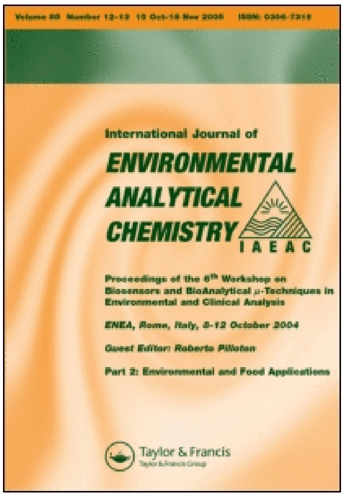

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Evaluation of an automatic sampling gas chromatographic-mass spectrometric instrument for continuous monitoring of trace anthropogenic gases

Michela Maione[a]; Jgor Arduini[a]; Giovanna Mangani[a]; Annalisa Geniali[a]
[a] Università degli Studi di Urbino, Istituto di Scienze Chimiche, 61029 Urbino, Italy

To cite this Article Maione, Michela , Arduini, Jgor , Mangani, Giovanna and Geniali, Annalisa(2004) 'Evaluation of an automatic sampling gas chromatographic-mass spectrometric instrument for continuous monitoring of trace anthropogenic gases', International Journal of Environmental Analytical Chemistry, 84: 4, 241 — 253

To link to this Article: DOI: 10.1080/03067310310001626740

URL: http://dx.doi.org/10.1080/03067310310001626740

Intern. J. Environ. Anal. Chem.
Vol. 84, No. 4, pp. 241–253, 15 March 2004

Taylor & Francis
Taylor & Francis Group

EVALUATION OF AN AUTOMATIC SAMPLING GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC INSTRUMENT FOR CONTINUOUS MONITORING OF TRACE ANTHROPOGENIC GASES

MICHELA MAIONE*, JGOR ARDUINI,
GIOVANNA MANGANI and ANNALISA GENIALI

Università degli Studi di Urbino, Istituto di Scienze Chimiche, Piazza Rinascimento 6,
61029 Urbino, Italy

(Received 12 December 2002; In final form 28 August 2003)

Continuous monitoring of the atmospheric volatile halogenated hydrocarbons is needed in light of the role played by these compounds in global climate change phenomena. The analytical methodology described in the following implies the use of a gas chromatographic–mass spectrometric system equipped with a sampling/pre-concentration unit, for the simultaneous and continuous analysis of a number of halogenated hydrocarbons present in the atmosphere at concentration levels ranging from a few to hundreds of part per trillion by volume. The optimization of the analytical procedure in terms of efficiency, linearity, and reproducibility is reported together with some of the results obtained in the frame of a monitoring activity carried out on a remote mountain station in central Italy.

Keywords: CFCs; Halocarbons; Greenhouse gases; GC–MS; Continuous monitoring

INTRODUCTION

Anthropogenic greenhouse gases include chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and SF_6. They are all characterized by elevated global warming potential (GWP) values, being capable of effectively absorbing long-wave radiation re-emitted by the Earth's surface within the spectral region from 8 to 11 μm, commonly defined as the 'atmospheric window' [1,2]. Their average atmospheric mixing ratios range from a few parts per trillion (ppt) for SF_6 to hundreds of ppt for CFC-12 and CFC-11.

---

*Corresponding author. Fax: +39-7222754. E-mail: michela@uniurb.it

ISSN 0306-7319 print: ISSN 1029-0397 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/03067310310001626740

Even though CFCs have been phased out under Montreal Protocol [3,4] since January 1996, they are still emitted into the atmosphere, as demonstrated by the variability in their concentration measured in non-remote areas [5–8]. HCFC emissions have been regulated by the Montreal Protocol since 1996; meanwhile, HFCs, PFCs, and SF_6 are not yet regulated, and so their atmospheric mixing ratios are increasing and are strongly affected by local emission sources [8–13].

To obtain a reliable picture of changes in atmospheric concentrations of anthropogenic greenhouse gases, and to better evaluate their source strengths on a regional scale, continuous monitoring of these compounds is necessary [5–7].

Capillary gas chromatography (GC) is the chosen technique for separation of extremely volatile organic compounds, provided that the stationary phase has the appropriate retention characteristics. Mass spectrometric (MS) detection is compulsory for the identification of a number of components in a complex mixture. Further, the extremely low concentration levels of the compounds to be monitored require an enrichment step prior to chromatographic separation [14,15].

In the following, the set-up and evaluation of a GC–MS analytical system equipped with an on-line sampling/adsorption device to be used for continuous monitoring of these compounds will be described.

Such an instrumentation is currently operating unattended in a remote mountain station (Mt. Cimone, Northern Apennines, Italy, 44° 11′ N–10° 42′ E, 2165 m asl), and it is run via modem from the laboratories of the University of Urbino. Air samples are collected every fourth hour to yield an actual picture of the atmospheric mixing ratio of 21 halogenated hydrocarbons. The list of compounds monitored is given in Table I, together with their main sources.

TABLE I Compounds monitored at Monte Cimone

Species	*Chemical formula*	*GWP*[a]	*Main sources*
CFC-11	CCl_3F	4680	Blowing agent
CFC-12	CCl_2F_2	10 720	Refrigerant, blowing agent
CFC-113	CCl_2FCClF_2	6039	Solvent
CFC-114	$CClF_2CClF_2$	9860	Solvent
CFC-115	CF_3CClF_2	7250	Solvent, refrigerant
H-1211	CF_2ClBr	1860	Fire retardant
H-1301	CF_3Br	7030	Fire retardant
HCFC-22	CHF_2Cl	1780	Refrigerant, air conditioning, foam blowing agent
HCFC-141b	CH_3CFCl_2	713	Foam blowing agent, solvent
HCFC-142b	CH_3CF_2Cl	1850	Foam blowing agent
HCFC-124	$CHFClCF_3$	599	Sterilant
HFC-125	CHF_2CF_3	3450	Specialized end use, air conditioning mix
HCFC-152a	CHF_2CH_3	129	Propellant
HFC-134a	CH_2FCF_3	1400	Refrigerant, air conditioning
HFC-143a	CF_3CH_3	440	Refrigerant
Perfluoroethane	C_2F_6	12 010	Refrigerant
Sulphur hexafluoride	SF_6	22 450	Insulator, cover gas
Methyl chloride	CH_3Cl	17	Natural, biomass burning
Methyl bromide	CH_3Br	2	Natural, Fumigant
Chloroform	$CHCl_3$	2.5	HCFC feedstock
Dichloromethane	CH_2Cl_2	10	Solvent

EXPERIMENTAL

Instrument Description

The instrumentation comprises an auto-sampling/pre-concentration unit, allowing the automated semi-continuous collection of atmospheric samples, coupled to a gas chromatograph with a quadrupole mass spectrometer as selective mass detector.

Auto-sampler

This consists of a mass flow controller with three sampling lines (blank, sample, and standard), equipped with a suction pump for collecting ambient air samples at ambient pressure. Furthermore, ambient air is dried by passage through a Nafion permeation dryer, whose purpose is to reduce the humidity of the gas before entering the desorption tube, preventing the water from condensing in the adsorbent resins.

Pre-concentration unit

The unit (UNITY-Air Server, Markes International Ltd, Pontyclun, UK) consisted of a sorbent-based focusing device for trapping and concentrating the compounds of interest. Three different sorbents were used to fill a glass tubing (1.6 mm i.d., 3.0 mm o.d., 120.0 mm long): a short bed (3.5 mm) of Tenax TA, a short bed (11.5 mm) of Carbopack B, and a longer bed (39.5 mm) of Carboxen 1000. The sorbent sequence in the sampling step respects the strength of each sorbent, from the weaker one to the stronger one, in order to trap the relatively less volatile compounds on to the weaker adsorbent, thus avoiding the irreversible adsorption of these compounds on strong adsorbents. The direction of flow is reversed during the desorption step. The trapping system is electrically cooled by means of a Peltier device, thus eliminating the inconveniences associated with the use of cryogenic fluids. Thermal desorption of the trapped analytes is obtained heating the trap up to 300°C at a rate of 60°C s^{-1}.

Gas chromatograph

The gas-chromatograph used was a HP 6890 GC system (Hewlett Packard, Palo Alto, CA, USA), with the following temperature programme: 10 min at 35°C, then 10°C min^{-1} up to 150°C, using UHP Helium as carrier gas at a flow rate of 2 mL min^{-1}.

Column

The gas chromatographic column was a GS-GasPro 30 m × 0.32 mm i.d. (J&W Scientific Inc. Folsom, CA, USA), i.e. a GSC column with cyclodextrin as stationary phase, working in adsorption gas chromatography [16,17]. Such a column showed extremely high retention and separation factor characteristics, also being able to strongly retain the more volatile compounds. The elution order is governed by a combination of factors, i.e. boiling point, hydrogen bonding, and number of chlorine atoms. Such a column is particularly able to strongly absorb molecules that can form hydrogen bonds, like those compounds with adjacent hydrogen and fluorine atoms, which is the case for many of the compounds in this research.

Mass Spectrometer

An HP 6890 Quadrupole Mass Selective Detector (Hewlett Packard, Palo Alto, CA, USA) operated in electron impact and in the selected ion monitoring (SIM) mode was used as detector. The employed SIM program is reported in Table II. For quantitation, the most abundant specific ion fragments were used. In a few cases (designated by superscript ‘c’ in Table II), the less abundant fragments were considered, to avoid any interferences with nearby eluting compounds having ion traces in common with the most abundant ones.

TABLE II SIM programme

Compound	*m/z*	*%RA*[a]	*AW*[b]
SF_6	127	100	0.0–3.8
	89	26	
C_2F_6	119	41[c]	
	69	100	
$CBrF_3$	69	100	3.8–5.9
	129	12	
CF_3CClF_2	85	100	5.9–7.6
	119	56	
CHF_2CF_3	101	53[c]	7.6–10.5
	51	100	
CF_3CH_3	65	38[c]	
	69	100	
CF_2Cl_2	85	100	
	87	32	
CHF_2Cl	51	100	
	67	15	
CH_3Cl	50	100	10.5–13.00
	52	31	
CF_3CFH_2	69	71	
	83	63	
$CBrF_2Cl$	85	100	13.0–15.0
	129	20	
CHF_2CH_3	51	100	
	65	50	
CF_2Cl	85	100	15.0–16.7
CF_2Cl	135	65	
CH_3Br	94	100	
	96	80	
CH_3CF_2Cl	65	100	
	85	14	
$CHFClCF_3$	67	100	
	101	40	
$CFCl_3$	101	100	16.7–19.8
	103	66	
CH_2Cl_2	49	100	19.8–20.2
	84	65	
CH_3CFCl_2	81	100	20.2–22.0
	61	28	
$CF_2ClCFCl_2$	101	100	
	151	68	
$CHCl_3$	83	100	22.0
	85	64	

[a]%RA = percent relative abundance; [b]AW = acquisition window (min); [c]See text.

Sampling Approach

To avoid any problems related to the irreversible adsorption of relatively non-volatile compounds on valves and tubing of the whole pre-concentration unit and on the chromatographic column, a 'protection' trap was placed on line with the sampling line. This consisted of a stainless steel tube (5 cm long, 0.6 cm o.d., 0.4 cm i.d.) filled with 50 mg of a very low-surface-area (s.a.) adsorbent material, i.e. Carbograph F, s.a. $5\,\mathrm{m^2\,g^{-1}}$. This weak adsorbent can adsorb the relatively less volatile compounds, but it cannot retain the most volatile compounds. To determine whether there is some degree of retention of the compounds of interest, the same aliquots of calibrated actual air were analysed with and without the 'protection' trap on the sampling line. Results showed that no adsorption of the most volatile compounds in this research takes place.

The sampling line is made of a stainless steel tube 1000 cm long (0.6 cm o.d., 0.4 cm i.d.). The Pyrex sample inlet, placed on the roof of the monitoring station 800 cm above ground level, is heated to a few degrees above 0°C, to avoid any clogging resulting from ice formation during the winter.

Calibration

One of the most important issues in trace analysis of atmospheric pollutants is the quantitation of the compounds of interest. In this case, calibration is performed against 'working secondary standards', i.e. actual air tanks currently linked to two absolute calibration scales for halocarbons which reside at the Scripps Institution of Oceanography (SIO98 scale-SIO, La Jolla, CA, USA) and at Bristol University (UB98 scale, University of Bristol, Bristol, UK), for seven and 14 compounds, respectively. The preparation of gravimetric primary standards by a two-step 'bootstrap' technique was described by Bullister and Weiss [18]. Working secondary standards were prepared using compressed clean marine air taken at Mace Head (Ireland), sent to the University of Bristol for calibration on the UB98 scale. To prevent liquid water from building up in the secondary tanks, air is pumped into 35-L stainless steel electropolished tanks to a pressure higher than 4×10^4 hPa (the pressure generally used in the tanks) and then expanded from a water-vapour trap down to 4×10^4 hPa. In this way, the water-vapour pressure in the tank remains below saturation. The use of such a scale is possible, since the halocarbons monitoring activity described takes place in the frame of a European Project named SOGE (System for Observation of halogenated Greenhouse gases in Europe), linked to the global monitoring network named AGAGE (Advanced Global Atmospheric Gases Experiment) [19].

Each sample run is bracketed between two standard runs. For quantification purposes, the areas of the peaks of the actual air are compared with the mean area of the two standard runs to correct the instrumental drift in the signal response of the mass spectrometer that normally decreases during working time, mainly due to the oxidation of the ion source.

Remote Control

The whole instrumentation operating at the remote mountain station is equipped to run continuously. As the site is located on a high mountain, it is frequently vulnerable to adverse weather conditions, such as thunderstorms, that can compromise the power supply. For this reason, the whole system is supplied with power-conditioning equipment that provides instantaneous voltage regulation and isolation from any kind of noise and suppressing transients and overloads on electric power. Furthermore, the power continuity is guaranteed by two UPS systems that provide power for at least 30 min (power failures often being 5–10 min long). In case of longer power failures, the power loads supplied by the two UPS systems are partitioned to prevent any serious damage that could eventually arise from irregular breakdown of the mass spectrometer.

The instrumentation is fully automated, and all operations related to the sampling unit, gas chromatograph, and mass spectrometer functions are controlled via software by a local PC. Remote control is achieved via a modem connection that allows daily checks and, when necessary, complete remote set-up of all parameters.

RESULTS AND DISCUSSION

The overall analytical procedure was evaluated in terms of the relative retention capability of the sorbent bed (generally expressed by the Break Through Volume (BTV)), range of linearity, reproducibility, and limits of detection.

BTV Evaluation

BTV, i.e. the maximum air volume that can be sampled using a given quantity of the adsorbent before the compound exits the trap, is one of the most critical parameters to be considered when analysing extremely volatile compounds.

A correct evaluation of BTV values of the most volatile compounds is essential, since it allows the maximum actual air volume to be sampled to be assessed, to quantitatively trap all the compounds of interest.

BTVs depend on many factors, among which temperature is crucial, since BTV decreases exponentially as the temperature of the sorbent material increases.

To assess the temperature at which the quantitative trapping of the analytes is achieved, 600 mL of calibrated actual air are enriched on to the multi-layer bed at temperatures ranging from −15°C up to 10°C. The BTV values for the single compounds at a given temperature were evaluated by sampling increasing volumes of calibrated actual air, another very important factor that influences the BTV being the simultaneous presence of more than one compound and their relative concentration in the air sample.

Results are reported in the graphs of Fig. 1(a) and (b), where the peak areas of selected test compounds are plotted against the trapping temperature. As can be seen from the graphs, at a temperature of −10°C, the degree of trapping of the analytes is not significantly lower than that obtained at −15°C, even for some extremely volatile compounds (i.e. HFC-125 and HFC-143a).

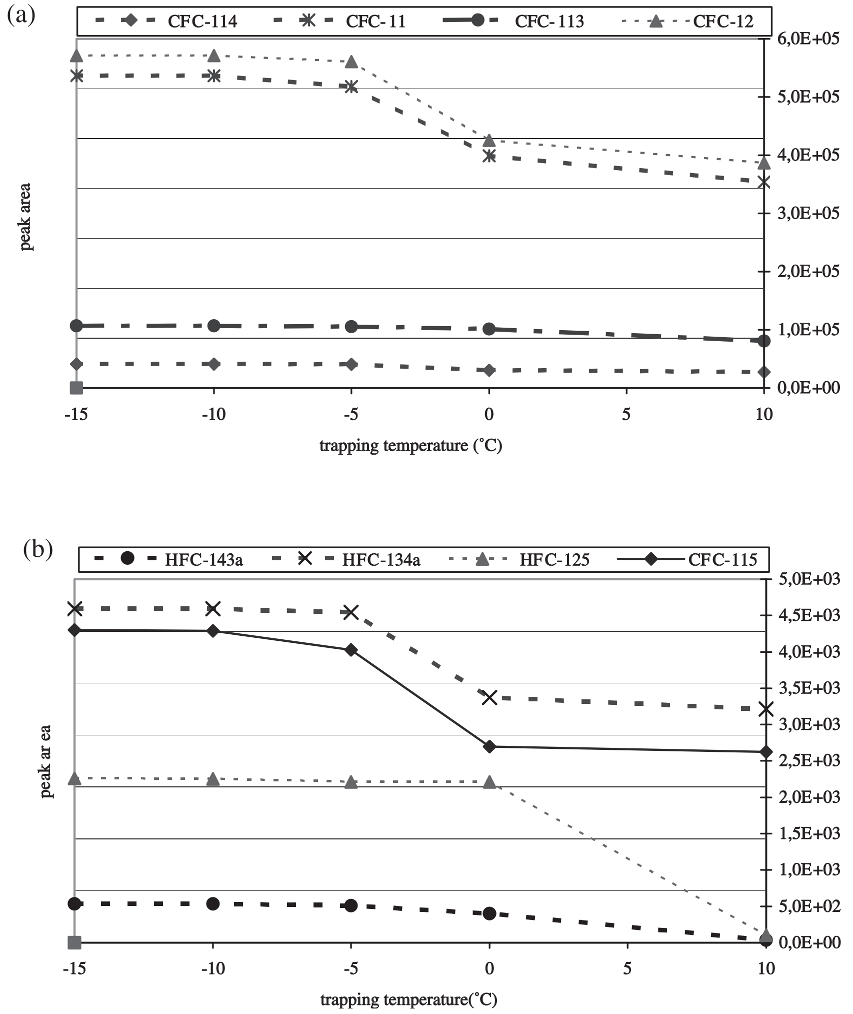

FIGURE 1 Dependence of peak areas on trapping temperature, obtained by enriching onto 600 mL of calibrated actual air.

The 'chromatographic efficiency' of the adsorbent bed is also affected, albeit at a lower extent, by the linear flow rate of the gas phase. Therefore, the BTV can be influenced by the velocity of the gas during sampling. At excessively high flow rates, the BTV is likely to decrease as a consequence of the non-interaction between the analytes and the pores of the adsorbent resin [20]. For this purpose, 500 mL of a standard mixture where HFC-134a was present at concentration levels of 100 pptv in UHP nitrogen were passed through the adsorbent bed at increasing flow rates, spanning from 5 to 60 mL min^{-1}. HFC-134a was chosen as it is one of the most volatile compounds studied. It has been found that a loss in trapping efficiency can be observed when the velocity of the sampling flow is increased. However, at a flow rate of 60 mL min^{-1}, the peak area is only 10% lower with respect to that obtained sampling at 5 mL min^{-1}. Therefore, a value of 25 mL min^{-1} was chosen, being a good compromise between trapping efficiency and speed of analysis.

To assess the maximum air volume that can be enriched on to the above described adsorption tube, linearity tests were performed enriching the multi-bed tube with increasing volumes of actual air (600, 750, 900, 1050, 1200, 1350, and 1500 mL), then performing the GC–MS analysis. The tests were carried out at two different trapping temperatures, i.e. −10 and −15°C. Correlation coefficients obtained plotting the sampled volume vs. the chromatographic peak area at −15°C are reported in Table III. Peak areas were measured on the single ion traces, selecting the most significant *m*/*z* value for each compound.

The calibration plots showed a fair agreement among data points with a correlation coefficient very close to linearity. R^2 values lower than 0.99 were obtained in a few cases, but only for sulphur hexafluoride and perfluoroethane, the most volatile among all the compounds considered. This is due to the loss of such compounds, which takes place when sampling air volumes higher than 1200 and 1050 mL, respectively, even when using an enriching temperature of −15°C. This is shown in the graph in Fig. 2, where the peak areas of SF_6 and C_2F_6 are plotted against the enriched volume. Linearity is obtained up to 1050 mL of air enriched. The R^2 value observed at −10°C for other compounds, among the most volatile, i.e. $CBrF_3$, is due to the loss occurring when enriching an air volume of 1500 mL. Therefore, to meet both the sensitivity of the analytical procedure, and the trapping capability of the adsorbent bed, a 1000-mL aliquot of air was enriched for actual sample analysis. A completely different matter lies at the base of the low R^2 value obtained at both temperatures for HCFC-141b. In this case, lack of linearity can be ascribed to problems related to peak shape, for which results are spoiled by an overloaded co-eluting peak. Such a peak, which is not detectable using the SIM mode, is likely to affect the chromatographic process.

TABLE III Correlation coefficients (R^2) obtained by plotting peak areas obtained enriching increasing air volumes at the temperature of −15°C, and reproducibility on 100 replicate analyses of calibrated actual air

Species	*Up to* 1000 mL *enriched*	*Up to* 1500 mL *enriched*	*%RSD*[a], $N = 100$ 1000 mL *enriched*
CFC-11	0.9993	0.9998	0.64
CFC-12	0.9991	0.9991	1.84
CFC-113	0.9981	0.9984	1.27
CFC-114	0.9998	0.9998	1.69
CFC-115	0.9981	0.9972	0.84
H-1211	0.9962	0.9968	1.51
H-1301	0.9930	0.9900	3.49
HCFC-22	0.9998	0.9991	2.47
HCFC-141b	0.9687	0.8804	6.85
HCFC-142b	0.9978	0.9974	1.12
HCFC-124	0.9964	0.9946	4.75
HFC-125	0.9998	0.9967	0.98
HCFC-152a	0.9956	0.9944	3.12
HFC-134a	0.9981	0.9978	1.07
HFC-143a	0.9972	0.9895	3.18
Perfluoroethane	0.9994	0.8315	2.97
Sulphur hexafluoride	0.9990	0.8900	0.94
Methyl chloride	0.9996	0.9997	0.88
Methyl bromide	0.9980	0.9912	1.47
Chloroform	0.9975	0.9991	1.77
Dichloromethane	0.9972	0.9977	4.11

[a] %RSD: percentage relative standard deviation.

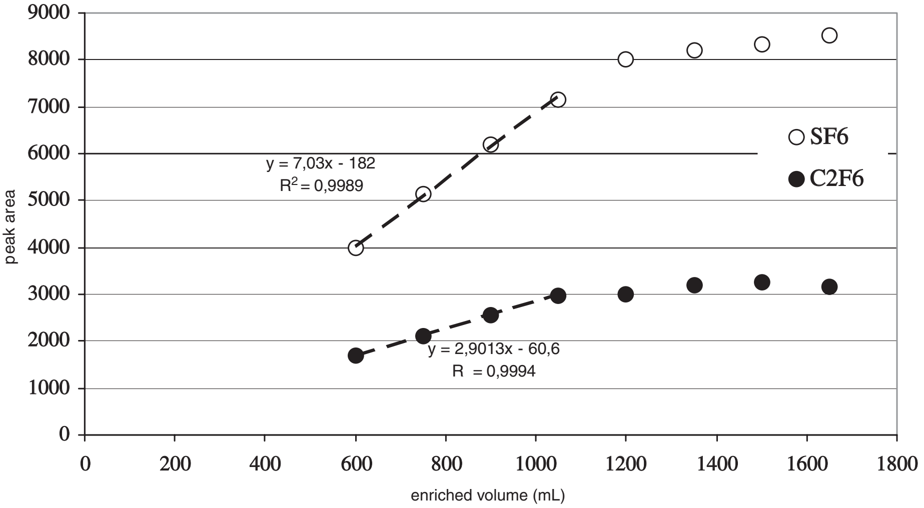

FIGURE 2 Calibration plots for SF_6 and C_2F_6 obtained by enriching onto the multi-bed adsorption tube increasing volumes of calibrated actual air at a temperature of $-15°C$.

A chromatographic run performed using the MS detector in the SCAN mode revealed the overloaded peak with a mass spectrum corresponding to the water spectrum, whose occurrence is not compatible with the use of the Nafion dryer. Further investigations are needed to overcome this problem.

Reproducibility

The reproducibility for this method was evaluated by using the operative parameters described above: 1000-mL aliquots of calibrated actual air, sampled at a flow rate of $25\,mL\,min^{-1}$, were enriched onto the multi-layer adsorption tube kept at the temperature of $-15°C$. An excellent agreement was found over more than 100 measurements, as can be seen from the percentage relative standard deviation (%RSD) values reported in Table III. As expected, the only compound for which a rather high %RSD value was found is HCFC-141b. This is the consequence of the peak-shape problems described above.

Limits of Detection

The minimum volume to be sampled to obtain a detector response three times greater than the background noise has been evaluated. To assess such volume, detection limits were evaluated for the single components of a standard mixture on the quadrupole mass-spectrometric detector, always operating in SIM mode. By enriching 1000 mL of calibrated actual air on the multi-bed adsorption tube, the halogenated halocarbons in 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.

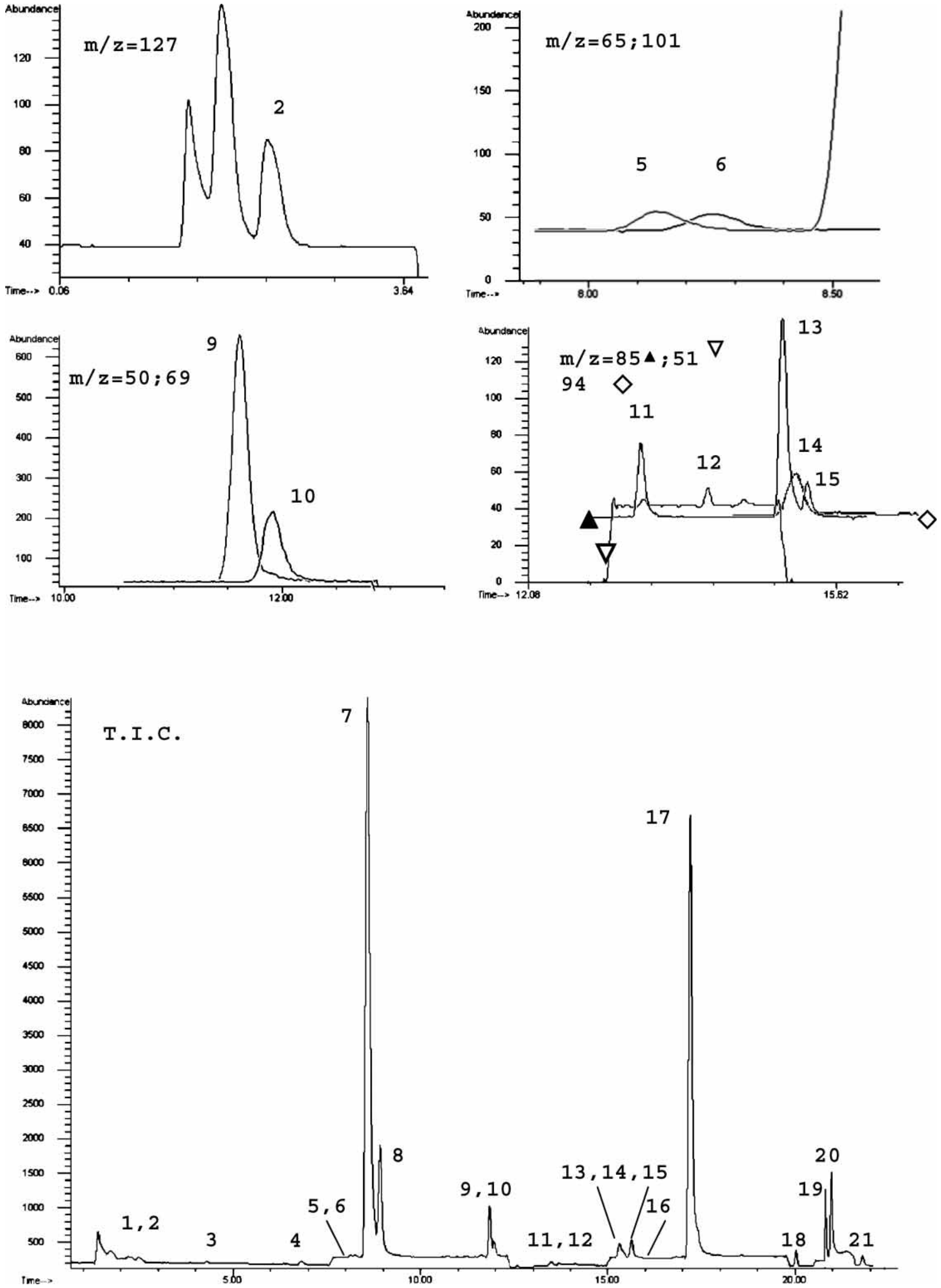

FIGURE 3 Reconstructed total ion chromatogram of a 1000-mL actual air sample collected at Monte Cimone enriched on the multi-layer trap kept at the temperature of −14°C. For chromatographic conditions, see text. The boxes show the enlarged portions of the TIC. Peak identification: 1. C_2F_6; 2. SF_6; 3. H-1301; 4. CFC-115; 5. HCFC-125; 6. HFC-143a; 7. CFC-12; 8. HCFC-22; 9. CH_3Cl; 10. HFC-134a; 11. H-1211; 12. HFC-152a; 13. CFC-114; 14. CH_3Br; 15.HCFC-142b; 16. HCFC-124; 17. CFC-11; 18. CH_2Cl_2; 19. HCFC-141b; 20. CFC-113; 21. $CHCl_3$.

Actual Sample Analysis

The reconstructed total ion chromatogram obtained analysing 1000 mL of actual air is reported in Fig. 3. As can be seen, the complete separation of the 21 compounds of interest is achieved, with almost all the compounds of interest chromatographically resolved at the baseline, with the exception of two pairs of compounds, i.e. CFC-114/CH_3Br and CH_3Br/HCFC-142b. In this case, the use of mass spectrometry by selecting ions characteristic of each compound helps in solving the problem. Furthermore, notwithstanding the high retention of the GSC column, the compounds are eluted in a reasonable length of time (22 min).

Table IV lists the mean concentration values measured in air samples collected at the Research Station of Monte Cimone over a 1-month period in August 2002. As can be seen, with the proposed method, it was possible to quantify the 21 compounds of interest that were present at concentration levels from a few to hundreds of ppt. Column 1 reports the average concentrations obtained, taking into account the whole data set of the month. However, a simple data-filtering procedure, implying the calculation of the average of the lowest 50% of the data of the monthly running mean, can be used to better define the background mixing ratios. The results are listed in column 2.

The concentration data, compared with those obtained in other 'non continental' stations of the SOGE network, sometimes appear higher. This can be ascribed to the location of Mt. Cimone station, which is affected more by the European continental emissions. In this respect, a comparison with data obtained in background stations, such as Mace Head (Ireland) and Mt. Zeppelin (Svalbard Islands, Norway), would

TABLE IV Concentration data, expressed in pptv, measured in two different sampling sites (progressive numbers as in Figs. 3 and 4)

Compound	*Enriched volume*	*August* 2002—*monthly mean* 1000 mL		*Antarctica* (*December 2000*) 300 mL
		All data set ($N = 87$)	*lowest* 50% *data*	
1	PFE	0.85[a]	0.81[a]	n.d.
2	SF_6	4.61	4.46	n.d.
3	H-1301 (CF_3Br)	3.26	3.10	n.d.
4	CFC-115 (CF_3CF_2Cl)	8.88	8.32	n.d.
5	HFC-125 (CF_3CF_2H)	3.85	3.44	n.d.
6	HCFC-143a (CH_3CF_3)	1.31[a]	1.15[a]	n.d.
7	CFC-12 (CF_2Cl_2)	551.52	536.60	513.9
8	HCFC-22 (CHF_2Cl)	173.53	168.12	214.3
9	CH_3Cl	535.63	522.52	540.2
10	HFC-134a (CF_3CFH_2)	42.13	29.42	11.9
11	H-1211 (CF_2ClBr)	4.54	4.43	n.d.
12	HFC-152a (CF_2HCH_3)	4.15	3.50	n.d.
13	CFC-114 (CF_2ClCF_2Cl)	17.30	17.10	16.3
14	CH_3Br	8.90	8.40	n.d.
15	HCFC-142b (CH_3CF_2Cl)	27.26	16.28	15.2
16	HCFC-124 ($CHFClCF_3$)	1.36	1.18	n.d.
17	CFC-11 ($CFCl_3$)	261.94	260.55	237.2
18	CH_2Cl_2	62.33	30.77	n.d.
19	HCFC-141b (CH_3CFCl_2)	23.25	17.93	11.8
20	CFC-113 ($CF_2ClCFCl_2$)	80.80	79.59	82.7
21	$CHCl_3$	11.23	8.97	4.2

[a] Ratio to reference, no calibration scale.

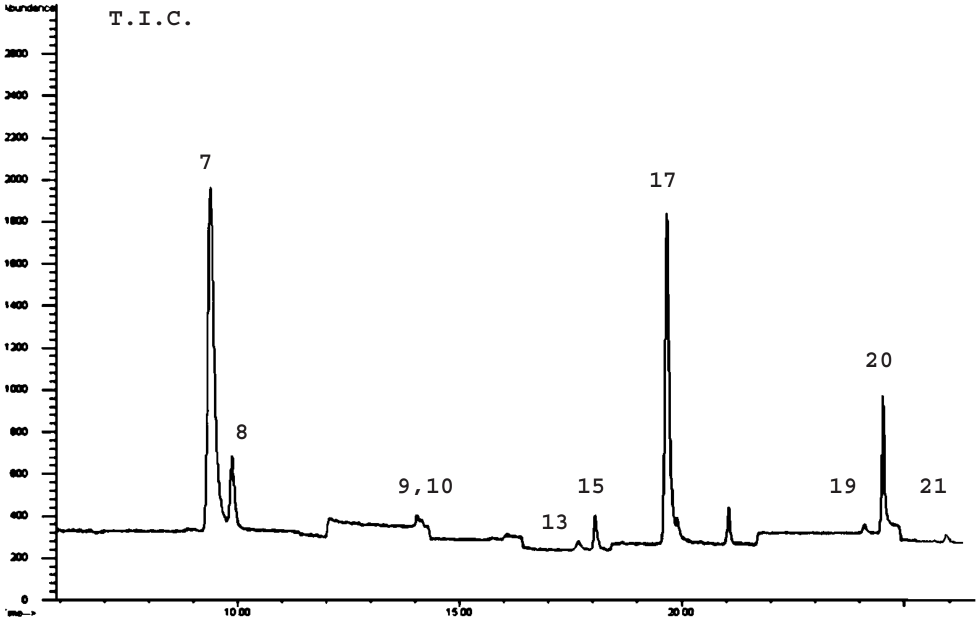

FIGURE 4 Reconstructed total ion chromatogram of a 300-mL actual air sample collected in Antarctica enriched on the multi-layer trap kept at a temperature of −14°C. For chromatographic conditions, see text. For peak identification, see Fig. 3.

be very useful in assessing emission-source strengths on a regional scale, when supported by the statistical analysis of air-mass back-trajectories.

The analytical methodology presented here can also be used to analyse grab samples, by simply connecting the sample inlet with a stainless steel flask filled with ambient air sampled elsewhere. Here are presented results obtained by analysing grab air samples collected in a remote site, i.e. Antarctica, in the frame of a research activity aimed at evaluating the background long-term trend of CFCs and their main substitutes [21,22]. In this case, only the most abundant halocarbons have to be determined, and therefore small flasks are used. For this purpose, 300-mL aliquots of air collected in the Northern Victoria Land (Antarctica) during the 2000–2001 austral summer were enriched on the adsorption trap. Notwithstanding the small enriched volume, it was possible to determine halogenated hydrocarbons present at concentration levels down to about 10 ppt. The reconstructed total ion chromatogram is shown in Fig. 4, and the concentration data are listed in Table IV.

CONCLUSIONS

The methodology presented here was found to be a reliable regime for continuous analysis of volatile halogenated hydrocarbons present in the atmosphere at concentration levels down to a few ppt. The concentration data can be used to determine the influence of anthropogenic sources of these compounds on a regional scale. At the same time, the method can be used effectively to analyse grab samples collected in those areas where the use of a continuous monitoring station is not applicable.

Acknowledgements

The present study was carried out in the frame of the EU Project SOGE (EVK2-2000-00674). Ray Weiss and the SIO98 scale, and the University of Bristol and the UB 98 scale are greatly acknowledged, as well as the colleagues participating in the SOGE consortium. Paolo Bonasoni, station chief, and all the staff of the CNR (Italian National Research Council) 'O. Vittori' research station at Monte Cimone are deeply acknowledged as well. Part of this work was performed as a result of our participation in the Italian National Programme for Research in Antarctica (PNRA).

References

[1] T.J. Wallington, W.F. Schneider, D.R. Worsnop, O.J. Nielsen, J. Sehested, W.J. Debruyn and J.A. Shorter, *Environ. Sci. Technol*, **28**, 320–326 (1994).
[2] S. Pinnock, M.H. Hurley, K.P. Shine, T.J. Wallington and T.J. Smyth, *J. Geophys. Res*, **100**, **D11**, 23, 227–23, 238 (1995).
[3] *Montreal Protocol to Reduce Substances that Deplete the Ozone Layer, Final Report*. UN Environmental Programme, New York (1987).
[4] Copenhagen Amendment to the Montreal Protocol. UNEP (United Nations Environment Programme) 1992. *Report of the Fourth Meeting of the Parties to the Montreal Protocol on Substances that Deplete the Ozone Layer*. United Nations, New York (1994).
[5] P.G. Simmonds, R.G. Derewent, A. McCulloch, S. O'Doherty and A. Gaudry, *Atmos. Environ.*, **30**, 4041–4063 (1996).
[6] R.G. Derewent, P.G. Simmonds, S. O'Doherty, P. Ciais and D.B. Ryall, *Atmos. Environ.*, **32**, 3703–3715 (1998).
[7] R.G. Derewent, P.G. Simmonds, S. O'Doherty and D.B. Ryall, *Atmos. Environ.*, **32**, 3689–3702 (1998).
[8] F. Mangani, M. Maione, L. Lattanzi and J. Arduini, *Atmos. Environ.*, **34**, 5303–5309 (2000).
[9] D.E. Oram, C.E. Reeves, S.A. Penkett and P.J. Fraser, *Geophys. Res. Lett.*, **22**, 2741–2744 (1995).
[10] A. Montzka, J.H. Butler, R.C. Myers, T.M. Thompson, T.H. Swanson, A.D. Clarke, L.T. Lock and J.W. Elkin, *Science*, **272**, 1318–1322 (1996).
[11] S.A. Montzka, R.C. Myers, J.H. Butler, J.W. Elkins, L.T. Lock, A.D. Clarke and A.H. Goldstein, *Geophys. Res. Lett.*, **23**, 169–172 (1996).
[12] D.E. Oram, C.E. Reeves, W.T. Sturges, S.A. Penkett, P.J. Fraser and R.L. Lagenfelds, *Geophys. Res. Lett.*, **23**, 1949–1952 (1996).
[13] S.A. Montzka, J.H. Butler, J.W. Elkins, T.M. Thompson, A.D. Clarke and L.T. Lock, *Nature*, **398**, 690–693 (1999).
[14] W.T. Sturges and J.W. Elkins, *J. Chromatogr.*, **642**, 123–134 (1993).
[15] P.G. Simmonds, S. O'Doherthy, G. Nickless, G.A. Sturrock, R. Swany, P. Knight, J. Ricketts, G. Woffendin and R. Smith, *Anal. Chem.*, **67**, 717–723 (1995).
[16] D.W. Armstrong, G.L. Reid, III and M.P. Gasper, J. *Microcolumn Separations*, **8**, 83–87 (1996).
[17] S.J. O'Doherty, G. Nickless, M. Bassford, M. Pajot and P. Simmonds, *J. Chromatogr. A*, **832**, 253–258 (1999).
[18] J.L. Bullister and R.F. Weiss, *Deep Sea Res*, **35**, 839–853 (1988).
[19] D.M. Cunnold, R.F. Weiss, R.G. Prinn, D. Hartley, P.G. Simmonds, P.J. Fraser, B.R. Miller, F.N. Alyea and L. Porter, *J. Geophys. Res.* **102**, **D1**, 1259–1269 (1997).
[20] M. Riba, B. Clement, M. Haziza and L. Torres, *Toxicol. Environ. Chem*, **31–32**, 235–240 (1991).
[21] F. Mangani, M. Maione and L. Lattanzi, *Ant. Sci.*, **11**(2), 259–262 (1999).
[22] F. Mangani, M. Maione, L. Lattanzi and J. Arduini, *Intern. J. Environ. Anal. Chem*, **74**, 273–282 (2001).