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GAS CHROMATOGRAPHIC DETERMINATION OF C_2–C_8 HYDROCARBONS AND HALOCARBONS IN AMBIENT AIR BY SIMULTANEOUS USE OF THREE DETECTORS

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SUMMARY

In order to determine trace amounts of several light non-methane hydrocarbons and halocarbons in ambient air a two-oven gas chromatograph was set up. This meets the requirements for the analysis of grab samples (stainless-steel containers) as well as of the contents of sorption tubes. The use of an alumina PLOT column enabled the separation of several substances with a wide range of volatility (ethane to xylene). A three-detector set-up gave additional information from the signal ratios of the different detectors.

INTRODUCTION

In recent years there has been considerable interest in the volatile organic compounds present in the atmosphere[1]. Intensive efforts have been made to improve sampling and analysing devices that meet the requirements for the determination of trace amounts of non-methane hydrocarbons (NMHC) and halogenated hydrocarbons (HalHC)[2–4]. The abundance of these species may vary considerably between polluted urban and industrial areas and remote rural and marine areas, as well as at different altitudes of the troposphere, particularly in and above the boundary layer.

The amounts of NMHC and HalHC found in air are normally in the low ppb-range, or even less. Their determination is mostly performed by sampling in the field with subsequent analysis in the laboratory. As sampling devices, cryo-traps, sorption tubes and grab samplers are used. The analysis is mostly carried out by gas chromatography (GC) with either mass spectrometric or ionization detectors. The chromatographic columns and detectors should be selected according to the compound or group of compounds to be analysed[5–8]. For complex mixtures it is feasible to use different types of detectors simultaneously. In that case different set-ups are possible due to the qualities of the detectors employed.

In general, the requirements of sampling and analysing devices can be summarized as follows:

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(1) regardless of the method employed, the sampling must be representative and quantitative

(2) the sampling procedure should be so simple that it can be performed by unskilled persons and under difficult circumstances, *e.g.*, aboard an airplane or in regions where no electric power supply is available

(3) no deterioration or losses of the sample between the sampling and the analysis most occur

In this paper a GC set-up for the routine analysis of light NMHC (ethane to xylene) and light HalHC collected in ambient air with sorption tubes as well as with grab samples is described. The advantages and difficulties in the use of a triple detector system are discussed.

EXPERIMENTAL

Sampling techniques

Electropolished stainless-steel containers (volume 2 dm^3) with metal bellow valves (Nupro) were used as grab samplers[4]. The containers were evacuated (10^{-5} hPa) under heating (150°C) for 12 h. The advantage of grab sampling is that no further equipment is needed (pumps, cooling devices, etc.). On the other hand, the sample volume is limited and collecting over a long period is not possible. For that reason sorption tubes [stainless steel, 15 cm × 1/8 in. O.D.; packing 5 cm Tenax TA (60–80 mesh) and 5 cm Carbosphere S (80–100 mesh) in series] were also used.

Fig. 1 shows a schematic diagram of the sampling devices for sorption tubes. For grab samples, the drying tube (magnesium perchlorate) is mounted between the container and the enrichment column (fig. 2), whereas for the sorption tubes the water has to be trapped in front of the tube. This is unavoidable, particularly when collecting at subambient temperatures, in order to prevent the tubes being blocked by condensed water. As cooling device, a copper jacket is attached to a copper bar immersed into liquid nitrogen. The temperature is regulated by the level of liquid nitrogen in the dewar vessel. The flow of air (100 ml min^{-1}) is controlled by means of a needle valve and monitored with a mass flow meter. The sorption tubes were purged in a stream of nitrogen (99.996%) at 300°C for 24 h. Subsequently they were conditioned by performing five adsorption/desorption circles with ambient air at subambient temperatures. After desorption of the samples, further reconditioning is not necessary. The sorption tubes are then closed with brass caps.

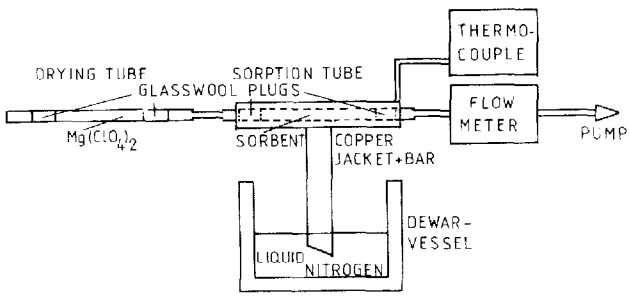

Fig. 1. Schematic drawing of the sampling devices for sorption tubes.

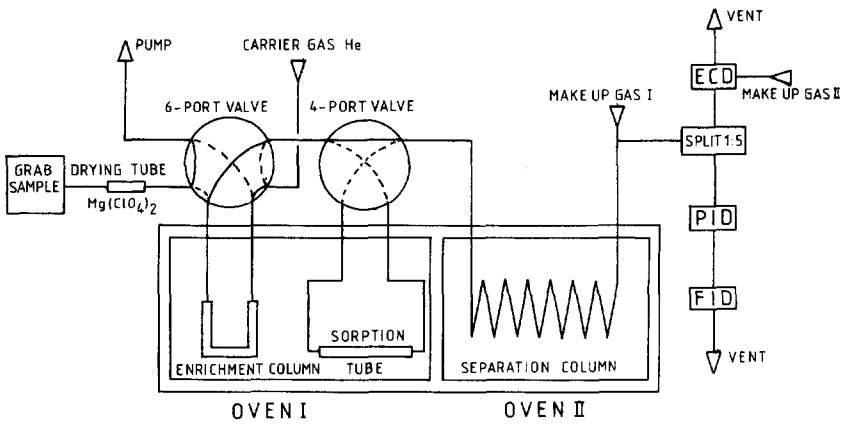

Fig. 2. Schematic drawing of the chromatographic set-up.

Analysis

A schematic diagram of the GC set-up is given in Fig. 2. The gas chromatograph is a Sichromat "2" (Siemens) with two insulated ovens. Both ovens can be operated at subambient temperatures. They are cooled by a stream of liquid nitrogen regulated by solenoid valves. Oven I contains the enrichment column for the analysis of grab samples and the sorption tube which can be analysed alternatively. The enrichment column (stainless steel, 15 cm × 1/8 in. O.D.) is packed with Spherosil XOA 200 (80–100 mesh) (Supelco) and Carbosieve B (60–80 mesh) (Supelco) in series. For the preconcentration step (dashed line) it is cooled to −100°C. Subsequently the six-port valve is switched into the "desorption" position (solid line) and oven I is heated to 280°C at a rate of 25°C min^{-1}. The sorption tubes are analysed similarly by using the separate circuit with the four-port valve.

The separation column is mounted in oven II. it is a 50-m alumina PLOT column (WGA) which separates the C_2–C_8 fraction of NMHC as well as the light halocarbons. In contrast to the formerly used packed columns with liquid stationary phases, no bleeding can occur even at high temperatures. Additionally, this column can be conditioned simply by temperature-programmed heating. The optimum carrier gas (99.996% helium) flow-rate was found to be 2.5 ml min^{-1}. After the column a flow-rate of 35 ml min^{-1} nitrogen is added as a make-up gas for the detectors. The gas stream is then split, since the electron-capture detector (Siemens) is mounted parallel to a tandem configuration of a photoionization detection (PID) system (HNU-PI 52, 10.2 eV) and a flame ionization detector (Siemens). A splitting ratio of 1:5 (ECD:PID + FID) was found to be suitable. It was then necessary to provide an additional make-up gas line for the electron-capture detector to achieve the optimum flow-rate of 25 ml min^{-1} nitrogen.

The three detectors were heated to 280°C. The analysis was performed by temperature programming. In order to achieve a preconcentration on the separation column, oven II was maintained at −80°C during the heating of the enrichment column (10 min). Then it was temperature programmed as follows: from −80 to 60°C at a rate of 25°C min^{-1}, from 60 to 250°C at a rate of 15°C min^{-1} and finally from 250 to 280°C at a rate of 20°C min^{-1}. It was then maintained at 280°C during the

entire analysis (40 min). For grab samples, 0.5–1.5 m^3 were analysed, for sorption tubes, up to 10 dm^3. The PID and FID signals were recorded on a Shimadzu C-R2A X two-channel recorder, ECD signals on a separate recorder (Linseis) attached to an Autolab Minigrator (Spectra Physics). The peaks were identified according to their retention times and the signal ratios of the different detectors. For quantitative evaluation the peak areas were compared with peak areas from the analysis of gas mixtures, prepared in a static dilution system using pure compounds and purified synthetic air.

RESULTS AND DISCUSSION

Since air samples from polluted areas as well as from unpolluted ones should be analysed, it was necessary to investigate whether the chromatographic set-up, particularly the combination of three detectors, meets the requirements of reproducibility, detection limits and range of detection. This is very important, since the compositions vary considerably, especially in and above the boundary layer. In addition, the concentrations of different groups of compounds differ according to their reactivity and residence time. Therefore different set-ups for more than one detector are possible. First, an in-series (tandem) construction is conceivable[7,8]. This means low detection limits, because the whole effluent stream from the separation column passes all detectors. However, only one destructive detector (*e.g.*, FID, FPD) can be employed. Additionally all the detectors must have approximately the same sensitivity because an overload of only one detector would always require a second run of the same sample but with a smaller volume. Another possibility is a parallel configuration of detectors[6]. The optimum linear dynamic range for each detector can be achieved by regulating the effluent flow-rate through each detector by means of the splitting ratio. Since the ECD has a considerably smaller dynamic range than the PID and the FID it is best to split the stream of effluent between the ECD and a tandem configuration of PID and FID. A typical chromatogram of an ambient air sample collected in an urban area (city of Darmstadt) is shown in Fig. 3. The FID trace (3a) has a negative baseline, since it was recorded with the PID trace (3b) on a two-channel recorder. The chromatogram shows a good separation for the C_2–C_8 fraction of NMHC. This is remarkable, since a co-elution of the C_2 fraction or the C_3-fraction often happened with the formerly used columns[6]. Thus the alumina PLOT column provides good separation properties for the compounds that have boiling points ranging from -104 to $+144$°C.

We decided to use a 10.2-eV lamp for the PID, since it promised the best detection limits for aromatics and alkenes[5]. A lamp of higher energy (*e.g.*, 11.7 eV) would yield a better response for light alkanes. This was, however, not considered necessary, because their determination by FID is reliable. The separation of light halogenated hydrocarbons (C_2Cl_4, C_2HCl_3, CCl_4, CH_3CCl_3, $CHCl_3$, F11, CH_2Cl_2, F12) is shown by the ECD trace in Fig. 3c. The ECD trace shows one major problem in analysing all compounds of a complex environmental sample in one experiment. While some peaks are hardly recognizable, others reach almost the upper detection limit. This problem is due either to the large differences in the concentrations or to the detector sensitivity which is effected by the number of halogen atoms in a compound. Therefore the splitting (1:5, ECD:PID + FID) of the carrier gas best meets

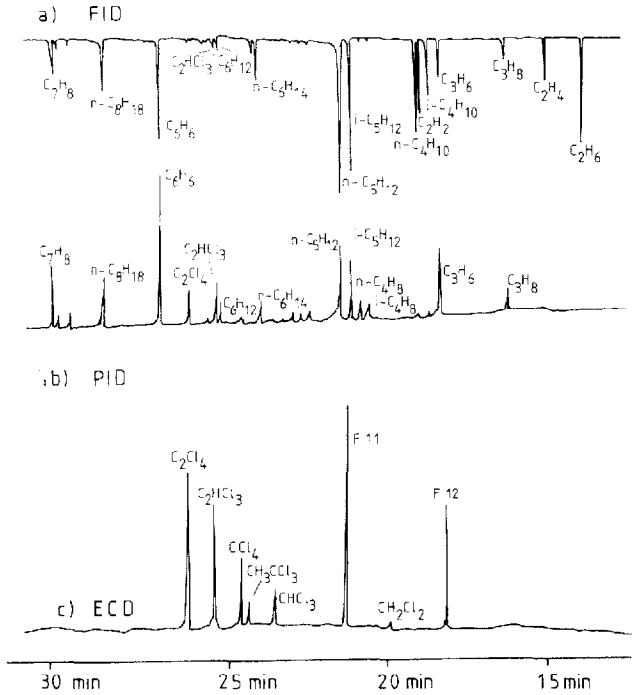

Fig. 3. Chromatogram of an ambient air sample recorded with three different detectors.

the requirements. No effect of the temperature program on the splitting ratio was observed.

For the evaluation of the detection limits, samples prepared in a static dilution system were analysed. Each sample was analysed five times in order to test the reproducibility. In Table I, the detection limits (3σ-value) and reproducibilities are listed. In general these detection limits are slightly higher than those reported for tandem set-ups[7]. This might result from the splitting of the effluent. Anyhow, the detection limits are well within the range for environmental samples, even from remote areas. One exception is that for ethyne, which has a considerable higher detection limit and poor reproducibility. A conceivable explanation is that this compound, due to its higher polarity, is irreversibly adsorbed on the container surface. This might result from ageing of the surface by means of water vapour or compounds of low volatility, since older containers which had gone through several sampling/heating circles showed higher losses than new ones.

Sorption tubes were employed for sampling over long periods at very low environmental concentrations. Since the whole C_2–C_8 fraction should be collected, in-series packing of organic polymer (Tenax TA, 60–80 mesh) and graphitized carbon black (Carbosphere S, 80–100 mesh) was used. This combination should ensure that the species of low volatility are adsorbed on the Tenax[2,3,9] while the more volatile species are unretained. The latter are subsequently trapped on the Carbosphere S. In this way an irreversible adsorption of compounds of low volatility on the Carbosphere S should be avoided. The thermal desorption is carried out with a reversed

TABLE I

DETECTION LIMITS (pptv) OF SOME NMHC AND HALHC AND REPRODUCIBILITIES (%) FOR DIFFERENT DETECTORS (1 dm^3 STANDARD TEMPERATURE AND PRESSURE)

Compound	*ECD*	*%*	*PID*	*%*	*FID*	*%*
C_2H_6	–	–	–	–	24	± 4.8
C_2H_4	–	–	–	–	24	± 4.3
C_3H_8	–	–	–	–	12	± 5.7
C_3H_6	–	–	12	±3.0	12	± 5.2
n-C_4H_{10}	–	–	100	±2.3	12	± 2.0
n-C_4H_8	–	–	12	±2.7	50	± 2.9
n-C_5H_{12}	–	–	50	±5.6	12	± 4.7
C_6H_6	–	–	5	±3.6	24	± 4.2
n-C_8H_{18}	–	–	90	±5.7	24	± 1.7
CH_2Cl_2	10	± 1.9	50	±7.1	–	–
CH_3Cl	90	±12.0	–	–	120	±13.2
CCl_4	5	± 0.9	–	–	–	–
$CHCl_3$	5	± 3.5	–	–	–	–
CCl_3F	10	± 7.0	–	–	–	–
C_2HCl_3	1	± 2.0	5	±2.0	24	± 1.9
C_2Cl_4	1	± 1.7	5	±2.9	–	–
C_2H_2	–	–	–	–	240	±13.2

gas stream. This is important, because the desorption temperature is limited by the gas chromatograph as well as by the Tenax. A direct comparison of grab sample and sorption tube was conducted by sampling from a 10-dm^3 stainless-steel container containing a synthetic mixture of NMHC and HalHC in approximately tropospheric concentrations. Table II lists the recoveries (percentage of synthetic mixture) for different sample volumes and temperatures. If it is required to collect only the high boiling compounds, this can be achieved by means of temperature regulation. All compounds can be determined quantitatively for a sampling temperature of −50°C, at which the sample volume can be increased to 10 dm^3 without significant losses.

TABLE II

RECOVERIES FROM SORPTION TUBES (%) FOR DIFFERENT SAMPLING VOLUMES AND TEMPERATURES

Compound	*ppbv*	*+21°C*		*0°C*		*−50°C*	
		0.5 dm^3	*0.25 dm^3*	*0.5 dm^3*	*0.25 dm^3*	*0.5 dm^3*	*0.25 dm^3*
C_2H_6	3.5	53 ± 5	34 ± 8	62 ± 1	60 ± 7	97 ± 5	100 ± 12
C_2H_4	0.5	42 ± 6	30 ± 3	52 ± 6	48 ± 8	88 ± 8	58 ± 12
C_3H_8	2.7	76 ± 5	58 ± 12	70 ± 8	69 ± 7	95 ± 8	88 ± 7
C_3H_6	1.5	71 ± 6	48 ± 7	60 ± 8	55 ± 5	94 ± 4	88 ± 7
n-C_4H_{10}	2.7	72 ± 9	55 ± 4	77 ± 5	50 ± 6	101 ± 3	92 ± 7
C_6H_6	4.5	98 ± 6	101 ± 5	98 ± 8	97 ± 5	98 ± 5	101 ± 7
CCl_4	0.25	66 ± 7	34 ± 8	78 ± 6	56 ± 7	82 ± 6	77 ± 8
C_2HCl_3	0.5	100 ± 8	100 ± 6	98 ± 5	95 ± 6	100 ± 8	87 ± 8
C_2Cl_4	0.5	88 ± 5	85 ± 9	89 ± 4	83 ± 4	87 ± 7	89 ± 6

Ethyne could not be detected with the sorption tubes, either from synthetic mixtures or from natural air samples. A major disadvantage is that aliquots of the samples cannot be analysed, *i.e.*, when the concentrations cannot be estimated in advance, always two or more samples must be collected. The application of sorption tubes requires considerable efforts concerning the equipment (pump, cooling device, power supply, etc.). Therefore it seems appropriate only for special tasks, *e.g.*, sampling of low concentrations of NMHC and HalHC above the boundary layer of the atmosphere or in remote areas.

CONCLUSIONS

A gas chromatographic set-up is presented that allows the routine analysis of trace amounts of light NMHC and light HalHC in one experiment. Good reproducibilities are achieved by employing a two-oven technique for the enrichment column and the separation column. The detection limits meet the requirements for ambient air samples collected in urban areas as well as in remote areas. The alumina PLOT column enables the separation of compounds having boiling points in the range from -104 to $+144$°C. The three-detector set-up gives additional information from the signal ratios.

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