



“Cold” solid-phase microextraction method for the determination of volatile halocarbons present in the atmosphere at ultra-trace levels

Giovanna Mangani^a, Arnaldo Berloni^b, Michela Maione^{b,*}

^aUniversity of Urbino, Faculty of Environmental Sciences, Scientific Campus “Sogesta”, 61029 Urbino, Italy

^bUniversity of Urbino, Institute of Chemical Sciences, 6 Piazza Rinascimento, 61029 Urbino, Italy

Received 25 July 2002; received in revised form 13 December 2002; accepted 13 December 2002

Abstract

Anthropogenic volatile halocarbons are compounds of great environmental concern because of their involvement in global change phenomena. They are present in the atmosphere at concentration levels in the order of parts per trillion by volume. The chosen analytical method for their determination is capillary gas chromatography coupled to mass spectrometry, preceded by an enrichment step on suitable adsorbent resins. The method here presented makes use of the solid-phase microextraction as a pre-analytical technique, using sub-ambient temperature in order to enhance the retention capability of the fiber coating. The proposed method was evaluated in terms of extraction efficiency, linearity, reproducibility, and limits of detection. Results obtained showed that trace atmospheric halocarbons are detectable even when enriching very small air sample volumes. A good chromatographic resolution is obtained as a consequence of the extremely low injection volume. Finally a standard GC–MS instrumentation equipped with a simple split-splitless injector was employed, thus avoiding the use of expensive dedicated apparatus. The method was also applied to the analysis of actual samples collected both in remote, and in semi-remote sites.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Air analysis; Halogenated compounds; Chlorofluorocarbons; Solid-phase microextraction; Environmental analysis; Volatile organic compounds

1. Introduction

Anthropogenic volatile halocarbons include chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and chlorinated solvents. All these compounds play a key role in global change phenomena, since they are stratospheric ozone depleting gases (CFCs, HCFCs,

and chlorinated solvents) [1] and powerful greenhouse gases (CFCs, HCFCs, and HFCs) [2]. These compounds are regulated under the “Montreal Protocol on Substances that Deplete the Stratospheric Ozone Layer” [3] and under the “Kyoto Protocol on Global Climate Change” [4], and therefore they are monitored on a global scale in different sampling sites, often by means of continuous and automated on-line instrumentations [5–7]. However, sometimes off-line methods are preferable. This is the case of grab sampling campaigns, especially in remote sites

*Corresponding author. Fax: +39-0722-2754.

E-mail address: michela@uniurb.it (M. Maione).

where automated on-line methods are not applicable because the instrumentation required for this kind of analyses is excessively sophisticated, or when the aim of the research is assessing long-term concentration trends [8]. In this case, weekly or monthly analyses of atmospheric grab samples are sufficient for establishing these trends.

In both cases, from an analytical point of view, two features have to be considered: the compounds of interest are characterized by a rather high volatility and by concentration levels spanning from a few up to hundreds of parts per trillion by volume (pptv). Therefore a pre-concentration step preceding the gas chromatographic–mass spectrometric (GC–MS) analysis is required. Both when using in-line [9], and off-line methods [10], such an enrichment step is performed using different combinations of adsorbent resins, whose retention characteristics must be carefully evaluated in terms of breakthrough volume (BTV), that is a rather critical parameter especially in the case of very volatile compounds. Therefore, sub-ambient temperatures have to be used in order to quantitatively trap all the compounds of interest, including the most volatile ones. The analytes are then introduced into the GC unit by thermal desorption.

Here is presented an innovative analytical methodology that makes use of the solid phase microextraction (SPME) as a pre-concentration technique. SPME is a rapidly growing pre-analytical method introduced as an extraction technique for organic micro-pollutants from aqueous matrices at the end of the 1980s by Pawliszyn and co-workers [11,12]. SPME involves exposing a fused-silica fiber that has been coated with a non-volatile polymeric coating to an aqueous sample or its headspace. The absorbed analytes are then thermally desorbed in the injector of a gas chromatograph for separation and quantitation. Therefore, no solvent extraction is required. Simplicity, speed of analysis and low cost are among the advantages of this technique, the use of which was subsequently extended to the analysis of gas-phase organic compounds [13–17]. However, when extremely volatile compounds have to be determined, this method lacks in retention capability [12]. Since the temperature-dependent partition coefficients decrease when temperature increases [13], the problem can be resolved by working at sub-

Table 1
List of the compounds considered and single ion monitoring (SIM) program

Compound	Chemical formula	<i>m/z</i>	Acquisition window (min)
HFC-23	CHF ₃	51–69	0.00–6.50
CFC-115	CF ₃ CClF ₂	85–69	
HFC-125	CHF ₂ CF ₃	101–51	6.50–8.00
HFC-143a	CF ₃ CH ₃	65–69	
CFC-12	CCl ₂ F ₂	87–85	
HCFC-22	CHF ₂ Cl	67–51	
HFC-134a	CH ₂ FCF ₃	83–69	8.00–10.40
Methyl chloride	CH ₃ Cl	50–52	
HFC-152a	CHF ₂ CH ₃	51–65	
CFC-114	CClF ₂ CClF ₂	135–101	10.40–11.50
HCFC -142b	CH ₂ CF ₂ Cl	65–85	
CFC-11	CCl ₃ F	101–103	11.50–13.00
HCFC 141b	CH ₃ CFCl ₂	81–83	13.00–16.20
CFC-113	CCl ₂ FCClF ₂	101–151	
Methyl chloroform	CH ₃ CCl ₃	97–117	16.20–

ambient temperature, resulting in an increasing of the coating partition coefficient.

The “cold” SPME method described below has proven to be an effective, fast and reliable method for the determination of volatile halogenated halocarbons down to ppt levels. A list of the compounds considered is reported in Table 1. Quantitative results obtained analyzing actual air samples using this methodology are described as well.

2. Experimental

2.1. Grab sampling

Air samples were collected, by means of a portable ultra-clean air pump (model FC-1121, Biospheric Research, Hillsboro, OR, USA), at the pressure of 3 atm in 0.85 l stainless steel canisters (Biospheric Research) whose internal walls were passivated to provide a surface chemically inert towards halogenated compounds (atm=101 325 Pa). Thus, the passivation, together with the stability of the compounds of interest, makes it possible to keep the air samples up to several weeks before the analysis, without any degradation of the compounds occurring [18]. Gas-tight connections between the

canister and the pump were assured by two Nupro valves (Nupro, Willoughby, OH, USA) and a purge-tee fitted with a pressure gauge. Due to its simplicity, this sampling apparatus is particularly suitable and advantageous for collecting air samples in remote areas.

2.2. Pre-concentration

A laboratory-made SPME apparatus was set up for enriching the halogenated hydrocarbons that are the object of this study. It consists of a conventional stainless steel inlet for packed columns (10 cm×0.4 cm I.D.), whose external surfaces were put in contact with a “cold finger” (Julabo Labortechnik, Seelbach/West Germany) refrigerating the inlet down to -40°C . The constant temperature of -40°C is maintained by a thermally insulated band wrapped around the apparatus. During the enriching step, the outlet of the canister is connected to the apparatus inlet, through a stainless steel line (0.2 cm I.D.).

A Nafion dryer (Perma Pure, Toms River, NJ, USA) is placed in-line as well as a glass tubing (10 cm×0.4 cm I.D.) containing an extremely weak

adsorbent, i.e. Carbograph 3 (Lara, Rome, Italy), whose surface area is about $5\text{ m}^2\text{ g}^{-1}$. This weak adsorbent is able to adsorb the relatively less volatile compounds, meanwhile it cannot retain the most volatile compounds. In this way, problems related to retention of relatively non-volatile compounds on the chromatographic column is prevented. The use of the Nafion dryer is aimed at reducing the relative humidity of the gas before the enrichment step, preventing the water from condensing on the fiber. Furthermore, it was demonstrated that the greater the relative humidity level, the lower is the mass of volatile analytes adsorbed [6]. A schematic diagram of the apparatus is reported in Fig. 1.

The sample is passed at a flow-rate of 5 ml min^{-1} , regulated by means of a needle valve. The SPME fiber is inserted in the inlet of apparatus, being exposed for 15 min to the air coming out from the canister. Therefore 75 ml air aliquots have been used in order to perform the analysis. After the exposure time had elapsed, the fiber was rapidly removed from the sampling room and quickly inserted in the inlet of the GC system maintained at 240°C for 2 min for quantitative desorption of the analytes. The time of

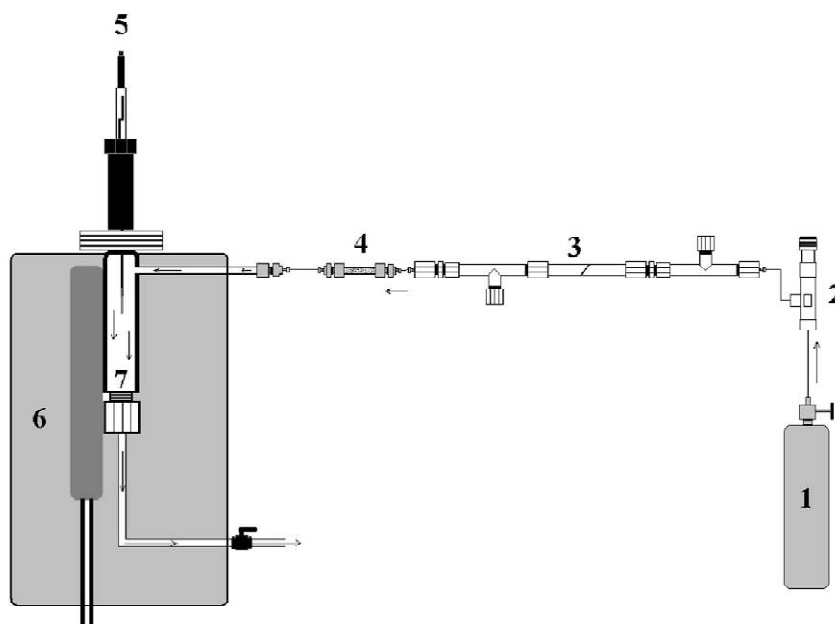


Fig. 1. Schematic diagram of the “cold” SPME device. (1) Stainless steel flask; (2) fine metering valve; (3) Nafion dryer; (4) graphitized carbon black adsorption tube; (5) SPME holder; (6) refrigerated sampling apparatus; (7) sampling room.

2 min is necessary in order to condition the SPME fiber. However, the flash desorption of the analytes is attained, together with a outstandingly low injection volume, as clearly demonstrated by the peaks shape.

A SPME fiber assembly 2 cm, 50/30 μm divinylbenzene (DVB)–Carboxen–polydimethylsiloxane (PDMS) (Supelco, Bellefonte, PA, USA) was used for this application. Such a mixed SPME coating is made of two layers of a liquid coating (i.e. PDMS) extracting the analytes via an absorption process. In the two PDMS layers two different adsorbents are suspended: a porous carbon (Carboxen) with a surface area of $720 \text{ m}^2 \text{ g}^{-1}$ and DVB (divinylbenzene) with a surface area of $750 \text{ m}^2 \text{ g}^{-1}$, the major difference between the two adsorbents being that the latter is primarily mesoporous with a moderate amount of macropores, meanwhile the first has a much higher percentage of micropores. These porous solids extract analytes via an adsorption process [19].

2.3. Gas chromatographic separation

An Agilent (Agilent Technologies, Palo Alto, CA, USA) 6890N gas chromatograph equipped with a splitless injector operated at 240°C was employed, with the following temperature programme: 2 min at 40°C , then up to 180°C at $10^\circ\text{C min}^{-1}$, hold for 1 min, then up to 300°C at $20^\circ\text{C min}^{-1}$, hold for 5 min. Ultra-high-purity (UHP) Helium was used as carrier gas at an average flow-rate of 41 cm s^{-1} .

The chromatographic column was a GS-GasPro 30 $\text{m} \times 0.32 \text{ mm}$ I.D. (J&W Scientific, Folsom, CA, USA), i.e. a GSC column with cyclodextrin as the stationary phase, working in adsorption gas chromatography, characterized by outstandingly high retention and separation factors [20]. The retention characteristics of the column avoided the cryofocusing step before the gas chromatographic run.

2.4. Mass spectrometric detection

An Agilent MSD 5973N quadrupole mass spectrometer with an electron impact (EI) source operated in SIM mode was used as selective detector. The employed SIM program is reported in Table 1.

For quantitative purposes the most abundant m/z values have been selected.

2.5. Calibration curves

In order to evaluate the linearity of the method, but not for quantitative purposes, calibration curves have been created. An apparatus for the preparation of diluted standard mixtures was set up, whose design is reported in Fig. 2. It comprises two needle valves connecting a stainless steel passivated 2 l cylinder with (a) a bottle containing a certified standard mixture prepared with a gravimetric method (SIAD, Bergamo, Italy) at ppt levels of the single compounds of interest in UHP nitrogen; and (b) a bottle containing chromatographic grade UHP Helium. A TIF digital pressure gauge (TIF Instruments, Miami, FL, USA) with a accuracy of 0.01 bar, able to measure also negative pressures in a range spanning from -1 up to $+9.99$ bar is provided too. Three toggle valves (Supelco, Bellefonte, PA) and two fine metering valves (Supelco) assure connections among the different elements. At the initial stage, the 2 l cylinder was evacuated by means of a rotative pump, evacuating at the same time all the stainless steel lines and valves. Vacuum was measured by means of the digital pressure gauge. Then, an accurately known pressure of the certified mixture was passed in the 2 l cylinder. In order to obtain subsequent dilutions, known pressures of the UHP Helium are added. Therefore, when the initial and the final pressures are known, the dilution factor can be measured with accuracy. In this way, even if an uncertainty related to the absolute initial amount exists, the dilution factor is known.

2.6. Quantitation

For quantitative purposes of actual air samples, a secondary standard was used. It consists of actual air, sampled in a clean site, and kept in a stainless steel canister [8]. This air in turn has been calibrated against a gravimetric primary standard [21]. Advantages of secondary standard calibration are in that concentration found in the standard are quite similar to those found in the actual sample and therefore within the linearity range of the method, thus allowing a reliable quantitation of actual samples.

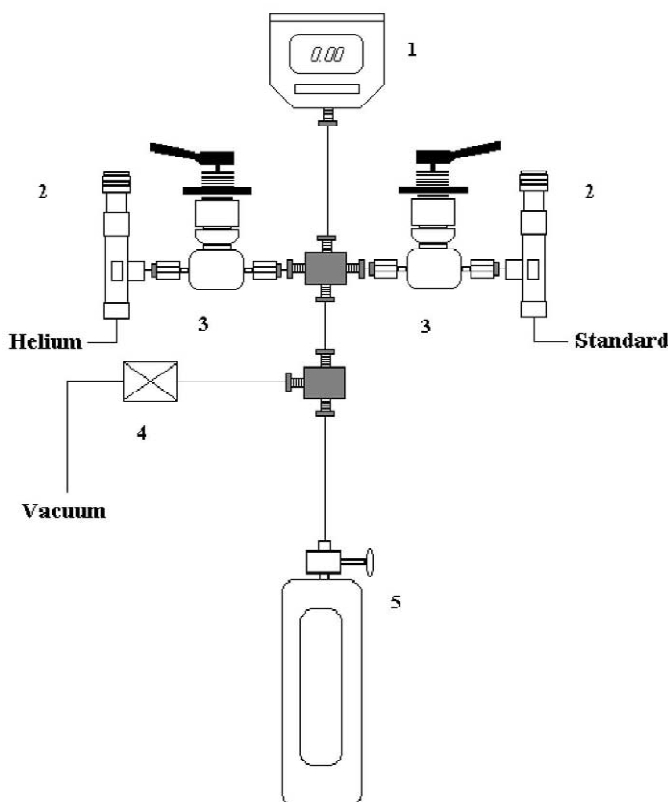


Fig. 2. Schematic diagram of the apparatus for the preparation of diluted standard mixtures. (1) Pressure gauge; (2) fine metering valve; (3) toggle valve; (4) on-off vacuum valve; (5) stainless steel flask.

3. Results and discussion

The proposed method has been evaluated in terms of extraction efficiency, linearity, reproducibility, and limits of detection (LODs). Furthermore, blank levels have been considered.

3.1. Extraction efficiency

Extraction efficiency was evaluated exposing the SPME fiber at increasingly longer time periods, i.e. 5, 15, 30, 45 and 60 min. It was observed that after 60 min, a complete extraction is not attained for all the compounds of interest. However, a time of 15 min was chosen for this application in order both to shorten the time of analysis, and to use an as small as possible sample amount, thus working in non-equilibrium conditions. This was possible because, in the 15 min. neighborhood, the extraction curve slope

is slight enough to obtain a good reproducibility, as shown by results obtained after replicate analyses (see the next sections). At the same time, the amount of analytes extracted is high enough to allow the quantitation of all the compounds of interest down to a few ppts level.

3.2. Linearity

To verify the linearity of the method, calibration curves for eight compounds characterized by different volatility were created. For this purpose, mixtures of the single components at increasing concentrations were prepared, following the previously described dilution procedure. Among hydrogenated halocarbons four compounds were chosen, i.e. HFC-134a, HCFC-22, HCFC-141b, HCFC-142b. The concentration levels considered were 20, 50, 100, 150, 200 pptv. The calibration curves for four fully halo-

generated hydrocarbons were created at different concentration ranges, i.e. CFC-12: 127.5, 170, 255, 510 pptv; CFC-114: 12.5, 16.6, 25, 50 pptv; CFC-11: 75, 100, 150, 300 pptv; CFC-113: 25, 33.3, 50, 100 pptv. Each point of the curve was obtained as an average of four replicate analyses. Fairly good correlation coefficients have been obtained for all the compounds considered thus confirming the linearity of the method. In details, R^2 values were 0.9958 for CFC-12, 0.9980 for HCFC-22, 0.9966 for HFC-134a, 0.9997 for CFC-114, 0.9891 for HCFC-142b, 0.9974 for CFC-11, 0.9916 for HCFC-141b, and 0.9275 for CFC-113.

3.3. Reproducibility

The method reproducibility was evaluated, analyzing the same actual sample following the above described procedure. A number of six replicated analyses was performed. An excellent agreement among the different measurements was found, as it can be seen from the percent relative standard deviations (RSD) values reported in Table 2, together with concentration values measured on that sample.

3.4. Limits of detection

The minimum concentration required to have the detector response three times greater than the background noise, has been evaluated. In order to assess such a concentration, detection limits were evaluated for the single components of a standard mixture on the quadrupole mass spectrometric detector, always

operating in the SIM mode. The halogenated halocarbons that are the object of this research were determined starting from a concentration of 1 pptv. In this case, the signal given by each compound was at least three times greater than the background noise.

3.5. System blanks

In order to evaluate the possible contamination of the overall system, blank analyses have been performed. For this purpose, the sampling procedure has been conducted, by exposing the “cold” SPME assembly to UHP Helium, and then performing the GC–MS analysis. In the obtained chromatogram no peaks are detected at the retention times of our interest, even when using an abundance scale much lower than that used in the actual sample chromatogram.

3.6. Actual sample analysis

In order to evaluate the applicability of the proposed method, actual samples from different sampling spots have been analyzed. Fig. 3 is referred to the qualitative analysis of an air sample collected in a semi-rural site in central Italy. A total number of 14 compounds have been identified, some of them being present at low ppt levels. As can be seen, the efficacy of the pre-analytical technique together with the retention characteristics of the chromatographic column provide an excellent separation of the compounds considered, even though no cryofocussing of the analytes on the top column was carried out. Fig. 4 reports the chromatogram obtained analyzing the actual air constituting the secondary standard, on which basis the quantitation of the single compounds was performed. In this case, 11 compounds were considered, whose concentrations ranged from 1.0 up to 547 pptv. After direct comparison with actual grab samples the quantitative analysis was possible. On each canister, sampled in different sites, at least three replicate analyses were performed, alternated with three replicate analyses of the secondary standard. Table 3 reports the results obtained analyzing samples collected in a semi-remote and in a remote area, i.e. a mountain site in central Italy and Northern Victoria Land in Antarctica, respectively. In order to

Table 2
Relative standard deviation (RSD) calculated on six replicate analyses

Compound	Concentration (pptv)	RSD%
CFC -12	546.7	2.4
HCFC-22	164.2	4.0
HFC-134a	21.1	6.0
CH ₃ Cl	544.6	12.0
CFC-114	17.3	3.6
HCFC-142b	15.1	7.2
CFC-11	260.2	4.5
HCFC-141b	16.6	6.1
CFC-113	81.4	4.6
CH ₃ CCl ₃	39.1	16.8

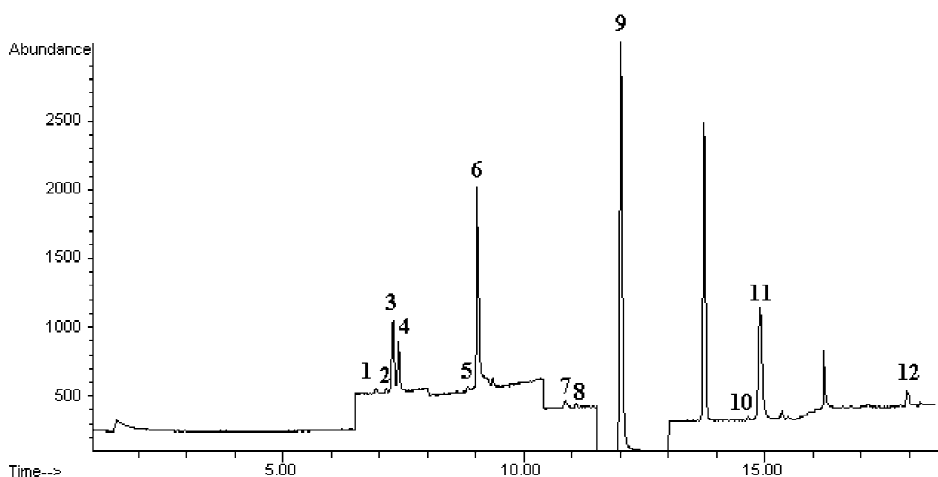


Fig. 3. Reconstructed total ion chromatogram of an actual air sample from a rural site. Peak identification: (1) HFC-125; (2) HFC-143a; (3) CFC-12; (4) HCFC-22; (5) HFC-134a; (6) CH_3Cl ; (7) CFC-114; (8) HCFC-42b; (9) CFC-11; (10) HCFC-141b; (11) CFC-113; (12) CH_3CCl_3 .

evaluate the reliability of the method, a comparison was made with concentration data obtained analyzing the content of the same flask sampled in Antarctica, using an analytical method that makes use of an on-line enriching device coupled to a GC–MS system [22] equipped with the same analytical column as in this work. Data are reported in the fourth column of Table 3. Notwithstanding two quite different analytical approaches have been used, a

fairly good agreement among the measured data has been obtained, thus demonstrating the effectiveness of the proposed method.

4. Conclusions

A fast, simple and reliable SPME–GC–MS method has been presented for the determination of very

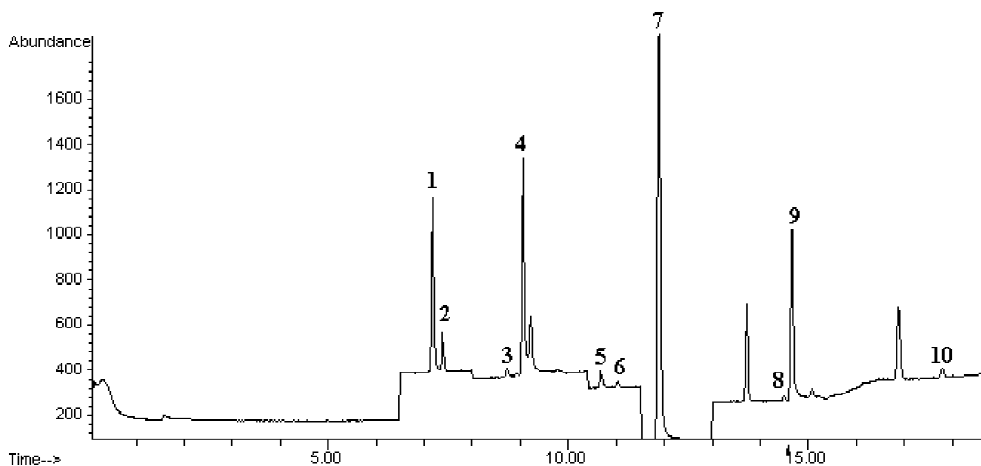


Fig. 4. Reconstructed total ion chromatogram of an actual air sample used as secondary working standard. Peak identification: (1) CFC-12 (546.7 pptv); (2) HCFC-22 (164.2 pptv); (3) HFC 134a (21.1 pptv); (4) CH_3Cl (544.6 pptv); (5) CFC 114 (17.3 pptv); (6) HCFC 142b (15.2 pptv); (7) CFC 11 (260.2 pptv); (8) HCFC 141b (16.6 pptv); (9) CFC 113 (81.4 pptv); (10) CH_3CCl_3 (39.1 pptv).

Table 3
Concentration (expressed in pptv) measured in two different sampling sites

Compound	Mountain site SPME method	Antarctica SPME method	Antarctica on-line method
CFC-12	599.2	556.5	539.7
HCFC-22	182.9	144.0	193.0
HCFC-134a	79.0	8.6	11.3
CH ₃ Cl	576.6	536.8	565.5
CFC-114	17.7	16.7	18.3
HCFC-142b	16.8	13.9	14.5
CFC-11	234.0	243.8	247.7
HCFC -141b	14.0	14.4	12.4
CFC-113	90.9	66.1	78.0
CH ₃ CCl ₃	36.8	30.4	n.d.

volatile halocarbons present in the atmosphere down to a few pptv levels. The method represents a good alternative to conventional methods when grab samples coming from different sampling sites have to be analyzed. Advantages of this method over conventional off-line and in-line methods can be summarized as follows:

1. Sample volumes down to 75 ml are sufficient in order to detect halocarbons at pptv levels. Such a volume is much lower than those necessary in off-line (200 ml) and in-line (1000 ml) methods. This feature is particularly appreciable since replicate analyses of the same sample can be performed, also when using small volume flasks;
2. The extremely small injection volume provides fairly good chromatographic resolution;
3. Sample contamination is negligible, as demonstrated by system blanks. Furthermore this method is less time consuming if compared with conventional adsorption tubes used in off-line methods. In fact, tubes must be desorbed and analyzed prior to every sample enrichment in order to assess contamination levels.
4. The analytical instrumentation required is a standard gas chromatograph coupled to a quadrupole mass detector, equipped with a simple split–splitless injection system; meanwhile conventional off-line methods require dedicated apparatus, such as a thermal desorber, equipped with a cryogenic device. In-line methods require in-itself expensive instrumentation.

Acknowledgements

Part of this work was carried out in the framework of the Italian National Program for Research in Antarctica (PNRA), whose financial support is acknowledged. Ray Weiss and the SIO (Scripps Institution of Oceanography (SIO, La Jolla, CA, USA) scale are greatly acknowledged.

References

- [1] M.J. Molina, F.S. Rowland, *Nature* 249 (1974) 810.
- [2] Intergovernmental Panel on Climate Change, *Climate Change 1994: The Science of Climate Change*, Cambridge University Press, Cambridge, UK, 1995.
- [3] Montreal Protocol to Reduce Substances that Deplete the Ozone Layer, Final Report, U.N. Environmental Programme, New York, 1987.
- [4] Kyoto Protocol on Climate Change, in: U.N. Framework Convention on Climate Change, Kyoto, December 11, 1997.
- [5] D.M. Cunnold, P.J. Fraser, R.F. Weiss, R.G. Prinn, P.G. Simmonds, B.R. Miller, F.N. Alyea, A.J. Crawford, *J. Geophys. Res.* 99 (D1) (1994) 1107.
- [6] P.D. Fraser, D. Cunnold, F. Alyea, R. Weiss, R. Prinn, P. Simmonds, B. Miller, R. Langenfelds, *J. Geophys. Res.* 101 (D1) (1996) 12585.
- [7] D.M. Cunnold, R.F. Weiss, R.G. Prinn, D. Hartley, P.G. Simmonds, P.J. Fraser, B.R. Miller, F.N. Alyea, L. Porter, *J. Geophys. Res.* 102 (D1) (1997) 1259.
- [8] F. Mangani, M. Maione, L. Lattanzi, J. Arduini, *Int. J. Environ. Anal. Chem.* 74 (9) (2001) 273.
- [9] P.G. Simmonds, S. O'Doherty, G. Nickless, G.A. Sturrock, R. Swaby, P. Knight, J. Ricketts, G. Woffendin, R. Smith, *Anal. Chem.* 67 (1995) 717.

- [10] F. Mangani, M. Maione, L. Lattanzi, J. Arduini, *Chromatographia* 51 (5/6) (2000) 325.
- [11] C.L. Arthur, J. Pawliszyn, *Anal. Chem.* 62 (1990) 2145.
- [12] Z. Zhang, M. Yang, J. Pawliszyn, *Anal. Chem.* 66 (1994) 844A.
- [13] M. Chai, C.L. Arthur, J. Pawliszyn, R.P. Belardi, K.F. Pratt, *Analyst* 118 (1993) 1501.
- [14] F. Mangani, R. Cenciarini, *Chromatographia* 41 (1995) 678.
- [15] M. Chai, J. Pawliszyn, *Environ. Sci. Technol.* 29 (1995) 693.
- [16] J. Koziel, M. Jia, J. Pawliszyn, *Anal. Chem.* 72 (2000) 5178.
- [17] L. Tuduri, V. Desauziers, J.L. Fanlo, *J. Chromatogr. Sci.* 39 (2001) 521.
- [18] R.A. Rasmussen, J.E. Lovelock, *J. Geophys. Res.* 88 (C13) (1983) 8369.
- [19] T. Górecki, X. Yu, J. Pawliszyn, *Analyst* 124 (1999) 643.
- [20] S.J. O'Doherty, G. Nickless, M. Bassford, M. Pajot, P. Simmonds, *J. Chromatogr. A* 832 (1999) 253.
- [21] J.L. Bullister, R.F. Weiss, *Deep Sea Res.* 35 (1988) 839.
- [22] F. Mangani, M. Maione, J. Arduini, *Int. J. Environ. Anal. Chem.* (submitted for publication).