ELSEVIER

Journal of Chromatography A, 725 (1996) 157–163

JOURNAL OF CHROMATOGRAPHY A

Determination of trihalomethanes in aqueous samples by means of a purge-and-trap system with on-sorbent focusing coupled to gas chromatography with electron-capture detection

Bogdan Zygmunt

Technical University of Gdańsk, Chemical Faculty, 11/12 Narutowicza Str., 80-952 Gdańsk, Poland

Abstract

A laboratory-built purge-and-trap device in which analytes desorbed from a primary trap (macrotrap) are focused in a microtrap (also with sorbent) and moisture is removed from purge gases by a Nafion tube (walls selectively permeable to water vapour) is described. The device is compatible with capillary GC columns. Purge parameters such as purge gas flow-rate and volume, purge temperature and ionic strength were optimized with respect to recovery efficiencies of trihalomethanes (THMs) and carbon tetrachloride (CCl_4) from aqueous samples. Sorption and desorption parameters of a macrotrap–microtrap system for THMs were selected. A procedure was developed whereby THMs and CCl_4 at the level of several ppt can be determined with good accuracy and precision in a variety of aqueous samples. The procedure was applied to the determination of THMs and CCl_4 in real samples, i.e., tap water, orange drinks and an infusion fluid.

Keywords: Purge-and-trap system; Trihalomethanes; Carbon tetrachloride

1. Introduction

Owing to their toxicity, possible carcenogenicity [1] and some other reasons, trihalomethanes (THMs) must be determined at very low levels in environmental and biological samples and in food products. The basic approach to such analytical problems is the application of gas chromatography with electron-capture detection (GC–ECD), ensuring high sensitivity and selectivity. A convenient sample introduction method, in such a case, is a direct aqueous injection (DAI) technique in which an aqueous sample is directly introduced into a GC column. Capillary columns used in such a technique are generally covered with a thick film of an apolar liquid phase to make water elute before the analytes. DAI–GC–ECD has been widely employed for the rapid screening of THMs and other volatile haloorganic compounds at the level of 0.01–10 ppb in aqueous samples with relatively simple matrices to prevent contamination of the GC column [2–8]. For lower concentrations and when samples are additionally heavily contaminated with low-boiling organic and inorganic compounds, isolation and/or preconcentration of analytes of interest, prior to the analysis proper, become necessary [9,10]. In the case of volatile analytes, to which THMs belong, this is most often performed by gas extraction techniques. Among them, the most popular for the determination of volatile compounds are headspace (HS) and

0021-9673/96/$15.00
SSDI 0021-9673(95)00892-6

purge-and-trap (PT) methods, although HS combined with solid-phase microextraction (HS–SPME) developed by Pawliszyn and co-workers [11,12] and the thin-layer headspace (TLHS) method proposed by Kozłowski et al. [13] are also very useful. Being gas extraction techniques, HS, PT, TLHS and HS–SPME are applicable to the selective introduction of volatile compounds into a GC column also from samples heavily contaminated with pollutants of low volatility.

Kozłowski and Polkowska [14] used the TLHS method at 90°C to isolate THMs from water; subsequently, water vapour in the extraction gas was condensed at 10°C together with a constant fraction of the analytes. A water condensate containing only volatile compounds (those extracted at 90°C) can be analysed by DAI–GC–ECD. Recoveries with the method were low but enrichment factors for THMs were fairly high (range 20–100).

The application of HS and PT, still the two basic gas extraction techniques, to environmental samples was compared by Voice and Kolb [15], who stressed that static HS is widely used in western Europe. In the USA, PT seems to be preferred. Past and present trends in PT have been comprehensively and critically discussed by Abeel et al. [16]. Not surprisingly, the PT technique has also been widely used to determine volatile haloorganic pollutants, including THMs, in various aqueous matrices [17–23]. Published procedures differ in the design of the purge vessels, sorbents for trapping purged analytes and ways to refocus bands of analytes desorbed from traps. Refocusing, which is a necessary step when PT is coupled with capillary GC, is generally performed with the help of a cooling medium. This can sometimes be a problem for smaller laboratories.

In this paper, a laboratory-built PT device is described in which refocusing is effected by use of a microtrap with a double bed of different sorbents. Water vapour from purge gases containing the analytes is removed by a Nafion drier, consisting of a tube whose walls are permeable to water vapour but not to the organic compounds of interest [24]. A procedure to determine THMs and related pollutants was developed and different real aqueous samples were analysed.

2. Experimental

2.1. Chemicals and reagents

Trichloromethane, tetrachloromethane, tribromomethane and sodium sulphate (all of "pure for analysis" grade) were obtained from POCh (Gliwice, Poland), bromodichloromethane and dibromochloromethane (both of purum grade) from Fluka (Buchs, Switzerland) and methanol (of Ultra Resi-Analyzed grade) from J.T. Baker.

Stock standard solutions of individual THMs (0.5–0.7 mg/ml) were prepared in methanol from the pure chemicals. Working standard solutions of a mixture of analytes (0.5, 1.0, 1.5, 2.0, 3.0 and 5.0 mg/l) were obtained by dilution of the stock standard solutions with methanol. They were stable for several weeks if stored at low temperature. Before use the solutions were allowed to reach room temperature. Aqueous standard solutions were prepared 15 min before purging by addition of a methanolic solution into so-called "zero water".

Water purified with a compact Milli-RO Plus 10 reverse osmosis system (Millipore) was boiled for 30 min to remove as many volatile contaminants as possible. Just before the addition of standards, 10-ml water portions were purged with argon for 30 min for further purification. Such water is called "zero water".

2.2. Apparatus and procedure

A laboratory-built purge-and-trap system (Fig. 1) was directly coupled to a Hewlett-Packard Model 5890 Series II gas chromatograph equipped with an electron-capture detector. The analytical procedure was as follows. An aqueous sample was poured into a 20-ml laboratory-made purge vessel with a medium pore size frit (1). The vessel can be thermostated if required. In configuration A, purge gas (ultra-pure argon additionally purified by passing it through a bed of Korbl catalyst) was successively passed through the purge vessel, a 1-m Nafion tube embedded in 5A molecular sieve desiccant (2), an eight-port rotary valve (3) and a macrotrap (4) kept at ambient temperature. In configura-

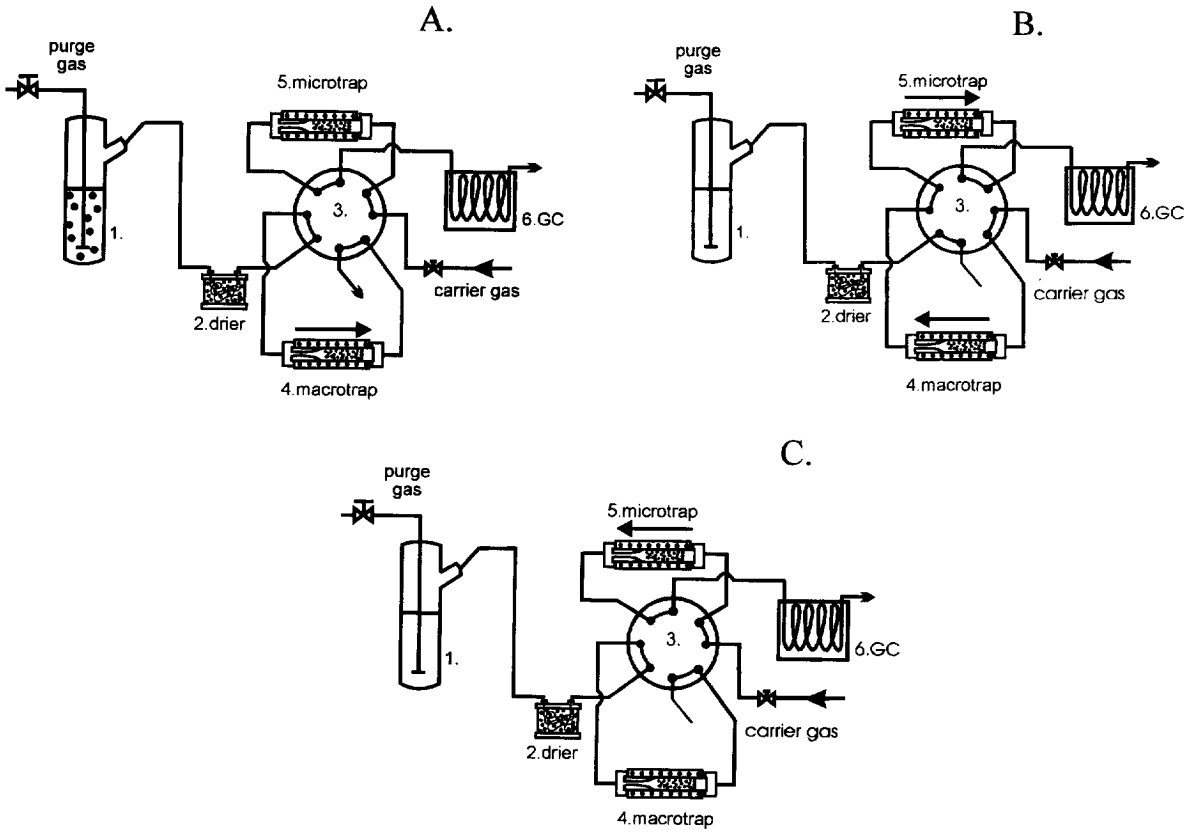

Fig. 1. Schematic diagram of the apparatus for the purge-and-trap technique: 1 = purge vessel; 2 = 1.2-m Nafion drier embedded in 5A molecular sieve; 3 = eight-port rotary valve; 4 = heated macrotrap; 5 = heated microtrap; 6 = gas chromatograph. Apparatus configurations: (A) purge-and-trap; (B) desorption from macrotrap and sorption in microtrap; (C) desorption into GC column.

tion B, carrier gas was passed through the macrotrap ballistically heated to desorption temperature and then through a microtrap (5) kept at ambient temperature. In this step, analytes liberated from the macrotrap were sorbed in the microtrap. In configuration C, the microtrap was rapidly heated and desorbed analytes were transferred by the carrier gas into a GC column (6) for analysis.

The instrumental conditions were as follows.

Purge and trap

Sample volumes 10 ml; macrotrap, glass tube (80 × 4 mm I.D.) packed with 105 mg of Tenax GC and 180 mg of Carbosieve III S; microtrap, glass tube (50 × 2 mm I.D.) packed with 15 mg of Tenax GC and 21 mg of Carbosieve III S; purge gas, argon at 30 ml/min purified on Korbl catalyst kept at 450°C; purge gas volume, 600 ml; trap temperature during sorption, ambient; trap temperature during desorption, 250°C; desorption time from macrotrap, 4 min; and desorption time from microtrap, 2 min.

Gas chromatograph

Analytical column, DB-1 (30 m × 0.32 mm I.D., 5 μm (dimethylpolysiloxane); carrier gas for column, helium (passed through a bed of deoxygenating agent at 250°C) at 2.0 ml/min; make-up gas for ECD, nitrogen at 70 ml/min; oven programme, 50°C for 2 min, increased to 200°C at 10°C/min, held at 200°C for 5 min.

The traps were conditioned every morning by baking for 10 min at 250°C under a flow of carrier gas; during this period, the column was kept at the final temperature of the programme.

A subsequent routine step was to carry out a blank run to check the cleanliness of the whole coupled system.

3. Results and discussion

3.1. Sorption in and desorption from a macrotrap–microtrap system of purged analytes

Transfer of analytes from an aqueous sample into a GC column was carried out in a three-step process: first, during the purge step analytes were sorbed in a macrotrap; then they were desorbed, transferred by carrier gas into a microtrap and sorbed there; in the third step, they were desorbed into the GC column. The desorption temperature (250°C) for both traps packed with Tenax GC and Carbosieve III S was optimized in previous studies [25]. Sorption was performed at ambient temperature. To select a suitable time of desorption from the macrotrap, recoveries were determined for 2- and 4-min desorption periods. For the former the recoveries ranged from 85 to 90% and for the latter the recoveries of all four THMs and CCl_4 were quantitative; a 4-min desorption time was selected as an operational parameter. The recoveries from the microtrap were studied for 60, 90 and 120 s and were quantitative only with a 120-s period, which was fixed as an operational parameter.

3.2. Optimization of purge parameters

Purging parameters (purge gas volume, sample temperature and ionic strength) were optimized with respect to purging efficiency. The purge gas volume is limited by the breakthrough volume (BTV) of the most volatile compound, trichloromethane. It was found not to exceed 600 ml at a flow-rate of 20 ml/min. Such a volume was sufficient to purge trichloromethane quantitatively but the recoveries of the other analytes were too low, at least at room temperature. Recoveries of these analytes were studied at higher temperatures and with the addition of sodium sulphate as a salting-out agent. The results obtained are given in Table 1. At 55°C the recoveries of all the analytes were quantitative but at this temperature the amount of water carried by the purge gas exceeded the capability of the Nafion drier and therefore a temperature of 35°C was selected for operation. Although the recovery of the least volatile compound, tribromomethane, from an aqueous solution was not

Table 1
Purging efficiency (%) of THMs and CCl_4 from aqueous solutions with different purging parameters

Purge temperature (°C)	Recovery (%)[a]				
	$CHCl_3$	CCl_4	$CHBrCl_2$	$CHBr_2Cl$	$CHBr_3$
Analyte concentration 50 ppt, without salt addition					
25[b]	99 ± 2.0	99 ± 1.0	95 ± 1.5	82 ± 5.4	63 ± 5.5
35	100 ± 2.4	100 ± 1.9	97 ± 2.4	94 ± 4.3	72 ± 3.3
Analyte concentration 500 ppt, without salt addition					
25[b]	100 ± 3.0	100 ± 2.0	94 ± 4.1	81 ± 5.8	62 ± 4.5
35	99 ± 3.4	100 ± 3.4	98 ± 3.5	93 ± 4.2	78 ± 4.0
55	99 ± 2.3	100 ± 4.0	99 ± 3.4	99 ± 4.1	95 ± 5.1
Analyte concentration 500 ppt, addition of sodium sulphate (2.5 g/l)					
25	99 ± 3.8	100 ± 4.0	99 ± 2.3	100 ± 4.6	92 ± 3.5
35	101 ± 3.8	100 ± 4.1	99 ± 3.5	99 ± 5.3	99 ± 3.6

[a] With confidence interval for $P = 95\%$, $n = 5$, except where indicated otherwise.
[b] $n = 7$.

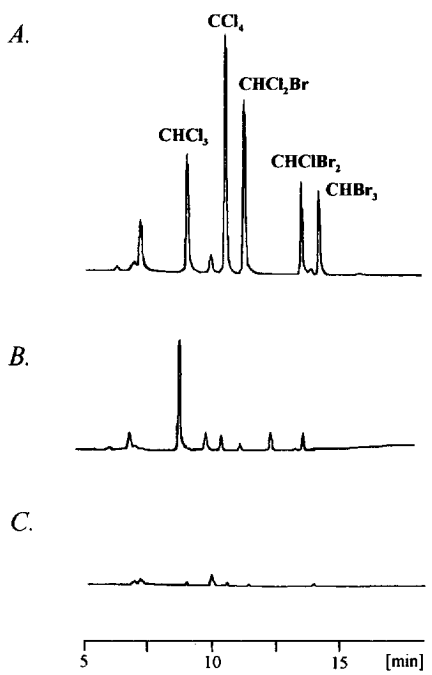

Fig. 2. Chromatograms showing influence of water preparation on water purity: (A) Aqueous solution containing analytes at 50 ppt concentration; (B) water after reverse osmosis; (C) water after boiling and purging with argon.

quantitative at this temperature, it can be improved by addition of Na_2SO_4.

The final purge parameters adopted are given in the preceding section.

3.3. Water quality

The degree of purification of water used in the experiments is presented in Fig. 2. Part A is a chromatogram of an aqueous standard solution containing THMs at 50 ppt, B that of water purified by reverse osmosis and C that of water boiled for 30 min and then purged with argon. It can be concluded that the described procedure reduces interfering contaminants to an acceptable level.

3.4. Performance of the coupled PT–GC–ECD system

For the optimum parameters, the total system response was determined for the concentration range 50 ppt–1 ppb. For this concentration range calibration graphs (peak area versus concentration) were linear with correlation coefficients (r) ranging from 0.9918 for $CHBr_3$ to 0.9987 for $CHCl_3$. Relative sensitivities (1 for $CHCl_3$), very similar to those obtained by Lepine and Archambault [17], were 3.3, 2.3, 0.7 and 4.1 for $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$, and CCl_4, respectively. The detection limits (concentration equivalent to a peak height three times the baseline noise) were at the level of 1 ppt. At 50 ppt the relative standard deviations (R.S.D.s) were in the range 2.9–4.1% for seven measurements.

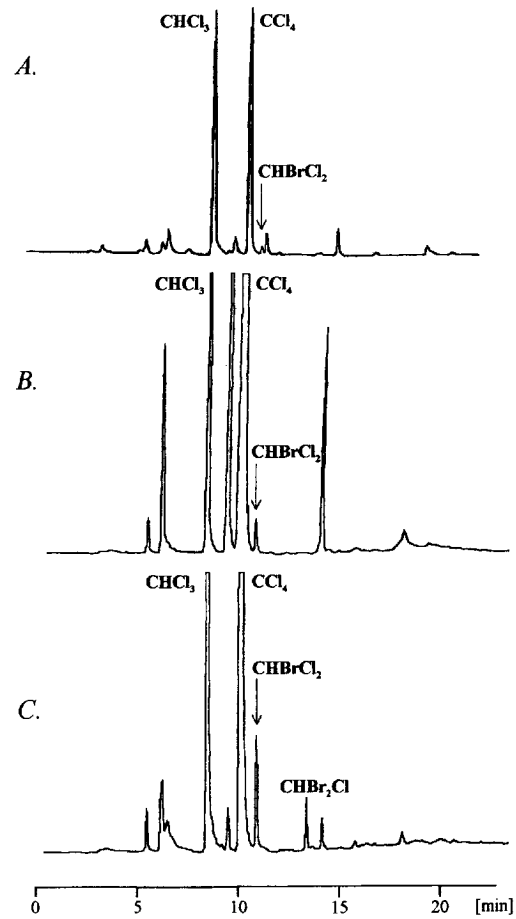

Fig. 3. Chromatograms for 10 ml of real samples: (A) orange drink 1; (B) orange drink 2; (C) infusion fluid.

Table 2
Level of contamination with THMs and tetrachloromethane of some real samples

Compound	Concentration (ng/l; ppt)			
	Orange drink 1	Orange drink 2	Infusion fluid	Tap water
$CHCl_3$	220	365	740	1140
CCl_4	60	1520	950	10
$CHBrCl_2$	20	25	45	720
$CHBr_2Cl$	ND[a]	ND	30	80
$CHBr_3$	ND	ND	ND	2

[a] ND = not detected.

3.5. Real samples

The developed method was used to determine THMs and CCl_4 in orange drinks from two different manufacturers, in tap water and in an infusion fluid. Chromatograms are presented in Fig. 3 and specific contaminant contents in Table 2. An attempt was made to analyse an orange juice. In such a case the addition of an anti-foaming agent is necessary, otherwise the system can undergo contamination because of intensive foaming.

4. Conclusions

The purge-and-trap device with a sorbent microtrap for refocusing of analytes desorbed from a primary trap (macrotrap) can be successfully coupled with capillary GC. Bands entering a GC column are narrow enough to be compatible with capillary GC. The approach seems simpler than that with cryofocusing since the freezing medium is eliminated. Being of the order of 1 ppt, the detection limits are sufficiently low for the described method for the determination of trihalomethanes and other volatile haloorganic compounds to satisfy majority of requirements. The precision (R.S.D.s 2.9–4.1% at 50 ppt) is also acceptable for most protocols. The R.S.D.s comparable to those obtained with commercial devices based on cryofocusing.

Acknowledgements

This research was supported by an internal grant from the Chemical Faculty of the Technical University of Gdańsk. The author thanks W. Janicki for technical assistance and helpful discussions and J. Serek for part of the experimental work.

References

[1] H.A.M. de Kruijf and J.H. Kool (Editors), Organic Micropollutants in Drinking Water and Health, Elsevier, Amsterdam, 1985.
[2] M. Biziuk, J. Czerwiński, E. Kozłowski and L. Torres, Int. J. Anal. Chem., 50 (1993) 109.
[3] T. Lung, C.J. Peters, R.J. Young and R. Perry, Environ. Technol. Lett., 1 (1980) 299.
[4] J.F.M.M. Temmerman and D.J.M. Quaghebeur, J. High Resolut. Chromatogr., 13 (1990) 379.
[5] M. Biziuk and Ż. Polkowska, Pollut. Environ., 3 (1993) 12.
[6] K. Grob, J. Chromatogr., 299 (1984) 1.
[7] K. Grob and A. Habich, J. High Resolut. Chromatogr. Chromatogr. Commun., 6 (1983) 11.
[8] D. Carmichael and W. Holmes, J. High Resolut. Chromatogr., 13 (1990) 267.
[9] J. Namieśnik, T. Górecki and M. Biziuk, Anal. Chim. Acta, 237 (1990) 1.
[10] J. Namieśnik, M. Biziuk, W. Wardencki and B. Zygmunt, Chem. Anal. (Warsaw), 40 (1995) 115.
[11] Z. Zhang and J. Pawliszyn, Anal. Chem., 65 (1993) 1843.
[12] B. MacGillivray, J. Pawliszyn, P. Folie and C. Sagara, J. Chromatogr. Sci., 32 (1994) 317.
[13] E. Kozłowski, E. Sieńkowska-Zyskowska, T. Górecki, Fresenius J. Anal. Chem., 339 (1991) 19.

[14] E. Kozłowski and Ż. Polkowska, in Proceedings of the Symposium "Organic Compounds in the Environment and their Analysis", Jachranka (Poland), May 1994, Library of Environment Monitoring, Warsaw, 1994, p. 183.
[15] T.C. Voice and B. Kolb, J. Chromatogr. Sci., 32 (1994) 306.
[16] S.C. Abeel, A.K. Vickers and D. Decker, J. Chromatogr. Sci., 32 (1994) 328.
[17] L. Lepine and J.-F. Archambault, Anal. Chem., 64 (1992) 810.
[18] X. Yan, K.R. Carney and E.B. Overton, J. Chromatogr. Sci., 30 (1992) 491.
[19] D.P. Lin, C. Falkenberg, D.A. Payne, J. Thakkar, C. Tang and C. Elly, Anal. Chem., 65 (1993) 999.
[20] S.A. Rounds and J. Pankow, J. Chromatogr., 629 (1993) 321.
[21] M.D. Driss and M.L. Bouguerra, Int. J. Anal. Chem., 45 (1991) 193.
[22] M.F. Mehran, M.G. Nickelsen, N. Golkar and W.J. Cooper, J. High Resolut. Chromatogr., 13 (1990) 429.
[23] M. Fujita, W.T. Jung, H. Tatematu, D.H. Sohn and T. Maeda, J. High Resolut. Chromatogr., 14 (1991) 83.
[24] W. Janicki, L. Wolska, W. Wardencki, J. Namieśnik, J. Chromatogr. A, 654 (1993) 285.
[25] W. Janicki, B. Zygmunt, L. Wolska, W. Chrzanowski and W. Wardencki, Chem. Anal. (Warsaw), 37 (1992) 599.