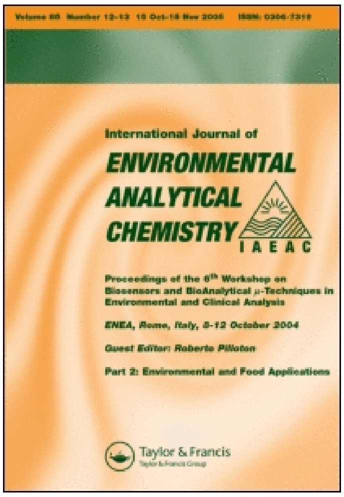

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Problems Connected with the Analysis of Halocarbons and Hydrocarbons in the Non-Urban Atmosphere†

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The problems connected with the measurement of hydrocarbons outside urban areas are considerable: The atmospheric mixing ratios of most of the hydrocarbons are very low—from a few ppb down to some ppt; the mixture of hydrocarbons is extremely complex, ranging from light *n*-alkanes to alkyl benzenes and terpenes; for measurements in remote areas the logistic conditions often restrict the instrumentation which can be used for sample collection or *in situ* measurements (such as lack of electric power supply, weight restrictions etc.). Nevertheless, sensitive and sufficiently reliable measurements of hydrocarbons in the non-urban atmosphere are important. Hydrocarbons are important factors in the tropospheric photochemistry (e.g. ozone formation) and can be used as valuable tracers for man-made atmospheric pollutants etc.

Other useful tracers for anthropogenic emission are halocarbons such as dichlormethane, tri- and tetrachloroethen etc.

The impact of man-made hydrocarbons on the chemistry of the troposphere can only be understood if the extent of natural (biogenic) contributions is known. From measurements of a large variety of hydrocarbons and halocarbons it is often possible to obtain information about the sources of the most important atmospheric hydrocar-

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bon species, even for trace gases with both significant anthropogenic and biogenic sources.

In this presentation some of the problems and their solutions connected with such measurements of atmospheric hydrocarbons and halocarbons are presented and discussed. Some of the results obtained by several series of measurements are described, indicating that man-made as well as biogenic hydrocarbons can be important factors for the chemistry of the atmosphere.

KEY WORDS: Non-urban atmosphere, hydrocarbons, halocarbons, tracers, background measurements, grab sampling, preconcentration, gas chromatography, photochemical history.

INTRODUCTION

During the past years the interest in measurements of hydrocarbons, halocarbons and related compounds in the non-urban atmosphere has been continuously increasing.[1-24]

This is due mainly to the observation that even outside polluted areas many of the hydrocarbons can play an important role for the chemistry of the atmosphere. Due to their high photochemical reactivity and complex photooxidation mechanisms many of the hydrocarbons are relevant participants in the photochemical atmospheric reaction chains and cycles even if they are present in levels as low as a few ppb or even fractions of a ppb. There is also an increasing concern about long-term effects on the climate caused by the impact of various trace gases on the tropospheric and stratospheric photochemistry and radiation budget.[25] But also for the purpose of air mass identification and characterization as well as the estimate of the "photochemical history" measurements of atmospheric trace gases have been used successfully.[1,11,14,15,26]

The trace gas pattern in the atmosphere is quite complex—even outside urban or industrialized areas. Engine exhaust, natural gas leakage, solvent evaporation, plant emissions, etc. contribute a large variety of different organic substances which can be observed at varying levels in the atmosphere. The mixing ratios of these trace gases may be as low as a few ppb or even down to a fraction of ppt over very remote areas. Due to the extremely complex trace gas pattern and the very low atmospheric mixing ratios of most of these trace gases such measurements require specially adapted or developed techniques. The most suitable method is probably gas chromatography in combination with a preconcentration step.[18,19,21,27-34]

However there is a lack of techniques which allow measurements of a wider range of trace gases on a routine basis with adequate precision, sensitivity and selectivity.

For some years our institute has been engaged in measurements of atmospheric hydrocarbons and—although to a lesser extent—halocarbons in the remote atmosphere. In this paper a gas chromatographic procedure is described which allows the measurement of a large variety of low and medium molecular weight hydrocarbons at the ppb and sub-ppb level. Some of the problems connected with such measurements and their solutions are discussed and examples of measurements in air masses of different pollution levels are presented.

GENERAL CONSIDERATIONS

As mentioned above, we have to deal with trace gas mixing ratios down to a few ppt. For low molecular weight hydrocarbons this corresponds to some ten picogram per dm^3 of air (at STP). This is roughly equivalent to the lower limit of detection for a reasonably narrow chromatographic peak if an ionization detector with good sensitivity (flame- or photoionization and electron capture detection) is used for detection. There are some compounds which could be measured with considerably higher sensitivity—such as some halocarbons with electron capture detection—but with the intention of measuring a broad range of different trace gases in mind we should base our considerations on a more general detection method, e.g. flame ionization detection, which gives a reasonable response for most organic trace gases. Consequently, we have to use a sample volume of 1–2 dm^3 of air (STP) for our measurements. This means that the halocarbons and hydrocarbons have to be separated not only from each other but also from some minor constituents of air—such as water vapor or carbon dioxide—which are several orders of magnitude more abundant in ambient air. An overview of the abundance of various atmospheric constituents is given in Figure 1.

There is another important point which has to be considered in the design of a measurement procedure for trace gases in the non-

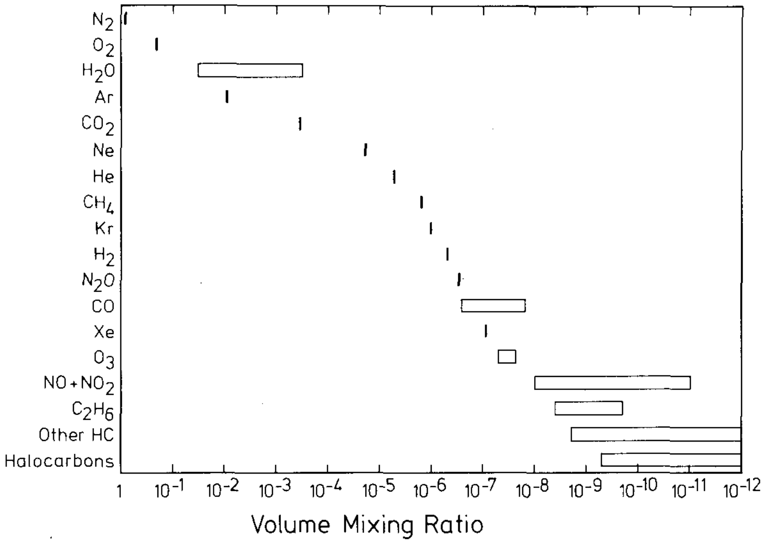

FIGURE 1 Abundance of different atmospheric constituents in non-urban air.

urban atmosphere. In order to avoid—or at least minimize—the influence of nearby anthropogenic trace gas sources it is necessary to make measurements in rather remote locations or on board ships or aeroplanes. This restricts considerably the type and amount of equipment which can be used (power requirements, space and weight limitations, etc.). Ideally the technique for the measurements or the collection of the samples in the field should be simple enough to be made by one operator and the equipment should be light enough to be transported by all usual means of transportation. Furthermore, it should be reliable and require no major preparations or checks in the field. This restricts the possible procedures considerably but it is equally important to have a method which allows sample collection or measurements at suitable places as to have a sufficiently sensitive and selective technique. It is evident that these conditions can be much easier met by a sampling procedure than by a complete mobile analytical instrument.

SAMPLE COLLECTION AND PRECONCENTRATION

The easiest way to collect air samples is the so-called "grab sampling". The collection procedure itself consists only in the opening and subsequent closing of the valve of a previously evacuated container. All other steps of the measurement procedure can be made in the laboratory. The disadvantage of this procedure is the limitation of the sample volume or the use of extremely large sample containers and the problem of the stability of the trace gases in the sample container.

Another rather simple way to collect samples of atmospheric trace gases is adsorptive sampling on solid sorbents such as Tenax, XAD-resins, Carbosieve, etc. However, the sampling efficiency of these adsorbents for light hydrocarbons, light fluorocarbons and comparable trace gases of high volatility is often not very good. Furthermore the formation of artefacts during sampling, storage or sample desorption has been reported.[35] For these reasons we decided to collect whole air samples in spite of the limited sample volume. There are several ways to increase the pressure in the sample container above ambient pressure and thus to increase the sample volume. Pumps are often used to pressurize air samples;[18,19,27] however, we observed that even "Metal-bellows" pumps cause a slight contamination of the air sample with light alkenes and some halocarbons in the ppt range. This is most probably due to the teflon sealings of the pump valves. Indications for similar contamination effects have been reported by Cronn and Robinson.[28] Another problem connected with the use of pumps is the substantial temperature increase in the air due to the fast—and thus "quasi adiabatic"—compression process. This causes the decomposition or rearrangement of thermally less stable trace gases.

Another technique to collect whole air samples at increased pressure is the so-called "cryogenic collection". This procedure is based on the fact that at ground level the partial pressure of air at the temperature of liquid nitrogen is only about one-half of the atmospheric pressure. This allows us to condense large volumes of air into a small sample container. The maximum pressure is only limited by the mechanical stability of the container. Since during this procedure the collected air has no contact with any pumps, valves etc. except the sample container, this method does not cause any additional contamination. However, this collection method requires quite substantial amounts of liquid nitrogen and thus causes considerable logistic problems—especially for remote areas.

Special care has to be taken with the containers used for collection and storage of the air samples. Stainless steel flasks with metal bellows valves have been successfully used for the collection of whole air samples and subsequent analyses of a variety of different trace gases.[2,6,7,9,18,19,21,23,27,29,30,31] The necessary pretreatment and cleaning procedure for this type of sampling flask has been described by Rudolph *et al.*[31] It should be noted that it is essential to avoid all contact of the air sample during storage with polymeric seals, gaskets, etc. The substantial contamination effects which can be caused by even very small parts of organic polymers in contact with the air sample is demonstrated by the results shown in Table I.

TABLE I

Relative change in the composition of an air sample collected in containers equipped with a metal bellows sealed valve with a Kel-F tip compared to containers with all stainless steel valves. Average and variance from five pairs of measurements.

Compound	Relative change (%)	Variance (%)
C_2H_6	+0.5	±0.7
C_2H_2	−0.2	±2
C_3H_8	−1	±1
C_3H_6	+1	±4
n-C_5H_{12}	+2	±3
n-C_6H_{14}	+88	±30
n-C_7H_{16}	+28	±15
C_6H_6	+7	±9
F-12	+2	±1
F-22	+80	±26
F-113	+6	±1
CH_3Cl	+12	±7
CH_2Cl_2	+6	±1
$CHCl_3$	+9	±8
CCl_4	−0.6	±1
C_2HCl_3	+133	±27
C_2Cl_4	+92	±70
CH_3CCl_3	+11	±9

This shows the comparison of sample containers with all stainless steel valves (the valves are closed by a high-precision stainless steel tip fitting into a stainless steel cone) and with valves equipped with Kel-F tips instead of stainless steel tips. Five pairs of sample containers were collected over the North Sea and the results of the measurements of the two types of containers compared. The trace gas mixing ratios were in the lower ppb and sub-ppb range. From the results it is evident that even an extremely small polymeric part can cause contamination in the lower ppb and sub-ppb range. This rules out the use of any type of polymeric seals, connections etc. in sample containers which are to be used for the measurement of trace gases in the lower ppb and sub-ppb range. It is evident that extreme care has to be taken in the collection of air samples with such low trace gas mixing ratios in order to ensure sample integrity.

SAMPLE PRECONCENTRATION AND INJECTION

As estimated in the previous chapter a rather large sample volume of about 1 dm^3 (STP) is necessary to achieve the desired lower limits of detection of some ppt for the various hydrocarbons and halocarbons in the atmosphere. Consequently some preconcentration procedure is necessary in order to reduce the sample size sufficiently to allow injection and separation in a gas chromatographic system. A separation of nitrogen and oxygen (and some of the very light trace components such as CO etc.) from the low and medium molecular weight hydrocarbons and halocarbons can be achieved simply by adsorbing the trace gases on some solid sorbent such as porous silica, alumina, graphite or even porous glass beads at subambient temperatures. A small stainless steel precolumn (15 cm length, 2 mm i.d.) packed with porous glass beads (0.35 micrometer) at about 80 K adsorbs all hydrocarbons—except methane—and halocarbons but does not retain nitrogen and oxygen. The advantage of this type of preconcentration column is that porous glass beads can easily be cleaned and cause neither detectable blank values nor any measurable memory effects from one sample to the next. Furthermore desorption is fast and complete at quite moderate temperatures (see below) and thus the risk of thermal decomposition of certain trace components during the desorption process is minimized. The preconcentration column is housed in a small dewar (4 × 7 × 12 cm) which can be cooled by injection of liquid nitrogen. The precolumn can be heated by direct resistance heating with the column itself as resistance. This allows a very fast heating rate of more than 25 K sec^{-1}.

The temperatures are measured with thermocouples and are electronically controlled. Subambient temperatures are constant within a range of ±2 K, temperatures above 300 K are constant within ±0.5 K. This system allows us to easily adapt the adsorption and desorption temperatures, heating rate etc. to the desired optimum conditions.

The sample preconcentration and injection procedure can best be described from Figure 2. The complete system, which also in-

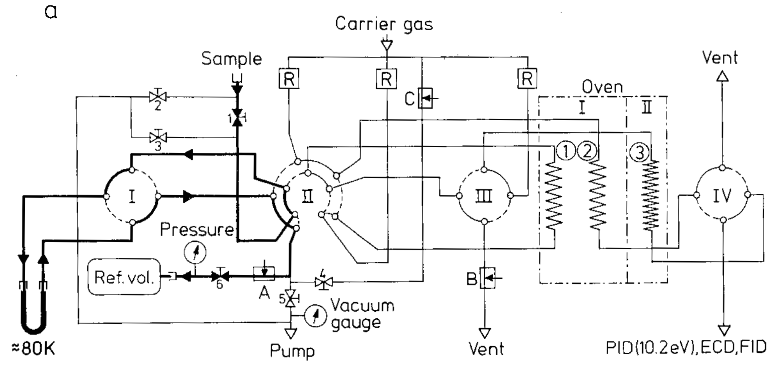

FIGURE 2(a) Sample preconcentration.

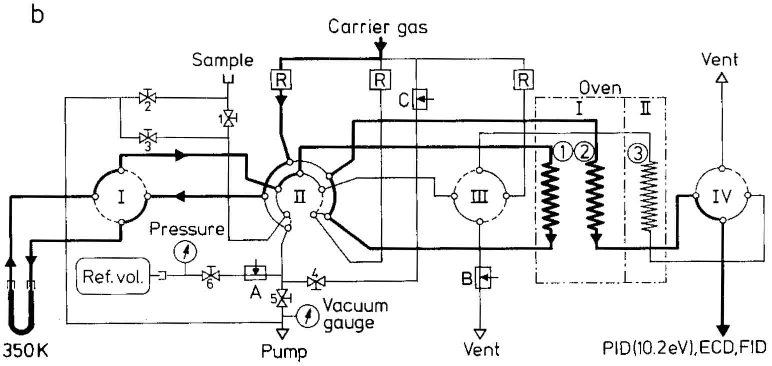

FIGURE 2(b) Sample injection and preseparation on first column.

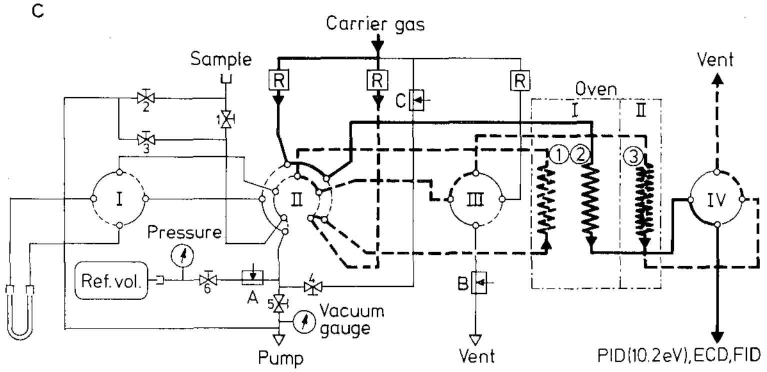

FIGURE 2(c) Separation of light fraction on second column and transfer of heavier fraction from first column to capillary column.

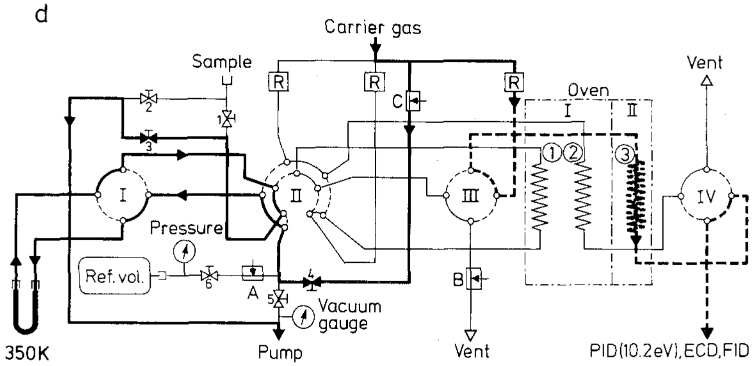

FIGURE 2(d) Separation of heavier fraction on capillary column and reconditioning of preconcentration column.

FIGURE 2 Schematic drawing of sample preconcentration and column switching system. I–IV: multi port valves; 1–6: shut off valves; R: pressure regulators; A, B, C: needle valves.

corporates the column switching and backflush valves, consists of four multi-port valves (three four-port and one ten-port valve) and six shut-off valves (Nupro metal bellows valves). All valves are pneumatically actuated and the complete system can be operated automatically. All valves, connecting lines etc. are kept at 350 K in order to minimize adsorption effects, wall losses, contaminations etc.

Prior to sample enrichment the dead-volume between valve 1 and the sample container is evacuated (about 10^{-2} mb) by opening valve 2 and then flushed twice with a small volume of the sample (roughly 5 cm^3 STP) in order to avoid contamination effects from laboratory air or previous samples. Then the sample is pumped via the four-port valve (I) and the ten-port valve (II) through the sample preconcentration loop into the previously evacuated reference volume. During this step the enrichment column is kept at 80 K, the sample flow rate adjusted to about 50 $cm^3 \, min^{-1}$ (STP) with a metal bellows sealed needle valve (A). The sample flow is schematically shown in Figure 2(a). The total sample volume is determined from the measured final pressure in the reference volume (10 dm^3). At these conditions the light hydrocarbons (C_2 and above) and the halocarbons are quantitatively retained in the preconcentration column. Immediately after preconcentration the sample loop is evacuated to a pressure of less than 0.1 mb with the sample loop still at 80 K (valves 1 and 6 closed, valve 5 open) in order to minimize the volume of the preconcentrated sample.

Then the four-port valve (I) and the ten-port valve (II) are rotated and the sample loop is heated to 350 K within less than 20 seconds. Directly after the final desorption temperature is reached, the four-port valve (I) is switched again and the sample injected into the carrier gas stream (Figure 2(b)). The separation of the sample loop from the carrier gas stream with four-port valve (I) during the heating of the sample loop ensures that all components are injected simultaneously onto the chromatographic column and avoids possible fractionation and tailing effects which might be caused by the 20 sec heating interval. From Figure 3 it can be seen that at a final desorption temperature of 350 K the injection of low and medium molecular weight hydrocarbons and halocarbons is complete within the reproducibility of the measurements (about 5%, see below). There is a slight indication that the yield for acetaldehyde is decreasing if the desorption temperature is increased to 400 K, most probably due to thermal decomposition. However even at 400 K this effect is rather small. The partial pressure of water at 350 K is only around 350 mb. If the sample contained substantial amounts of water, water would not be completely injected directly but over a considerable period of time. If the sample contained 10 mg of water vapour—which is not even much for a 1 dm^3 STP air sample—this would be

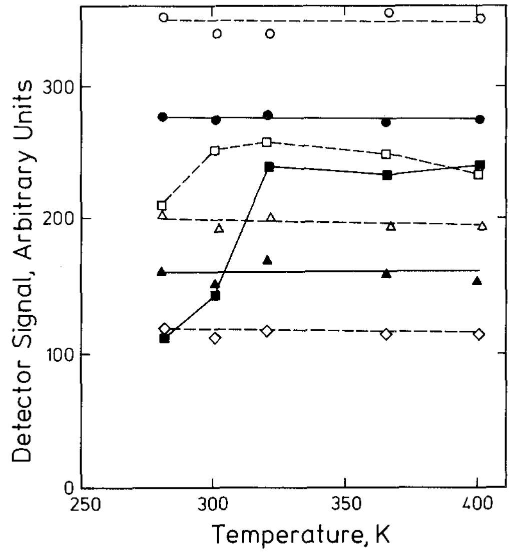

FIGURE 3 Desorption efficiency of different compounds from a precolumn packed with porous glass beads as function of temperature. ○, C_2Cl_4; ●, C_2H_6; □, CH_3CHO; ■, *p*-xylene, △, toluene; ▲, benzene; ◇, CH_3CCl_3.

sufficient to saturate about 35 cm^3 of carrier gas with water vapour at 350 K. To prevent such an extreme tailing the four-port valve (I) is rotated back after 5 cm^3 of carrier gas have passed through the sample loop. This is more than ten times the dead volume of the preconcentration column and thus more than sufficient to transfer all components to the separation column, which are not strongly adsorbed by the packing of the precolumn (porous glass beads) at 350 K. The maximum amount of water which is injected onto the separation column in this way is about 1.5 mg instead of the total amount of water in the original sample which might be 10 mg or even more. This not only substantially reduces the tailing of water but also limits the amount of water which is transferred from the preconcentration loop onto the separation column. This is essential in order to avoid the overloading of the separation column in the case of large sample volumes of high humidity air.

SEPARATION

As mentioned above the sample which is injected onto the separation column contains a substantial amount of water (up to 1.5 mg). It also contains all the carbon dioxide from the original air sample, about 0.7 mg for each dm^3 (STP) of air. The presence of a still substantial amount of water prohibits the use of a capillary column since at the temperatures which are necessary to separate the very light components of the sample from each other water would condensate and clog any small bore capillary column. For the measurement of a number of trace gases this problem has been solved by removing the water from the sample with a drying agent such as $Mg(ClO_4)_2$ or K_2CO_3.[30-32] However, the use of such drying agents causes severe changes in sample composition for a number of trace gases as can be seen from Table II. The use of a drying agent would restrict considerably the type of trace gases

TABLE II
Effects of $Mg(ClO_4)_2$ drying tube on sample composition

Compound	Temperature of drying tube (peak area relative to undried sample)	
	(25°C)	(60°C)
C_2H_2	1.005	1.04
C_2H_4	0.98	1.05
C_2H_6	0.97	1.03
C_3H_6	1.04	1.03
C_3H_8	0.97	1.02
CH_3Cl	1.02	0.94
CH_3CHO	0.03	1.15
i-C_5H_{12}	0.98	1.04
n-C_6H_{14}	0.90	1.07
C_6H_6	0.57	1.12
C_7H_8	0.15	1.05
CH_2Cl_2	0.80	0.73
C_2Cl_4	0.78	0.81
F-113	0.88	0.99
CH_3CCl_3	0.92	1.00

which could be reliably measured. By raising the temperature of the drying agent to 330 K the adverse effects of a drying agent can be reduced but not completely avoided.

If a packed column or a wide-bore capillary column is used for the separation, the reduced separation efficiency of these columns compared to a small-bore quartz capillary would cause considerable problems for the reliable identification and quantification of the medium molecular weight trace gases (C_5-C_{10}) due to the complexity of the sample. The best solution of this problem is to separate the light fraction of the trace species and water from the heavier fraction on a packed column and subsequently separate both fractions on two different columns, both optimized for the two different separation problems.

The operation of the separation system is shown in Figure 2. After injection, the preconcentrated sample is separated into two fractions on column 1 (3 m length, 0.8 mm i.d. packed with Porapack QS, 100–120 mesh). The lighter fraction including the hydrocarbons up to butane and water is transferred to another packed column (6 m length, same type as column 1). The gas flow pattern is shown in Figure 2(b).

After the elution of *n*-butane from column 1 and transfer to column 2, the ten-port valve (II) is rotated into the "backflush" position and the heavier fraction of the sample transferred to column 3, a 60 m long DB-1 capillary. Columns 1 and 2 are housed in the same column oven whereas column 3 is in a second oven which can be operated at different temperatures independent of the first one. This allows us to separate the light fraction on column 2 and simultaneously to focus the heavier fraction at the head of column 3 by cooling this column down to 175 K. The packed columns are kept at 283 K for 4 min after sample injection and then the temperature is increased with a rate of 4 K min^{-1}. The preseparation on column 1 takes 20 min, the total separation of the light fraction about 35 min (the very light components of the sample such as ethane, acetylene etc. are eluted from column 2 even before *n*-butane has left column 1). After completion of the separation of the light fraction the two four-port valves (III) and (IV) are turned. Now the substances eluted from column 3 are monitored by the detection system and also the carrier gas for column 3 is controlled by a separate pressure regulator. This allows us to select the optimum flow conditions for column 3 independent of the operation of the other columns. Then the capillary column (3) is rapidly heated from 175 K to 250 K (at 25 K min^{-1}) and from 250 to 460 K at a rate of 3 K min^{-1}.

The capillary column is operated at a constant pressure of 0.5 bar, the packed columns with a flow of 7 $\mathrm{cm}^3\,\mathrm{min}^{-1}$. As carrier gas high purity nitrogen is used which is further purified with a molecular sieve (5 A and 13 X mixture) adsorber at dry ice temperature. Directly at the end of columns 2 and 3 make up gas is added to obtain total flow rate of 20 $\mathrm{cm}^3\,\mathrm{min}^{-1}$ for both columns.

DETECTION

Due to the, in many cases, very low amounts of the individual substances in the samples, detectors with high sensitivity have to be used. With respect to the identification of the different species in the sample mass-spectrometry would be by far the best choice. However, this method is far too expensive to be used for large series of measurements. Furthermore the sensitivity of mass spectrometric detection is not for all types of compounds comparable to state of the art ionisation detectors. For this reason we decided to use a combination of three different ionization detectors: photoionization-, flame ionization- and electron capture detection, in order to obtain sufficient selectivity and sensitivity for the analysis of a complex mixture of substances at sub-nanogram amounts. Similar detection systems have already been successfully used for the analysis of complex samples.[1,30,36,37] The detectors are combined in series: PID-ECD-FID. This avoids splitting of the column effluent and the resulting decrease of the detection limit and the problem of possible variation of the split ratio with temperature etc. Problems are the possible decomposition of thermally unstable compounds in the detectors or the transfer lines between the detectors and the risk of peak broadening. However, these problems are mostly avoided due to the very low dead volume of the complete system (valves, detectors, transfer lines etc.). The total dead time from the end of one of the chromatographic columns to the last of the three detectors is only about 0.3 seconds.

The combination of different types of detectors provides considerable advantages over the use of a single detector. The sensitivity of the different detectors varies considerably for different types of compounds. The sensitivity of the ECD for many halocarbons is by orders of magnitudes better than for the PID or FID and the PID responds to aromatic hydrocarbons much better than the FID. Thus the lower limits of detection are considerably decreased for a number of compounds if we compare a combination of several detectors with any one of the individual detectors. Furthermore the linear range for compounds with high electron capture sensitivity is considerably improved. Many of the halocarbons can be measured by EC detection at picogram or even sub-picogram levels. Due to the limited linear range of an ECD (about 3 orders of magnitude) the ECD signal for these compounds could not be evaluated quantitatively if these compounds are present at higher levels. Since atmospheric samples contain a variety of halocarbons with very good ECD sensitivity at levels varying considerably this might often prevent the quantitative determination of several of the trace components. But the FID signal for halocarbons can be easily evaluated if the signal is above the lower limit of detection which is nearly always the case if the linear range of the ECD is exceeded.

A further advantage of a combination of different detectors can be seen from Table III. In this table the ratio of the FID response to the PID response (10.2 eV photonenergy) is listed for a number of different compounds.

It can be seen that the response ratio varies by orders of magnitude for different classes of compounds. This can be used to verify the identity of a given peak and to detect unexpected interferences by comparing the response ratio from the measurements with that of the pure substance. It is even possible to "unfold" a peak caused by two substances with the same retention time into its two components on the basis of the response in the different detectors. However, this increases the error of the quantitative evaluation, and such a procedure should only be used if the relative detector responses for the two substances differ considerably.

INSTRUMENT PERFORMANCE

Figure 4 shows chromatograms for the separation of the lighter fraction on the small-bore packed column and Figure 5 of the

TABLE III
Ratio FID/PID signal (arbitrary units)

C_2H_6	>15
C_3H_8	4.8
n-C_4H_{10}	1.8
n-C_5H_{12}	0.98
n-C_6H_{14}	0.90
n-C_7H_{16}	0.70
n-C_8H_{18}	0.54
n-C_9H_{20}	0.42
n-$C_{10}H_{22}$	0.36
n-$C_{11}H_{24}$	0.3
i-C_4H_{10}	2.1
i-C_5H_{12}	1.2
cyclopentane	1.3
cyclohexane	0.4
3-methylpentane	0.8
methylcyclopentane	1.1
methylcyclohexane	0.3
C_2H_4	1.3
C_3H_6	0.14
1-butene	0.10
cyclopentene	0.085
C_6H_6	0.13
C_7H_8	0.12
o-xylene	0.10
$C_6H_5.C_2H_5$	0.11
$C_6H_3(CH_3)_3$	0.07
CH_3CHO	0.24
C_2HCl_3	0.05
C_2Cl_4	0.06

heavier fraction on the capillary column. As expected the three detectors show a quite different selectivity: the major peaks in the ECD trace are halocarbons, the PID is most sensitive for alkenes (except ethene) and aromatic hydrocarbons. The air sample was collected over a rural area of Germany (Eifel) and showed only very little influence of pollution. With the exception of ethane, propane and n-butane all peaks represent compounds which are present at the sub-ppb level. Sample volume was 1 dm^3 (STP). The separation efficiency both of the packed and the capillary column is sufficient even for rather complex environmental samples. There is no indica-

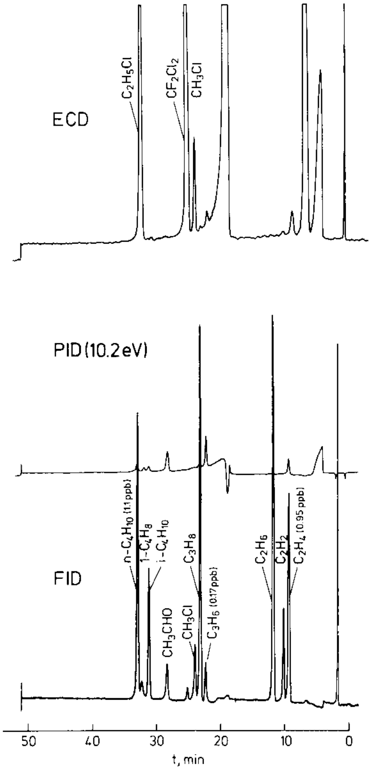

FIGURE 4 Separation of light fraction on packed column (Porapack Q), rural air sample, 1 cm^3 STP.

tion that the in-series connection of the three detectors adversly affects the chromatographic resolution of the system.

The main performance characteristics of the instrument are shown in Table IV. The given values—especially for the detection limits—represent the range which includes the majority of the components, but there are a few compounds with significantly higher or lower detection limits. For example some of the fluorocarbons have theoretical detection limits far below 0.1 ppt whereas they have an extremely poor FID response and thus for FID detection a lower limit of considerably more than 20 ppt (packed column) or 5 ppt (capillary).

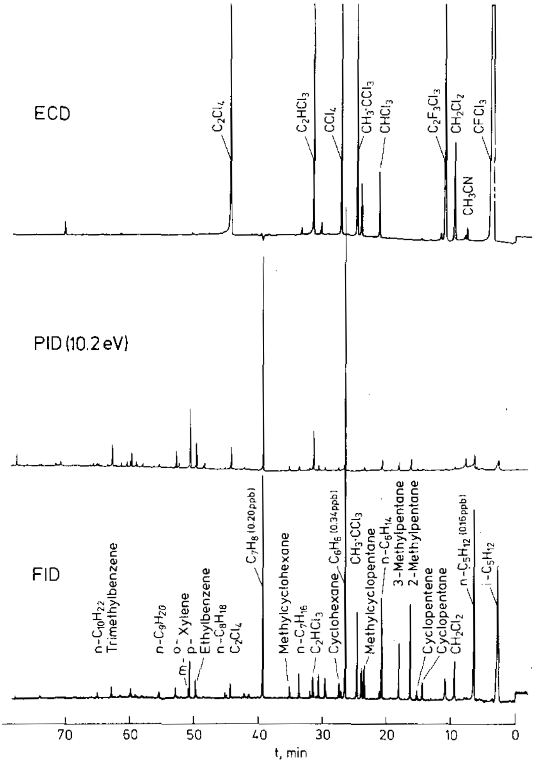

FIGURE 5 Separation of heavier fraction on capillary column (60 m DB-1), same sample as Figure 4.

If desired—and a sufficiently large sample volume is available—the lower limit of detection can be decreased by increasing the sample volume. For air samples with high humidity the maximum sample volume is limited by the amount of water which can be frozen out in the preconcentration column to roughly 2 dm^3–3 dm^3 (STP) of air. In the case of air samples with low water vapour content (e.g. from the free troposphere) considerably larger sample volumes could be used for the enrichment procedure, however, the size of the available sample and the increasing time for the concentration step limits the sample volume to less than 5 dm^3 (STP) of air.

TABLE IV

Instrument performance

Packed column
- Peak width (50% height): 10–15 s
- Distance of adjacent *n*-alkanes: 10–12 min
- Detection limits (3σ, 1 dm^3 STP air sample):
  - FID: 10–20 pptC
  - PID: 2–10 pptC (alkenes, CH_3CHO, etc.)
  - ECD: 0.1–1 pptv (fluorocarbons)
    - 5 pptv (CH_3Cl)
    - 20 pptv (COS)
- Reproducibility 5–10%
- Linearity: $>10^5$ (FID and PID)
  - $\approx 10^3$ (ECD)

Capillary column
- Peak width (50% height): 3–4 s
- Distance of adjacent *n*-alkanes: 12–15 min
- Detection limits (3σ, 1 dm^3 STP air sample):
  - PID: 0.5–2 pptC (alkenes, aromatics)
  - ECD: 0.1–0.5 pptv (halocarbons)
  - FID: 3–5 pptC
- Reproducibility and linearity same as packed column

MEASUREMENTS

The described method has been successfully used for several series of measurements of hydrocarbons and halocarbons in the non-urban atmosphere. A presentation and detailed discussion of the results would be beyond the scope of this paper. Instead a few results will be presented to demonstrate the advantage of measurements of rather broad trace gas profiles with respect to the evaluation and interpretation of such data.

In Figure 6 the results of two measurements of several trace halocarbons and hydrocarbons in air samples collected at Amsterdam Island (a very small isolated island located in the Indian Ocean at about 30 °S) are shown. Figure 6(a) represents the trace gas pattern for conditions with extremely low continental influence. This is indicated by the extremely low content of Rn-222 in the air mass which is far below the Rn-222 level observed over continents.[29,38]

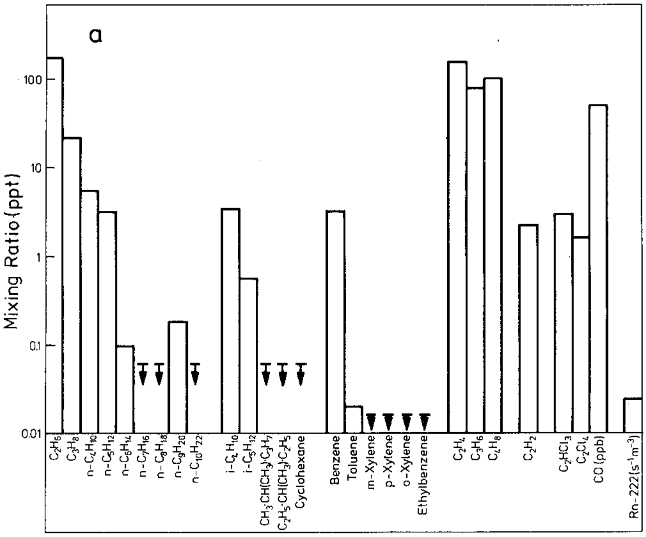

FIGURE 6(a) Trace gas profile for various trace gases, measured on Amsterdam Island on 15th January, 1984.

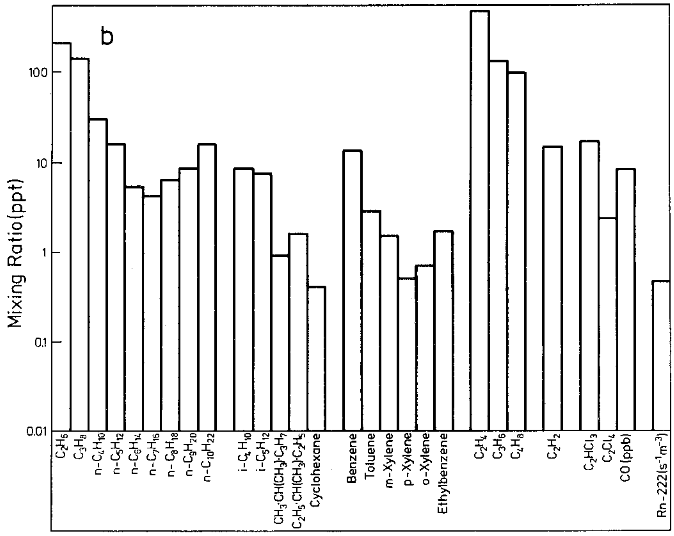

FIGURE 6(b) Same as Figure 6(a), but from 26th May, 1984.

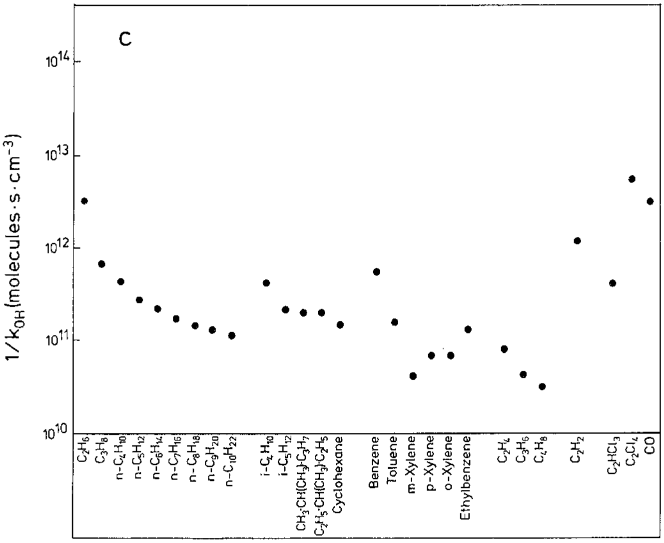

FIGURE 6(c) Inverse rate constants for the reaction of several hydrocarbons and halocarbons (same species as shown in Figures 6(a) and 6(b)) with OH-radicals.

For comparison the results of hydrocarbon and halocarbon measurements in a sample from the same location but a different time is shown in Figure 6(b).

As can be seen from the by more than an order of magnitude higher Rn-222 content of the air mass, this second sample showed considerable continental influence. This is also visible in the substantially increased mixing ratios of the halocarbons and aromatic hydrocarbons.

It is interesting to note that not only the absolute values for the trace gas mixing ratios changed, but also the pattern of the trace composition changed considerably. In the "clean air" sample (Figure 6(a)) the ratio of ethane to *n*-hexane is about 2000 and of benzene to toluene more than 100, whereas in the other sample (Figure 6(b)) the ratio of ethane to *n*-hexane is less than 50 and of benzene to toluene less than 5. This systematic change in the trace gas pattern has been observed in a quite similar way in continental air masses with varying anthropogenic impact and can be explained by the different photochemical reactivity—and consequently differing atmospheric lifetime of the individual trace species. The main atmospheric removal mechanism for these hydrocarbons is the reaction with OH-radicals; therefore, their atmospheric lifetime will be inversely proportional to the reaction rate constant with OH-radicals. In Figure 6(c) this inverse reaction rate constant is plotted for the different trace gases shown in Figures 6(a) and 6(b). It can be seen that the difference between the two measurements for a given trace gas is—as a general rule—increasing with decreasing atmospheric residence time (or increasing rate constant for the reaction with OH-radicals). For example, the relative change in C_2H_6 and C_2Cl_4—which belong to the longest lived of the trace gases shown in Figure 6—is less than 50%. The xylenes—which are removed from the atmosphere around 50 times faster than C_2H_6 or C_2Cl_4, differ by about two orders of magnitude in their mixing ratios between the two measurements.

However, there is one group of trace constituents which does not fit into this pattern. The light alkenes do not only show rather high atmospheric mixing ratios but also a rather small difference between the two samples. For the reaction rate constants with OH-radicals this is rather surprising since the alkenes are among the most reactive of the trace gases from Figure 6. This is most probably due to the existence of significant oceanic sources for these atmospheric trace gases.[2] Thus it is not surprising that the light alkenes do not fit into the pattern of trace gases with predominantly continental sources.

The behaviour of trace gases over continental areas is in several aspects quite similar. In Figure 7 the trace gas patterns from five measurements over a rural area about 50 km northwest of Aachen are shown. Four of the samples were collected inside a forested area, the fifth sample about 3 km away in an open field. Sample 1 (from 18th January, 1985) was collected during a period of several days with stagnant weather conditions and extremely little horizontal and vertical exchange (during this time heavy smog was reported for most major German cities). Samples 2 and 3 (collected on June 6th and June 7th) were taken during moderate winds from southwest, whereas on 13th April (Samples 4 and 5) strong winds from southwest prevailed.

As a result of the restricted exchange conditions on 18th January Sample 1 shows—compared to the other samples—considerably elevated trace gas mixing ratios.

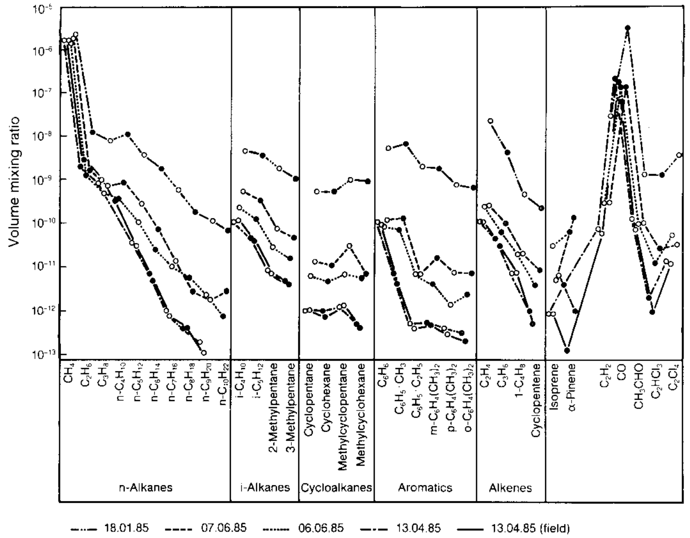

FIGURE 7 Trace gas profiles measured in a rural area 50 km southeast of Aachen under different meteorological conditions (see text). Sample 1 (—··—) (18.01.85) inside forest; Sample 2 (– – – –) (07.06.85) inside forest; Sample 3 (····) (06.06.85) inside forest; Sample 4 (—·—) (13.04.85) inside forest; Sample 5 (——) (13.04.85) open field 3 km from sampling locations for Samples 1–4.

On 13th April extremely clean air was observed—indeed the mixing ratios for many of the trace gases are comparable to those observed in oceanic air masses (see for example Figure 6). The data from 6th and 7th June may be characterized as "average" and represent values which are similar in the hydrocarbon mixing ratios to measurements made over other remote, rural areas of Germany.[23]

Again we can see from a comparison of the five measurements, that a lower level of pollution is most strongly seen in the mixing ratios of the most reactive of the different trace species, e.g. the alkylbenzenes. The longer-lived species such as C_2H_6 show much less pronounced relative changes between the five samples.

There are some details in the trace gas pattern which deserve interest. The two measurements from 13th April show—within the precision of the data—no difference in the trace gas mixing ratios with the exception of α-pinene. This agrees with an observation made by various authors[5,6,12] that substantial amounts of monoterpenes—including α-pinene—are emitted from vegetation, especially trees. α-pinene and isoprene—also a trace gas emitted from vegetation—are the only species shown in Figure 7 which show lower values on 18th January than for the other four samples. The very good agreement between the two measurements from 13th April shows also that these two samples—which were taken at locations about 3 km distance from each other—are not influenced by nearby trace gas sources, with the exception of emissions from vegetation.

CONCLUSIONS

The described gas chromatographic technique—including the sampling procedure—is suitable for measurements of low and medium molecular weight hydrocarbons and halocarbons in the atmosphere at ppt levels and for several species even below. The sampling method—grab sampling—in the field is easy to handle and requires only a minimum of logistic efforts. This provides excellent possibilities for measurements at truly remote locations. The measurement-instrument in the laboratory is completely automated and provides a good reproducibility of the results. The technique is suitable for routine measurements; however, both the preparation of the sample containers for field sampling and the measurements themselves are rather time-consuming.

The results obtained from measurements provide valuable information on the atmospheric abundance and distribution of a large number of different hydrocarbons and halocarbons. The measurement of a broad spectrum of trace gases allows inferences on possible sources and sinks for the different trace gases.

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