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Analysis of volatile organic compounds in air using retention indices together with a simple thermal desorption and cold trap method

Eeva Kivi-Etelälä¹, Olli Kostianen¹, Mariitta Kokko*

Department of Chemistry, P.O. Box 55, Fin-00014 University of Helsinki, Finland

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Abstract

A simple, low-cost thermal desorption and cold trap device was constructed and tested with a two-channel gas chromatograph equipped with SE-54 fused-silica capillary columns or a $\text{Al}_2\text{O}_3/\text{KCl}$ column and flame ionization, nitrogen–phosphorus or electron-capture detectors. Good repeatability was obtained in the identification of ten aromatic compounds, with use of *n*-alkanes as index compounds for the determination of retention indices. The performance of the equipment and method with real samples was evaluated for the determination of volatile halogenated compounds and small alcohols in urban air, and for the determination of N,N-dimethylformamide (DMF) in air nearby a chemical plant. A collection method was developed for highly volatile halogenated hydrocarbons and small polar alcohols. At ambient temperature they were not easily trapped completely and humidity was a problem. Drying tubes were needed in front of the sampling tubes, which were placed inside copper tubes refrigerated in a cold box. Compounds were reliably identified, and some of the halogenated compounds and DMF were determined quantitatively. © 1997 Elsevier Science B.V.

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1. Introduction

Monitoring of volatile organic compounds in air has increased considerably. Often these trace compounds need to be concentrated before high-resolution (HR) GC analysis, through collection onto solid adsorbent. Thermal desorption followed by cold trapping and flash heating offers significant advantages over solvent desorption, especially for automated on-site monitoring [1–14]. As well as

sample handling and preparation, thermal desorption eliminates the interfering solvent peak, allowing better recovery of the compounds. The whole sample can be analysed at one time with maximum sensitivity. Further, the sampling tubes can be re-used after desorption and purification. On the negative side the “one-shot” nature of the analysis means that all conditions have to be right the first time round. Many of the sorbents available for thermal desorption also are poorly adsorptive for polar compounds.

Thermal desorption of trapped compounds from an adsorbent is normally effected by electrical heating. To improve peak shape and resolution, the desorbed compounds are cryofocused then into a narrow band

*Corresponding author.

¹Present address: Finnish Institute for the Verification of Chemical Weapons Convention.

by cooling either the whole capillary column or just the first part. Pankow [8] and Pankow and Rosen [9] have shown that whole column cooling is effective for highly volatile compounds. However, the oven cooling requires a high consumption of liquid nitrogen or carbon dioxide and special construction of the oven.

Cryofocusing methods in which a small mantle is placed around either a short pre-column or the first part of the analytical column [13,14] are common in commercial systems. The column is cooled by leading liquid nitrogen as coolant through the mantle. Heating of the cooled section is done by direct electrical supply or by leading heated air through the trap in the same direction as the carrier gas flow.

The quantitative trapping of desorbed compounds must be assured. Short open tubular cryotrap do not always allow quantitative trapping of highly volatile compounds even at liquid nitrogen temperature. The retention in cooled traps can be improved by packing the traps with adsorbent material such as Tenax GC, Chromosorb W, Porapak Q or porous layer sieve. Alternatively thick-film columns (up to 100 μm) can be used as the cold trap, with the advantage of a reduced need for cooling.

In this paper we describe an efficient and low-cost thermal desorption and cold trap device, which can easily be constructed from readily available materials and is suitable for any GC system. The performance of the device was tested in the analysis of air samples for volatile halogenated hydrocarbons and small alcohols and for *N,N*-dimethylformamide (DMF). Retention index monitoring is shown to be reliable used in conjunction with the thermal desorption and cold trap method in identification of aromatic compounds common in ambient air.

2. Experimental

2.1. Sampling tubes and materials

Sampling tubes made of Pyrex glass tubing (200 mm \times 4 mm I.D.) were washed before use with Deconex, distilled water and diethyl ether and dried at 140°C for several hours. The tubes were filled with 300 mg of Tenax GC resin (60–80 mesh) or some other resin, held in place with small plugs of

purified silanized glass wool. Silanized glass wool was purified by Soxhlet extraction for 8 h with diethyl ether and dried at 140°C overnight. Solvents were analytical grade and redistilled before use. Four sampling tubes were simultaneously preconditioned by heating to 250°C in the GC oven for 8 h under purified helium gas purge of 50–100 ml/min. Before being led to the sample tubes, the helium was passed through a gas trap cooled in liquid nitrogen. After preconditioning, the tubes were equipped with Swagelok fittings and PTFE ferrules and stored in a freezer. Tenax GC is a suitable adsorbent for compounds like DMF with boiling points above 60°C. Its adsorption of water is negligible, and thermal stability is better than for the other porous polymers tested. For the halogenated compounds and alcohols, use was first made of sampling tubes filled with Tenax GC at the entrance and with Porapak N resin (80–100 mesh) at the exit. Later, Hayesep Q resin (80–100 mesh) was used because it is polar and better trapped the polar alcohols. The resins were purchased from Chrompack. Hayesep resins were also relatively clean and easy to purify. Water constitutes a problem, however, and to overcome this a drying tube was placed in front of the sampling tube. K_2CO_3 , MgCO_3 and $\text{Mg}(\text{ClO}_4)_2$ tubes were tested. The carbonate tubes can be dried and reused several times, but $\text{Mg}(\text{ClO}_4)_2$ tubes can be used only once. None of the tubes absorbs the investigated compounds irreversibly and no artefacts were found. $\text{Mg}(\text{ClO}_4)_2$ tubes proved to be most effective; no water was found when the air sampling velocity was between 50 and 200 ml/min and all joints were tightened with PTFE tape.

Highly volatile halogenated hydrocarbons and small polar alcohols were not easily trapped completely at ambient temperature. To overcome this problem, a cold box was constructed with three copper tubes attached to the walls and a poly(vinyl chloride) (PVC) tube connected to the lid (Fig. 1). Sampling tubes filled with Hayesep Q resin were placed inside the copper tubes and the box was filled with dry ice. The temperature inside the resin was -60°C at the beginning and nearly the same after 100 min; then it began to rise. CO_2 evaporated from dry ice in the box was conducted by the PVC tubing far away from the collection point. To avoid moisture, it is important that the collection tubes stay

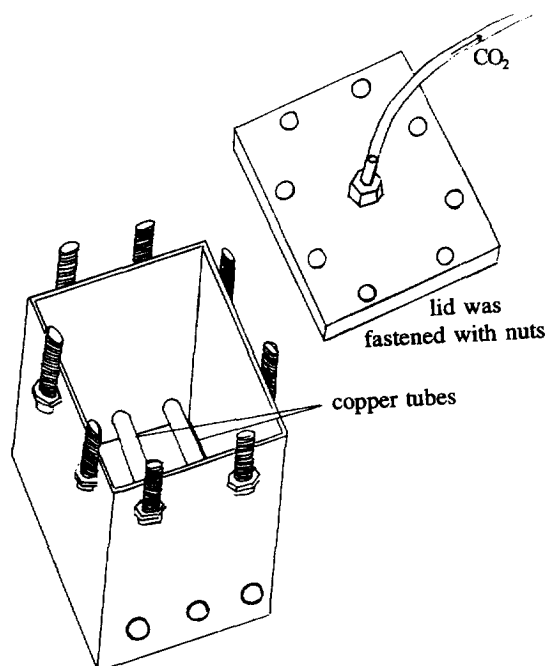


Fig. 1. Cold box filled with dry ice used to refrigerate the sampling tubes for collection of highly volatile compounds.

attached to the drying tubes until all the dry ice has evaporated from the box.

2.2. Instrumentation and chromatographic conditions

All samples were analysed with a Micromat HRGC 412 microcomputer-controlled gas chromatograph (HNU-Nordion) with two-channel integration and printing software. Two fused-silica capillary columns 50 m×0.32 mm I.D. with 1 μm cross-linked SE-54 film (dimethylpolysiloxane, 5% phenyl with 1% vinyl groups), from HNU-Nordion, were used with FID (flame ionization detection), ECD (electron-capture detection) or NPD (nitrogen–phosphorus detection). Standard chromatographic conditions were as follows: injector and detector temperature, 250°C (FID/NPD); carrier gas (He) flow-rate, 2 ml/min; splitting ratio, 1:10; septum purge, 10 ml/min; starting point of the temperature programme, 40°C for 2 min; temperature programming rate, 10°C/min; and end temperature, 220°C for 5 min. A flame ionization detector and an electron-

capture detector or two electron-capture detectors were used for highly volatile halogenated compounds, and since some of the compounds could not be separated with the SE-54 column, an Al₂O₃/KCl column (50 m×0.32 mm I.D.) from Chrompack was sometimes used in the second channel. With the Al₂O₃/KCl column the temperature was programmed from 100°C (2 min) to 200°C (5 min) at a rate of 10°C/min. Since 200°C is the maximum temperature of the column, the temperatures of injector and detectors were kept at 200°C.

The gas chromatograph was equipped with the simple, laboratory-made, thermal desorption and cold trap unit depicted in Fig. 2a [15]. Thermal desorption of the sample from the adsorbent was effected by connecting the sampling tube to the carrier gas stream with Swagelok-type fittings and PTFE ferrules and by heating it in an electrically regulated heating-block. The carrier gas was earlier purified by

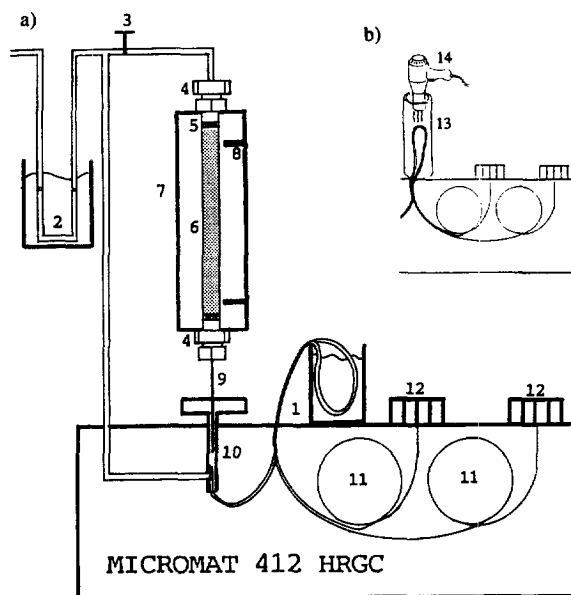


Fig. 2. (a) Schematic view of the thermal desorption and cold trap unit with standard gas chromatograph. 1=Dewar vessel containing liquid nitrogen; 2=trap filled with adsorbent; 3=shut-off valve; 4=Swagelok fitting; 5=silanized glass wool; 6=sample tube (200 mm×4 mm I.D.); 7=aluminium block; 8=heater; 9=needle; 10=injector; 11=column; 12=detector. (b) Injection of high boiling compounds is started by removing the column sections from the liquid nitrogen and leading hot air onto the cooled column sections through an open tubular tube (13) with a hot air gun (14).

leading it through a trap filled with Porapak N resin and immersed in liquid nitrogen. The sample was desorbed directly into the two columns of the GC system and immediately entered the cold trap where it was cryofocused into a narrow band. Without use of the cold trap, peaks were broad and the resolution poor. The cold trap unit consisted of one revolution of each of the fused-silica capillary columns, pulled out of the oven of the GC system and immersed into a Dewar vessel containing liquid nitrogen. After the desorption period the carrier gas flow was switched from the desorption block straight to the injector. The chromatographic run was started by removing the column sections from the liquid nitrogen to ambient temperature. Because of the low thermal mass of the fused-silica column, this is sufficient for compounds with boiling points below 80°C. For compounds with higher boiling points the run was started by leading hot air through an open tubular tube with a hot air gun onto the cooled column sections (Fig. 2b). The latter method was used because air samples also contain high boiling compounds.

2.3. Desorption conditions

During desorption of the sampling tube, the split valve of the gas chromatograph was kept closed. Desorption temperatures were 190–200°C, desorption flow-rate 4 ml/min, desorption times 10 min for aromatic standards and halogenated hydrocarbons and 15 min for DMF and polar alcohols, injection temperature about 250°C, temperature of the cold trap –186°C and injection time 2 min. Injection times of 1 to 10 min were tested and 1.5 min found to be sufficient. With the Al₂O₃/KCl column, the injection temperature had to be below 200°C.

3. Results and discussion

3.1. Analysis of aromatic compounds

The suitability of our laboratory-made thermal desorption and cold trap device for analysis of urban air was first tested by performing repeatability studies on ten aromatic compounds common in ambient air. Liquid standard mixtures of benzene,

toluene, ethylbenzene, styrene, *o*-xylene, isopropylbenzene, propylbenzene, *m*-ethyltoluene, 1,3,5-trimethylbenzene and 1,2,3-trimethylbenzene, and of seven alkanes (C₅–C₁₁) were prepared in glass bottles. Gas standard mixtures were prepared into Tedlar bags that had been filled with nitrogen gas (purity 99.98%) and several times evacuated with a water aspirator. After the purity of the bag was confirmed by GC, and the bag was filled with nitrogen, a known volume of liquid standard mixture was injected. After 30 min, and again 1.5 min before the standard mixture was used, the standards were mixed by hand-pressing the bag.

Two series of measurements were made. In the first series the gas standards in the Tedlar bag were injected with a gas-tight syringe onto the Tenax GC resin bed and the tube was immediately thermally desorbed and analysed; in the second series the liquid standards in glass bottles were spiked into the sampling tube and 10 l of urban air was sucked through the tube before thermal desorption and analysis. Compounds were identified by the retention index method, introduced by van den Dool and Kratz [16] and for many years used in our laboratory [17,18]. Alkanes (C₅–C₁₁) were used as the retention index standards. The equipment gave reliable results: for nine of the ten aromatic compounds the values of the retention indices, calculated from the two measurement series together, were highly reproducible (S.D. about 0.1 except for isopropylbenzene) (Table 1).

Table 1
Repeatability of retention indices of aromatic compounds common in ambient air when samples were analysed with laboratory-made thermal desorption and cold trap equipment

Compound	Retention index	S.D.
Benzene	654.1	0.1
Toluene	762.9	0.0
Ethylbenzene	860.9	0.1
Styrene	890.0	0.1
<i>o</i> -Xylene	892.1	0.1
Isopropylbenzene	928.7	0.2
<i>n</i> -Propylbenzene	960.7	0.1
<i>m</i> -Ethyltoluene	974.5	0.0
1,3,5-Trimethylbenzene	984.3	0.1
1,2,3-Trimethylbenzene	1027.0	0.0

3.2. Determination of halogenated hydrocarbons and small alcohols

As a next step in testing the method, real air samples were analyzed for halogenated hydrocarbons and small alcohols. Liquid standards of halogenated compounds were prepared in glass bottles. Compounds were measured into the bottles with a calibrated pipette or a microlitre syringe, the highly volatile compounds being injected below the liquid surface. Gas standards were prepared in Tedlar bags filled with purified helium (400 ml). The bags were handled similarly as for the gas standards of the aromatic hydrocarbons. Three different mixtures of standards were prepared: the first contained dichloromethane, trichloromethane, 1,2-dichloroethane, tetrachloromethane, trichloroethene and 1,1,2,2-tetrachloroethane and, into this, small alcohols (methanol, ethanol, propanol, isopropanol) were injected. The second mixture contained trichlorofluoromethane, dichloromethane, trichloromethane, 1,1,1-trichloroethane, tetrachloromethane and tetrachloroethene, and the third contained dichloromethane, trichloromethane, tetrachloromethane, 1,2-dichloroethane and trichloroethene.

The stability of the halogenated standards was tested using three different Tedlar bags and the third standard mixture. After three days the concentrations of halogenated methanes were greater than 95% and after seven days still about 80%. 1,2-Dichloroethane and trichloroethene were effectively adsorbed on the bag walls, so that after three days the concentrations were about 80% and after seven days only about 60%. Thus, whereas the standards prepared in glass bottles can be preserved for weeks in a refrigerator, those in gas bags should be prepared the day of the analysis.

Suitable injection volumes of the gas standards were investigated using a gas-tight syringe with PTFE tip plunger and the third standard mixture. Examination of the injection volumes against peak areas in gas chromatograms showed the correlation to be linear up to 3 μ l. Perhaps the syringe was not wholly gas tight or perhaps the larger gas volumes did not pass quantitatively into the syringe. In quantitative determinations injection volumes of standards were accordingly kept smaller than 3 μ l.

Fig. 3 displays chromatogram of the standard

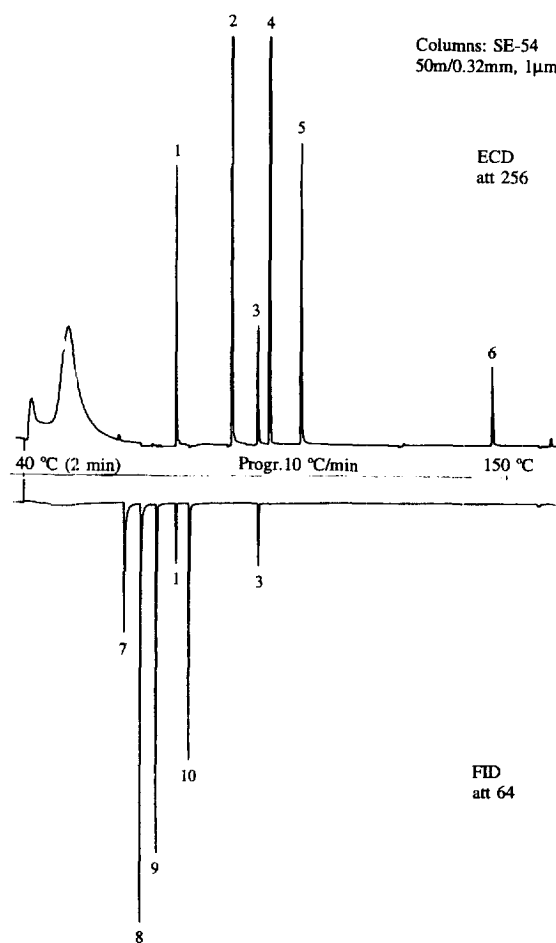


Fig. 3. Chromatogram of a standard mixture of halogenated hydrocarbons and alcohols. 1=Dichloromethane; 2=trichloromethane; 3=1,2-dichloroethane; 4=tetrachloromethane; 5=trichloroethene; 6=1,1,2,2-tetrachloroethane; 7=methanol; 8=ethanol; 9=isopropanol; 10=propanol.

mixture of volatile halogenated hydrocarbons and polar small alcohols and Fig. 4 the chromatogram of the second standard mixture of highly volatile halogenated hydrocarbons. The halogenated hydrocarbons were detected with ECD and the alcohols with FID; dichloromethane and 1,2-dichloroethane were also found with FID; the other halogenated hydrocarbons were not detected with FID because of their low concentrations.

In quantitative analysis the adsorption temperature, the concentration of the compound and the

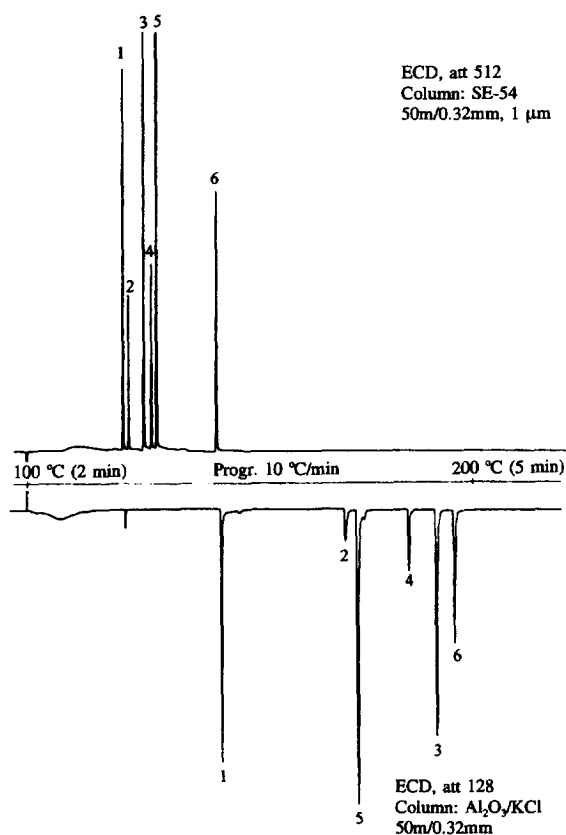


Fig. 4. Chromatogram of the second standard mixture of highly volatile halogenated hydrocarbons. 1=Trichlorofluoromethane; 2=dichloromethane; 3=trichloromethane; 4=1,1,1-trichloroethane; 5=tetrachloromethane; 6=tetrachloroethene.

flow-rate of the sampling markedly affect the retention volumes. The effects of humidity and of vapour concentration below 100 ppm, in turn, are not very significant [19]. The safe sampling volume can

be estimated in several ways, but usually it is at most 50–80% of the retention volume [19–24].

The effect of adsorption temperature was tested with dichloromethane, tetrachloromethane and vinyl chloride using XAD-2, Porapak N, Chromosorb 102 and Tenax GC resins (300 mg resin in sampling tube). The breakthrough volume (BTV, the volume of gas that can be passed through the adsorbent before the analyte begins to elute from the sampling tube) was determined at four different temperatures and extrapolated to 20°C by means of the linear relationship $\log V=1/T \cdot 10^3$. The sampling tube was connected between the GC injector and detector in the GC oven and stabilized at oven temperature over a period of 2 h. Injector temperature was kept the same as the oven temperature. Samples (about 100 ng) were led to the injector in gas form. The carrier gas flow was 50 ml/min, corresponding to the sampling velocity for low boiling compounds. The retention volume was calculated from the retention time, which is the time in which a single injection of the vapour emerges from the tube. As can be seen from Table 2, Porapak N resin gave the largest BTVs for dichloromethane and tetrachloromethane and it was also able to trap vinyl chloride (b.p. -13°C).

Effect of sampling velocity on BTV (7.7, 24, 92 and 248 ml/min) was tested with tetrachloromethane at concentration level 640 pg–800 ng. The increase of velocity did not markedly effect BTV, which was maximum at flow-rate of 24 ml/min.

When purification of sampling tubes filled with Porapak N proved complicated, a similar type resin, Hayesep Q, was tested as sampling material. Now retention volumes of the halogenated compounds were determined using the third standard mixture and two sampling tubes filled with Hayesep Q resin

Table 2

BTVs for dichloromethane, tetrachloromethane and vinyl chloride extrapolated to +20°C

Resin	BTV (l/sampling tube) ^a		
	Dichloromethane	Tetrachloromethane	Vinyl chloride
XAD-2	0.63	4.2	–
Porapak N	8.32	30.2	0.83
Chromosorb 102	3.02	15.8	–
Tenax GC	0.87	–	–

Samples were about 100 ng and the amount of resin in the sampling tube was 300 mg.

^a BTV the volume of gas that can be passed through the adsorbent before the analyte begins to elute from the sampling tube.

connected end-to-end. The standard mixture from the Tedlar bag was injected into the first tube, and pure helium from another Tedlar bag was sucked through both tubes while the latter was set in a cold box filled with dry ice. If the amount of helium was less than 3.6 l there was no breakthrough into the second tube. Thus, in real determinations our sample volumes were kept below 3 l.

Table 3 shows the concentrations of highly volatile halogenated hydrocarbons determined in air samples from a busy street. The sampling tubes were refrigerated during sampling and compounds were desorbed with our laboratory-made instrument. In quantitative analysis using external standard method, desorption percentages of investigated compounds have to be determined if the standards are injected directly into the GC injector. However, if the standards are injected into the sampling tube, as here, the conditions are the same for standards and real samples and the desorption percentages do not need to be determined. Measured by the relative standard deviations, the precision in the quantitation of trichlorofluoromethane, dichloromethane, trichloromethane and tetrachloromethane was closely similar, while the precision for 1,1,1-trichloroethane was a little better.

3.3. Analysis of DMF

As a further test of our thermal desorption and cold trap method, we determined DMF nearby a chemical plant employing it as a process solvent (Table 4). DMF was a suitable test compound because there were no other sources near the plant. In earlier work [25], DMF was measured by trapping it onto XAD-2 resin and extracting with diethyl ether, but the method proved time-consuming due to

slow solvent evaporation during concentration. The ventilation system in the plant was changed a few years after this work and today there is a 30 m-high chimney stack for gaseous emissions.

The BTV of DMF was determined using similar arrangements as for the halogenated hydrocarbons. The standard vapour pressure of DMF was obtained by bag dilution method: DMF was injected into a Tedlar bag filled with nitrogen, the contents of the bag were gently heated with a hot air gun and thoroughly mixed, and a sample of vaporized DMF (about 500 ng estimated by the standard solution) was taken from the bag in a gas-tight syringe. The sample was then injected through the GC injector, onto the resin bed of a sampling tube that was connected between the injector and detector, inside the GC oven. The carrier gas flow was 50 ml/min and the effluent was monitored with an NPD.

Retention volumes were calculated from retention times of DMF measured at six different temperatures ranging from 60 to 90°C and extrapolated to ambient temperature by means of the linear relationship $\log V = 1/T \cdot 10^3$. The slope of the line was 3.492, the intercept -7.161 and the correlation coefficient 0.993. The extrapolated retention volume was about 56 l/sampling tube (300 mg Tenax GC) at 20°C. An increase in the flow-rate from 50 to 700 ml/min had no significant effect on the BTV.

Quantitative standards of DMF were prepared by diluting DMF with analytical grade pentane. Quantitation was done by an external standard method. The standard solution of DMF was spiked onto the Tenax resin bed and most part of the solvent was removed by passing air through the sampling tube for 15 min. The DMF trapped on the resin was determined by the same method as the DMF in environmental samples. Standard tubes with variable DMF con-

Table 3
Concentrations of highly volatile halogenated hydrocarbons on a busy street

Compound	Concentration ($\mu\text{g}/\text{m}^3$)	S.D. ($\mu\text{g}/\text{m}^3$)	R.S.D. (%)
Trichlorofluoromethane	15.1	5.4	36
Dichloromethane	373	86.6	23
Trichloromethane	35.0	10.5	30
1,1,1-Trichloroethane	13.9	1.5	11
Tetrachloromethane	16.5	5.3	32

Five samples were collected and sampling volumes varied between 0.2 and 1.0 l.

Table 4
Amounts of DMF in air nearby a chemical plant

Sampling area/tube	Amounts of DMF (ng/m ³)	Distance between the sampling point and the plant (m)	Meteorological observations	
			Wind velocity; direction (degree)	Air pressure; temperature
1/1	250	300	3 m/s; 230–280°	1026 mbar; 9°C
1/2	1070	300	·	·
1/3	320	400	·	·
1/4	+	400	·	·
1/5	940	400	·	·
1/6	610	400	·	·
1/7	720	500	·	·
2/1	+	750	4–5 m/s; 280–340°	1024 mbar; 21°C
2/2	+	750	·	·
2/3	320	800	·	·
2/4	290	800	·	·
3/1	+	400	1 m/s; 280–340°	1020 mbar; 13°C
3/2	+	400	·	·
3/3	320	400	·	·
3/4	280	350	·	·
3/5	200	200	·	·
3/6	340	200	·	·
3/7	+	300	·	·
3/8	210	300	2 m/s; 160–200°	1022 mbar; 26°C
4/1 ^a	–	450	4 m/s; 280–340°	1018 mbar; 17°C
4/2 ^a	+	450	·	·
5/1	+	4000	4 m/s; 200–250°	1000 mbar; 15°C
5/2	–	5000	·	·
5/3	–	6500	·	·
5/4	–	7000	·	·

– DMF not found, + DMF found, but the amount below 5 ng/sample.

^a During this sampling the plant was closed for repairs and cleaning.

centrations were analysed before each sample series, for the preparation of calibration curves. The response range was linear between 5 and 40 ng.

Tests with retention indexes showed that DMF could be identified almost equally well on the basis of absolute retention times since there were no interfering peaks in chromatograms of the samples when the NPD was used. Usually, absolute retention times are not reliable enough due to changes in the chromatographic conditions. The temperature dependence of retention indexes is not so marked and retention index monitoring (RIM) is recommended, especially when samples are complex [16–18].

Retention index monitoring with a calibration

detector method may assist identification in certain cases [26]. For this, the effluent of one column is led to two capillaries, one connected to an analytical detector and the other to a calibration detector, or else two similar columns are connected in parallel to the same injector. When the “retention index” of DMF was calculated at the NPD channel using toluene and ethylbenzene as index standards at the FID channel, the reproducibility of the retention indexes in the sample runs was ± 0.9 index units. The reproducibility of absolute retention times of DMF calculated from the same runs was only slightly poorer: ± 1.4 s.

Samples were collected in the summer, when

temperatures were 9 to 26°C. Sampling areas (2 to 8 sampling points each) were located downwind from the plant at distances ranging from a few hundred metres to 3–7 km (Table 4). The meteorological observations were made at a synoptic weather station 10 km from the plant. Fig. 5a shows the chromatogram of a sample collected 300 m from the plant. A chromatogram of the background air (Fig. 5b) showed that there were no peaks interfering with DMF on the NPD channel. The sampling time was varied from 1 to 4 h and the sample volumes varied between 26 and 35 l. Our sampling times were too short to allow us to estimate the total or average emissions of DMF per day; the results describe only occasional emissions, which changed considerably from day-to-day.

Desorption efficiency was tested by spiking 0.5 µl of the standard solution onto the Tenax resin bed at the same concentration level as the actual samples. Then 30 l air was sucked through the tube and the

tube was analysed thermally. The absence of the DMF peak in a further analysis of the tube indicated complete desorption of DMF.

Recovery of DMF at the atmospheric concentration level was measured by injecting the DMF standard into the resin tube and sucking 10 l of air through the tube. The recovery was calculated by comparing the peak area with that in a direct injection of a standard solution through the injector and into the cold trap. The recovery was $81 \pm 3\%$ ($n=5$). Thus DMF was easily and reliably determined in air at a concentration level of 200 ng/m³ or greater.

4. Conclusions

Use of the thermal desorption method allows many samples to be analysed in a short time, without sample preparation and with no loss of easily volatile compounds. The amount of air collected can be smaller than when solvent extraction and larger amounts of resins are used. One disadvantage is that the analysis cannot be repeated.

Use of the thermal desorption and cold trap method together with the retention index method appears to provide reliable identifications of compounds. The repeatability of the retention indices of ten aromatic compounds was good; standard deviations below 0.06 index units.

Compounds were successfully desorbed with our laboratory-made device from various sampling tubes and adsorbents. Tenax GC was suitable for the sampling of non-polar compounds with boiling points above 60°C. It does not trap water and the thermal stability is good. Hayesep Q resin proved better for the sampling of small polar compounds and volatile halogenated hydrocarbons. To improve the collection of highly volatile compounds, a method of refrigerating the sampling tubes was developed. A drying tube connected in front of the sampling tube was required. Mg(ClO₄)₂ was the best of the drying materials tested. No humidity was found in samples at sampling rates of 50–200 ml/min.

DMF was collected into Tenax GC resin and the GC analysis was made with SE-54 columns (50 m×0.32 mm I.D. with 1.5 µm film). Halogenated

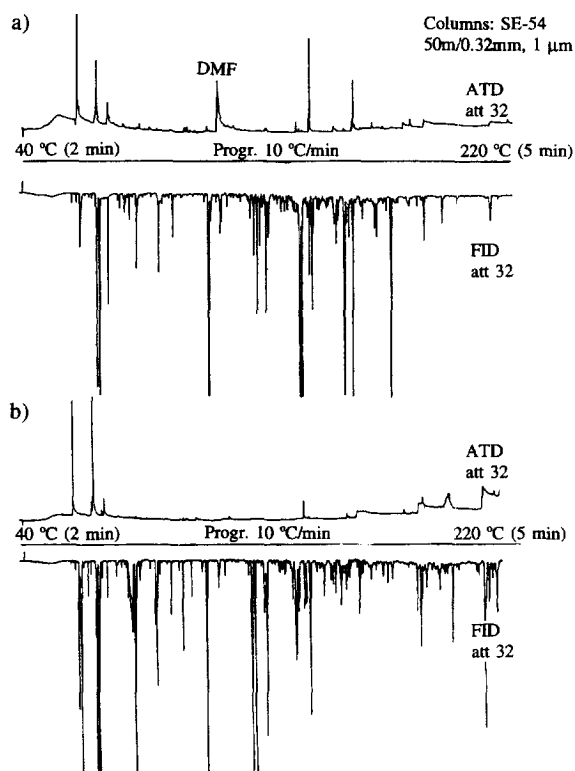


Fig. 5. (a) Chromatograms of the sample collected from in sampling point 1/2. (b) Background air nearby the chemical plant.

hydrocarbons and small alcohols were collected into refrigerated tubes containing Hayesep Q resin and analysed with the same SE-54 columns or with $\text{Al}_2\text{O}_3/\text{KCl}$ column (50 m \times 0.32 mm I.D.) replacing one SE-54 column. The BTV for DMF was about 56 l, but for selected halogenated compounds less than 3 l.

Our thermal desorption and cold trap device also proved rapid and convenient for quantitative analysis of DMF, which was easily and reliably determined in air at a concentration level of ng/m³. Quantitative determinations were also made for some halogenated hydrocarbons.

Acknowledgements

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