss and liver cancers. Therefore, a lot of countries have been introducing regular measurements of HAA concentrations in drinking water and during its treatment, setting standards that govern HAA permissible levels in the water supplied to consumers. In 2008, The United States Environmental Protection Agency set a permissible level of 60 μg/dm^3 for the total of 5 HAAs i.e. MCAA, DCAA, TCAA, MBAA, DBAA. In the future, howev-

er, the standard is going to be decreased to 30 μg/dm^3 due to the carcinogenic hazard HAAs effect on people and animals [6]. According to WHO guidelines on the quality of drinking water, the permissible concentrations of dichloroacetic and trichloroacetic acids must not exceed 50 μg/dm^3 and 100 μg/dm^3, respectively [7]. In Poland, the regulation of the Minister of Health dated 20 April 2010 on the conditions drinking and household water must meet (J. L. from 2007, No. 61, item 417) mentions monochloroacetic acid whose permissible concentration is 30 μg/dm^3 [8].

Haloacetic acid assays involve the acidification of a water sample to pH < 2. This reverses acid dissociation, which enables their extraction to an organic solvent (Liquid – Liquid Extraction – LLE) insoluble in water. Normally, methyl tert-butyl ether (MTBE) is used to carry out the task. The extraction of haloacetic acids and other compounds of such polarity, is enhanced by the derivatization procedure. Extracted acids are derivatized to methyl esters which are separated by gas chromatography, using an electron capture detector. The limits of quantification for that technique are around 0.5 μg/dm^3, except for monochloroacetic acid whose limit is about 1 μg/dm^3 [9].

This study employed US EPA 552.2 [10] to prepare water samples of haloacetic acids and GC-MS to analyze qualitatively and quantitatively the extract. The inclusion of GC-MS in haloacetic acid assays is a modification of classic techniques.

2. METHODS

Materials

Methyl tert-butyl ether was supplied by Acros Organics while sulfuric acid, sodium sulfate and sodium carbonate (Na_2CO_3) A.R. grade were produced by POCH (Poland). Monochloroacetate, trichloroacetate and monobromoacetate standard solutions were manufactured by Fluki and dichloroacetate, tribromoacetate and dibromoacetate standard solutions were produced by Sigma-Aldrich. The haloacetic acid stock solution (1.0 mg/cm^3) and working solution (100 ng/μl) were prepared in methyl tert-butyl ether.

Liquid – liquid extraction and haloacetic acids derivatization

The haloacetic acids were separated introducing 1.5 cm^3 H_2SO_4, 12 g solid Na_2S_4 and 3 cm^3 methyl tert-butyl ether into a water sample and shaken intensively for 5 minutes in a separator. After separating the organic fraction, 2.5 cm^3 of the extract was collected and placed in a test tube, adding 1 cm^3 of 10% H_2SO_4 in CH_3OH. For derivatization purposes, a sample thus prepared was placed in a dryer heated to 50°C for 30 minutes. Then 4 cm^3 of 10% aqueous Na_2SO_4 solution was added and transferred again into the separator. Following the separation, the organic fraction was analyzed by GC-MS. The procedure is given in Fig. 1.

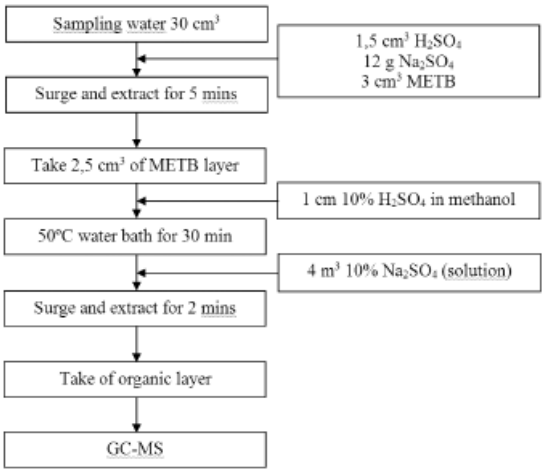

Figure 1.
Water sample preparation procedure

GC-MS analysis

The assays were carried out employing a Saturn 2100 T gas chromatographer (Varian) coupled with a mass detector (GC-MS, ion trap). The parameters of the chromatographic assays are given in Table 1. The quantitative analysis was conducted using FS (full scan) at a mass range of 50 to 250 a.m.u.

Table 1.
Parameters of GC-MS assays

GC	Column	Varian SLB™ – 5ms 0.25 mm *i.d.* x 30 m., *df*: 0.25 mm
	Temperature setting	40°C (10 min), 20°C/min to 210°C (1.5 min)
	Injection volume Injector	1 μm 210°C, *splitless*
	Gas Flow	helium 1.1 ml/min
MS	Ionization Ionization energy	EI 70 eV
	Temperature of ion source	200°C

Table 2.
The physico-chemical properties of the water

Parameter	Tap water	Surface water
pH	6.50	7.91
Absorbance in UV_{254}, cm^{-1}	0.12	0.31
Total organic carbon, mgC/dm^3	4.82	7.56

Table 3.
Limits of detection and quantitation, assays and linearity of mass detector response in LLE-derivatization-GC/MS technique

Compound	LOD[a] ($\mu g/dm^3$)	LOQ[b] ($\mu g/dm^3$)	Correlation coefficient (R^2)[c]
Monochloroacetic acid MCAA	15	60	0.958 (30 – 1500)
Bromoacetic acid MBAA	15	60	0.921 (30 – 1500)
Dichloroacetic acid DCAA	30	90	0.923 (60 – 1500)
Trichloroacetic acid TCAA	30	90	0.934 (60 – 1500)
Dibromoacetic acid DBAA	15	30	0.968 (30 – 1500)

[a] Limit of detection (S/N = 3);
[b] Limit of quantitation (S/N > 10);
[c] the values in brackets show a linear range of calibration curves (ng/cm^3)

Recovery and repeatability of assays

The recovery of the compounds was calculated as an arithmetic mean for four runs of tap and surface water samples extraction (n=4), Table 2. The concentrations of the standard solutions were 500, 1000 and 1500 $\mu g/dm^3$. Prior to extraction, the water was monitored for haloacetic acids occurrence. The repeatability of the assays was expressed as a relative standard deviation (*R.S.D.*, %).

3. RESULTS

Fig. 2A shows a chromatogram of a mixture of derivatized haloacetic acids. The assumed chromatographic conditions enabled a separation of all the components of haloacetic acid ester derivatives. The chromatographic peaks corresponding to the mixture components had varied retention times. The proper course of esterification was confirmed by the presence of m/z 59 ion in the mass spectrum of monochloroacetic acid derivative (Fig. 2B) connected to the presence of $[COOCH_3]^+$ structure.

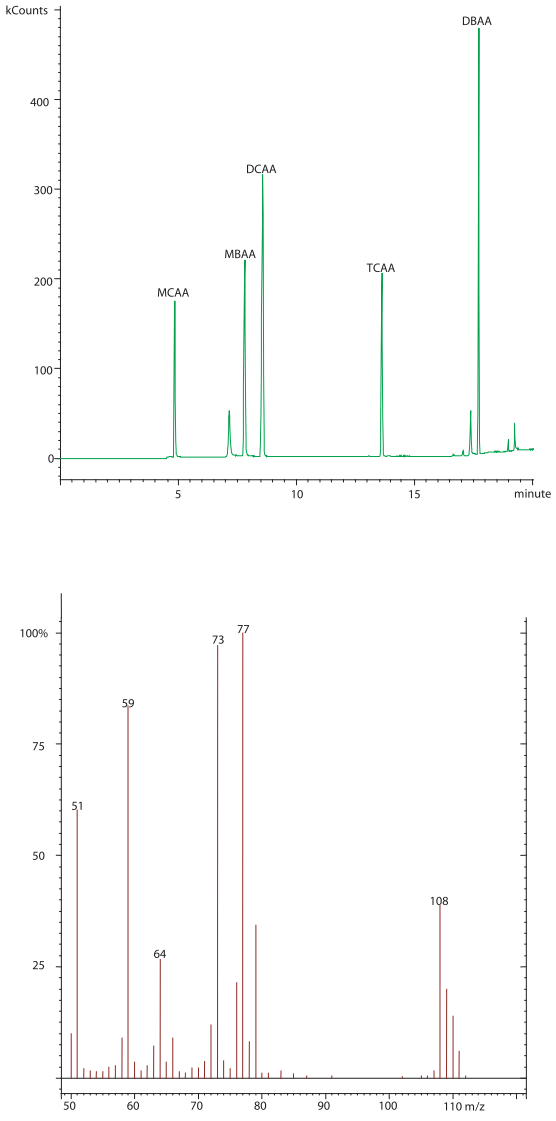

Figure 2.
GC-MS chromatogram of haloacetic acid derivatives (standard solution concentration of 1000$\mu g/dm^3$) (A) and mass spectrum of monochloroacetic acid methyl ester (B)

The detection limit for the technique was 15 $\mu g/dm^3$ for monochloroacetic, bromoacetic and dibromoacetic acids and 30 $\mu g/dm^3$ for dicholroacetic and trichloroacetic acids, Table 3. The linear range of the mass detector response was determined for a range of 30-1500 $\mu g/dm^3$ for monochloroacetic, bromoacetic and dibromoacetic acids and 60-1500 $\mu g/dm^3$ for dichloroacetic and trichloroacetic acids. The linear correlation coefficient (R^2) exceeded 92.1%.

Table 4.
Recovery of haloacetic acids and repeatability of LLE-derivatization-GC/MS technique

Compound	Water sample	Recovery (%)[a] (mean ± *R.S.D.*) at a haloacetic acid concentration, μg/dm^3		
		500	1000	1500
MCAA	tap	70 ± 12	74 ± 5.7	82 ± 1.1
	surface	74 ± 9.2	85 ± 5.1	88 ± 6.1
MBAA	tap	74 ± 15	79 ± 2.0	80 ± 3.5
	surface	77 ± 10	73 ± 0.1	100 ± 0.4
DCAA	tap	90 ± 16	89 ± 14	88 ± 13
	surface	89 ± 11	60 ± 12	98 ± 13
TCAA	tap	80 ± 4.4	81 ± 2.6	84 ± 5.3
	surface	82 ± 5.2	74 ± 2.3	80 ± 10
DBAA	tap	84 ± 6.1	85 ± 10	87 ± 11
	surface	86 ± 13	87 ± 6.7	91 ± 8.4

[a]recovery and accuracy of assays were determined by repeating the procedure four times (n=4).
R.S.D.– relative standard deviation

Table 4 gives data on the quantitative assays carried out by LLE-derivatization-GC/MS procedure. The efficiency of extraction and repeatability of the assays were determined conducting the procedure four times using two types of water (tap and surface) with standard solutions of the following haloacetic acid concentrations: 500, 1000 and 1500 μg/dm^3. The results thus obtained were used to calculate the recovery (%) of the compounds. Its mean values fell within 70%-100%. The water samples did not affect significantly the efficiency of extraction. The repeatability of the results produced by this procedure expressed as relative standard deviation (*R.S.D*) did not exceed 16%.

4. CONCLUSIONS

The analytical procedure presented herein enables the separation of a 5-component mixture of haloacetic acids and their quantitative assays in water at a concentration level of 15-30 μg/dm^3. The assays carried out for two types of water (concentrations of haloacetic acids – 500, 1000 and 1500 μg/dm^3) produced a satisfactory repeatability of 0.1-16%.

The technique developed for assaying haloacetic acids in water turned out to be less sensitive than standard techniques [9]. Nevertheless, it can be applied to screening analysis.

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