DETERMINATION OF C_2–C_5 HYDROCARBONS IN THE ATMOSPHERE AT LOW PARTS PER 10^9 TO HIGH PARTS PER 10^{12} LEVELS

SUMMARY

By far the most abundant hydrocarbon in unpolluted air is methane (mixing ratio *ca.* 1.6 ppm). The mixing ratios of other hydrocarbons are typically in the low parts per 10^9 (ppb) and parts per 10^{12} (ppt) ranges. Although methane is several orders of magnitude more abundant in clean air, it is conceivable that other hydrocarbons are still of considerable importance to clean air photochemistry, because their reaction with hydroxyl radicals proceeds much faster than that of methane.

Owing to this high reactivity of many of the light non-methane hydrocarbons (NMHC), mixing ratios of NMHC as low as a few ppb or several ppt can have a considerable influence on the photochemistry of unpolluted air. For this reason a gas chromatographic method has been developed that permits the determination of several C_2–C_5 hydrocarbons with detection limits of a few ppt from grab samples of 0.5–2 dm^3 (STP).

The samples are collected in evacuated 2-l stainless-steel containers with metal bellows-sealed stainless-steel valves. These sample collection and storage cans are specially pre-treated and cleaned to avoid changes in sample composition during transport of the samples to the laboratory. In the laboratory the samples are analysed by enrichment of the hydrocarbons on a packed pre-column at sub-ambient temperatures (*ca.* −35°C) and subsequent separation on a 7 m × 0.8 mm I.D. packed column (Spherosil X0B 075). A flame-ionization detector is used. This method allowed survey measurements on a global scale of C_2–C_5 hydrocarbons, which gave an estimate of the contributions of light hydrocarbons to atmospheric photochemical reactions.

INTRODUCTION

With a mixing ratio of about 1.6 ppm, methane is by far the most abundant hydrocarbon in unpolluted air. The mixing ratios of other hydrocarbons are several orders of magnitude lower at a few parts per 10^9 (ppb) or fractions of 1 ppb[1]. However, this does not necessarily mean that the non-methane hydrocarbons (NMHC) are of no importance to the chemistry of the unpolluted atmosphere. The importance of an atmospheric trace component to atmospheric photochemistry is determined not only by its abundance but also by its participation in photochemical reaction chains and cycles. According to current understanding of atmospheric chem-

istry, the main starting reaction step for hydrocarbons in a photochemical reaction chain is the reaction with OH radicals. Olefinic hydrocarbons also react with ozone, but in unpolluted ground-level air the ozone concentrations are low (30–50 ppb)[2] and the reactions of alkenes with ozone are generally less important than the reaction with OH radicals.

Thus, for a better understanding of the relative influence of hydrocarbons on atmospheric photochemistry, the atmospheric mixing ratios of hydrocarbons should be weighted according to their reaction rate constants with radicals. As the reaction rate constants of olefinic NMHC are up to 3 orders of magnitudes greater than that of methane (Table I), the mixing ratios of these gases in the low ppb range could have an importance to the photochemistry of air comparable to that of methane. There are few data available on the mixing ratios of NMHC in unpolluted air and therefore measurements of NMHC in clean air on a more global basis are needed in order to allow any conclusions about their importance to be drawn.

TABLE I

MIXING RATIOS OF LIGHT HYDROCARBONS EQUIVALENT TO 1.6 ppm OF METHANE BASED ON REACTION RATE CONSTANTS WITH OH RADICALS

Hydrocarbon	*Reaction rate constant*		*Mixing ratio (ppb)*
	Value (cm^3 $molecules^{-1}$ sec^{-1})	*Reference*	
CH_4	$8 \cdot 10^{-15}$	3	–
C_2H_6	$2.9 \cdot 10^{-13}$	4	44
C_2H_4	$8.1 \cdot 10^{-12}$	5	1.6
C_2H_2	$1.6 \cdot 10^{-12}$	6	98
C_3H_8	$1.5 \cdot 10^{-12}$	7	8.5
C_3H_6	$1.5 \cdot 10^{-11}$	8	0.85
n-C_4H_{10}	$2.5 \cdot 10^{-12}$	7	5.1
iso-C_4H_{10}	$2.4 \cdot 10^{-12}$	7	5.3
n-C_5H_{12}	$3.7 \cdot 10^{-12}$	7	3.5
iso-C_5H_{12}	$4.6 \cdot 10^{-12}$	7	2.8

As a first step towards a survey of the global distribution of hydrocarbons, we decided to make measurements of light NMHC in unpolluted areas. The first step is to estimate the limits of detection and the precision and accuracy necessary to achieve this purpose.

The only hydrocarbon whose global distribution and importance to atmospheric chemistry are well known is methane, so we used methane as a "reference" by comparing the NMHC mixing ratios with methane mixing ratios, but weighted according to their reaction rate constants with OH radicals for the reasons mentioned above. For the purpose of comparison, in Table I are listed the mixing ratios of some light hydrocarbons which are equivalent to 1.6 ppm (the average background mixing ratio) of methane. Also included are the reaction rate constants for the reactions with OH radicals. As a crude assumption, we consider hydrocarbon mixing ratios or changes in hydrocarbon mixing ratios of less than 1% "methane equivalent" to be negligible. This is a low limit, but it must be borne in mind that owing to the large

number of light hydrocarbons small effects and small errors in mixing ratios may accumulate to give substantial effects. Thus a useful analytical procedure for the determination of light NMHC in background air should have detection limits of about 1% of the mixing ratios listed in Table I and the analytical error for mixing ratios which are 10% of the "methane equivalent" should not exceed 10%. Another point should be considered for the development of a method for the measurement of trace components in background air: for a representative picture of the abundance of species such as NMHCs, measurements for different locations, seasons, meteorological conditions, etc., are necessary. Thus any analytical procedure should allow measurements in remote areas.

Many methods for the determination of light hydrocarbons in the atmosphere are described in the literature (see, *e.g.*, ref. 9), but nearly all of them were designed with measurements in polluted areas in mind and are not sufficiently sensitive for measurements in clean air. Very few procedures sensitive enough for the analysis of light hydrocarbons in unpolluted air are reported (*e.g.*, refs. 10–13). However these methods use *in situ* cryogenic enrichment which requires some cryogenic liquid, in most cases liquid oxygen, and this puts some restrictions on the sampling locations and causes considerable logistic problems for sampling in areas remote to any anthropogenic activity.

EXPERIMENTAL AND RESULTS

Sample collection

The most convenient way to collect air samples is "grab sampling" in evacuated containers. The problem of this kind of sampling is the possibility of sample degradation (*e.g.* by reaction of trace constituents with the container material or by internal outgassing of the container). Ehhalt *et al.*[14] have described all stainless-steel sampling flasks which enabled the storage of clean environmental air samples with chlorofluoromethane mixing ratios of several hundred ppt.

All joints were vacuum welded and the insides of the containers were electropolished. After cleaning with acetone the containers were subjected to the following treatment:

(1) evacuated to a pressure of less than 10^{-5} mbar and kept for at least 2 days at 200°C;

(2) filled with synthetic air (1 bar) and maintained at 200°C for 24 h;

(3) evacuated ($p \leqslant 10^{-5}$ mbar) and heated at 100°C for a short period;

(4) helium leak tested (including the valves); the leak rate must be less than 10^{-8} mbar dm^3 sec^{-1};

(5) evacuated ($p \leqslant 10^{-5}$ mbar) and heated at 100°C for at least 36 h.

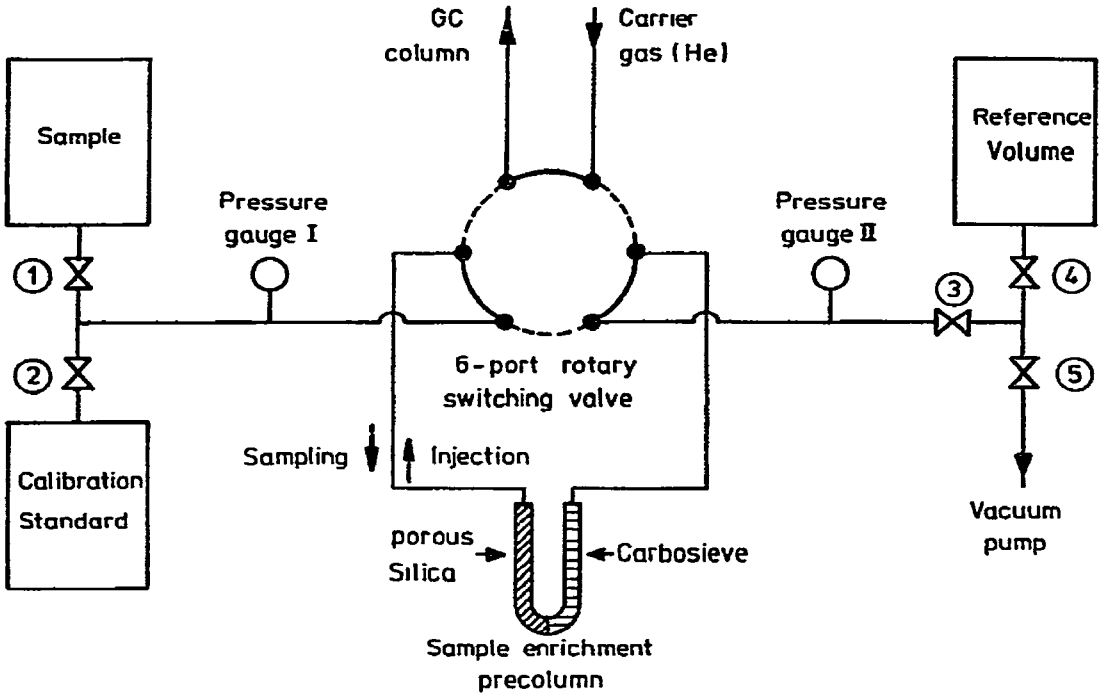
Steps (4) and (5) were repeated every time prior to the use of the sample containers for clean air sampling.

Sample containers prepared in this way did not give any detectable blank values for C_2–C_5 hydrocarbons (s. detection limits beyond). No sample degradation was observed for samples stored for more than 3 months in these containers.

Sample enrichment

For analyses the sample containers are transferred to the laboratory. To obtain a sufficiently low detection limit an enrichment step is included in the procedure.

The sample inlet system is adopted from the design of the generally used gas injection systems, with the sample-loop replaced by an enrichment column. The combined sample inlet and enrichment system is shown in Fig. 1. It is made completely of stainless steel with the exception of the rotor of the six-port valve (Valco valve), which is made of a fluorocarbon polymer. All other valves are metal-bellows-sealed stainless-steel valves.



Rotary valve:
—— sample enrichment position
--- sample injection position

Fig. 1. Schematic diagram of sample enrichment and injection system for hydrocarbon analysis.

For packings of enrichment columns for light hydrocarbons the use of various adsorbents is reported (*e.g.* Carbopack, Carbosieve, porous polymers, porous silica and porous alumina, see *e.g.* refs. 14–17).

Carbon molecular sieves provide a very good sampling efficiency even for low-molecular-weight compounds. The disadvantages are that rather high temperatures are needed for thermal desorption, especially of heavier molecules, and thus thermal decomposition of less stable molecules can occur[15]. Experiments showd that at the temperatures necessary for the desorption of C_4 and C_5 hydrocarbons, the thermal decomposition of heavier components of air is no longer negligible. This resulted in increasing blank values for the light hydrocarbons with the number of samples analyzed. The probable reason is the gradually increasing amount of heavier hydrocarbons on the Carbosieve, the thermal decomposition products causing the blank values. Porous silica is a less efficient adsorbent, but has also been successfully used for the concentration of hydrocarbons from air samples[17]. From the known properties of porous silica however it is evident, that at temperatures necessary for the quantitative enrichment of C_2 hydrocarbons, carbon dioxide is adsorbed as well (see, *e.g.*, ref. 19). This would cause difficulties in the subsequent chromatographic separation.

A combination of both adsorbents solves these problems:

The enrichment pre-column is a 12 cm × 1/8 in. I.D. stainless-steel tube, 5 cm being packed with porous silica (100–200 μm) and 5 cm with Carbosieve B. During sample (or standard) enrichment this pre-column is kept at −30 to −35°C.

For sample enrichment the reference volume (10 dm^3) is evacuated (valve 3) closed, valves 4 and 5 open). Then, with the six-port valve in the enrichment position, valve 5 is closed and valves 3 and 1 are opened. Owing to the pressure difference between the sample container and the reference volume, the sample is drawn through the enrichment column and the C_2 and higher hydrocarbons are adsorbed on the pre-column.

Sample volumes for one analysis are typically between 0.5 and 1 dm^3. The sample volume is determined from the reading of pressure gauge II and the reference volume. The error of the determination of the sample volume is about 1 %.

For sample desorption, the six-port valve is switched into the "sample injection" position, the enrichment pre-column is heated at *ca.* 250°C for 20 min by direct resistance heating and the enriched sample is transferred to the separation column.

Separation and detection

We use a Packard 419 chromatograph equipped with a flame-ionization detector. The inlet system of the chromatograph is replaced with the sample inlet described above. The pressure and flow regulation is replaced with all-stainless-steel pressure controllers, and the flows of hydrogen and synthetic air for the detector are controlled via the pressure by micro-orifices. The carrier gas (helium) flow is only pressure controlled. The carrier gas and the hydrogen are purified in cold traps with porous silica at liquid nitrogen temperature. The synthetic air is passed through a molecular sieve (13X) adsorbent cartridge at ambient temperature.

A very large number of different types of stationary phases, including modified and unmodified porous silica, and different column dimensions are described in the literature for the separation of light hydrocarbons (see, *e.g.*, refs. 9, 13, 17 and 18). We have decided to use an uncoated and untreated porous silica (see, *e.g.*, refs. 17 and 18) to minimize all negative effects from column bleeding such as baseline drift and detector noise which would adversely effect the detection limits.

The column dimension, temperature program and carrier gas pressure were optimized with respect to separation efficiency, detection limit and speed of analyses.

The separation column is a 7 m × 0.8 mm I.D. stainless-steel column packed with untreated porous silica (Spherosil X0B 075) (40–100 μm). A similar type of column but packed with a different adsorbent (a modified porous silica) was used by Westberg *et al.*[12] for the separation of C_2–C_6 hydrocarbons. It is known that porous silica changes its separation properties with its content of moisture[19]. To avoid changes in the column properties a short (12 cm) drying tube containing magnesium perchlorate is installed between the sample inlet and the separation column. The use of comparable drying tubes with various drying agents has been described by several authors (*e.g.*, refs. 12, 13). This drying tube is located outside the column oven and maintained at ambient temperature. Tests showed that this method of removing water from the enriched sample did not cause any detectable changes in the content of C_2–C_5 hydrocarbons in the sample. The carrier gas pressure is *ca.* 12 bar.

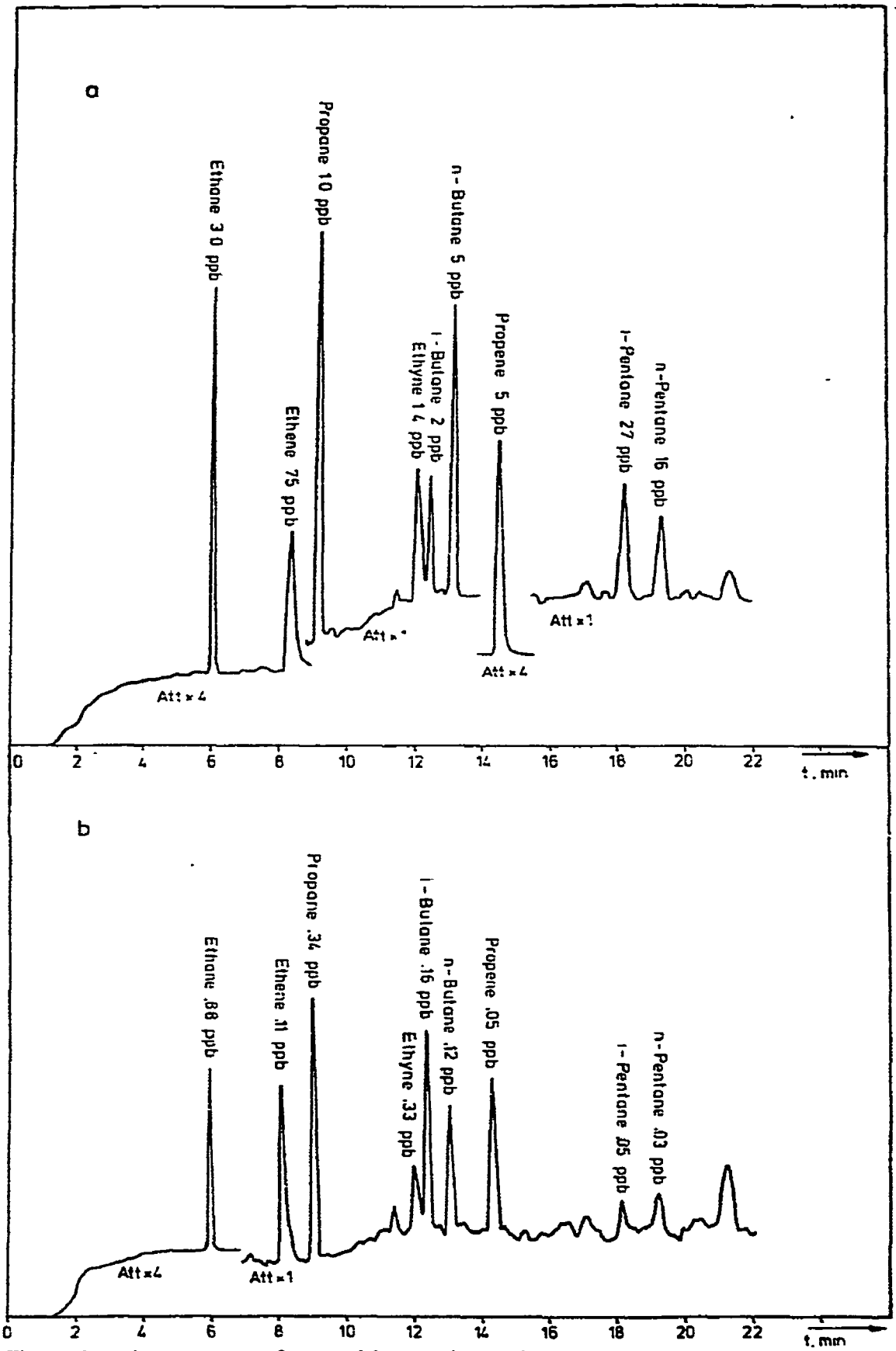


Fig. 2. Two chromatograms from enrichment air samples: (a) sample from a semi-rural site near Jülich (G.F.R.), 51°N 6°E, 5/3/79; (b) sample of marine air collected aboard the F.S. Meteor over the Atlantic at 9°N 28°W, 10/24/80.

During sample desorption, the separation column is kept at −90°C in order to concentrate the C_2–C_5 hydrocarbons at the head of the separation column. Then the column oven is heated at 30°K/min to 10°C and at 7.5°K/min from 10 to 70°C. The separation takes about 20 min and a complete analysis, including enrichment, about 1 h.

Fig. 2 shows two chromatograms of air samples. One of the samples (Fig. 2a) was collected in a semi-rural area and the other (Fig. 2b) was a sample of marine air. It can be seen that the separation and sensitivity of the method is not only sufficient for the measurement of hydrocarbons outside polluted areas in continental Europe, but even allows the determination of C_2–C_5 hydrocarbons in clean marine air.

Evaluation

The chromatograms are recorded with a strip-chart recorder and evaluated manually. For the C_2–C_5 hydrocarbons, with the exception of ethene, peak-height measurements proved to be sufficient, but for ethene peak-area determination gives better results.

The hydrocarbon mixing ratios are calculated by comparison with the corresponding peak heights (or peak areas) of a standard of known hydrocarbon content. The standard is analysed in the same way as the samples. At least once a day a chromatogram of the standard is run.

The standard is calibrated with mixtures of the individual hydrocarbons in synthetic air. These calibration gases with hydrocarbon mixing ratios between 0.5 and 5 ppb are prepared by a usual three-step static dilution. The measuring procedures for the calibration mixtures are identical with those for samples or standards.

Reproducibility, detection limit and linearity

Before the method can be applied to field measurements, it is necessary to ascertain that it is sufficiently sensitive and reliable for the required purpose, namely the determination of the possible importance of light NMHC in unpolluted air.

The reproducibility and the theoretical detection limit (for a signal better than three times the baseline noise) are listed in Table II. The reproducibility was determined from six replicate measurements (0.5 cm^3 of air per measurement) of an air sample collected near this Institute.

TABLE II

REPRODUCIBILITY AND DETECTION LIMIT

Hydrocarbon	*Mixing ratio (ppb)*	*Relative standard deviation (%)*	*Detection limit (ppt)*
C_2H_6	10.9	1.9	12
C_2H_4	1.19	7.5	7
C_2H_2	16.8	3.7	45
C_3H_8	4.20	3.0	11
C_3H_6	0.68	3.3	4
n-C_4H_{10}	4.13	2.2	8
iso-C_4H_{10}	3.2	1.2	7
n-C_5H_{10}	1.44	2.0	12
iso-C_5H_{10}	3.03	2.9	18

The linearity of the peak height (or peak area) with hydrocarbon mixing ratio was tested with six different dilutions of an air sample with synthetic air. Two examples of such dilution curves are shown in Fig. 3. The regression coefficient for the nine light hydrocarbons was always better than 0.9995.

It can be concluded that the method fully meets the requirements.

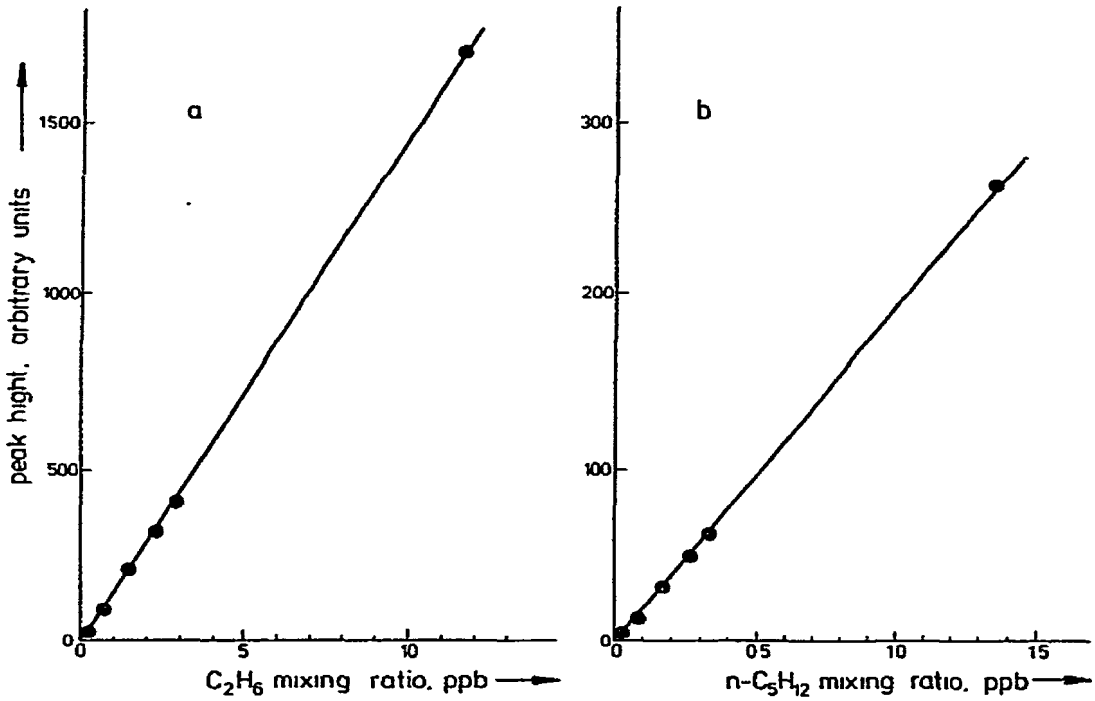


Fig. 3. Peak height *versus* hydrocarbon mixing ratio for different dilutions of an air sample: (a) ethane; (b) *n*-pentane.

Atmospheric measurements

In applying the method, we started with survey measurements of light NMHC on a global basis. A complete presentation and discussion of the results is beyond the scope of this paper, but one series of measurements is presented in order to illustrate the potential of the combination of field sampling in evacuated containers ("grab sampling") and highly sensitive analyses in the laboratory. During the end of October and early November 1979 we made three airplane flights over the Cologne–Bonn–Ruhr area and over the Eifel (G.F.R.; 51°N 6°E) and collected nearly 30 air samples at altitudes between ground level and 5 km. The vertical profiles of light hydrocarbons (for comparison some other trace gases are included) are presented in Fig. 4. During this period winds from north-west to west dominated. At an altitude of 3 km (700 mbar level) the wind velocity was 35–40 km/h and cold air masses from northern Europe dominated the weather situation. This brought relatively clean air into the western parts of G.F.R., as can be seen from the low carbon monoxide mixing ratios of 100–150 ppb above 2 km. These carbon monoxide mixing ratios are low for *ca.* 50°N and an altitude of 2–5 km[20]. All these trace gases, with the exception of chloromethane, exhibit similar vertical profiles with a significant decrease in mixing ratios at *ca.* 2 km. These vertical profiles are a good demonstration of the upward transport of

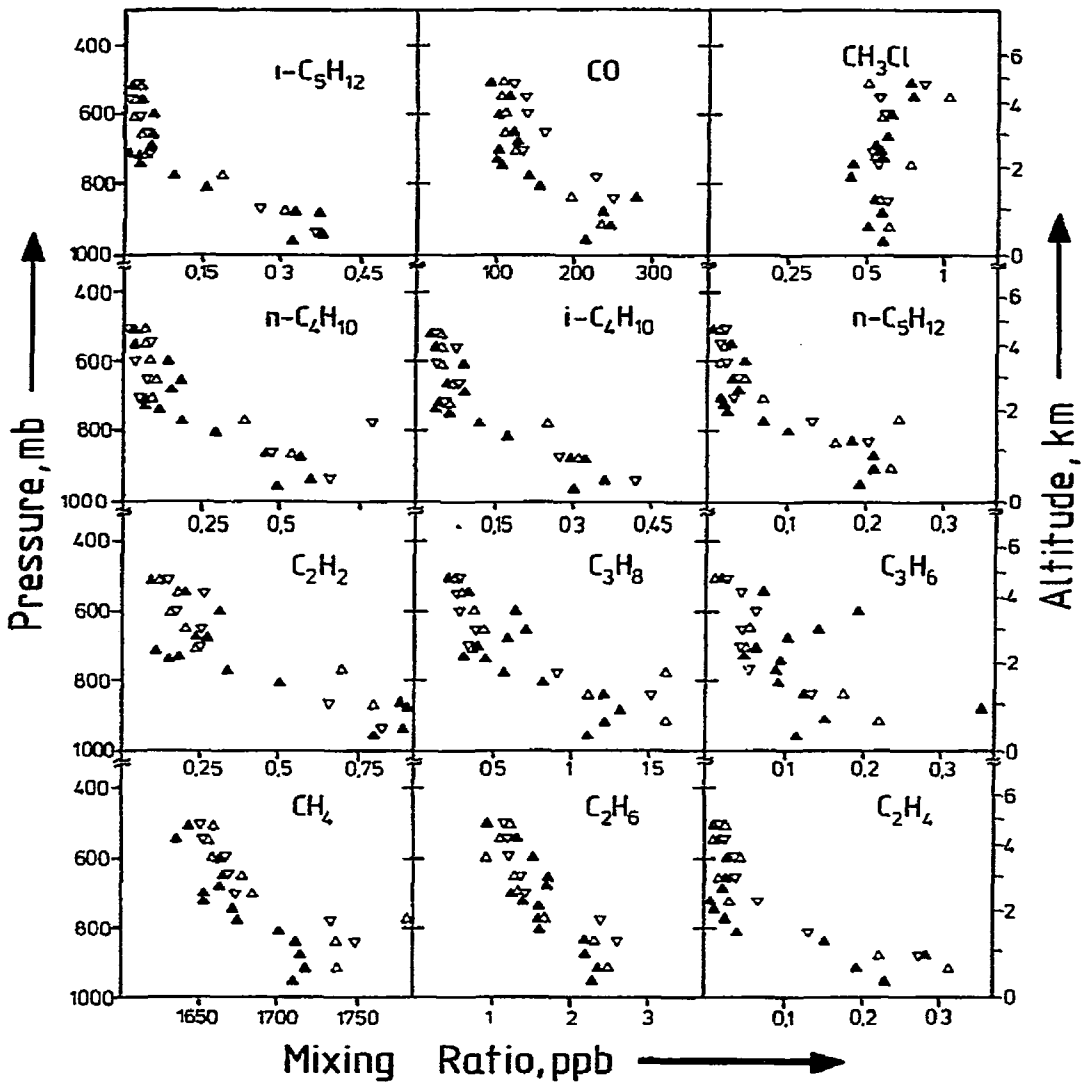


Fig. 4. Synoptic representation of the vertical profiles of several trace gases in the atmosphere. △, Cologne–Bonn–Ruhr area (30/10/79); ▽, Eifel (30/10/79); ▲, Eifel (7/11/79).

trace gases from ground-level sources and mixing with cleaner air masses above the tropospheric boundary layer. From a more detailed discussion of these vertical profiles, it can be shown that indeed vertical transport and mixing dominate the observed profiles and that photochemical removal is not of significance[21] for the given meteorological siluation. For chloromethane, the vertical profiles do not indicate significant continental ground-level sources. This is in agreement with the observations that chloromethane seems to be of oceanic origin and that chloromethane mixing ratios seem to be lower in air masses of continental origin than in those of marine origin[22].

It is important to note that for the given meteorological situation the contribution of C_2–C_5 hydrocarbons to atmospheric photochemistry is comparable to that of methane within the boundary layer, and still 20% that of methane in the free troposphere above 3 km.

CONCLUSIONS

The mixing ratios of light NMHCs (C_2–C_5) in unpolluted air are low (ppb to fractions of 1 ppb), but still of considerable interest for atmospheric chemistry. The fact that there is very little information available on the background distribution of light NMHCs seems to be due mainly to the analytical problems connected with such measurements. The method presented for the determination of light NMHCs in air meets the requirements for measurements of background levels of NMHC on a global basis: easy sampling in remote areas, sufficiently low detection limits (*cf.*, Tables I and II) and good precision.

One further problem should be mentioned: most of the light NMHCs in unpolluted air have individually only a slight influence on the photochemistry in the atmosphere, but their cumulated effect should not be neglected. With our measurements we can determine only part of the whole range of hydrocarbons, and it is desirabel to develop methods adequate for the measurement of other hydrocarbons in background air.

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