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Characterization of a commercial gas chromatography–flame ionization detection system for the in situ determination of C_5–C_{10} hydrocarbons in ambient air

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Abstract

A commercial automated gas chromatograph with preconcentration on solid adsorbents (AirmoVoc HC1010) was coupled with a mass spectrometer in parallel with the flame ionization detection (FID) system and characterized for its suitability for quasi continuous measurements of atmospheric hydrocarbons (HCs) with a time resolution of 20 min. Of the 50 identified HCs in the range C_5–C_{10}, 15 elute in isolated peaks and 20 in groups of two or more HCs. The remaining 15 HCs suffer from coelution by oxygenated and halogenated compounds. Procedures to minimize and quantify the blanks and the memory from the adsorbents are described. Calibration was based on a custom-made diffusion source. The accuracy of this calibration ($\pm$10%, 2σ) was verified by analysis of a certified 70-component standard (average deviation: -4.3 ± 2%). During a field experiment in Summer 1998, the HC1010 system was compared with a custom-made GC system with cryogenic preconcentration and much better separation properties but lower time resolution. In ambient air, good agreement (2σ deviation $<$14% or 10 ppt) was found for HCs and groups of HCs that are free from coelution with oxygenated compounds, whereas large discrepancies (in some cases more than a factor of three) were found for those HCs that coelute with oxygenated compounds, as identified by MS. Analysis of the mass spectra from those peaks via specific target ions showed much better agreement with the FID system of the reference GC within 25%. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Volatile organic compounds (VOCs) play an important role in the photochemical production of ozone and other photooxidants in urban air [1,2]. Therefore, accurate measurements of hydrocarbons (HCs) and other organic compounds are prerequisite for the interpretation of field experiments addressing the chemical development of photooxidants in urban plumes. VOC measurements have also become an important task for air pollution monitoring networks. In the sunlit atmosphere, degradation of the HCs occurs mainly by reaction with hydroxyl radicals (OH) [3].

The chemical lifetime of the HCs due to reaction with OH varies from almost 10 years for methane to

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a few hours for the most reactive compounds. Because of its long life time, the atmospheric distribution of CH_4 is relatively homogeneous (1.6–1.9 ppm, v/v, [4]) whereas the mixing ratio of a reactive compound such as, e.g., toluene varies between 75 ppb (v/v) in urban areas [5] and values of a few ppt (v/v) or less in remote areas [6–9].

While the HC reactivity in maritime air is predominated by CH_4, reactive olefinic and aromatic compounds dominate the total HC reactivity in the urban environment. There, the total reactivity is distributed over more than 100 hydrocarbons [5]. In addition, reactive VOCs of biogenic origin such as isoprene, terpenes and a number of oxygenated compounds, have been identified to contribute significantly to the total VOC reactivity in suburban and rural air masses [10].

Because of their different reactivities, hydrocarbon measurements can be utilized to obtain an estimate of the time integrated OH concentration in an air mass [6,11–15]. The subset of compounds utilized in such an experiment must be measured unequivocally with sufficient accuracy and with sufficient time resolution in order to follow an air mass in a quasi-Lagrangian approach, e.g., Refs. [15,16].

HC measurements are usually made by gas chromatography (GC), either off-line on samples collected in special canisters (e.g., Refs. [7,8,11,17,18]) or on adsorption tubes [5,19,20] or by deploying in situ GC systems in the field (e.g., Refs. [10,17,21–23]). For measurements in urban/suburban air, the instrument should ideally have a time resolution of about 10–20 min, a detection limit of $<$10 ppt (v/v) and sufficient resolution for separation of about 100 compounds. The required detection limit is usually achieved by using large air volumes in combination with preconcentration on solid adsorbents or cryogenically. Relatively long columns with high plate numbers must be used in order to achieve the required separation efficiency which results in analysis times of 1 h or more. The use of narrow bore columns [24] is difficult because of the large sample volume required for achieving a sufficient detection limit for the very reactive but less abundant compounds. While this conflicting situation can principally be resolved by off-line sampling, the amount of containers or adsorption tubes needed for large field experiments and the necessary tests for sample integrity place high logistic demands.

Among the different commercial systems that have become available for automated VOC measurements, the AirmoVoc HC1010 (Airmotec, Illnau, Switzerland, [25]) combines the advantages of small size, low logistic demands (no liquid N_2), and high time resolution. For this reason, it has been used in several scientific projects [13–15,26–31] and has also been implemented in monitoring networks [32].

During the Berlin Ozone Experiment (BERLIOZ) in Summer 1998, we have deployed a HC1010 system for quasi continuous measurements of selected hydrocarbons in the range C_5–C_{10} with a time resolution of 20 min. The HC1010 system was operated side by side with a custom-built instrument, which employs cryogenic preconcentration and has much better separation efficiency due to its longer analytical cycle of 90 min. The column outlet of the HC1010 system was coupled to a mass spectrometer in parallel with the flame ionization detection (FID) system in order to investigate its analytical performance. In this paper, the performance of the HC1010 system, including peak identification, FID response and quantification of blanks and memory, is evaluated from measurements performed on synthetic mixtures and by comparison with the reference GC system in ambient air. On the basis of these exercises, it is outlined for which compounds the HC1010 system can be used in urban/suburban air.

2. Experimental

A schematic diagram of the HC1010 system and the coupling to the MS system is shown in Fig. 1. A detailed description of the instrument's technical aspects is given in Ref. [25]. Briefly, samples are collected on adsorption tubes containing Carbotrap and Carbosieve SIII (3:1, Supelco, Bellefonte, PA, USA) at ambient temperature. Six adsorption tubes are installed on a revolving cylinder and can be moved into enrichment, desorption, purge/rinse or one of three waiting positions. Only three tubes are used in our experiments. While a sample is collected on the first tube the second tube is desorbed and the third tube is purged with H_2 5.0 (Linde, Höllriegelskreuth, Germany) thus providing a quasi continuous measurement with a cycle of 20 min.

The sample is aspirated through the adsorption tube at a flow-rate of about 100 ml/min which is

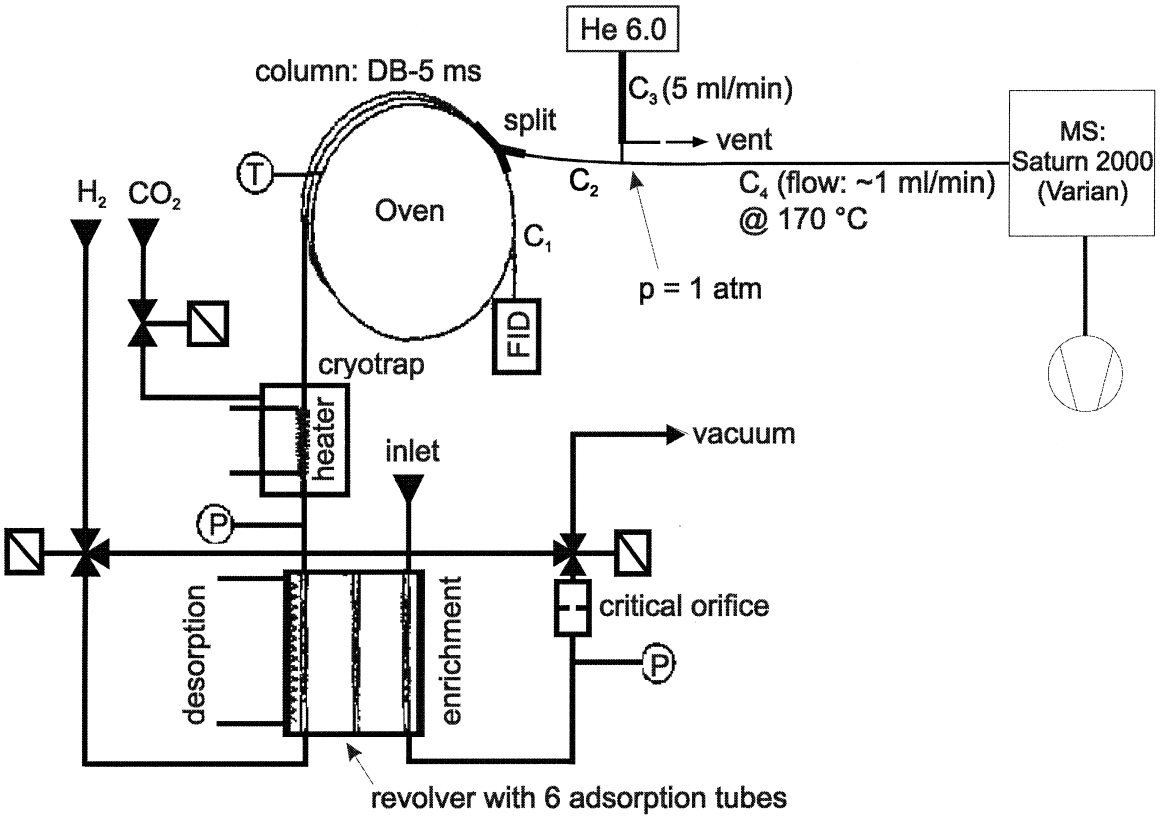

Fig. 1. Schematic flow diagram of the AirmoVoc HC1010 system and the coupling to the mass spectrometer. *T*: temperature measurement, *P*: pressure measurement. For details see text.

limited by a critical orifice downstream of the tube. The sample volume is calculated from the pressure, which is measured upstream of the orifice, and the sampling time. After sampling for 1130 s, the tube is moved into the desorption position by revolving the cylinder. Desorption occurs at reversed flow by heating the sampling tube to 250°C. The hydrocarbons are then re-focused on a cryotrap consisting of a micro packed capillary (18 cm×0.78 mm O.D.×0.50 mm I.D., 5 cm packing of Carbopack B, Supelco). The cryotrap can be cooled with CO_2 in order to improve the trapping efficiency for hydrocarbons $\leq C_5$. Injection onto the analytical column occurs by flash heating of the cryotrap to 350°C within <1 s. Note that the instrument design does not allow backflushing of the cryotrap. The GC column (DB-5 ms, 9 m×250 μm I.D., 1 μm film, J&W Scientific, Folsom, CA, USA) is fixed on a copper plate. Heating of the column at rates up to 30°C/min is achieved with a heater foil on the bottom side of the plate. Cooling is achieved with ambient air by a fan.

The following modifications were made to the HC1010 system. A heat exchanger, which was fed from a cryostat, was mounted below the fan in order to achieve a faster cooling rate and a lower starting temperature of the analytical column. The GC system was coupled to an ion trap mass spectrometer (Saturn 2000, Varian, Walnut Creek, CA, USA) in parallel to the FID system in order to join the FID mass response with the information on the chemical composition provided by the mass spectrometer. As the HC1010 system is not equipped with a constant flow regulator, a simple open coupling as reported by Traitler and Horman [33] would result in a column temperature dependent split ratio which would make calibration of the FID system more difficult. In order to maintain a constant split ratio between the FID

system and the ion trap throughout the chromatogram, an open coupling with make-up gas addition was chosen (Fig. 1).

The effluent of the analytical column (2 ml/min at 30°C) is split via a glass Y-piece and two fused-silica capillaries (C_1 and C_2; split ratio FID:MS=3:1). C_1 is directly introduced into the FID system. C_2 is connected to the transfer line to the MS system (fused-silica capillary C_4 at 170°C) via a low-mass zero dead volume Tee for the addition of the make-up gas. The flow-rate in the transfer line (1 ml/min) is always larger than the maximum flow provided by C_2. The make-up gas (He 6.0) is supplied at an excess flow (5 ml/min, controlled by pressure regulator and capillary C_3). It is added at ambient pressure, with the excess flow being vented through a Tee mounted upstream in the He flow. The capillaries C_1 and C_2 and the connectors are mounted on the column oven and the transfer line is heated to 170°C to avoid condensation of the eluting compounds.

The mass spectrometer was operated in the scan mode (35–250 u) with electron impact ionisation (70 eV) and a scan rate of 3 s^{-1}. For data acquisition and control a personal computer with the commercial Varian software 4.1 was used. The mass spectrometer could be started either manually or by a trigger signal from the GC system. Control and data acquisition of the HC1010 system was performed with a second personal computer via the Software AirmoVista 3.11. All important GC parameters, i.e., column temperature, start and end of sampling, revolving of the adsorption tubes, start and end of desorption and data acquisition were individually programmed. The results from the automatic peak integration provided by the GC software were only used for the measurements of synthetic mixtures, as the AirmoVista software does not allow the manual setting of start and end points of the peaks nor setting of the baseline. The analysis of chromatograms from ambient samples was always made manually with the software from PE Nelson analytical.

Several temperature programs were tested to optimize the separation efficiency for a cycle of 20 min. Although an external refrigeration unit was installed for cooling of the air flow to the column, the column initial temperature could not be reliably reduced below 30°C within the measuring cycle of 20 min during the field measurements, because of the fairly high ambient temperature in the mobile laboratory. Under these conditions the following temperature program yielded the best separation: 1 min at 30°C, 30–140°C at 10°C/min, 1 min at 140°C.

During the BERLIOZ experiment, the HC1010 system was operated side by side with a custom-made GC system based on a HP5890 [23,34] (Hewlett-Packard, Palo Alto, CA, USA, referred to as HP-GC). Briefly, the HP-GC system is appropriate for measuring hydrocarbons in the range C_2 to C_{10}. After drying of the sample air in a Silco Steel tube at −20°C (water trap), the hydrocarbons are preconcentrated at −190°C in a custom-made cryogenic sampling device similar to that described in Refs. [17,35]. Samples are taken for 20 min at a flow-rate of 50 ml/min. After thermal desorption at 80°C, the hydrocarbons are re-focussed and separated on a capillary column (DB-1 ms, 90 m×320 μm I.D., 3 μm film, J&W Scientific) followed by FID. A complete measuring cycle requires about 85 min. In addition to the better separation on the longer column [plate numbers range from ~340 000 (C_5) to 2 300 000 (C_{10})] and with a moderate temperature program (2 min at −50°C, −50–200°C at 5°C/min, 15 min at 200°C), the cryogenic sampling method, which is widely used for measuring hydrocarbons in ambient air (e.g., Refs. [7,17,35,36]), suffers very little from memory effects and blanks. The memory effect in consecutive chromatograms was found to be less than 0.2% for all compounds. The blanks are well below the detection limits, which range from 8 ppt for the C_5 hydrocarbons to 4 ppt for the C_{10} hydrocarbons.

2.1. Diffusion source

A diffusion source similar to that described in Refs. [37] and [38] was used for peak identification and for quantitative calibration. A schematic outline is shown in Fig. 2. Hydrocarbons of high purity (>99%, Sigma–Aldrich, Deisenhofen, Germany) are stored in 1/4 in. (1 in.=2.54 cm) O.D. stainless steel vials, topped with stainless steel capillaries (0.17 and 0.53 mm I.D., 1.5–4 cm long) using Swagelok reducing unions. The vials are positioned in an electro-polished stainless steel vessel (V=0.8 l)

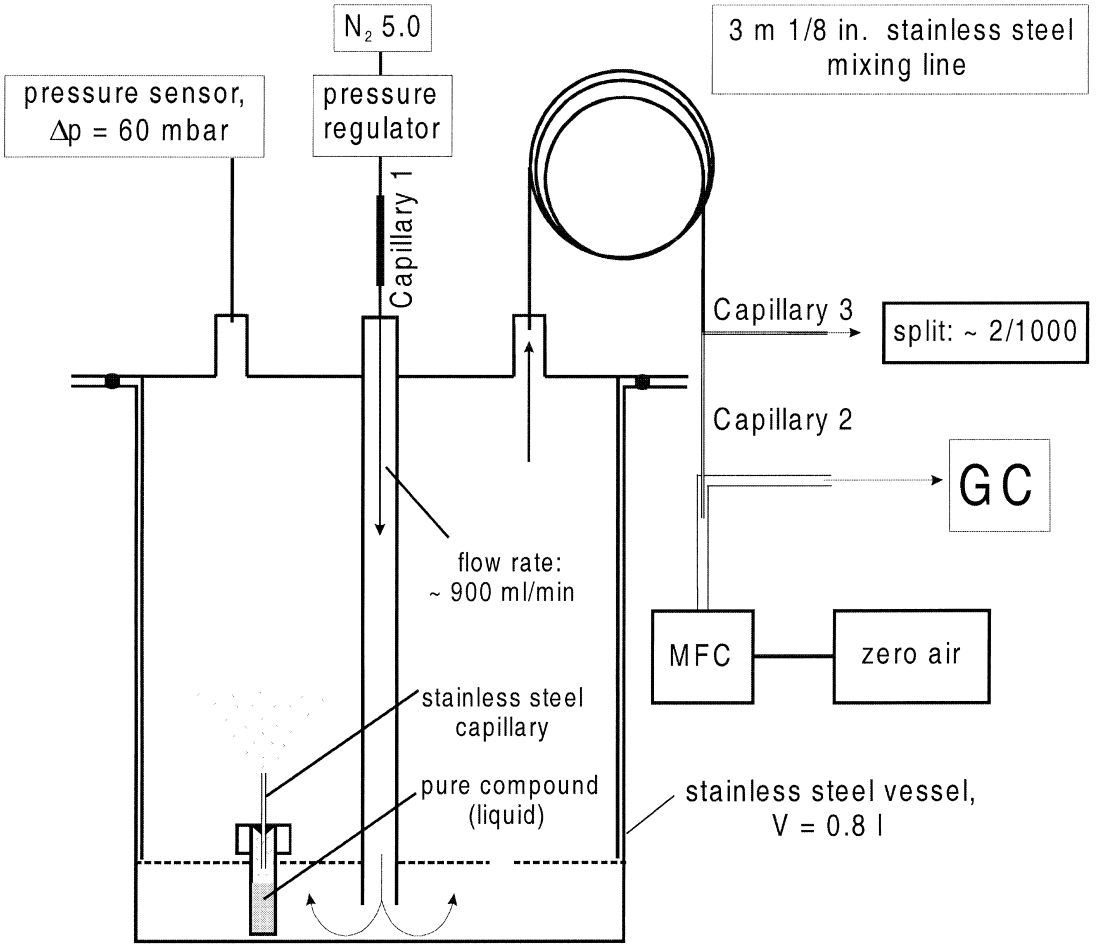

Fig. 2. Schematic outline of the diffusion source. For details see text.

which is continuously flushed with nitrogen (Linde, 5.0). It is supplied through a 1/4 in. O.D. stainless steel tube which ends about 1 cm above the bottom of the vessel. The N_2 flow (900 ml/min) is maintained constant through a capillary and a pressure regulator (Δp~5 bar). A 3 m long 1/8 in. O.D. stainless steel tube at the outlet ensures a homogeneous mixture before the flow is split for further dilution by two capillaries at a ratio of 2:1000. The combination of capillaries yields a pressure inside the source of 60 mbar above ambient. It is continuously monitored with a pressure transducer (BTE4005G4, Sensortechnics, VA, USA) mounted on the top flange. Further dilution of the flow through capillary 2 is achieved with catalytically purified air (zero air) adjusted by a mass flow controller (5850TRC, 0–2 l/min, Brooks, Veenendaal, The Netherlands). The mixing ratios in the final calibration mixture range between 0.2 and 3 ppb.

The source is temperature controlled by peltier elements and a heater foil which are fixed on the outer walls of the vessel (not shown in Fig. 2). The temperature can be adjusted between 15 and 60°C and is stable within 0.2°C. All experiments were conducted at a temperature of 23°C, i.e., close to the laboratory temperature to minimize the time for temperature equilibration when the source is opened for weighing of the vials.

The concentration of the hydrocarbons in the effluent of the source were calculated from the flow-

Table 1
Diffusion rates of the individual compounds between April and June 1998

	Diffusion rates (mg/day)									
	26 March–9 April	9–21 April	21 April–5 May	5–13 May	13–26 May	26 May–8 June	8–15 June	15–26 June	Mean	SD[a] 1σ (%)
2-Methylpentane	1.09	0.98	0.93	0.89	0.86	0.83	0.81	0.79	0.896	11.1 (2.5)
n-Hexane	1.38	1.44	1.45	1.41	1.40	1.38	1.40	1.39	1.408	2.0
2,2,4-Trimethylpentane	1.06	1.06	1.02	1.04	1.03	1.03	1.05	1.03	1.037	1.6
Methylcyclohexane	0.57	0.55	0.53	0.53	0.53	0.50	0.49	0.49	0.524	5.4 (0.7)
Toluene	1.62	1.71	1.62	1.62	1.62	1.62	1.63	1.62	1.632	2.0
n-Octane	0.63	0.63	0.61	0.62	0.61	0.60	0.61	0.61	0.613	1.8
Ethylbenzene	0.44	0.45	0.43	0.45	0.44	0.44	0.45	0.44	0.442	1.2
n-Nonane	0.21	0.20	0.19	0.21	0.21	0.19	0.20	0.20	0.202	3.0
Isopropylbenzene	0.19	0.19	0.17	0.19	0.18	0.18	0.19	0.18	0.183	4.3
1,3,5-Trimethylbenzene	0.35	0.36	0.34	0.35	0.35	0.33	0.34	0.34	0.343	2.4
1σ error of diffusion rates	0.005	0.006	0.005	0.010	0.005	0.005	0.010	0.010	–	–

[a] The numbers in parentheses give the standard deviation after removal of the systematic trend.

rate of N_2 and the mass loss in the different vials. The latter was determined with a microbalance (AT 201, Mettler Toledo, Giessen, Hessen, Germany) in intervals of 7–14 days. The error of an individual diffusion rate, as estimated from the precision of the weighing of an empty vial (0.1 mg, 2σ) and the uncertainty in the flow-rates (1%, 2σ), propagate into a total uncertainty of 2–10% (2σ). This is in the same range as the experimentally determined standard deviation of the diffusion rates determined from the eight time intervals in 1998 (see Table 1). For most compounds, the standard deviation (1σ) is well below 5%. Exceptions are 2-methylpentane and methylclohexane which show a systematic decrease in the diffusion rate. After removal of the trend, these compounds exhibit similar standard deviations as the rest. Therefore, calibration of the GC system was based upon the diffusion rates during the actual measuring interval. We have presently no explanation for the decrease in the diffusion rates of 2-methylpentane and methylcyclohexane.

3. Peak identification

A chromatogram of an ambient air sample is shown in Fig. 3. Identification of the different hydrocarbons was based upon retention times, using static synthetic standards of known composition and mixtures made with the diffusion source. The identification was verified with the mass spectrometer in ambient samples, i.e., by comparison with mass spectra from the National Institute of Standards and Technology library (NIST 92) and with those obtained from synthetic mixtures.

Table 2 lists all peaks identified so far on the HC1010 system. Of the 50 identified HCs in the range C_5–C_{10}, 15 elute in isolated peaks and 20 in groups of two or more HCs. The remaining 15 HCs are subject to coelution by oxygenated and halogenated compounds. The C_4 hydrocarbons are not investigated here, since experiments in the past had shown that separation of these compounds is very poor unless a lower starting temperature of the column is achieved. In addition, the cryotrap must be cooled to temperatures below −25°C in order to avoid breakthrough of the C_4 hydrocarbons. Due to a failure of the CO_2 injection system, this was not possible during the BERLIOZ campaign.

4. Calibration

The signal of a properly operated FID system is proportional to the total mass of a hydrocarbon in the carrier gas flow and thus a unique calibration factor (RF_m, Eq. (1)), can be applied with deviations on the order of a few percent [39] (with the exception of

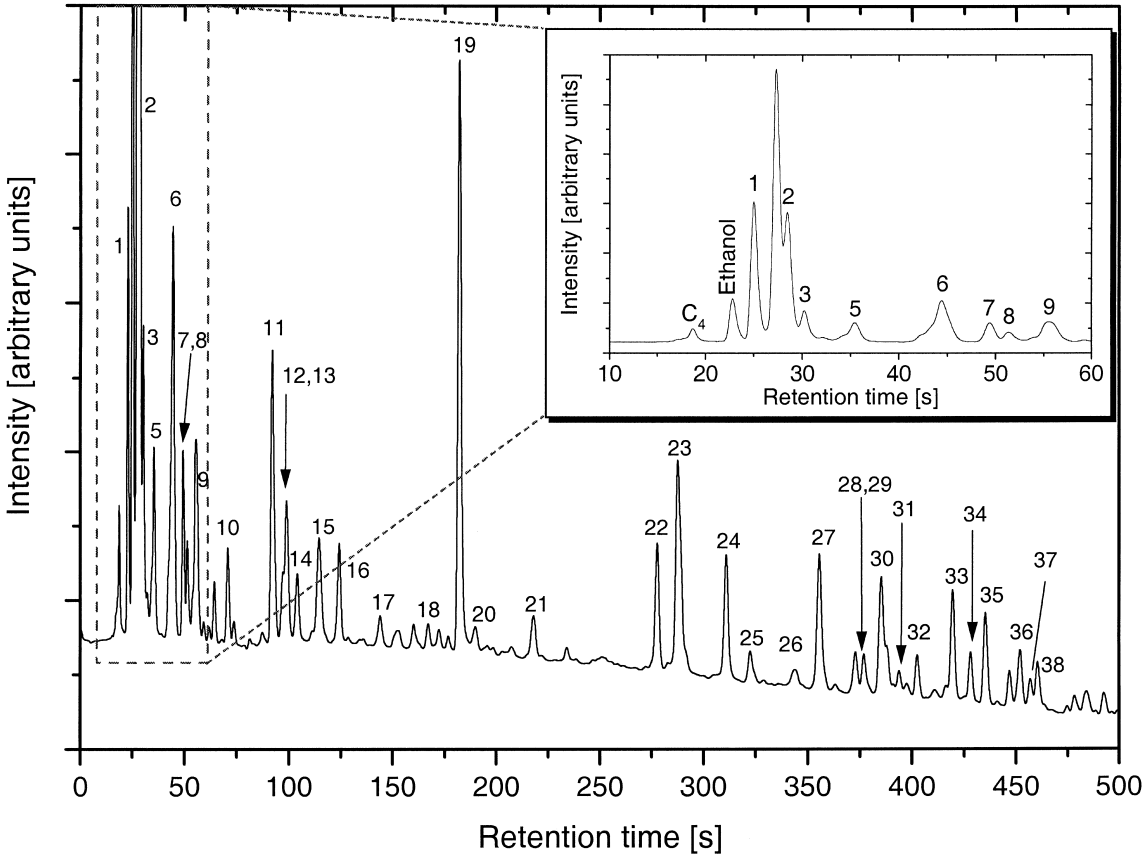

Fig. 3. Chromatogram of an ambient air sample during the BERLIOZ campaign on 21 July 1998, 06:56–07:15 GMT. Numbers refer to the substances listed in Table 2.

acetylene, for which the response factor seems to depend strongly on the operating conditions of the FID system [40–43]).

$$\mathrm{RF_m} = \frac{A_i}{\mu_i M_i} \cdot \frac{RT}{V_S p_S} \left[\frac{\mathrm{A\,s}}{\mathrm{g}} \right] \quad (1)$$

where A_i = peak area (A s), μ_i = mol fraction of the compound in the sample (ppb), M_i = molar mass of the hydrocarbon (g/mol), $V_S p_S / RT$ = sample size (mol).

The response of the HC1010 system was investigated for compounds in the range C_6–C_9 using both, a certified standard [BOC No.: 292662, certified against standards from NPL (National Physical Laboratory, Teddington, UK); quoted accuracy ±5%] and the diffusion source. The BOC standard (BOC Gase, Stuttgart, Germany) which contains (as certified) 494 ppb acetylene, 462 ppb ethene, 469 ppb propene, 452 ppb 1-butene, 472 ppb *n*-butane, 415 ppb 1-hexene, 431 ppb *n*-hexane, 393 ppb benzene, 579 ppb toluene and 606 ppb *n*-octane was dynamically diluted with zero air via mass flow controllers (MFCs) at a ratio of 1:200. The MFCs were calibrated with an automated soap bubble flow meter (The Gilibrator, Gillian Instrument, NJ, USA). Subsequent measurements of the zero air were made to ensure the absence of significant contamination in the dilution gas. The diffusion source described above produced the following hydrocarbon mixing ratios (before the final dilution of 2:200): 171 ppb 2-methylpentane, 295 ppb *n*-hexane, 167 ppb 2,2,4-trimethylpentane, 91 ppb methylcyclohexane, 322 ppb toluene, 97 ppb *n*-octane, 76 ppb ethylbenzene,

Table 2
Compounds identified on the HC1010 system in order of elution

Peak No.	t_R (s)	Main hydrocarbon in ambient air[a]	Coeluting compounds[a]	PC
1	25.0	2-Methylbutane (a)	–	+
2	28.4	*n*-Pentane (a)	*Propanone (c)*, 2-methyl-1-butene (a), 1-pentene (a)	#
3	30.2	Isoprene (a)	*trans*-2-Pentene (a)	+
4	32.1	*cis*-2-Pentene (a)	2-Methyl-2-butene (b), *+ unknown (c)*	*
5	35.4	2,2-Dimethylbutane (a)	3-Methyl-1,2-butadiene (a)	+
6	44.4	2-Methylpentane (a)	2,3-Dimethlybutane, cyclopentane, *2-methoxy-2-methylpropane (c)*	#
7	49.4	3-Methylpentane (a)	–	+
8	51.3	1-Hexene (a)	2-Methyl-1-pentene (b), *C_4H_6O (c)*	#
9	55.5	*n*-Hexane (a)	*Butanone (c)*	#
10	70.8	Methylcyclopentane (a)	2,4-Dimethylpentane (a)	+
11	92.1	Benzene (a)	Cyclohexane (a), *tetrachloromethane (c)*	(+)
12	97.2	2-Methylhexane (a)	12+13 are separated by one half width in standard but coelute with butanol in ambient air (c)	#
13	98.9	2,3-Dimethylpentane (a)		#
14	104.0	3-Methylhexane (a)	–	+
15	114.5	2,2,4-Trimethylpentane (a)	C_7H_{14} (c), *2-pentanone (c)*	#
16	124.2	*n*-Heptane (a)	*Trichlorethylene (c), $C_5H_{10}O$ (c)*	#
17	143.9	Methylcyclohexane (a)	–	+
18	167.1	2,3,4-Trimethylpentane (a)	–	+
19	182.2	Toluene (a)	2+4-Methylheptane (a), negligible in ambient air	+
20	189.7	3-Methylheptane (a)	*Unknown, $m/z=43$, 60 amu (c)*	#
21	218.0	*n*-Octane (a)	*Tetrachloroethylene (c), hexanal (c)*	#
22	277.7	Ethylbenzene (a)	–	+
23	287.6	*m*-Xylene (a)	*p*-Xylene (a), C_9H_{20} (c), negligible in ambient air	+
24	311.0	*o*-Xylene (a)	Ethenylbenzene (a)	+
25	322.5	*n*-Nonane (a)	*Heptanal (c)*	#
26	343.8	Isopropylbenzene (a)	+, Unknown terpene (c)	*
27	355.7	α-Pinene (a)	–	+
28	373.0	Camphene (c)	–	+
29	377.0	*n*-Propylbenzene (a)	*Unknown (c)*	*
30	385.3	3-Ethyltoluene (a)	4-Ethyltoluene (a), separated by one half width in standard but coelute with unknown compound in ambient air (c)	*
31	393.8	1,3,5-Trimethylbenzene (a)	–	+
32	402.5	2-Ethyltoluene (a)	Unknown terpene (c)	*
33	419.5	1,2,4-Trimethylbenzene (a)	–	+
34	428.1	*n*-Decane (a)	–	+
35	435.3	3-Carene (c)	–	+
36	452.0	*p*-Cymene (c)	–	+
37	456.9	Limonene (c)	–	+
38	460.4	Eucalyptol (c)	–	+

[a] (a): Identification by t_R and MS. (b) Identification by t_R. (c) Identification by MS. –: No indication for coelution found. Non hydrocarbons are in italics.

PC = Peak category. +: Unambiguously identified pure hydrocarbon peak, #: coelution with oxygenated compounds, *: coelution with unknown compounds.

29 ppb *n*-nonane, 29 ppb isopropylbenzene, 51 ppb 1,3,5-trimethylbenzene.

The RF_m values derived from the measurements are displayed in Fig. 4 as a function of the molar mass of the compounds. The diffusion source confirms the assumption of a constant RF_m within the estimated 2σ uncertainty of 10% (see Table 1). The lower panel of Fig. 4 reveals a slight increase of RF_m with retention time (t_R). For quantification, we used the linear regression of RF_m versus t_R shown in Fig.

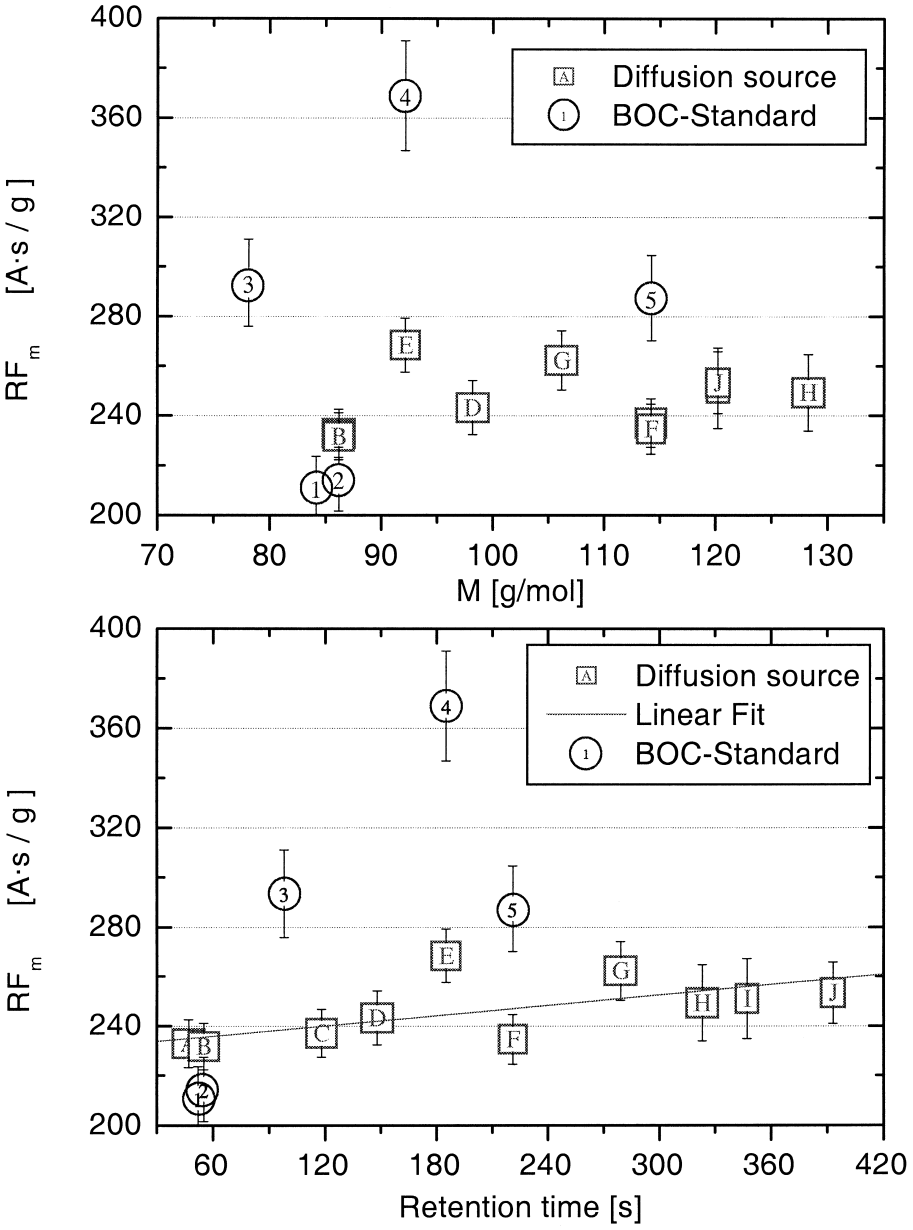

Fig. 4. Mass response factors (RF_m) as obtained from the diffusion source (squares) and the BOC standard (circles) versus the molar mass (upper panel) and the retention time (lower panel) of the compounds. The error bars (1σ) from the propagation of errors include contributions from weighing (or BOC certificate), dilution factors and peak integration. The solid line in the lower panel is a linear fit of RF_m values derived from the diffusion source versus t_R. Characters inside the symbols: 2-methylpentane (A), *n*-hexane (B), 2,2,4-trimethylpentane (C), methylcyclohexane (D), toluene (E), *n*-octane (F), ethylbenzene (G), *n*-nonane (H), isopropylbenzene (I), 1,3,5-trimethylbenzene (J), 1-hexene (1), *n*-hexane (2), benzene (3), toluene (4), *n*-octane (5).

4. Deviations of the individual compounds from the regression line are within the 1σ uncertainty of the diffusion source ($\leq$5%), except for toluene (+9%) and *n*-octane (−6%).

In contradiction to the certificate, the standard deviation of the average RF_m values calculated from the BOC standard is about five-times larger. Consequently, we corrected the concentrations in the BOC standard with the linear regression for RF_m from the diffusion source and used the thus corrected BOC standard for the regular calibration checks in the field.

During BERLIOZ, the calibration of the different participating laboratories was harmonized by comparison of the individual working standards with a primary standard containing 70 hydrocarbons in the lower ppb and sub ppb range, which was prepared at the National Center for Atmospheric Research (NCAR) (Boulder, CO, USA). It is referred to as NCAR-BERLIOZ standard. The standard was measured on 3 different days with both the HC1010 and the reference GC systems. For these measurements, the starting temperature of the column was lowered to 25°C by extending the analytical cycle to 30 min in order to improve the separation of toluene from 2- and 4-methylheptane. Unfortunately, the orifice in CO_2 line to the cryotrap was plugged at the beginning of the campaign and could not be repaired due to time constraints. Therefore, the C_4 hydrocarbons could not be captured and the quality for the C_5 hydrocarbons was not as high as for the other compounds. On one of the days, significant losses of the C_5 hydrocarbons were observed due to exceptionally high temperatures in the mobile laboratory.

The comparison between NCAR certificate [44] and our analysis with the HC1010 system is shown in Fig. 5. The results are averages over 12 individual chromatograms, except for the C_5 hydrocarbons (eight measurements), where the day with significant breakthrough is excluded. Our own calibration was based on the corrected BOC standard using a slightly retention time dependent value for RF_m (see above). For quantification of coeluting hydrocarbons, e.g., (benzene+cyclohexane) and (isoprene+*trans*-2-pentene), average molar masses were used for calculating RF_m. This procedure introduces only small errors because of the similar molar mass of most of the coeluting hydrocarbons present in the standard. We should like to note, however, that in ambient samples coelution of hydrocarbons with oxygenated compounds constitutes a much larger problem because of the much lower FID response for oxygenated compounds as compared to hydrocarbons [45,46].

In general, good agreement is found between the NCAR certificate and our own calibration. Large deviations are observed for 1,2,4-trimethylbenzene (−41%) and for α-pinene (−72%). When neglecting these compounds, the standard deviation (SD) of the individual ratios (HC1010/NCAR) is 6% and the average systematic deviation of our calibration from the NCAR certificate is $-4.3\pm2\%$ (2σ), in reasonable agreement with the above stated accuracy of the calibration with the diffusion source. The measurements with the reference GC system give a systematic deviation of $-2.3\pm2\%$ (2σ) and a standard deviation of the ratios of 6% without obvious discrepancies for 1,2,4-trimethylbenzene (−10%) and α-pinene (−20%).

The large underprediction of α-pinene by the HC1010 system is most likely the result of isomerization on the adsorbents as suggested by Refs. [47] and [48]. Indeed, significant concentrations of camphene, 3-carene and limonene, which are not present in the NCAR-BERLIOZ standard, are observed. The sum of all terpene peaks in the chromatogram comprises approximately 80% of the NCAR specification for α-pinene and agree within 10% with the value for α-pinene determined by the HP-GC system. We have no explanation for the large deviation of 1,2,4-trimethylbenzene. Isomerization was not observed during the test on the diffusion source.

In addition to the absolute calibration, the accuracy of the measurements may be influenced by blanks and a memory effect from the adsorption tubes of the HC1010 system. In an earlier investigation [49], the memory effect was found to depend on the desorption temperature, which was subsequently optimized. In order to quantify the memory effect for the instrument as used in BERLIOZ, each tube was probed three times with the NCAR-BERLIOZ standard and then three times with zero gas (N_2 5.0, Linde).

The results are summarized in Table 3. For most compounds, the ratio of the peak area in the first zero gas sample to that in the last sample of NCAR-

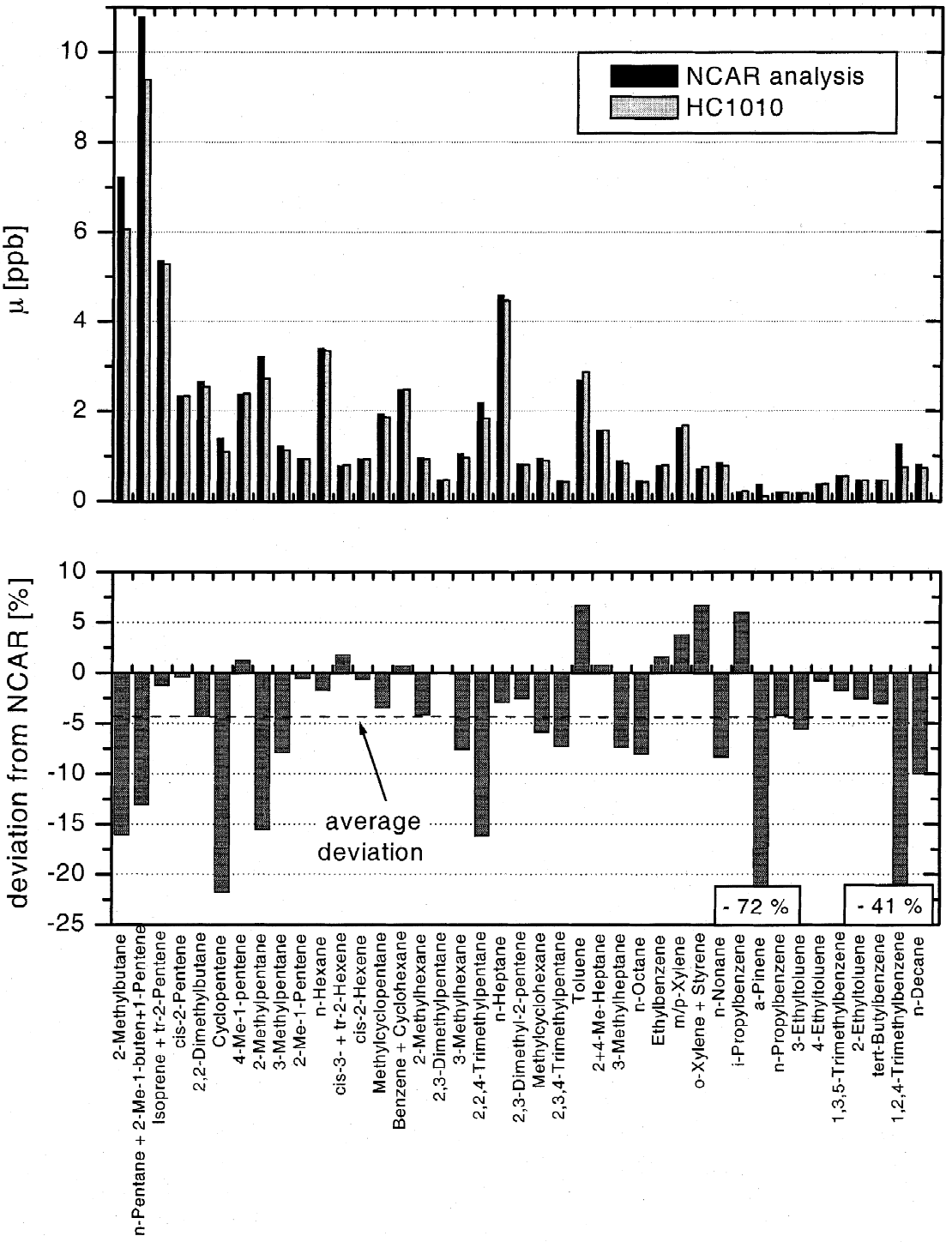

Fig. 5. Comparison of our analysis of the NCAR-BERLIOZ standard with the NCAR certificate. The lower panel gives the relative deviations.

value for taking no sample lies quite well on the linear regression line through the other samples. It should thus be possible to simplify the blank determination procedure by just analyzing a sample ''without sampling'', after the instrument has been probed with zero gas until the memory effect has disappeared.

The blanks were determined three times during the campaign. Significant blanks were found for benzene, toluene, ethylbenzene, *m*/*p*-xylene and *o*-xylene (6, 3, 2, 2 and 2 ppt, respectively) and were subtracted from the ambient air samples. The detection limits as calculated from the SD of the blanks (3σ) were 8, 6, 2, 3 and 2 ppt, respectively. For the other compounds, the sum of blank and contribution from zero gas and inlet line was well below 1 ppt. No blank correction was made for these compounds, and the detection limits were assumed to be 1 ppt, corresponding to 5σ of the baseline noise.

A possible solution for further reduction of the blanks would be a higher desorption temperature or a longer desorption interval.

5. Performance in ambient air

During the BERLIOZ experiment, both GC systems were housed in the mobile laboratory of the ICG-2, which also contained the instrumentation for other chemical compounds (NO, NO_x, NO_y, PAN, HNO_3, O_3, CO and CH_2O), and meteorological parameters. The mobile laboratory was installed near to the small village Pabstthum (52°51′ N, 12°56′ E) about 60 km north-east of the center of Berlin.

A schematic overview of the experimental set up of the GC systems is given in Fig. 7. The inlet was located 9 m above ground on a pneumatic mast. The inlet line (1/8 in. O.D. Silco Steel, Restek, Bad Soden, Germany) was heated to 50°C. Between the inlet line and the junction to both GC systems, a 2 m section of 1/8 in. O.D. stainless steel tubing, heated to 90°C, was installed as an O_3 scrubber [50]. The lines behind the junction were also made of 1/8 in. O.D. Silco Steel tubing. Calibration of both GC systems was done every 2–4 days with the BOC standard (corrected as described above), which was dynamically diluted with N_2 (5.0, Linde) at a ratio of 1:75. The calibration gas was added to the sample line via a three-port valve upstream of the O_3 scrubber at a flow-rate of ~500 ml/min. The excess flow was vented through the inlet line. In order to reduce the memory from the relatively high concentrations in the calibration gas (5–9 ppb), the sample volume of the HC1010 system was reduced by a factor of 10 during calibrations by reducing the

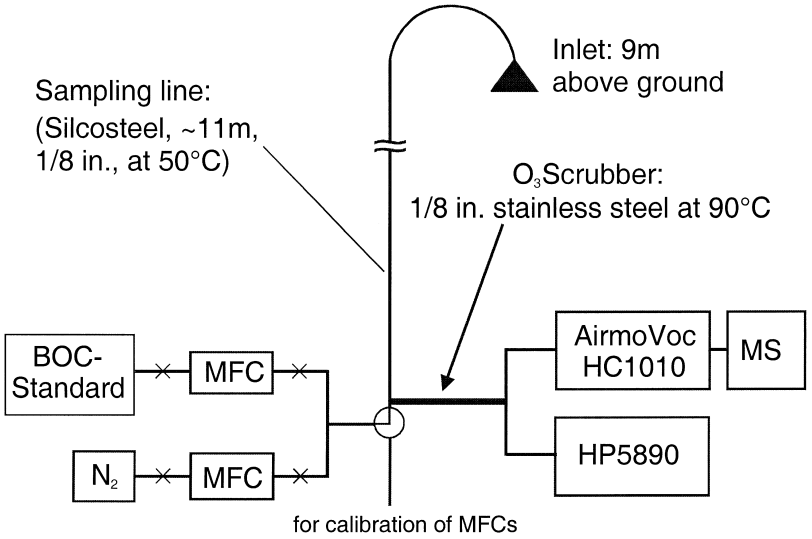

Fig. 7. Experimental set-up of both GC systems in the mobile laboratory during BERLIOZ. For details see text.

sampling time. Sampling was done in the middle of the analytical cycle.

The efficiency of the O_3 scrubber was checked by diluting the BOC standard with zero air that contained 110 ppb of ozone, i.e., somewhat larger than the maximum O_3 mixing ratio of 83 ppb encountered during BERLIOZ in ambient air. The peak areas of the tested alkenes (ethene, propene, 1-butene and 1-hexene) were slightly smaller (<10%) than in absence of O_3, without systematic differences between the different alkenes.

After the BERLIOZ campaign, the Silco Steel inlet line, which had been used before during several campaigns [51,52] was checked for losses of hydrocarbons. A first test was made with the NCAR-BERLIOZ standard which was subsequently sampled by the HP-GC system with and without the (11 m long) Silco Steel line. No special cleaning was applied before the tests. The results with the sampling line in place agreed with the measurements without sampling line within the precision of the GC system. Possible losses of the C_2–C_{10} hydrocarbons in the standard at mixing ratios between 0.20 and 7 ppb were <3%. Similar results were obtained in ambient air, using two almost identical versions of the HP-GC system, one of which sampled through the long inlet line, whereas the other GC system had a short inlet line of ~1 m. Both GC systems were calibrated with the same standard by calculating average RF_m values. The errors of the RF_m values for each GC system were ~5% yielding a standard error of the ratio between both GC systems of 7%. Possible systematic differences between the two inlet lines were found to be <15% or <10 ppt for hydrocarbons with mixing ratios <100 ppt. The larger scatter is consistent with the lower concentrations in ambient air and with the somewhat larger integration errors in more complex mixtures. For hydrocarbons with large peak areas that could be integrated with higher accuracy, e.g., ethane, *n*-butane, benzene, toluene, the deviations between the two GC systems were indeed <7% as expected from calibration.

5.1. Comparison of the HC1010 and HP-GC systems in ambient air

The BERLIOZ intensive observational periods (IOPs) 20, 21 and 23 July and 3, 8 and 9 August 1998 were selected for the comparison of the two GC systems. Because of the different measuring cycles of the two instruments, only those samples were considered where the sampling intervals of the two GC systems differed by less than 4 min. This criterion was fulfilled for 24 measurements of the HP-GC instrument on the 6 days. Quantification of the HC1010 data was performed as described above using average molar masses for multi-hydrocarbon peaks. The toluene peak was evaluated with the molecular mass of toluene since the coeluting compounds (2- and 4-methylheptane) were below the detection limit of the HP-GC system in all but three samples. In these three samples the sum of 2- and 4-methylheptane comprised less than 8% of toluene. Peaks for which coelution with oxygenated or halogenated compounds was found with the mass spectrometer were quantified using the molar mass of the hydrocarbon. The concentrations determined with the HC1010 system were blank corrected.

Fig. 8 shows the ratio between HC1010 and HP-GC systems as a function of the mixing ratio given by the HP-GC instrument. For multi-hydrocarbon peaks, the corresponding sum of the individual peaks was calculated for the HP-GC system (e. g. benzene+cyclohexane). The upper panel contains only peaks of the category "+" in Table 2 and the lower panel contains those HCs that are affected by coelution with oxygenated or unknown VOCs. At high concentrations, the ratio of the pure hydrocarbon peaks converges to values of 1±0.1. At low concentrations, the scatter increases as expected due to the increasing influence of errors from peak integration and blanks. A systematic underestimation of more than 10% is found for the C_5 HCs and for α-pinene. The underestimation of the C_5 HCs is a result of incomplete sampling on the uncooled adsorbent of the HC1010 system. The underprediction of the HC1010 system for α-pinene in ambient air (−15%) is much less pronounced than at the NCAR standard (a factor of 2.5). A possible explanation might be that isomerization on the HC1010 system is suppressed in moist samples. Another possibility is that the isomerization equilibrium established in ambient air with a larger variety of terpenes is accidentally in favor of higher α-pinene concentrations than in the standard, which contains only α-pinene.

The scatter in the rest of the data displayed in the

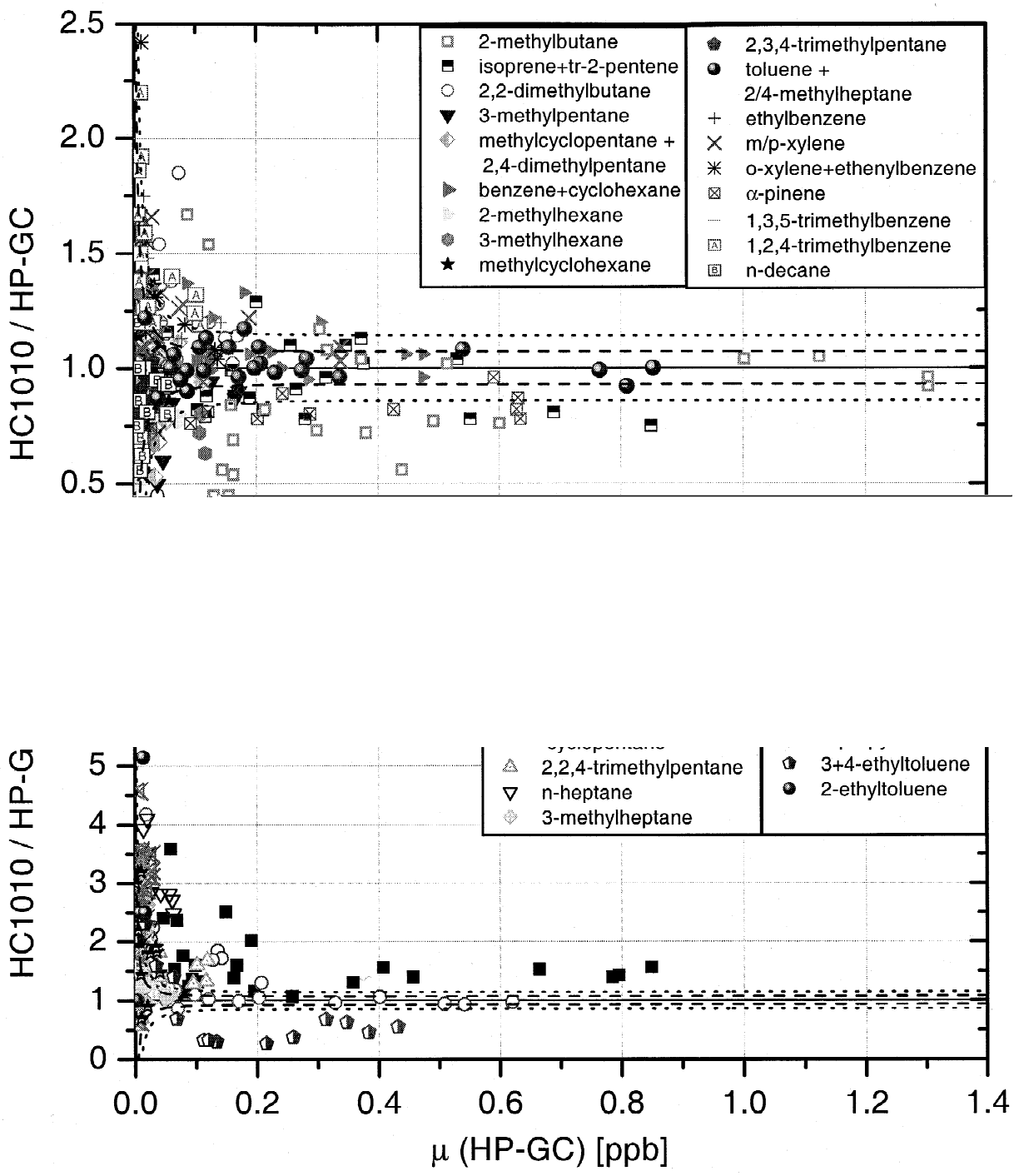

Fig. 8. Comparison of the HC1010 and HP-GC systems in ambient air during BERLIOZ. The upper panel gives the ratio between the two measurements as a function of the concentration for the pure HC peaks. The lower panel shows the ratio for compounds that are subject to coelution with oxygenated or unknown VOCs. The dashed and dotted lines are the estimated 1σ and 2σ errors arising from a relative error of 7% and a constant error of 5 ppt. Note the different scales on the ordinates.

upper panel of Fig. 8 can be described by a relative 1σ error of ±7% and a constant contribution of ±5 ppt (1σ) to the total uncertainty (dashed lines in Fig. 8). About 65% of the data fall inside the dashed lines and 90% of the data fall inside the corresponding 2σ limits (dotted lines in Fig. 8). When assuming equal contributions from both GC systems, the resulting relative error of 5% in each instrument is in accordance with the expectation from the measurements of synthetic standards. The absolute error of ±5 ppt is somewhat larger than what would be estimated from the blanks. In this sense, Fig. 8 provides a more realistic estimate of the uncertainties arising from the integration of small peaks in real atmospheric samples with an unknown mixture of compounds.

The lower panel of Fig. 8 highlights the large errors introduced by coelution with oxygenated compounds, in particular at HC concentrations below 0.2 ppb. The respective oxygenated VOCs are not detected by the HP-GC instrument as they are retained in the water trap. The apparent underestimation of 3+4-ethyltoluene is due to coelution with an unknown substance in the peak flanks of the HP-GC system.

The results of the correlation between the HC1010 and the HP-GC instruments are summarized in Table 4. For most of the pure hydrocarbon peaks the slopes between the two GC systems range between 0.8 and 1.2 (in most cases 0.9–1.1) and correlation coefficients of $R^2>0.9$ (in most cases >0.95). Even

Table 4
Results from the correlation analysis between HC1010 and HP-GC systems in order of elution[a]

Hydrocarbons in ambient air	Fit parameters from linear regression						Range HP (ppt)		
	m	Δm	b (ppb)	Δb (ppb)	R^2	N	Min. (HP)	Max. (HP)	PC[b]
2-Methylbutane	1.01	0.04	−0.053	0.024	0.96	24	9	1300	+
n-Pentane	1.44	0.05	0.019	0.019	0.97	24	43	850	#
Isoprene + *trans*-2-pentene	0.81	0.05	0.033	0.015	0.93	24	30	850	+
2,2-Dimethylbutane	1.13	0.06	0.002	0.004	0.94	24	10	169	+
2-Methylpentane + 2,3-dimethylbutane + cyclopentane	0.91	0.04	0.037	0.010	0.96	24	20	620	#
3-Methylpentane	0.95	0.03	−0.003	0.002	0.98	24	8	205	+
Methylcyclopentane + 2,4-dimethylpentane	1.01	0.04	−0.004	0.002	0.97	24	9	116	+
Benzene + cyclohexane	1.01	0.04	0.011	0.009	0.98	22	87	475	+
2-Methylhexane	0.85	0.03	0.000	0.001	0.98	19	6	75	+
3-Methylhexane	0.71	0.04	0.005	0.002	0.95	21	6	116	+
2,2,4-Trimethylpentane	1.50	0.08	0.000	0.004	0.94	24	7	118	#
n-Heptane	2.69	0.12	0.002	0.003	0.96	21	6	63	#
Methylcyclohexane	1.01	0.09	−0.001	0.002	0.9	15	6	57	+
2,3,4-Trimethylpentane	0.96	0.07	−0.001	0.001	0.95	14	5	30	+
Toluene + 2 + 4-methylheptane	0.97	0.02	0.008	0.006	0.99	24	17	850	+
3-Methylheptane	2.22	0.31	−0.001	0.004	0.86	10	4	21	#
n-Octane	3.52	0.23	−0.008	0.003	0.94	18	5	27	#
Ethylbenzene	1.11	0.03	0.000	0.002	0.99	22	6	142	+
m/*p*-Xylene	1.06	0.02	0.005	0.003	0.99	19	10	340	+
o-Xylene + ethenylbenzene	1.04	0.03	0.006	0.002	0.99	18	5	150	+
n-Nonane	0.99	0.03	0.000	0.000	0.99	14	4	35	#
Isopropylbenzene	3.00	0.65	0.007	0.005	0.68	12	4	14	*
α-Pinene	0.85	0.02	−0.002	0.007	0.99	17	4	630	+
n-Propylbenzene	1.64	0.21	−0.001	0.005	0.87	11	4	40	#
3 + 4-Ethyltoluene	0.48	0.06	0.012	0.014	0.81	15	8	430	*
1,3,5-Trimethylbenzene	1.25	0.55	0.003	0.007	0.47	8	4	23	+
2-Ethyltoluene	4.88	1.81	−0.008	0.020	0.59	7	4	16	*
1,2,4-Trimethylbenzene	1.22	0.03	0.004	0.002	0.99	15	5	108	+
n-Decane	0.91	0.04	−0.001	0.001	0.98	14	4	56	+

[a] Values below the detection limit are discarded.
[b] See Table 2.

the C_5 hydrocarbons 2-methylbutane and (isoprene+ *trans*-2-pentene) show a good correlation with the HP-GC system. For most hydrocarbons that coelute with oxygenated or unidentified compounds on the HC1010 system (cf. Table 2), the slopes are significantly larger than one. Surprising is the tight correlation ($R^2>0.94$) that is observed for many of the peaks (e.g., *n*-octane, *n*-heptane). Obviously, a relatively high degree of correlation must exist in ambient air between the hydrocarbons and the coeluting oxygenated compounds.

The diurnal variation of selected hydrocarbons on 21 July as measured by the HC1010 (FID and mass spectrometry) and the HP-GC systems is displayed in Fig. 9. This day is chosen as it provides the largest dynamic range of the entire campaign. The calibration is based on measurements of the NCAR-BERLIOZ standard on the day before, using compound specific calibration factors for the mass spectrometer and average RF_m values for the FID systems as described above.

With the exception of 2-ethyltoluene, the con-

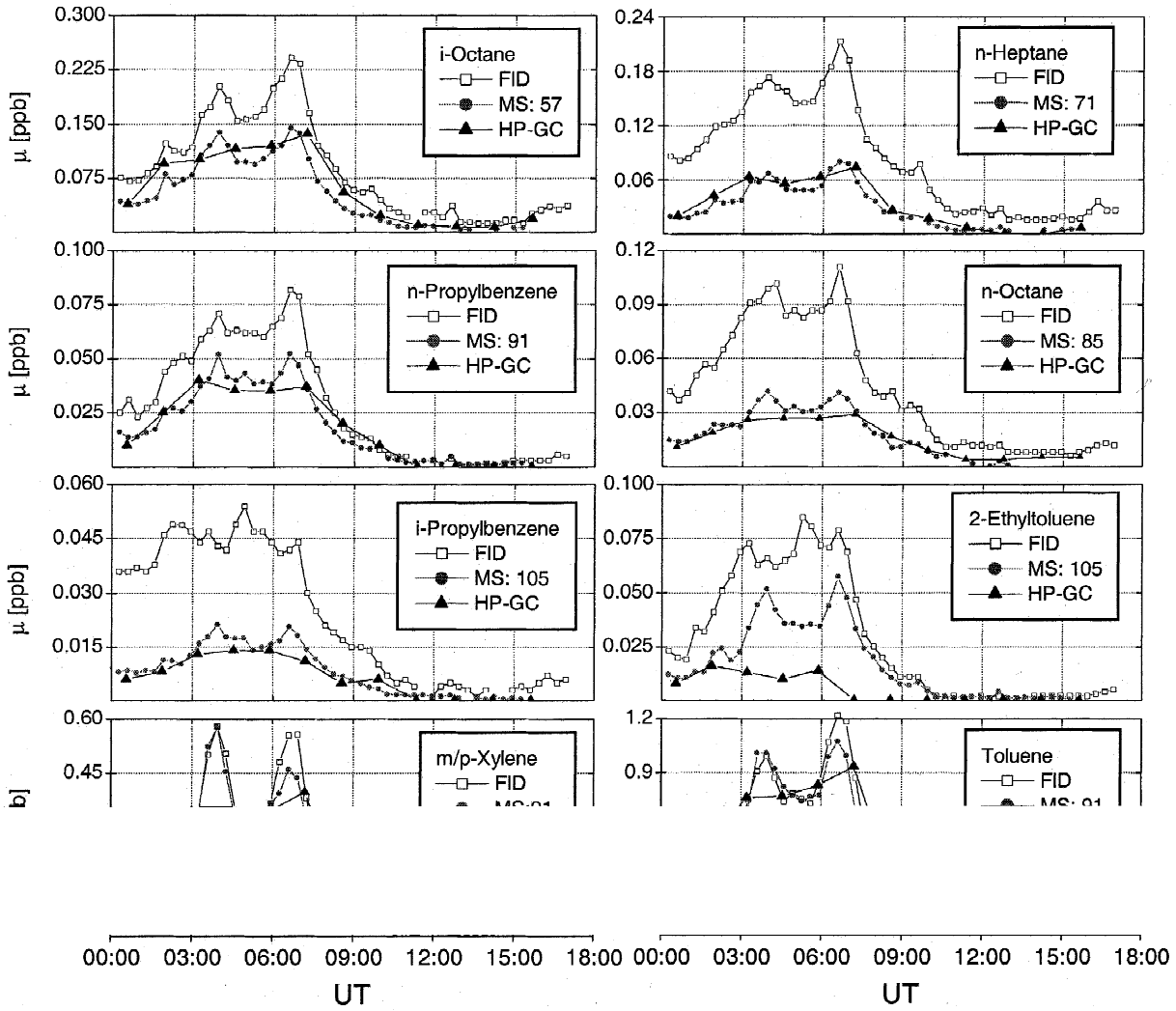

Fig. 9. Comparison between HC1010–FID (open squares), HC1010–MS (solid circles) and HP-GC (solid triangles) systems on 21 July 1998 at Pabstthum. The MS data are based on specific target ions. Note that the VOCs show two significant maxima from the Berlin plume in the early morning, which are missed by the HP-GC system because of its low time resolution.

centrations derived from specific target ions in the mass spectra agree with the HP-GC system within 25% or 10 ppt, without significant differences between pure hydrocarbon peaks and peaks that are subject to coelution by oxygenated compounds. The generally larger scatter of the mass spectrometer derived concentrations as compared to the FID measurements in case of unequivocally assigned peaks is presumably due to the adverse environmental conditions in the mobile laboratory during the field campaign, such as strong changes in ambient temperature (20–40°C). We have presently no explanation for the large disagreement between the mass spectrometer data and HP-GC data for 2-ethyltoluene. Clearly, the diurnal variation of the mass spectrometer derived concentrations is in much better agreement with that of the other aromatic compounds (e.g., toluene and *m*/*p*-xylene).

The data in Fig. 9 clearly demonstrate the importance of time resolution for representative ambient VOC measurements. Due to its long analytical cycle of 85 min, the HP-GC system misses most of the structure in the advected air and significantly underestimates the peak concentrations of the more reactive compounds in the city plume of Berlin.

6. Conclusions

The commercial GC–FID system HC1010 was coupled with a mass spectrometer and compared to a reference GC system in order to investigate its suitability for continuous measurements of C_5–C_{10} HCs in ambient air with a time resolution of 20 min. The memory effect from the adsorption tubes in the HC1010 system was found to be negligible for atmospheric measurements, except for situations when strong changes in air masses occur on relatively short time scales, after calibrations with high concentrations or after transportation of the instrument. More serious for accurate measurements is the quantification of the blanks and the unequivocal assignment of the peaks. From our experience we recommend diffusion sources for absolute calibration in addition to certified standards which can undergo changes during usage and upon strong temperature fluctuations.

The comparison between both GC systems in ambient air during BERLIOZ showed that the HC1010 system is well suited for the determination of a number of hydrocarbons in the range of C_5–C_{10}. Of the 29 peaks that were analyzed, 18 are due to individual HCs or mixtures of different HCs. For these peaks, the HC1010 results agreed with those of the reference GC system within 14% or 10 ppt (2σ). In the city plume of Berlin, the 28 HCs comprised in these peaks accounted for about 65% of the total HC reactivity towards OH as determined by the HP-GC system. The measurements demonstrated the importance of time resolved and continuous VOC measurements in such field experiments.

Large deviations up to a factor of 3 were found for hydrocarbons which, on the basis of the mass spectra, coelute with oxygenated or unidentified compounds. A better separation efficiency might be achieved by choosing longer and somewhat less polar columns and/or a starting temperature significantly below 30°C. A new oven for the HC1010 system which allows cooling by an external refrigerator is currently under development.

The C_5 HCs were found to be underestimated by about 10% because of losses on the uncooled cryotrap. Despite the relative good agreement with the reference GC results in ambient air, the adsorbtion materials in the normal configuration of the HC1010 system are likely not suitable for measuring terpenes as isomerization of α-pinene was observed on standard mixtures.

Acknowledgements

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