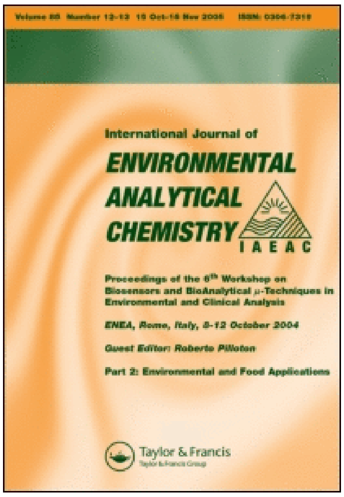

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Measurement of Atmospheric Monocyclic Aromatic Hydrocarbons and Chlorinated C_1- and C_2-Hydrocarbons at NG.M^{-3} Concentration Levels

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MEASUREMENT OF ATMOSPHERIC MONOCYCLIC AROMATIC HYDROCARBONS AND CHLORINATED C_1- AND C_2-HYDROCARBONS AT NG.M^{-3} CONCENTRATION LEVELS

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An air sampling and analysis technique for thirteen monocyclic aromatic hydrocarbons (MAHs) and chlorinated C_1- and C_2-hydrocarbons (CHCs) at ng.m^{-3} concentration levels is presented. Sampling was done on Carbopack B/Carbosieve SIII adsorbent tubes. The analysis on an automated on-line purge and trap (P&T) apparatus equipped with a thermal desorption unit proved to be not reproducible because of water interference and because of contamination from the apparatus itself. An off-line desorption unit, combined with thermal desorption by means of the on-line apparatus gave reproducible measurements with relative standard deviations (% SD, n = 4) from 0.9 to 8.3 at 2.2–4.1 µg.m^{-3} (±670 pptv). Limits of detection (LODs) at a signal/noise ratio equal to three were below 5.7 ng.m^{-3}. For chloroform, benzene and toluene the LODs were 41.4, 96.0 and 48.7 ng.m^{-3} respectively because of background levels of these compounds.

Next to this analysis, a simple calibration method is presented which proved to be accurate and precise. A dynamic vapour pressure (DVP) calibration technique on the contrary, was tested and showed significant bias.

The sampling and analysis method allowed to determine all mentioned volatile organic compounds (VOCs) in duplicate field measurements with 0.6–7.3% SD at 124–1374 ng.m^{-3} concentrations and with 21.3 to 39.4% SD for 29 to 95 ng.m^{-3} concentrations.

KEY WORDS: Volatile organic compounds (VOCs), chlorinated hydrocarbons (CHCs), monocyclic aromatic compounds (MAHs), atmospheric pollution.

INTRODUCTION

In ambient VOCs analysis, two critical points have to be considered. First, a good sampling technique together with an appropriate analysis method is necessary. Secondly, accurate calibration is needed. Different sampling techniques are reported in literature. Air sampling methods like canister sampling[1–4] and Tedlar bag sampling[5] are used. Further on, VOCs concentration methods like cryogenic trapping[6–9] and adsorbent trapping[10–13] are applied.

All these sampling methods have some disadvantages with respect to contamination, recovery and water interference. Canisters need a thorough cleaning[14,15] in order to measure low environmental concentrations. Interactions with the internal sample holder surface have to be considered when air with low relative humidity is sampled[16,17]. Sampling with cryogenic trapping can be disturbed by the formation of ice in the trap during the concentration step[7]. This can be encountered with more complicated cryogenic sampling methods as the double cryogenic trapping method of Greenberg *et al.*[6]. Sorbent sampling reduces the water problem if hydrophobic materials are used. However, the disadvantage of this method is a limited safe sampling volume for highly volatile compounds due to breakthrough losses[13,18]. At low environmental concentration levels, contamination originating from degradation of the sorbent itself, especially of Tenax[19] can cause inaccurate results.

Due to the development of new sorbent materials a new impulse to the sorbent sampling technique is given. Carbon based materials such as Carboxen 1000, Carboxen 1001, Carbotrap, Carbotrap C, Carbosieve SII and Carbosieve SIII are in use[20–22]. The application of different sorbents in series allows sampling and analysis of a wide range of VOCs. They show a good thermal stability and assure low background levels[21], but some of them such as Carbosieve SIII retain substantial amounts of water (breakthrough volume of 2.3 L/g[23]).

The calibration method is the second important point in the determination of atmospheric VOCs. Several calibration methods for VOCs analysis in air at $\mu g.m^{-3}$ or $ng.m^{-3}$ level are described such as external calibration with direct liquid injection[12,21], calibration with cylinders containing certified gas mixtures or with dilutions of these cylinders[7,16,24], the dilution method[4,7,8,22,25] and the dynamic vapour pressure (DVP) method[26]. Briefly, the DVP system consists of a clean air stream passing over the top of a capillary. At the bottom of the tube a vessel with the liquid VOC is installed. The vapour concentration entering the gas stream can be calculated from the vapour pressure and the diffusion coefficient of the VOC, from the pressure and the temperature in the system, and from the length and the diameter of the tube[26].

In this work a sampling and analysis technique for atmospheric CHCs and MAHs at $ng.m^{-3}$ levels is described. For this purpose an automatic on-line P&T system equipped with a cartridge desorber is evaluated. Further on, an off-line desorption step is combined with desorption in the on-line P&T system. The reproducibility of the sampling technique and the analysis are examined. Next to this, the accuracy and the precision of a new and simple calibration technique is investigated and compared with the DVP method. Finally, the applicability of the method is illustrated at concentration levels of 30 to 1400 $ng.m^{-3}$ by measurements at a rural site.

EXPERIMENTAL

Materials

Adsorbents 170 mg Carbopack B (graphitized carbon black, 100 m^2/g, 60/80 mesh, Supelco) and 350 mg Carbosieve SIII (carbon molecular sieve, 820 m^2/g, 60/80 mesh, Supelco) were used as sorbents in series. They were hold separately with glass wool plugs in open glass tubes (length 16 cm, OD 1/4"). The tubes were sealed with 1/4" brass end caps and 1/4" teflon ferrules (Alltech Ass.) Before sampling, the adsorption tubes were conditioned at 270°C with Helium (±50 ml/min) during four hours. At the same time, the teflon ferrules placed in a glass tube (ID 1 cm) were conditioned (270°C/4h/ ±50 ml/min). This was necessary because it was proven that unconditioned teflon and vespel ferrules contaminated adsorption tubes with VOCs. Teflon showed to be better than vespel in this respect.

VOCs, internal standard and solvent The CHCs chloroform, 1,1-dichloroethane, 1,2-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene (Janssen) and tetrachloromethane (Merck), and the MAHs benzene, toluene (Merck), ethylbenzene and m-, p- and o-xylene (Aldrich) were used as VOCs in the experiments. They were applied without further purification. Toluene-d8 (> 99.95 atom% D, Fluka) was used as internal standard. Methanol was obtained from Merck (for Chromatography, 99.8%).

Apparatus

The microprocessor controlled P&T system, CDS Peakmaster (CDS Analytical Instruments, Oxford, USA) was coupled with a gas chromatograph-mass spectrometer (GC-MS) Carlo Erba QMD 1000 (Carlo Erba Instruments, Milan, Italy) by a heated transferline with a cryogenic focuser at the GC injection port. The P&T system was provided with a 60 ml vessel, a wet trap and a sorbent trap, and a cartridge desorber. In some experiments the cartridge desorber was replaced by a Chrompack desorber TCT1 with a control unit (Chrompack, Middelburg, The Netherlands). As sorbent trap in the CDS instrument a Vocarb 4000 trap (1/8" OD, 8.5 cm Carbopack C, 10 cm Carbopack B, 6 cm Carboxen 1000 and 1 cm Carboxen 1001) was used. All parts and also the carrier gas and the transferline were connected to an 8-port switching valve. Separation of the VOCs was done on a RTX-502.2 capillary column (Restek) (length 60 m, ID 0.32 mm, film thickness 1.8 μm, carrier gas helium, inlet pressure 12 psi), detection was done using the mass spectrometer in the single ion monitoring (SIM) mode. M- and p-xylene were not separated and were determined together. The selected ions and time windows are reported in a previous work[27].

Next to the on-line system, an off-line desorption unit was constructed. It consisted of a Chrompack desorber connected to a wet trap. The wet trap in the construction was a 1/4" stainless steel tube (length 1.5 or 3 m) or a 2 m 1/4" glass column submerged in a temperature controlled ethylene glycol bath (–10 to –15°C). The end of this wet trap was connected to a Vocarb 4000 trap. Helium purge gas was led through a liquid nitrogen trap before entering the off-line system.

Preparation of the internal standard and the calibration mixture, and loading of the sampling tubes with the internal standard and the calibration mixture

9 μl toluene-d8 was added to 25 ml methanol. From this solution 40 μl was added to 20 ml deionized water in a 118 ml glass bottle. Immediately after the addition, the bottle was sealed with a mininert valve (Alltech Ass.). This closed two-phase system (CTS) was incubated upside down in a thermostatic water bath at 25.0 ± 0.1°C during at least 3 hours. In order to know the headspace concentration at equilibrium the dimensionless Henry's law constant for toluene-d8 was determined with the modified EPICS-method (equilibrium partitioning in closed systems)[28] as 0.183 ± 0.005 (n = 9). Knowing the mass M added, the gas and liquid volumes V_s and V_w, and Henry's law constant H, the headspace concentration C_g is calculated from the mass balance:

$$C_g = \frac{M}{V_g + V_w/H}$$

With a gastight syringe (Hamilton Gastight 1750, 500 μl) 250 μl headspace from the CTS was injected on the adsorption tube via an injection system as illustrated in Figure 1. After injection, the gas stream (250 ml/min) was held on for 2.5 minutes.

For the calibration tubes 250 μl headspace from a second CTS was brought on the IS-enriched sorption tubes. The second CTS was prepared similar to the first CTS but

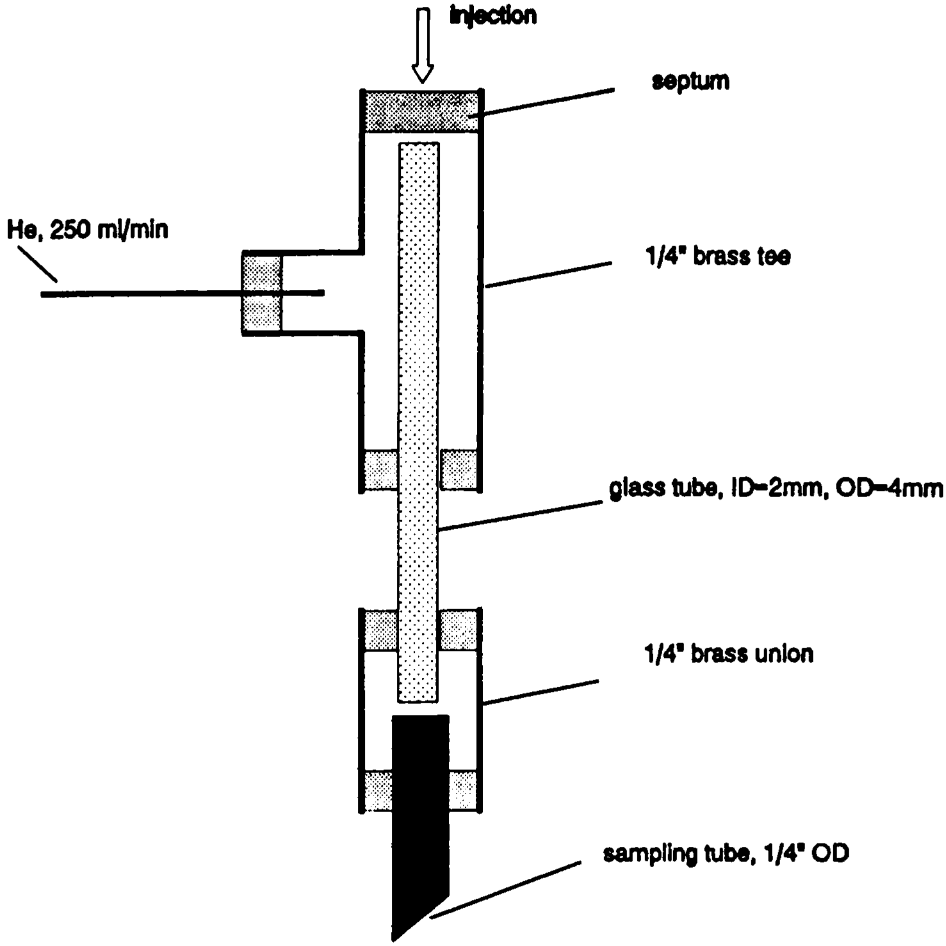

Figure 1 Injection system.

contained all VOCs. The amounts added were so that the masses in 250 µl headspace corresponded with 2.2–4.1 $\mu g.m^{-3}$ (645 till 698 pptv) in 61 samples (Table 1).

Instrumentation for the test of the accuracy and precision of the CTS and DVP calibration methods

In order to check the accuracy and the reproducibility of the calibration masses of the CTS and the DVP method, a gas chromatograph (GC) Varian model 3700 equipped with a thermal desorption unit was used[29]. The calibration masses could be verified versus liquid injection since this analytical instrument functions as well for thermal desorption of 750 mg Tenax TA tubes as for direct liquid injection[29]. The GC operated with an injector temperature of 220°C and a detector (FID) temperature of 250°C. Separation of

Table 1 Volumes V (nl) of VOCs brought in the CTS, density d (g/cm^3), Henry's law constant H at 25°C (dimensionless), mass m in 250 μl headspace (ng) and corresponding concentration C in 6 l (μg.m^{-3}).

VOC	*V*	*d*	H^*	*m*	*C*
Chloroform	12.0	1.490	0.153	19.54	3.26
Tetrachloromethane	7.2	1.593	1.048	24.49	4.08
1,1-Dichloroethane	11.2	1.174	0.206	16.85	2.81
1,2-Dichloroethane	30.4	1.253	0.0412	16.32	2.72
1,1,1-Trichloroethane	8.0	1.310	0.608	20.02	3.34
Trichloroethylene	8.8	1.464	0.351	20.78	3.46
Tetrachloroethylene	8.8	1.622	0.601	27.18	4.53
Benzene	12.0	0.879	0.194	13.11	2.19
Toluene	13.6	0.867	0.224	15.74	2.62
Ethylbenzene	14.4	0.867	0.270	18.14	3.02
o-Xylene	17.6	0.881	0.173	18.15	3.02
m/p-Xylene	14.4	0.863	0.248	17.39	2.90
Toluene-d8	14.4	0.944	0.183	16.39	2.73

* Data from Dewulf *et al.*[28], except for toluene-d8

the compounds was done on a RSL 150 fused silica column (30 m, film thickness 5 μm, ID 0.53 mm) and integration by an HP3388A integrator. During analysis the GC oven temperature was kept at 50°C for five minutes, then followed by heating till 200°C at a rate of 7°C/min. He-carrier gas flow rate was 2 mL/min, the FID was fed with air at 400 mL/min and H_2 at 40 mL/min.

Dynamic vapour pressure (DVP) system

A DVP system was set up as described by Schoene and Steinhanses[26]. A fused silica capillary tube with ID = 0.18 mm was obtained from Alltech Ass.. The length for the toluene and chloroform tubes were 5.0 and 7.5 cm respectively. They were held at 24.9 ± 0.1°C and a total pressure of 256 kPa was measured. Concentrations of 11.8 ng/l toluene and 89.6 ng/l chloroform are calculated from the formulas

$$m = D\,.\,M\,.\,(\frac{P_t}{R.T})\,.\,\frac{A}{l}\,.\,\ln(\frac{P_t}{P_t - P_s})$$

and

$$D = (\frac{b_o}{P_t})\,.\,T^{3/2}\,.\,\frac{(\frac{1}{M}+\frac{1}{M_a})^{0.5}}{(V^{1/3}+V_a^{1/3})^2}$$

with D = diffusion coefficient (cm^2/min), M = molecular mass (g/mol), P_t = total pressure at the top of the capillary tube (kPa), R = gas constant (8314.46 ml.kPa/mol.K), T = temperature (K), A = cross section of the capillary tube (cm^2), l = length of the capillary tube (cm), P_s = vapour pressure of the VOC (kPa), b_o = 26.133, M_a = average molecular mass of air (29 g/mol), V = molar volume of the VOC at boiling point (ml/mol) and V_a = molar volume of air at boiling point (29.9 ml/mol).

Sampling storage and analysis

Samples were taken by pumping air through the sorption tube at a flow rate of ±240 ml/min during 25 minutes. After sampling they were sealed and stored in the laboratory till analysis. Samples, blank tubes and calibration tubes were placed and desorbed in the CDS cartridge desorber, in the on-line Chrompack desorber or in the off-line installed Chrompack. In the off-line desorption of sampling tubes, the Vocarb 4000 trap with sorbed VOCs was replaced in the on-line system for desorption. The Vocarb 4000 trap was desorbed during 6 minutes at 250°C. After desorption the trap was conditioned at 260°C for 4 minutes. The cryofocussing temperature was held at −150°C during the desorption.

After the desorption the cryogenic focuser was heated to 260°C (rate 800°C/min) and held at this temperature during 5 minutes. Temperature programming of the GC and data acquisition were started simultaneously. Temperature of the GC oven was held at 50°C during 10 minutes, then increased to 190°C at a rate of 10°C/min.

RESULTS AND DISCUSSION

On-line versus off-line analysis

The original P&T unit was equipped with a cartridge desorber for analysis of sorption tubes. Desorption of empty tubes at 230°C for 8 minutes in the cartridge desorber gave constant contamination of MAHs: benzene: 4.56 ± 0.63, toluene: 0.89 ± 0.05, m/p-xylene: 0.103 ± 0.016 and ethylbenzene: 0.068 ± 0.012 ng (n = 3). With the same analysis without heating the cartridge desorber contamination was under control.

Subsequently the original cartridge desorber was replaced by a Chrompack desorber on the on-line P&T system. The blanks were now under control but peak shape was poor in the time window from chloroform till benzene due to water interference and secondly, incomplete desorption of the internal Vocarb 4000 trap was found since a second desorption of the trap gave MAHs up to 42% (benzene) of the first desorption.

On the contrary, when 250 µl of air containing 20 ng chloroform, 20 ng 1,2-dichloroethane, 20 ng toluene and 20 ng m-xylene was brought on the Vocarb 4000 trap via a Helium stream in an off-line construction, the desorption of the replaced trap was complete. An off-line construction was set up including the Chrompack desorber, a wet trap and the Vocarb trap in order to analyse sampling tubes. Finally, complete desorption of the whole system was obtained by desorption in the desorption unit at 250°C for 14 minutes and purging for 18 minutes at 30 ml/min.

In the literature, some solutions are mentioned to minimize water interference. By decreasing the sampling volume, the moisture problem in the analysis is decreased, but the LODs as well[1-3]. Secondly, cryogenic traps with large internal diameter can be used in order to avoid clogging by ice[4]. Thirdly, the installation of a 5 ml water vessel between the cryogenic trap and the sorbent trap kept the water amount entering the desorption unit constant[4]. The desorption was preceded by a dry purge[4]. As a fourth solution, Farmer *et al.*[2] mentioned nickel tubing with glass beads and Chromosorb A. Further on, Greenberg *et al.*[6] avoided water entering the analytical instrument in cryogenic sampling by slowly heating up the trap to 80°C in order to transfer only the VOCs. Finally, the technique most often applied is the installation of a water removing trap. Haszpra *et al.*[9] installed a granular magnesium perchlorate tube at 60°C before the cryogenic trap. Widely applied are Perma Pure dryers with a tubular hygroscopic ion-exchange membrane (Nafion). They can be used if two assumptions are made. First, the water retaining cartridge is supposed not to trap VOCs. One study reported the loss of methyl chloride[4]. Secondly, it may not set free VOCs in order to avoid contamination. McClenny *et al.*[7] reported no loss of MAHs and halogenated C_1-C_4-halocarbons at ±100–1000 $\mu g.m^{-3}$ but the dryers had to be cleaned by heated outgassing in order to reach zero air levels. Moreover, Boudries *et al.*[22] reported the impossibility of the quantification of butenes, benzene and toluene with Nafion, but later on, quantification was performed by a substraction of 145, 250 and 495 $ng.m^{-3}$ i-butene, benzene and toluene respectively.

Using 170 mg Carbopack B and 350 mg Carbosieve SIII and the breakthrough volume data of Mosesman *et al.*[23] 86.4% of water in a 6 l air sample is already lost during the sampling step. However, the water retained still disturbed the analysis in the on-line desorption, similar to the analyses of McCaffrey *et al.*[30]. The water trap used in our off-line construction, similar to the trap of Lai *et al.*[24], is a simple and efficient method. A glass trap is preferred because stainless steel traps showed unreproducible measurements for C_2-substituted MAHs after a series of analyses. It was demonstrated that the wet trap did not retain VOCs. A thermal desorption system as described by Van Langenhove *et al.*[29] was provided with and without the wet trap. Tenax tubes were loaded with 10 l humidified gas and with VOCs from a CTS (chloroform, 1,1,1-trichloroethane, tetrachloromethane, toluene, ethylbenzene and p-xylene). When the tubes were analysed in the system equipped with the wet trap, mean recovery values from triple analysis varying from 91.3 to 98.3% were noticed for all VOCs, when compared with analyses executed on the system when it was not provided with the wet trap.

Calibration method

In order to obtain an accurate and precise calibration system, the DVP method was evaluated for chloroform and toluene and a CTS calibration technique was developed.

Accuracy of DVP and CTS calibration The two calibration methods rely on the calculation of the mass brought on the adsorbent. In order to check the validity of the calculation, a GC-FID system equipped with a thermal desorption unit was used. So, the calculated mass from the DVP or from the CTS brought on a sorption tube could be verified versus direct liquid injection.

From a DVP system, 5 l air containing 59 ng toluene and 448 ng chloroform was sampled and analysed. The measured amount significantly exceeded the calculated mass for chloroform (% recovery 138.1 ± 8.6) as well as for toluene (128.8 ± 2.1) (n = 6). Possible explanations for this overestimation could be the difference between the real and the stated diameter of capillary tubes of 0.18 mm ID.

In Table 2, the analysed masses from the adsorption tubes loaded with chloroform, 1,2-dichloroethane, toluene and m-xylene from a CTS system are presented and compared with the calculated values. As can be seen, the measured masses match very well the calculated masses for chloroform and toluene. It can be concluded that the CTS calibration technique gave satisfactory accurate results with recoveries of 95.5 to 111.2% (n = 4) when masses equal to 3.23 till 4.73 ppbv in a 6 l sample were applied.

Precision of the DVP and the CTS calibration method The precision of both the DVP and the CTS calibration method were satisfactory. The % SD was 6.2 for chloroform and

Table 2 Calculated masses from a CTS and measured calibration masses from sampling tubes with corresponding standard deviation (ng) (n = 4).

VOC	*Calculated mass*	*Measured mass*	*Recovery*
Chloroform	149.4	151.3 ± 2.5	101.3 ± 1.7
1,2-Dichloroethane	95.5	106.2 ± 1.9	111.2 ± 2.0
Toluene	84.4	84.4 ± 1.4	100.0 ± 1.7
m-Xylene	88.2	84.2 ± 1.2	95.5 ± 1.4

1.6 for toluene in the DVP method (n = 6). In Table 2 the precision of the calibration mixture from the CTS is presented and ranges from 1.4 (m-xylene) to 1.8% SD (1,2-dichloroethane) (n = 4).

When compared to the DVP method and with other methods found in literature, it is clear that the CTS calibration technique is a valuable method since the technique is accurate, reproducible, easy applicable to several compounds and inexpensive. It is clear that the DVP method requires the knowledge of a lot of physical parameters. Permeation tubes are also based on a diffusion process, but knowledge of the parameters governing the mass flux are not required[31]. The diffusion rate can be calculated by measuring the tube weight loss over a long period. In this method regular and very precise weighing of the tube by means of an automatic microbalance is needed. Of all methods, direct liquid injection on the analytical column is the most simple technique[12,21] but it doesn't cover the sampling stage and the thermal desorption. Certified gas cylinders are used directly or after dilution[7,16,24]. However, McClenny *et al.*[3] reported for 10 compounds of the CHC and MAH target compounds a bias ranging from 4.2 to 21.2% at ±10–20 $\mu g.m^{-3}$ concentrations with this methodology. The preparation of a gas calibration mixture by diluting a liquid into a gas cylinder is a third calibration method[4,7,8,22,25]. For this method, Boudries *et al.*[22] reported average deviations of 20% if dilution down to the $ng.m^{-3}$ level is done.

Limits of detection

The limits of detection (LODs) ($ng.m^{-3}$) are defined as the total amount of VOC at a signal/noise ratio of three (s/n = 3) and the blank level. The VOC masses corresponding to s/n = 3 were determined by analysing a calibration mixture containing all 13 VOCs at 2.2–4.1 $\mu g.m^{-3}$ (±670 pptv)[61]. The blank levels of chloroform, benzene and toluene had to be considered (0.026, 0.159 and 0.062 ng respectively) in order to calculate the LODs. In this way LODs from 2.16 $ng.m^{-3}$ (m/p-xylene) to 5.73 $ng.m^{-3}$ (o-xylene) were obtained, except for chloroform (41.4 $ng.m^{-3}$), benzene (96.0 $ng.m^{-3}$) and toluene (48.7 $ng.m^{-3}$) (Table 3).

This obtained LODs are similar to LODs of Boudries *et al.*[22] for FID-detection. With the same detection (MS in SIM-mode), McClenny *et al.*[3] determined LODs of ±105 $ng.m^{-3}$ (1,1,1-trichloroethane) to ±1650 $ng.m^{-3}$ (toluene) for the same target compounds. Better benzene and toluene LODs (±1.2 $ng.m^{-3}$) are reported by Greenberg *et al.*[6] with cryogenic sampling and FID-detection. Helmig and Greenberg[21] suggest their adsorbent sampling with GC-MS analysis is able to detect below pptv levels though no exact determination of LODs is reported. Finally, it has to be mentioned that ECD-detection is capable to detect lower concentration levels of CHCs[8], but it doesn't cover all target compounds of this work.

Table 3 Limits of detection (ng.m^{-3}).

VOC	*LOD*
Chloroform	41.4
Tetrachloromethane	3.97
1,1-Dichloroethane	3.60
1,2-Dichloroethane	3.31
1,1,1-Trichloroethane	4.06
Trichloroethylene	2.53
Tetrachloroethylene	4.40
Benzene	96.0
Toluene	48.7
Ethylbenzene	3.65
o-Xylene	5.73
m/p-Xylene	2.16
Toluene-d8	3.68

Reproducibility of the analysis

A calibration mixture from a CTS was used to verify the reproducibility of the analysis. The masses analysed were equal to concentrations of 2.2–4.1 μg.m^{-3} (± 670 pptv) in a 6 l sample. The relative standard deviation ranged from 0.9 (chloroform) to 8.3% (1,1-dichloroethane) (Table 4).

Several precision levels are found in literature. With FID- and ECD-detection, deviations of up to 20% were observed for concentrations down to ±20 μg.m^{-3} (CHCs) and ±200 μg.m^{-3} (MAHs)[1]. Wiedmann *et al.*[12] obtained similar reproducibility for tetrachloroethylene at 7–70 ng.m^{-3}.

Better reproducibility data are reported as well. Hsu *et al.*[4] measured 2–5% SD for the same target compounds with GC-MS analysis at 5.6–27.8 μg.m^{-3}. At concentrations between ±4 and ±40 μg.m^{-3}, %SD below 4.5 are reported by Hisham and Grosjean[25] with ECD and by Lai *et al.*[24] with FID.

In conclusion, no reproducibility data for the measurements of this target compounds at levels below 4 μg.m^{-3} (about 1 ppbv) are found. Comparable measurements are done

Table 4 Reproducibility of analysis at 2.2–4.1 μg.m^{-3} (±670 pptv) in %SD (n = 4).

VOC	*%SD*
Chloroform	0.9
Tetrachloromethane	5.5
1,1-Dichloroethane	8.3
1,2-Dichloroethane	5.1
1,1,1-Trichloroethane	5.0
Trichloroethylene	4.0
Tetrachloroethylene	6.2
Benzene	2.6
Toluene	1.1
Ethylbenzene	4.0
o-Xylene	8.1
m/p-Xylene	7.1

by McClenny *et al.*[3] with 2.4 (toluene) to 15.1%SD (tetrachloromethane) at average concentrations of ±4.4 μg.m^{-3}.

Reproducibility of the sampling procedure

The sampling reproducibility was checked for toluene at a concentration level of 9.25 μg.m^{-3} and at a 930 ng.m^{-3}. A gas stream was made by application of a DVP system. Gas was sampled on two adsorption tubes in parallel connected, with one common inlet using a Y-shaped teflon tube. Though the standard deviation on one parallel sampling proved to be quite variable (1.9 to 20.7%SD) the mean of the parallel samples is reproducible with 3.2 (n = 4) and 3.8%SD (n = 4) for 9.25 μg.m^{-3} and 930 ng.m^{-3} respectively. In this view it is recommended to take air samples in duplicate in a parallel construction in order to improve the precision.

Field measurements

The developed technique was applied for measuring the 13 CHCs and MAHs at a rural site, Nukerke, 35 km south-west of Ghent (Belgium) on 16 February 1995. Two parallel samples were taken in duplicate. In Table 5 the mean concentration and the standard deviation of the two parallel samples are presented. A typical chromatogram is presented in Figure 2. The average %SD for all compounds ranges from 0.6%SD (tetrachloroethylene) to 7.3%SD (1,1,1-trichloroethane) except for chloroform and 1,2-dichloroethane. Their %SD (39.4 and 29.0 for chloroform, 21.3 and 25.2 for 1,2-dichloroethane) could be due to the low concentration levels detected, being 69 and 95 ng.m^{-3} for chloroform and 29 and 38 ng.m^{-3} for 1,2-dichloroethane respectively.

In the literature, sampling and analysis reproducibility for urban air samples (average concentration ±12 μg.m^{-3}) of 7.9 (ethylbenzene) to 22.9%SD (tetrachloroethylene) are found in one monitoring programme while reproducibility of 5.8 (benzene) to 15.9%SD (o-xylene) are found in a second programme (average concentration ±2.4 μg.m^{-3})[3]. Lai *et al.*[24] obtained %SD values below 3.51 for urban air MAHs measurements at

Table 5 Field sampling results at a rural site, Nukerke, 35 km south-west of Ghent (Belgium) on 16 February 1995 (ng.m^{-3}).

VOC	*1st Parallel sampling*	*2nd Parallel sampling*	*Average %SD on parallel sampling*
Chloroform	69 ± 27	95 ± 27	34.2
Tetrachloromethane	475 ± 33	435 ± 2	3.7
1,1-Dichloroethane	126 ± 3	124 ± 15	7.2
1,2-Dichloroethane	29 ± 6	38 ± 10	23.2
1,1,1-Trichloroethane	827 ± 114	571 ± 5	7.3
Trichloroethylene	902 ± 62	822 ± 13	4.2
Tetrachloroethylene	220 ± 0.5	239 ± 3	0.6
Benzene	738 ± 621	777 ± 25	5.8
Toluene	1374 ± 109	1217 ± 24	4.9
Ethylbenzene	447 ± 29	432 ± 15	5.0
o-Xylene	435 ± 43	428 ± 14	6.6
m/p-Xylene	694 ± 55	677 ± 19	5.4

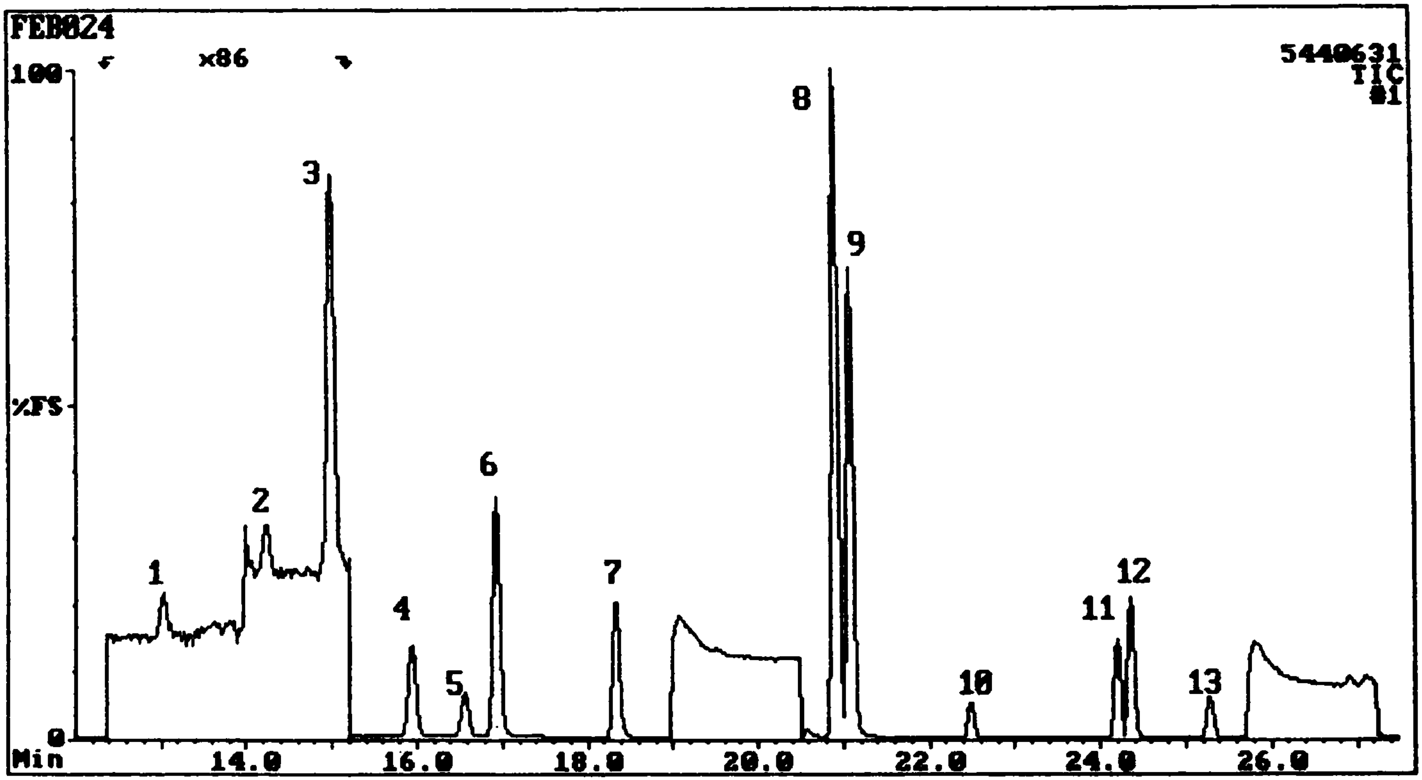

Figure 2 Chromatogram of an air sample taken at Nukerke, a rural site (Belgium). **1**: 1,1-dichloroethane; **2**: unidentified compound; **3**: chloroform; **4**: 1,1,1-trichloroethane; **5**: tetrachloromethane; **6**: benzene and 1,2-dichloroethane; **7**: trichloroethylene; **8**: toluene-d8; **9**: toluene; **10**: tetrachloroethylene; **11**: ethylbenzene; **12**: m/p-xylene; **13**: o-xylene. Ions 17 and 18 are added in time windows 19.00–20.25 and 25.75–27.25 min. to verify water background levels.

concentration levels of ±3.5–85 μg.m^{-3}. The data for field measurements at a rural site presented here at concentrations of 124 to 1374 ng.m^{-3} are satisfactory. The data of chloroform and 1,2-dichloroethane at 29 to 95 ng.m^{-3} of 21.3 to 39.4%SD are capable of improvement.

CONCLUSIONS

The presented technique consisting of sampling on Carbopack B/Carbosieve SIII sorbents and of a desorption-GC-MS analysis allowed the measurement of 13 CHCs and MAHs at ng.m^{-3} levels. This was not achieved by the application of an on-line P&T instrument equipped with a cartridge desorber because of water interference and because of contamination originating from the instrument. On the other hand, the combination of the on-line instrument together with an off-line desorption including a simple water trap, proved to operate reproducibly with 0.9 to 8.3%SD at 2.2–4.1 μg.m^{-3} (±670 pptv) (n = 4).

LODs were determined as ±4 ng.m^{-3} (2.16–5.73) for all compounds except for chloroform, benzene and toluene (41.4–96.0 ng.m^{-3}). This was caused by contamination originating from the P&T instrument. Storage of sampling tubes was checked. No contamination from outside on the stored tubes was found.

Next to the optimization of the sampling and analysis procedure, a simple calibration technique is presented. It is based on the equilibrium partitioning in a closed air-water system (Henry's law). The accuracy and precision were tested and proved to be good with a recovery of 102.0 ± 6.6% (n = 4) and with a reproducibility for each compound of 1.4 to 1.8%SD. On the contrary the measured concentrations generated by the DVP system[26] exceeded the expected concentrations.

Finally, the technique was applied in field measurements at a rural site. The reproducibity of the whole sampling and analysis technique showed average %SD for all VOCs of 0.6–7.3 at concentrations of 124 to 1374 ng.m^{-3}. Chloroform and 1,2-dichloroethane were detected at concentrations of 29 to 95 ng.m^{-3} with %SD from 21.3 to 39.4.

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