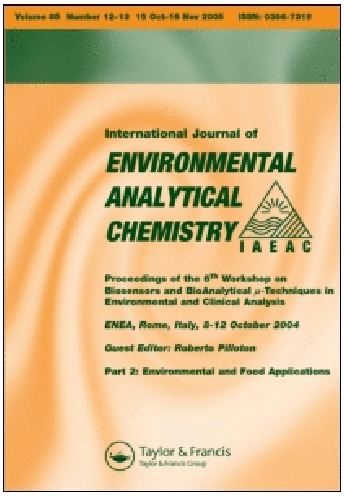

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AUTOMATED ANALYSIS OF LIGHT HYDROCARBONS IN AMBIENT AIR USING THE COMMERCIALLY AVAILABLE SYSTEM AAR-KA 5890A:

Technical Adaptations and Experience from Field Measurements

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An automated analytical system is used for the analysis of light hydrocarbons in ambient air. Sample pretreatment is performed with the instrument AAR-KA 5890A, manufactured by AMA(FRG). Sorbent materials (Tenax TA, Carbosieve S II, Molecular sieve) are used for sampling and enrichment of the hydrocarbons, which are analyzed by capillary gas chromatography with FID detection. In addition, an instrument was developed in our laboratories, in which the dehydration of the air samples and the thermal regeneration of the drying agent (K_2CO_3) were automated.

The experience from field measurements, in which nine light hydrocarbons from ambient air were quantified, is used to discuss the performance of the instrument.

INTRODUCTION

Hydrocarbons are important precursors for the formation of ozone in tropospheric air. It has been speculated that ethylene, a plant hormone, may contribute to forest decline, which was a topic of major concern in central Europe, especially during the first half of the 1980s, when observed damage increased very rapidly. The aim of this study was the analysis of light hydrocarbons (C_2–C_5) in ambient air as single compounds. Since continuous monitoring of these compounds was intended, an automated instrument was required.

Using conventional chemical techniques the following steps are normally performed in the analysis of light hydrocarbons from ambient air:

- ambient air sampling;
- enrichment of the species;
- cryofocusing;
- analysis with capillary GC.

Three different approaches are used to measure the concentrations of volatile hydrocarbons in ambient air:

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1) In the state-of-the-art technique, ambient air is sampled into electropolished stainless-steel bottles. After transport the samples are analyzed in the laboratory.[1–6] This sampling and analysis procedure is not suitable for complete automation.

2) Sampling and enrichment of the components can be performed in one step: The compounds are frozen out in a cold trap, the usual refrigerant being liquid nitrogen. In this method the sample is analyzed on the spot in a field laboratory.[7] Minimal sampling artifacts are associated with this approach. For automation the required liquid nitrogen supply must be minimized. Only recently this concept has been automated.[8]

3) For sampling and enrichment of volatile air components, suitable sorbent material can be used. This procedure is well established and tested using activated carbon followed by chemical desorption of the compounds to be analyzed.[9] Also well-documented is the sampling of hydrocarbons with Tenax and subsequent thermal desorption.[10, 11] This method has been criticized because of possible sampling artifacts;[12,13] however, the approach was carefully tested.[11] The technique of sampling volatile air components from ambient air using sorbent material was automated by Doulson[14] and Lambeth *et al.*[15] The apparatus of Doulson is commercially produced by AMA (Apparate für Mess- und Analysentechnik, Hilden, FRG). The instrument appears to be used successfully by others without further modifications.[16] To our knowledge this was the only commercially available instrument possibly suitable for the purpose of our study at the start of the project.

Although techniques for the automated analysis of hydrocarbons are available, the moisture in the air sample is still a challenge when dealing with the analysis of those compounds from ambient air. We describe in this paper an approach, in which the dehydration of the sample by K_2CO_3 and the regeneration of the dehydration agent were automated. Beside other modifications of the commercially available instrument, the experience of the performance of the analytical system during a measuring campaign of about 2 months (March and April, 1988) is described. Because of strong variations of the meteorological conditions during this campaign, the measurements allowed conclusions about the possibilities and limitations of such an analytical system for field measurements.

EXPERIMENTAL

Materials and Chemicals

Gases for the GC analysis: He, 99.999% purity; N_2 and pressurized air, technical grade; H_2, supplied by a hydrogen generator of an instrument measuring SO_2.

K_2CO_3, toluene, cyclooctamethyltetrasiloxane: Analytical grade.

Sorbent materials: Tenax TA (mesh: 35–60); Carbosieve SII (mesh: 60–80); Molecular sieve 5A (mesh: 40–60).

Calibration gases: Scott calibration gases (calibrated mixtures of several hydrocarbons, 10–20 or 100 ppm in N_2), supplied by Supelco.

Ni capillary: 1/16" i.d., coated on the inside with silicium, received from Mettler Inc., Greifensee, Switzerland (F. Behm).[17]

Copper tubes were used for all lines supplying gases such as the purge gas; the connections were soldered.

Materials used for the construction of the air drying instrument, which is described in the Appendix: Valves with direct contact with the air sampled for analysis, Nupro (SS-6BK-MM-1C) pneumatically driven; other valves, Huba 332.992, electrically driven. All lines of the air sampled for analysis were stainless steel.

Control device: Eberle Schaltung, PLS 509S.

Gas Chromatographic Analysis

Gas chromatograph: Hewlett-Packard, 5890. Integrator: Hewlett-Packard, 3393A. Detection: FID, using H_2 and compressed air as combustion gases and N_2 as make-up gas.

Cleaning of He (carrier and purge gas): Precleaning with hydrocarbon and oxygen trap from Chrompack. The purge-carrier gas stream was divided in two symmetrical units, each containing a cryogenic trap filled with Molecular sieve. One was immersed in a dewar tube containing liquid nitrogen to freeze out remaining impurities. To regenerate the other trap, the accumulated impurities were flushed out at room temperature by a small regulated He flow. The two traps were exchanged once a week. For convenience, a valve was positioned after the oxygen trap.

Analytical column: PLOT fused silica column, Al_2O_5/KCl, 50 m, 0.32 mm i.d. (Chrompack).

Temperature program used: 3 min at 60 °C; increase at a rate of 12 °C/min up to 120 °C, afterwards at 15 °C/min up to 200 °C, then kept constant for 10–20 min at 200 °C.

Description of the Deactivation of the Silicium-coated Nickel Capillaries[17]

2 ml of cyclooctamethyltetrasiloxane was drawn through the tubes. Remaining liquid was blown through the tubes by N_2 gas. The tubes were closed and heated up to 380 °C and kept at this temperature for 3 h. Afterwards they were slowly cooled to room temperature. The tubes were immersed in toluene, then N_2 was blown through the tubes with a low flow rate. The temperature was slowly increased again and kept constant for 10 min at 380 °C, with a small flow of N_2 flushing the tube.

Short Description of the Instrument AAR-KA 5890A and the Measuring Conditions Used

Figure 1 shows the whole analytical system used, including modifications from the commercially available instrument described in this paper. The sample pretreatment part consisted of the following parts: the sampling and enrichment unit (AR)

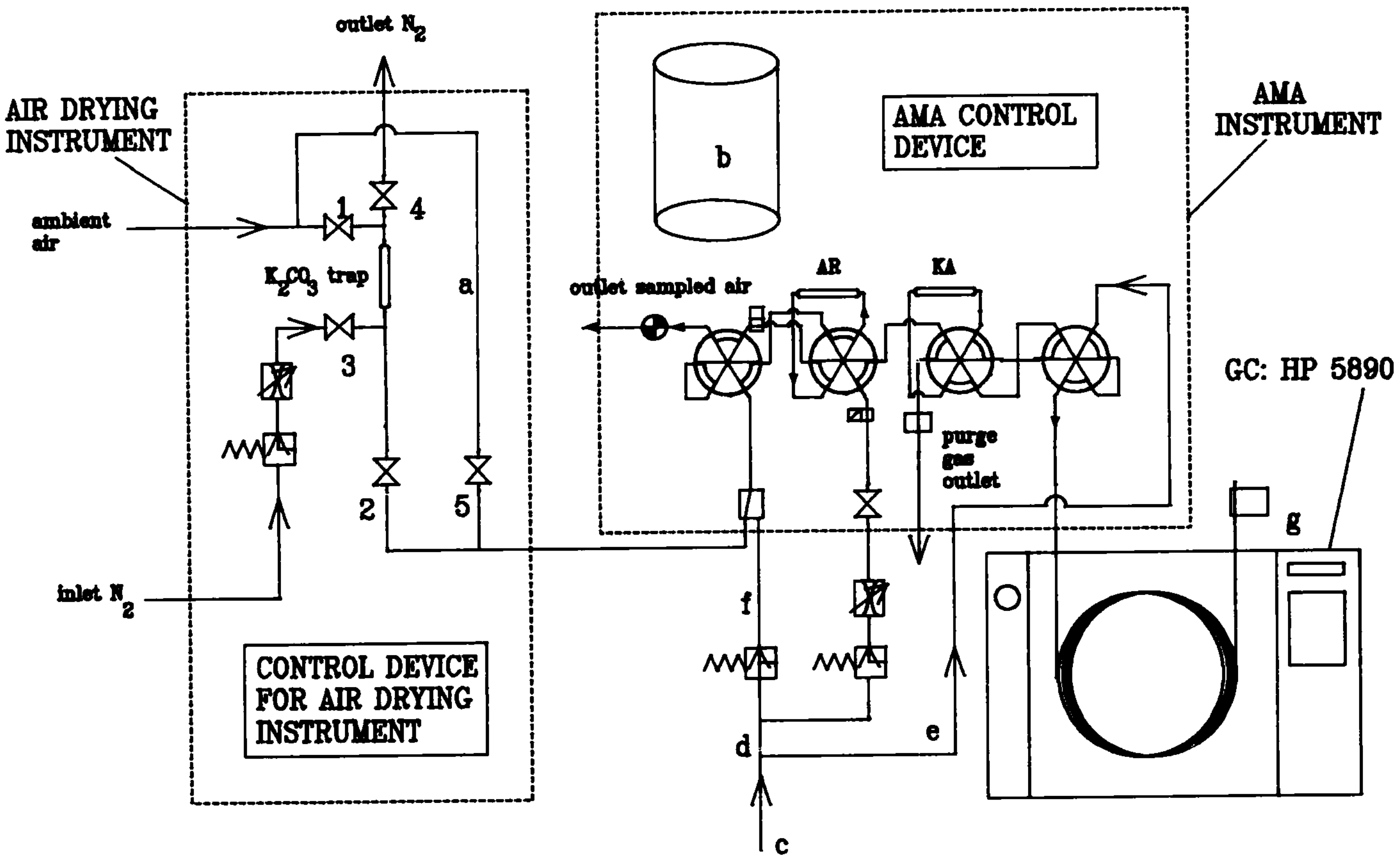


Figure 1 Overview of the apparatus used for automated sampling, sample pretreatment and analysis of light hydrocarbons in ambient air, including the commercially available instrument AAR-KA 5890A (AMA). (a) Bypass to avoid unnecessary exhaustion of the drying agent; (b) Refrigerant tank (50 l); (c) Purge gas inlet.

Table 1 Short description of the different steps in the analytical cycle of the automated analysis of the light hydrocarbons[a]

Step	*Duration*
1. Sampling (500 ml): AR unit slightly cooled (10–20 °C)	2 min
2. Short backflush of the AR unit by purge gas	20 sec
3. Thermal desorption of the sample from the AR unit (up to 200 °C) and cooling of the KA unit (to −120 °C)	several min
4. Transfer of the sample from the AR to the KA unit by the purge gas stream (flow rate about 10 ml/min)	2 min
5. Evaporation of the hydrocarbons from the hot KA unit (up to 200 °C) and reconditioning of the hot AR unit (200 °C)	2 min/20 min
6. Injection of the sample on the GC column by the carrier gas stream and start of the temperature program of the GC	10 min

[a] Conditions used for our analysis in parentheses.

was a glass tube (0.63 cm o.d., 18 cm long) containing the suitable sorbent material (length of the sorbent material: 11.5 cm). For the sampling of the hydrocarbons from ambient air, a combination of Tenax TA, Carbosieve and Molecular sieve was used. The cryofocusing unit (KA) was originally a glass-lined stainless-steel capillary (0.16 cm diameter, 13 cm long) filled with Tenax TA. The AR and KA units could be heated electrically or cooled using liquid nitrogen. Gas flow rates for the different steps of the sampling pretreatment were governed by four pneumatic 6-port valves. The sample pretreatment unit was mounted on top of the GC.

The steps performed in the analytical cycle are summarized in Table 1.

Blanks and Calibration Procedure

An accessory valve was used to determine the system blanks and the calibration which were measured by incorporating the complete sampling pretreatment. One side of the valve was connected to the purge gas supply. A pressure regulator and a septum were installed in-line. System blanks were measured using 500 ml purge gas. Instrument calibration was performed by adding suitable volume of calibration gases to the purge gas stream through the septum by syringes.

DISCUSSION

Instrument Development

The design of the AAR-KA 5890A seemed suitable for the analysis of light hydrocarbons from ambient air. A less sophisticated, but similar type of instrument (without cooling of the sorbent material, using only packed columns and constant-temperature GC analysis) had been developed and successfully used for many years at Ciba-Geigy for indoor monitoring of toxic substances in the air of chemical production plants.[18,19] Many technical problems, however, had to be solved to use the AAR-KA 5890A[20] for our purposes. In addition, two major modifications to the instrument were necessary for our measurements:

1) To prevent blockage of the cryofocusing unit (KA) we redesigned the unit using 1/16" Ni tubes which were coated inside with Si and deactivated (see Experimental part) and filled with Tenax. In contrast to previous experience with the unchanged unit, no blocking of the air flow was observed. Calibrations performed after a 2-month measuring campaign showed that the coating was still in good condition.

2) An important problem is the effect of moisture on the Molecular sieve.[15] In the original design of AMA, silica was used before the Molecular sieve to dry the sampled air. However, drying agents such as silica and $Mg(ClO_4)_2$ have been tested but rejected by others for drying of samples for the analysis of light hydrocarbons from ambient air.[5,21] The possible lack of sufficient drying capability of silica was also of concern to us. Other groups used K_2CO_3 for the drying of the air samples for the analysis of light hydrocarbons;[3,6] however, the drying capacity of K_2CO_3 was also small. In the case of humid air samples, the maximum amount of K_2CO_3 that could be used without interfering with the hydrocarbon analysis could be exhausted after drying only about 2 liters of ambient air. Therefore we decided to use a reconditioning approach. At about 100 °C, K_2CO_3 was reconditioned in a stream of an inert gas. These steps were automated. The design and function of the reconditioning apparatus are described in the Appendix. This instrument worked without any problems during our measuring campaign.

Performance of the Analytical System During a Measuring Campaign

About 120 measurements of light hydrocarbons from ambient air were performed during March and April, 1988. The instrument was located in a van of the Institute for Applied Plant Biology at Schönenbuch, a rural place about 5 km to the north-east of the city of Basel (Switzerland). We measured alternatively ambient air samples and system blanks. The sampling frequency of the AMA system was one per 1.5 or 2 h. During the measurement of the system blank the K_2CO_3 in the drying trap was regenerated. The duration of each different step is listed in Table 2. Observed concentrations of the light hydrocarbons in ambient air were corrected by subtracting the means of the compound concentrations in the blanks measured before and after each sample.

The peaks of the ambient air samples were identified by comparing the retention times with chromatograms of calibration runs, which were performed by addition of Scott Calibration Mixtures to the purge gas. The qualitative composition of the air samples of the measuring campaign was always very similar. The peaks of the nine quantified compounds listed in Table 3 could usually be tentatively identified without any problems; sometimes it was necessary to use relative retention times. Coeluting peaks could not be excluded completely using the retention times from only one analytical column. To solve this problem, GC/MS analysis could be used; however, GC/MS analysis of these light hydrocarbons is not an easy task and was not attempted.

Table 2 Signals from the control device of the automated instrument to dry air samples and to regenerate the drying agent[a]

Step	*Position of the valves*					*Heating trap*
	1	*2*	*3*	*4*	*5*	
Sampling of ambient air (30/20)	open	open	closed	closed	closed	off[b]
	closed	closed	closed	closed	open	off[c]
Regeneration of the drying agent (60/40)	closed	closed	open	open	open	on
Cooling of the drying trap (150/120)	closed	closed	open	open	open	off

[a] Numbers of the valves refer to Figure 1, left side. The time periods used in this work are given in parentheses (min).
[b] The ambient air is sampled for analysis by the AMA system.
[c] The air pumped by the AMA instrument is not used for analysis.

Table 3 Results of a 2-month field measuring campaign (concentrations in ppb (v/v)) at Schönenbuch (Switzerland)[a]

	Median	*25% quantiles*	*75% quantiles*	*Max. value*	*No. of observ.*	*Corr. coeff. vs.* $[NO_x]$
Propane	1.51	1.16	1.92	3.63	117	0.509
Propene	0.79	0.40	1.30	7.16	101	0.192
Acetylene	0.54	0.28	0.87	1.83	72	0.383
Isobutane	1.17	0.75	1.82	8.32	119	0.681
n-Butane	1.20	0.74	2.21	6.72	120	0.390
1-Butene	0.42	0.26	0.64	3.73	90	0.044
Methylbutane	1.25	0.47	2.43	9.94	119	0.477
n-Pentane	1.23	0.56	2.06	5.28	119	0.521
1-Pentene	0.47	0.27	0.86	3.35	94	0.166

[a] A significant number of runs yielded results below the detection limits; they are not included in the number of observations.

Typical results of the measurement of a system blank, a calibration run, and two samples of ambient air are shown in Fig. 2(a)–(d). After eliminating a mechanical problem (leaking of a valve in the purge gas system), the blanks were acceptable and calibration runs yielded acceptable results.

The chromatograms of the air samples in Figure 2 do not show optimal resolution of a PLOT capillary column. The following facts may explain these observations:

- the dead volume of the KA unit and the lines between the KA unit and the analytical column was rather large;
- due to the design of the KA unit the flow characteristics during the transfer of the sample from the KA unit to the capillary column were not optimal.

However, the separation of the peaks was usually sufficient for quantification of those light hydrocarbons in ambient air samples, which were measured in this study.

Memory effects could be substantial as shown in Figure 2(e), which is the blank

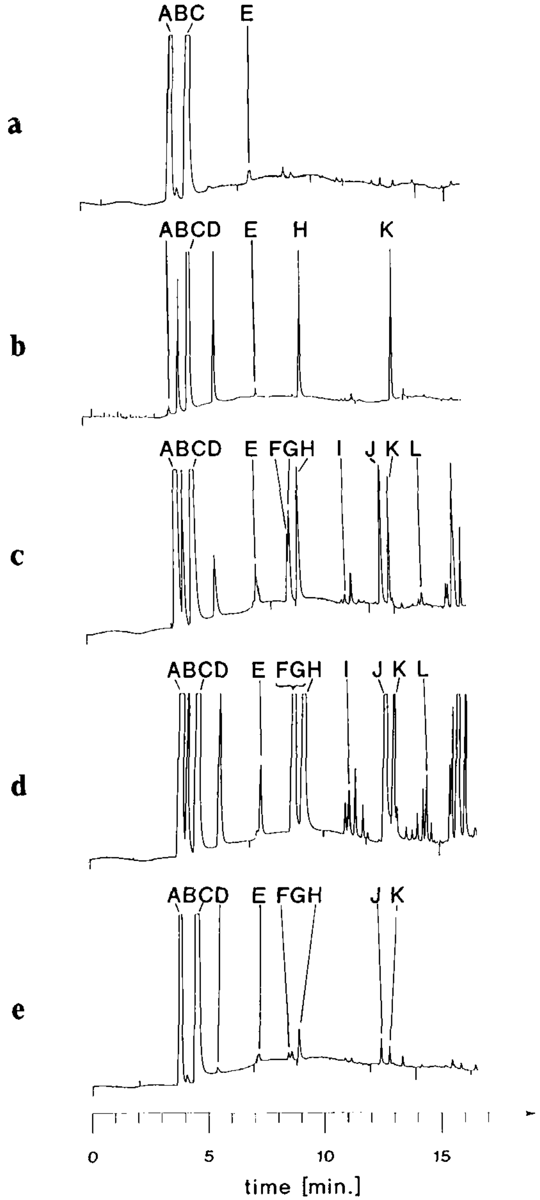


Figure 2 Chromatograms measured with the analytical system used in this work. Sampling site: Schönenbuch (Switzerland).

(a) Typical system blank (500 ml purge gas), 22 April 1988 (01.25).

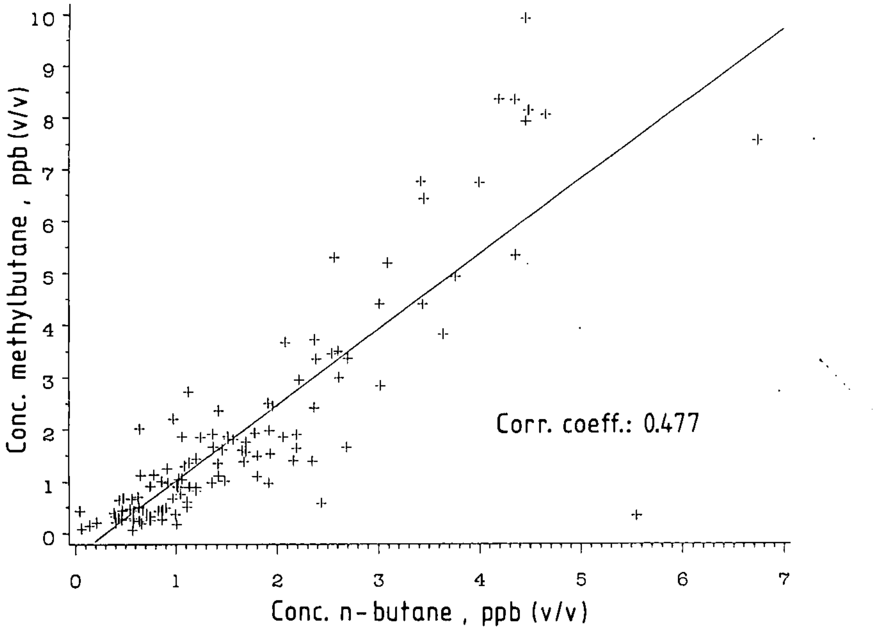
(b) Calibration: 100 μl of a mixture of *n*-alkanes (about 100 ppm) in 100 ml purge gas.

(c) 500 ml ambient air, 22 April 1988 (03.25).

(d) 500 ml ambient air, 25 April 1988 (10.25).

(e) System blank (500 ml purge gas), measured immediately after chromatogram (d).

A, methane; B, ethane; C, ethylene; D, propane; E, propene; F, acetylene; G, isobutane; H, *n*-butane; I, 1-butene; J, methylbutane; K, *n*-pentane; L, 1-pentene (tentatively identified).



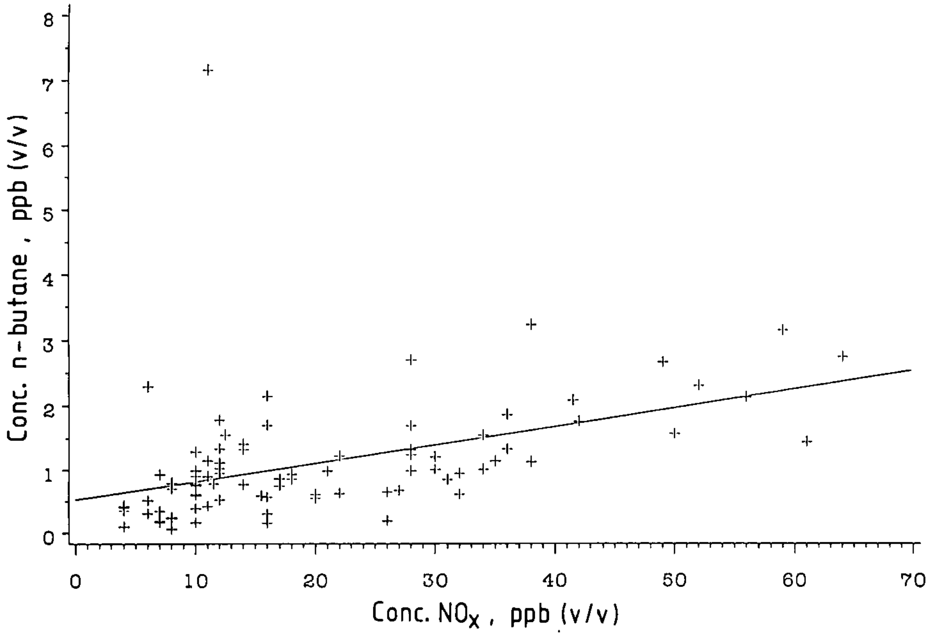


Figure 3 Examples of correlation of concentrations of different species measured during the field measuring campaign.

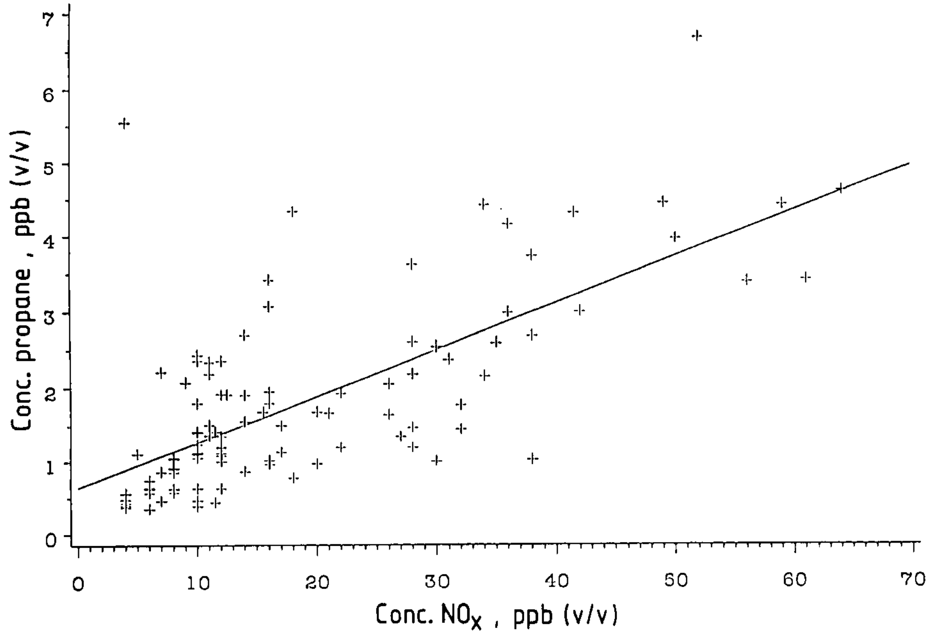


Figure 4 Examples of correlation of concentrations of different species measured during the field measuring campaign.

value measured immediately after the chromatogram of Figure 2(d), the observation with the highest concentrations found during the measuring campaign. In the case of isobutane and *n*-butane the concentrations calculated from Figure 2(e) are about 4% of the concentrations of the field observation presented in Figure 2(d). The absolute values of those concentrations were higher than 1 ppb (v/v), implying that memory effects can have a strong influence, if a measurement with low concentrations would follow directly after an observation such as shown in Figure 2(d). Because we always performed a system blank in-between two air samples, these memory effects lead to only a slight overestimation of the blank values in our procedure to calculate the concentrations of the hydrocarbons.

Detection limits were defined by the blank values, which differed from compound to compound. They were usually much less than 1 ppb (v/v).

The results of the field measurements summarized in Table 3 showed large differences in concentrations which offered the opportunity to evaluate the potential and limitations of the present analytical system. Very low concentrations of the measured hydrocarbons (often below the detection limit in case of 1-butene and 1-pentene which caused the relatively large number of non-listed values in Table 3) were observed when strong westerly winds occurred. In those cases the winds approached the sampling site from the Burgundische Pforte, which is only a sparsely populated region. The highest concentrations were measured when the winds came from the north-east to the south, which can be explained by close downwind sources.

In some cases high correlations between the concentrations of hydrocarbons were observed as exemplified in Figure 3(a). The correlations between the concentrations of the hydrocarbons and the simultaneously measured NO_X depend strongly on the species (see Table 3 and Figures 3(b) and 4. As shown in Figure 3(b), low correlation coefficients can be caused by outliers and/or large scatter of the data. However, the observed pattern of correlations between the concentrations of the air pollutants is expected for ambient samples, because of the complex interactions of meteorological influences, different emission sources and atmospheric chemical processes.

For the validation of complex numerical atmospheric chemical models and the monitoring of the air quality, extended data sets of hydrocarbon measurements are required. After complete development of such an automated system, sensitive analysis of light hydrocarbons with low manpower costs can be performed. The instrument was usually unattended for about 1 week. About 1 day per week was required to fill the nitrogen dewars, to change the cryogenic traps used to clean the purge gas and to start the system again, carefully checking the performance of the analytical system, especially all flow rates.

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APPENDIX

Design and Function of an Automated Instrument to Dry Air Samples and Recondition the Drying Agent

The apparatus was designed and manufactured by the Department of Measuring Technique and Automation of Ciba-Geigy, Basel. The instrument consisted of the following parts (compare Figure 1, left side):

- The trap containing the drying agent (K_2CO_3 in our study) was a glass tube (1.1 cm i.d., 10 cm length); the desiccant was held by a glass frit.
- The drying trap was surrounded by an oven of alumina. The front plate could be removed, simplifying replacement of the drying agent. Oven temperature were controlled by adjusting the power dissipated through the heating coil.
- A bypass for the ambient air was installed, to avoid rapid exhaustion of the K_2CO_3 drying capacity, because the ambient air was pumped continuously by the AMA instrument.
- Inert gas (N_2) was used to recondition the drying agent; the flow from the supplying bottle was controlled by a pressure regulator and a flow regulator.
- Five valves controlled the flow of the ambient air and the inert gas.
- An easily programmable control device controlled the function of the instrument, including the position of the valves and the heating of the trap of the drying agent. The time periods of the different steps could be set individually (in min).

To avoid condensation of water vapour inside the AMA instrument, a conventional silica trap was additionally installed in the bypass.

The following steps were used to dry the sampled air and to recondition the drying trap, the signals from the control device (positions of the valves, heating) being shown in Table 2.

1) *Sampling step.* In this period, the air could flow through the drying tube containing K_2CO_3. However, to avoid unnecessary exhaustion of K_2CO_3, the incoming air continuously pumped by the AMA instrument flowed through the bypass during most of the time. The signal to position the valves governing the air flow through the K_2CO_3 trap came from the AMA control device (air sampling step of the AMA instrument).

2) *Regeneration step.* To regenerate the drying agent (K_2CO_3), the trap was heated (100 °C) while under inert gas flow.

3) *Cooling step.* Inert gas flowed through the trap which was no longer heated.