Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1077 (2005) 181–187
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Improved analysis of volatile halogenated hydrocarbons in water by purge-and-trap with gas chromatography and mass spectrometric detection

Lelio Zoccolillo*, Luca Amendola, Claudia Cafaro, Susanna Insogna

Dipartimento di Chimica, Università Degli Studi di Roma "La Sapienza", Ple Aldo Moro 5, 00185 Rome, Italy

Received 25 February 2005; received in revised form 20 April 2005; accepted 22 April 2005

Abstract

An analytical system composed of a purge-and-trap injection system coupled to gas chromatography with mass spectrometric detection (PTI-GC–MS) specific for the analysis of volatile chlorinated hydrocarbons (VCHCs) (chloroform; 1,1,1-trichloroethane; tetrachloromethane; 1,1,2-trichloroethylene; tetrachloroethylene) and trihalomethanes (THMs) (chloroform; bromodichloromethane; dibromochloromethane; bromoform) in water was optimised. Samples were purged and trapped in a cold trap (−100 °C) fed with liquid nitrogen (cryo-concentration). In order to make this method suitable also for only slightly contaminated waters, some modifications were made to PTI sample introduction, in order to avoid any air intake into the system. PTI, GC and MS conditions were optimised for halogenated compound analysis and limits of detection (LOD) were evaluated. The proposed method allows analysis of samples whose concentrations range from μg/L to ng/L. It is, therefore, applicable to drinking waters, in analyses required by law, and to slightly contaminated aqueous matrices, such as those found in remote areas, in environmental monitoring. Moreover, by changing cold trap temperature, even sparkling mineral waters can be analysed, thus avoiding CO_2 interference during the cryo-concentration phase. Our method has been successfully used on real samples: tap water, mineral water and Antarctic snow.

Keywords: Water analysis; Volatile halogenated compounds; PTI-GC–MS

1. Introduction

One current environmental issue is the growing concern about the fate of anthropogenic compounds such as volatile halogenated hydrocarbons. These substances include volatile chlorinated hydrocarbons (VCHCs) and trihalomethanes (THMs), which are typical contaminants of water. VCHCs (chloroform; 1,1,1-trichloroethane; tetrachloromethane; 1,1,2-trichloroethylene; tetrachloroethylene) are used in a wide variety of industrial and commercial processes. This extensive use can lead to the release of VCHCs into the environment during their production, distribution, storage, handling and final use, and can pollute ground and surface waters, with serious attendant health risks. Apart from accidents and illegal discharges that can cause local pollution (μg/L), VCHC applications are potentially dispersive and so VCHCs are released into the atmosphere in large amounts (hundreds of thousands of t/year) [1–4]. This fact and their physico-chemical properties [5,6] mean that VCHCs are present in low concentrations (ng/L) in all aqueous matrices as a result of atmospheric fall-out. These compounds may consequently be considered as global contaminants and as pollution indicators in remote areas. Their volatility contributes to their global diffusion because, while non-volatile compounds are deposited and accumulate close to their source, more volatile compounds undergo long-range atmospheric transport before deposition in colder regions [7–10]. THMs (chloroform; bromodichloromethane; dibromochloromethane; bromoform) are a class of disinfection by-products formed when chlorine reacts with natural organic matter and bromides found in drinking water [11]. To

* Corresponding author. Tel.: +39 064 991 3327; fax: +39 064 90631.
E-mail address: lelio.zoccolillo@uniromal.it (L. Zoccolillo).

0021-9673/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2005.04.076

rid drinking water of harmful bacteria and viruses, disinfection by chlorine is usually necessary. This treatment is only allowed in tap water and thus THMs only occur in that kind of water. Chloroform is present in both groups because it is produced during disinfection but it is also widely used in industry. VCHCs and THMs have become a public health concern due to their suspected carcinogenic nature (a large population is exposed to them, in particular persons served by public water systems) and their acceptable concentration limits in drinking water are fixed by law [12].

The most common technique for analysing VCHCs and THMs in water, and the one expressly provided for in the legislation, is a liquid–liquid extraction with an organic solvent (hexane or pentane) and a subsequent analysis of the extract via gas chromatography with electron-capture detection (LLE-GC-ECD). Unfortunately, the LLE-GC-ECD technique has many quali-quantitative limitations. In a previous work [8], the LLE-GC-ECD method was optimised by an extraction carried out with hexane (hexane/water, 1/1000) in order to attain limits of detection (LODs) of ppt for some VCHCs. But LLE-GC-ECD, although specified in the existing legislation, has several limitations [13]. Liquid–liquid extraction is time consuming and requires extremely pure solvents; nevertheless, solvents are not totally free from halocarbons and these impurities can cause severe chromatographic interference leading to trace analysis problems. The extraction phase requires intensive manual handling which can be a source of many errors. Moreover, LLE-GC-ECD does not provide unequivocal identification of substances nor does it accurately quantify some of the compounds. Indeed if the extraction is carried out with *n*-hexane, compounds like chloroform and 1,1,1-trichloroethane are eluted from the column together with the solvent, and are therefore underestimated. Conversely, if the extraction is carried out with *n*-pentane, its high volatility causes the overestimation of less volatile compounds. Furthermore, this method requires at least 0.5 L of water sample; smaller quantities of sample make extract recovery difficult. So there are restrictions on samples that are hard to collect or hard to collect in large amounts (e.g. samples from remote areas, Antarctic snow). Other methods for the extraction of VCHCs and THMs from aqueous matrices are headspace (HS) and solid phase microextraction (SPME) [14,15]. Of the other techniques provided for by law, the purge-and-trap-GC–MS method is the most satisfactory in terms of qualitative and quantitative analysis and sensitivity level. Current PTI-GC–MS methods are not specific for VCHCs and THMs and have relatively high detection limits that range from 0.1 to 0.04 μg/L probably due to the difficulty in recovering small amounts of analytes when cartridges are used as a trap [16,17]. Although these LODs are compliant with existing legislation, they do not allow the analysis of water that has only been contaminated at a low level (e.g. samples from remote areas).

This work proposes a technique based on a modified purge-and-trap injection system coupled with gas chromatography–mass spectrometry (PTI-GC–MS) operating in SIM mode, specific for the analysis of VCHCs and THMs in water. The modification entails sample introduction into the purge-and-trap injector, in order to avoid any air intake into the system, which could otherwise alter the final results. Modified PTI-GC–MS overcomes the LLE-GC-ECD's limitations and lowers the detection limits of classic PTI-GC–MS by using a cold trap that allows even small amounts of analyte to be concentrated and recovered.

2. Experimental

2.1. Chemicals and reagents

Standard solutions were prepared with analytical grade 1,1,1-trichloroethane, tetrachloromethane, 1,1,2-trichloroethylene, tetrachloroethylene supplied by Merck (Darmstadt, Germany); analytical grade chloroform, bromodichloromethane, dibromochloromethane, bromoform for analysis supplied by Fluka (Buchs, Switzerland). Mixtures of the various volatile compounds were made up to different concentration levels in analytical grade methyl alcohol supplied by Carlo Erba Reagenti [Rodano (MI), Italy]. Appropriate amounts of stock solutions were diluted with a mineral water having a very low VCHC content (mineral waters are free from THMs but a VCHC-free water does not exist, because these substances are always present in all aqueous matrices) to obtain the final working standards (50, 35, 20, 10, 5 and 2 ppt v/v). These were analysed in order to draw six-point calibration curves. Highly concentrated standard solutions (3000, 1000, 500, and 50 ppt v/v) were also prepared and analysed to test the linear range of the detector.

2.2. Apparatus

The injector was a Chrompack CP-4010 purge-and-trap thermal desorption system (Middelburg, The Netherlands) equipped with a Chrompack Cryo-bath condenser and a keyboard controller. This PTI unit was coupled directly to a Hewlett-Packard 5890 series II gas chromatograph (equipped with a cryogenic oven system) connected to a Hewlett-Packard 5989 A mass spectrometer operating in electron impact mode and equipped with a Hewlett-Packard data system (Chemstation 59940 A) (see Fig. 1).

A sample volume of 10 mL was purged with a stream of Helium N55 (99.9995%), supplied by Air Liquid (Rome, Italy) purified through a Hewlett-Packard mass spectrometer gas purifier (Avondale, PA, USA) for 10 min at ambient temperature and at 10 mL/min. The purge flow, containing volatile and water vapour, was passed through a moisture trap kept at −10 °C by a Chrompack Cryo-bath with ethylene glycol, in which water vapour was condensed to avoid blockage of the cold trap. The flow, through a glass liner, arrived at the cold trap, a portion of a Hewlett-Packard HP-1 capillary column (methylsilicone gum) (15 cm × 0.53 mm, 2.65 μm),

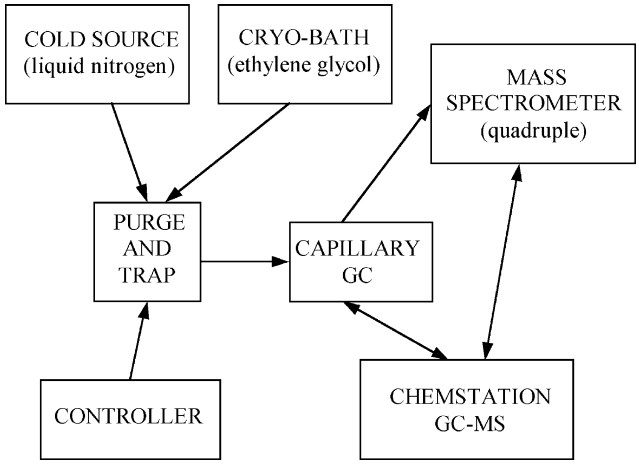

Fig. 1. On line analysis system (block diagram) for water and snow samples via coupled PTI-GC–MS. Each block is described in Section 2.2.

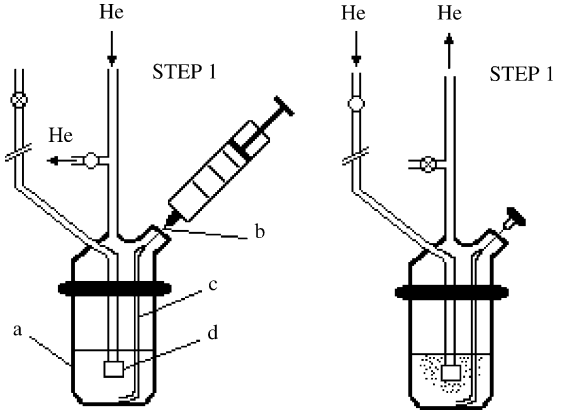

Fig. 2. PTI sample introduction system. Step 1: sample loading. Step 2: purge phase, (a) vessel; (b) fixed needle; (c) small tube connecting the needle to the bottom of the vessel, used both for sample introduction and removal; (d) porous septum.

cooled by a stream of liquid nitrogen (self-pressurising Dewar vessel, 25 L) at a temperature of −100 °C. At this temperature the VCHCs and THMs were trapped. At the end of the purge, a flash heating of the cold trap (200 °C) injected the substances into the capillary GC. The gas chromatograph was equipped with a Hewlett-Packard HP-5MS capillary column (crosslinked 5% PH ME Siloxane, 30 m × 0.25 mm i.d., 0.25 μm film thickness) and helium N55 (99.9995%) was used as carrier gas. The oven was set at 10 °C for 1.50 min and raised to 120 °C at 40 °C/min. The final temperature was maintained for 1.25 min and the total run time was 5.50 min. On exiting from the column, the eluted substances entered the mass spectrometer source (200 °C). Electron impact mode (EI) was performed at 70 eV. The quadrupole MS system was operated in selected ion monitoring (SIM) mode, see Table 1 for GC–MS spectral information. Between two consecutive analyses, the carrier gas was analysed in order to clean the system and eliminate carryover effects.

2.3. Optimisation of purge-and-trap

To remove air interference it was necessary to modify PTI sample introduction. Usually the vessel was first filled with the aqueous sample and then connected to the PTI system. This procedure causes air intake into the apparatus. Since VCHCs are always present in the atmosphere, the analysis results may therefore not be accurate, especially in the case of only slightly contaminated samples. We therefore modified the purge adaptor to allow sample introduction and removal without having to open the system (see Fig. 2). A fixed needle, inserted into a screw cap with a septum (PTFE and rubber), was placed in one purge adaptor entrance. The needle tip was

Table 1
Investigated compounds ordered by boiling point, retention time, retention time window

Id. no.	Compound	Formula	Boiling point (°C)	Retention time (min)	Retention window (min)	Ions (*m*/*z*)	
1	Chloroform	$CHCl_3$	61	2.52	2.30–2.65	83	85
						118	120
2	1,1,1-Trichloroethane	$C_2H_3Cl_3$	74	2.75	2.65–3.15	97	99
						117	119
3	Tetrachloromethane	CCl_4	77	2.90		82	84
						117	119
4	1,1,2-Trichloroethylene	C_2HCl_3	87	3.23	3.15–3.50	95	97
						130	132
5	Bromodichloromethane	$CHBrCl_2$	88	3.29		83	85
						127	129
6	Dibromochloromethane	$CHBr_2Cl$	117	3.95	3.50–4.30	127	129
						208	210
7	Tetrachloroethylene	C_2Cl_4	121	4.04		129	131
						164	166
8	Bromoform	$CHBr_3$	149	4.52	4.30–5.50	171	173
						252	254

In the last column ions detected in SIM mode are listed.

inserted into a small tube (diameter 1 mm) which reached down as far as the bottom of the vessel. The cone needle was closed with a stopper. When introducing the sample, the stopper was replaced with a syringe containing the water to be analysed (10 mL). This phase was carried out in backflush mode, in which the outgoing helium flow prevented simultaneous air intake. Following vessel loading, the cone needle was closed again with the stopper, and the analysis carried out. After this, the small tube was used to remove the sample: the pressure generated in the vessel by backflush flow, was used to push the water in the tube as far as an empty syringe that replaced the stopper.

2.4. Sample introduction and removal procedure

Sample introduction is carried out in several stages: set PTI controller to backflush mode; loosen screw cap; replace the stopper with the syringe containing the sample; introduce water sample into the vessel; remove syringe and close cone needle with the stopper; tighten screw cap; set PTI controller to standby mode. Now the apparatus is ready for analysis.

At the end of analysis, the sample is removed from the vessel following a similar procedure: set PTI controller to backflush mode; loosen screw cap; replace the stopper with the syringe containing the sample; tighten screw cap (water enters the syringe through the small tube under the internal pressure created by helium flow); loosen screw cap; remove syringe and close cone needle with the stopper; tighten screw cap; set PTI controller to standby mode. After a purge phase without any sample to clean the system, the vessel is ready to be filled with a new water sample.

2.5. Sample storage

Commercial bottled mineral water was analysed straight after opening. Tap water, surface water and groundwater were collected in 250 mL Duran glass bottles equipped with a screw cap with a PTFE gasket supplied by Schott (Mainz, Germany), which was completely filled up and stored at 4 °C until the analysis. Analyses were carried out within one month after sampling. Snow was collected in a stainless steel scoop, free from VCHCs and THMs, in 600 mL Duran glass bottles equipped with a screw cap with a PTFE gasket supplied by Schott (Mainz, Germany) that were completely filled up. The samples were stored at −20 °C; at the time of the analysis the snow was melted at 4 °C.

3. Results and discussion

The PTI system does not require any sample preparation, but in order to obtain satisfactory analyte recovery it is necessary to optimise several parameters, such as sample volume, purge time, cold trap temperature. Recovery is an important parameter to ensure an optimal performance of the analysis; it should be as high as possible, although its exact value is not important because the standard solution and the sample are treated and measured in the same way [18]. In order to study recovery we carried out analyses using different purge times (10 and 20 min). A purge time of 10 min was chosen because doubling purge time improved recovery only by about 10%. On the other hand after 13–15 min purging, the system flow decreased since the steam not removed by the moisture trap partly blocked the cold trap. Flow variation during the purge phase influences analysis reproducibility. The calibration curves obtained by analysing standard solutions at different concentrations showed that linearity was guaranteed from 1 ng/L to 1 μg/L. Thus the recovery did not depend substantially on sample concentration. In order to verify this result we subjected the same water sample to six consecutive 10 min purge operations; this test was carried out on two kinds of water, a standard solution (500 ppt v/v for each VCHC and THM) and a real sample (tap water). For the same compound the extraction curves of the standard solution (Fig. 3A) and of the real sample (Fig. 3B) have the same profile. In order to calculate the recovery for each compound, the signal of the first purge was compared with the summation of the signals obtained from all the extractions. The recovery percentages after the first extraction were different for VCHCs and THMs: for $C_2H_3Cl_3$, CCl_4, C_2HCl_3 and C_2Cl_4 the values were about 90%; for $CHCl_3$ the value was about 75%; for $CHBrCl_2$, $CHBr_2Cl$ and $CHBr_3$ the values were respectively about 60, 40 and 30%. The relationship between recovery and sample volume was also investigated. Volumes higher than 15 mL did not allow quantitative recovery, while volumes of less than 5 mL were too small for a correct purge phase; the optimum level was found to be 10 mL.

After many tests the optimal trap temperature (high trapping for all substances and acceptable liquid nitrogen consumption) was found to be −100 °C. Unfortunately this condition does not allow analysis of sparkling waters, because at −100 °C the CO_2 present in the sample solidifies in the cold trap in large amounts and blocks the purge phase. There are two ways of preventing this problem: sample pre-treatment or changing trap temperature. In the first case CO_2 is eliminated from sparkling water by adding NaOH (in alkaline solution $CaCO_3$ precipitates) just before the analysis, which allows the water to be analysed without any problem. The second possibility consists of modifying the instrument conditions, raising trap temperature to −70 °C in order to avoid CO_2 sublimation. As a result, the correct functioning of the purge is restored and a good trapping of analytes is guaranteed because the boiling points of the substances investigated range from 61 to 149 °C (see Table 1). Of course, also the standard solutions have to be analysed under these conditions too. According to the authors, the second method should be used as it does not involve any sample handling that could alter the water.

The PTI-GC–MS method dedicated to VCHCs and THMs has many advantages. It affords an on-line analysis of the sample without using extracting solvents, thus avoiding problems relative to solvent impurities and sample manipulation

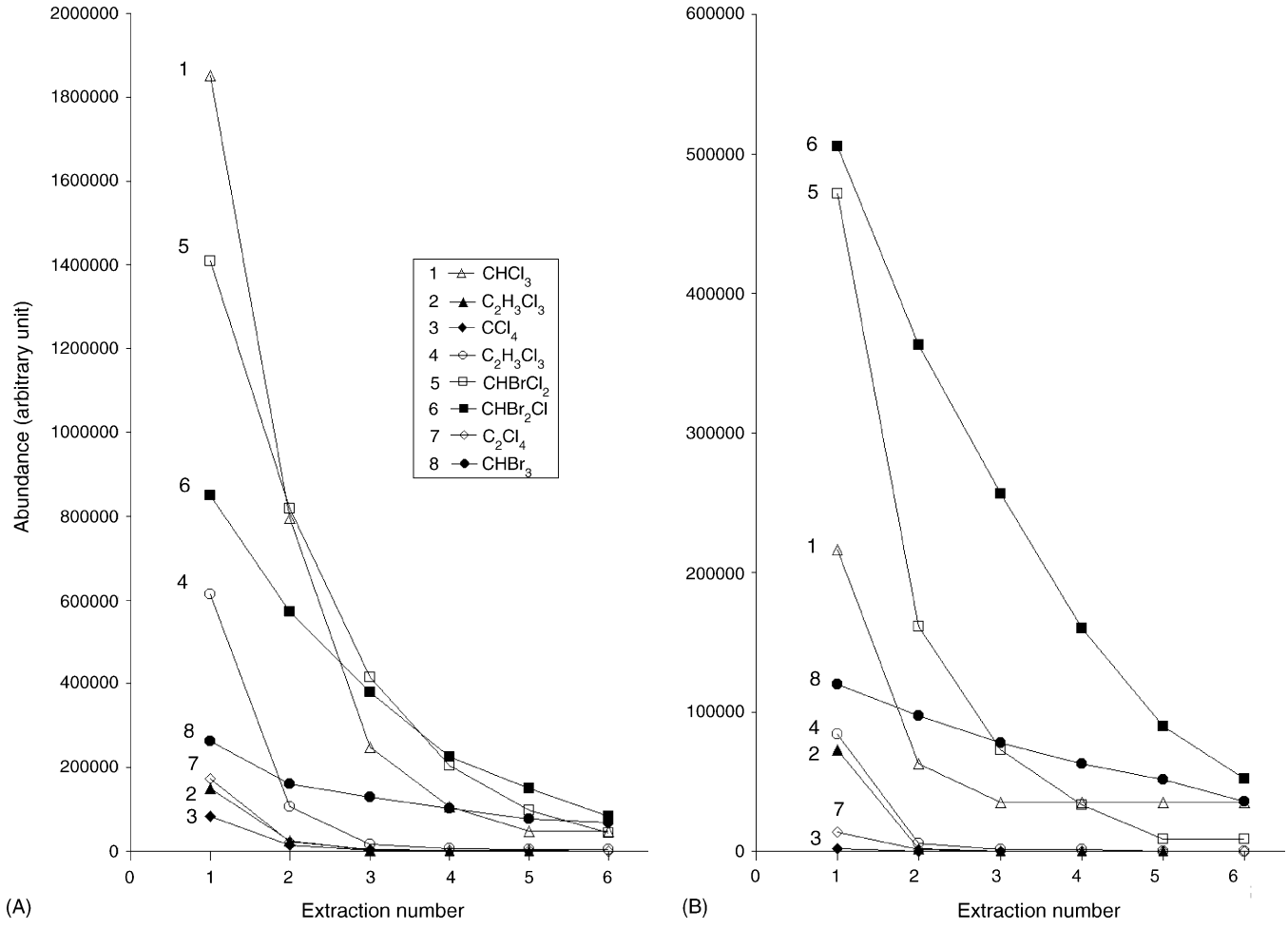

Fig. 3. Extraction profile from a single sample (A: 500 ppt v/v standard solution; B: tap water) submitted to six consecutive 10 min purge phases.

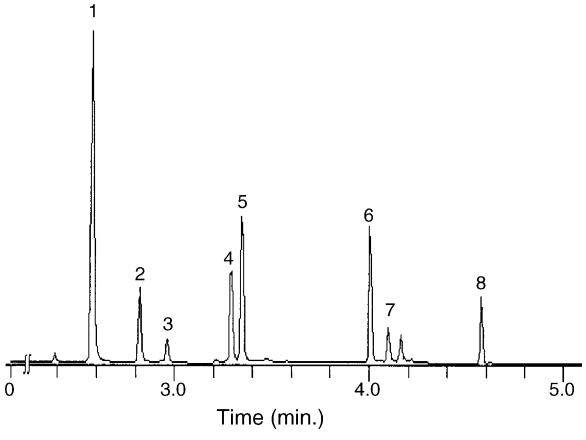

Fig. 4. Chromatogram of tap water sample obtained by modified PTI-GC–MS operating in SIM mode according to *m/z* reported in Table 1. (1) Chloroform; (2) 1,1,1-trichloroethane; (3) tetrachloromethane; (4) 1,1,2-trichloroethylene; (5) bromodichloromethane; (6) dibromochloromethane; (7) tetrachloroethylene; (8) bromoform. Sample volume 10 mL; purge time 10 min; moisture trap −10 °C; cold trap −100 °C; oven program: initial temperature 10 °C, initial time 1.50 min, ramp 40 °C/min, final temperature 120 °C, final time 1.25 min.

and increasing column life. A pre-treatment step is not necessary so analytic procedure is faster. Furthermore PTI-GC–MS provides very sharp and symmetrical peaks (see Fig. 4) and allows accurate analysis of all the compounds studied, even for chloroform and 1,1,1-trichloroethane; peak identification is certain: for each compound the retention time and spectral information may be acquired simultaneously [14]. With

Table 2
Concentration averages (ng/L) of three analysis carried out with modified PTI and classic PTI are compared, in order to stress air contribution, in only slightly contaminated mineral water and in highly contaminated mineral water

	$CHCl_3$	CCl_4	C_2HCl_3	C_2Cl_4
Modified PTI	17.8	5.07	1.46	2.19
Classic PTI	47.3	7.63	2.41	4.23
Concentration percentage increase (%)	166	50	65	93
Modified PTI	98.6	10.8	1350	1050
Classic PTI	143	11.4	1400	1050
Concentration percentage increase	45	6	4	0

Concentration percentage increase is also reported for evaluating air contribution.

Table 3
Concentration values (ng/L) of VCHCs and THMs in water and snow analysed with modified PTI-GC–MS (RSD% < 10%)

	$CHCl_3$	$C_2H_3Cl_3$	CCl_4	C_2HCl_3	$CHBrCl_2$	$CHBr_2Cl$	C_2Cl_4	$CHBr_3$
Typical Italian tap water	44.9	130	8.82	95.3	249	571	40.4	394
Typical Italian mineral water	14.9	12.2	8.92	1.72	<1	<1	2.43	<1
Contaminated mineral water	164	<1	18.7	2790	<1	<1	1690	<1
Typical Italian superficial snow	12.7	1.63	2.74	2.07	<1	<1	3.81	<1
Typical Antarctic superficial snow	236	9.66	52.2	58.2	<1	<1	9.50	<1

PTI-GC–MS sample volume is reduced to 10 mL (LLE-GC-ECD requires at least 0.5 L); this is fundamental for water and snow that are hard to sample.

With modified sample introduction in PTI-GC–MS, air intake into the apparatus is avoided and accuracy is enhanced. As mentioned above, VCHCs are known to be ubiquitous and are consequently present also in air. So, if the apparatus is open and air can enter, the volatile analytes trapped inside would consist both of those purged from water and those from the air. This contribution is negligible in the case of concentrated samples (μg/L or higher), but not for only slightly contaminated samples (ng/L). Moreover uncontrolled factors could alter precision, for example vessel substitution speed and the concentration of analytes in the air.

With modified PTI-GC–MS, there can be no air contribution so the compounds detected and quantified can derive only from water. In order to stress the air contribution, both only slightly contaminated mineral water and highly contaminated mineral water analysed with modified PTI and classic PTI are compared (see Table 2). A useful parameter for evaluating air contribution is concentration percentage increase, which displays a concentration increase on going from the modified to the classic PTI system. For highly contaminated water this percentage increase is negligible for all compounds except chloroform, because CCl_4 C_2HCl_3 and C_2Cl_4 air concentration is lower than water concentration, whereas $CHCl_3$ air concentration is significant. Conversely, for only slightly contaminated water, the air contribution is considerable for all compounds, and so concentration percentage increase values are extremely high, leading to very different results obtained using the classic PTI or the modified PTI. For only slightly contaminated samples, it is fundamental to use the modified PTI method as it affords accurate analyses and results that always correspond to the real water content of the contaminants. Moreover, analyses carried out using the proposed method are reproducible for all investigated substances and LODs in the order of ng/L units are obtained whereas detection limits reported in literature for other purge-and-trap methods for the same compounds range from 0.1 to 0.04 μg/L [17,18]. The linearity range was tested from ng/L units to μg/L units, in order to establish the validity and applicability of this method both for water with relatively low concentrations and water with concentrations close to the legal limits.

In order to demonstrate the versatility of the proposed method, the results of tests on different kinds of aqueous matrices are reported in Table 3. Trihalomethanes were found only in tap water as it is subjected to chlorination.

4. Conclusions

A modified PTI-GC–MS was optimised to analyse volatile halogenated hydrocarbons in water. The accuracy and reproducibility obtained using the modified PTI together with the sensitivity achieved by GC–MS make this method appropriate for the trace analysis of all the compounds studied.

Detection limits were very low, so even samples from remote areas (whose concentrations ranged from 0.5 to 100 ng/L) could be analysed in global contamination studies. Moreover, mineral and tap waters can finally be characterized because it is possible to discriminate among different waters, whose concentration levels range from 1 ng/L to 1 μg/L. It is significant to be able to distinguish a water containing 1 ng/L of any contaminant from another containing 100 ng/L, taking into account that the compounds studied are potentially toxic and dangerous (for human health and for the environment).

References

[1] The Handbook of Environmental Chemistry, in: P. Fabian, O.N. Singh (Eds.)„ in: Part E: Reactive Halogen Compounds in the Atmosphere, vol. 4, Springer, Berlin, Heidelberg, New York, 1999, p. 155.
[2] The Handbook of Environmental Chemistry, in: P. Fabian, O.N. Singh (Eds.)„ in: Part E: Reactive Halogen Compounds in the Atmosphere, vol. 4, Springer, Berlin, Heidelberg, New York, 1999, p. 45.
[3] A. McCulloch, P.M. Midgley, Atmos. Environ. 30 (1996) 601.
[4] A. McCulloch, M.L. Aucott, T.E. Graedel, G. Kleiman, P.M. Midgley, Y.-F. Li, J. Geophys. Res. 104 (1999) 8417.
[5] F.T. Campbell, R. Pfefferkorn, J.F. Rounsaville (Eds.), Ullmann's Encyclopedia of Industrial Chemistry, VCH, Weinheim, 1985 (fifth completely revised ed.).
[6] W.B. DeMore, J. Phys. Chem. 100 (1996) 5813.
[7] L. Zoccolillo, M. Rellori, Int. J. Environ. Anal. Chem. 55 (1994) 27.
[8] L. Zoccolillo, L. Amendola, G.A. Tarallo, Int. J. Environ. Anal. Chem. 63 (1996) 91.
[9] L. Zoccolillo, C. Abete, L. Amendola, R. Ruocco, A. Sbrilli, M. Termine, Int. J. Environ. Anal. Chem. 84 (2004) 513.
[10] W.A. Ockenden, A.J. Sweetman, H.F. Prest, E. Steinnes, K.C. Jones, Environ. Sci. Technol. 32 (1998) 2795.
[11] P.C. Singer, Water Sci. Tech. 40 (1999) 25.
[12] D. Lgs. n 31 02/02/2001, Absorbing 98/83/CE, Gazzetta Ufficiale 52, 03/03/2001.
[13] B. Buszewski, T. Ligor, Water Air Soil Pollut. 129 (2001) 155.

[14] S.K. Golfinopoulos, T.D. Lekkas, A.D. Nokolaou, Chemosphere 45 (2001) 275.
[15] T. Nilsson, R. Ferrari, S. Facchetti, Anal. Chim. Acta 356 (1997) 113.
[16] L.S. Clesceri, A.E. Greenberg, A.D. Eaton (Eds.), Standard Methods for the Examination of Water and Waste Water, American Public Health Association, American Water Association, Water Environment Federation, 20th ed., 1998.
[17] E. Martinez, S. Lacorte, I. Llobet, P. Viana, D. Barcelò, J. Chromatogr. A 959 (2002) 181.
[18] C.J.H. Miermans, L.E. van der Velde, P.C.M. Frintrop, Chemosphere 40 (2000) 39.