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C₂–C₈ Hydrocarbon measurement and quality control procedures at the Global Atmosphere Watch Observatory Hohenpeissenberg

C. Plass-Dülmer*, K. Michl, R. Ruf, H. Berresheim

Meteorological Observatory, German Weather Service (DWD), Albin Schwaiger Weg 10, 82383 Hohenpeissenberg, Germany

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Abstract

A new automated on-line GC–flame ionization detection system for long-term stationary measurements of atmospheric C₂–C₈ hydrocarbons in the lower ppt range is described. The system is operated at the Global Atmosphere Watch Observatory Hohenpeissenberg (47°48'N, 11°01'E) in rural south Germany. Atmospheric mixing ratios of more than 40 different hydrocarbons can be continuously measured in 80 min time intervals. Corresponding detection limits are below 3 ppt, except for propene, butenes and benzene (about 10 ppt). Detailed quality assurance and quality control protocols are described which are applied to routine operation and data analysis. The various error contributions, overall precision, and accuracy for all measured compounds are discussed in detail. Typical ambient air mixing ratios are in the range of a few ppt to a few ppb, and corresponding measurement accuracies are below 10% or 10 ppt. For less than 20% of the analyzed compounds measurement accuracies are worse, mainly because of insufficient peak separation, blank values or reduced reproducibilities. The present system was tested in international intercomparison experiments (NOMHICE, AMOHA). For most of the C₂–C₈ hydrocarbons analyzed, our results agreed better than ±10% (20% NOMHICE phase 5) or ±10 ppt with the corresponding reference values. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The importance of nonmethane hydrocarbons (NMHCs) for tropospheric chemistry has been addressed in numerous publications, e.g., Refs. [1–7], and dedicated books [8,9]. Briefly, atmospheric NMHCs are mainly important for the following reasons: (1) NMHCs significantly contribute to atmospheric photochemical processes leading to the formation of secondary photo-oxidants (e.g., ozone,

and/or aerosol particles. (2) Reactions involving NMHCs influence the concentrations of key atmospheric free radicals (in particular, the hydroxyl radical OH) and, thereby, the oxidizing capacity of the troposphere. (3) Photo-oxidation of NMHCs is a major source of CO and OVOCs (oxygenated volatile organic compounds). (4) Some NMHCs (such as benzene or 1,3-butadiene), or OVOCs (e.g., peroxyacetylnitrate, PAN) are potentially toxic for plants, and/or humans and animals.

Atmospheric mixing ratios of NMHCs typically range from tens of ppb (parts per billion, mixing ratios based on volume are used throughout the text) in urban atmospheres to well below 10 ppt (parts per

*Corresponding author.

E-mail address: christian.plass-duelmer@dwd.de (C. Plass-Dülmer).

trillion) in remote environments. NMHCs are emitted into the atmosphere by a number of anthropogenic and natural sources and are processed in the atmosphere through chemical reactions, and atmospheric transport including mixing, dilution, and deposition. NMHCs are of special interest for atmospheric chemistry research because the complex NMHC patterns in combination with a wide range of atmospheric residence times for the various NMHCs may provide valuable information about emissions, and about chemical aging and mixing of air masses during transport.

In recent years, substantial progress has been achieved both in NMHC measurement techniques and in understanding the role of NMHCs in atmospheric chemistry, e.g., in the evaluation of atmospheric chemistry models, analysis of the global distributions and seasonal cycles of NMHCs, the assessment of the contribution of biogenic and anthropogenic NMHCs to photochemical processes, characterization of air mass histories, establishing NMHC emission inventories, and the development of control strategies for ambient levels of ozone and other primary and secondary pollutants (e.g., Refs. [3–15]). The increasing demand for high quality NMHC data and long-term monitoring has led to international programs like EMEP (European Monitoring and Evaluation Program), NARSTO (North American Research Strategy on Tropospheric Ozone) and the World Meteorological Organization's Global Atmosphere Watch (GAW) program [16]. These measurement programs require a high standard of quality assurance (QA) and quality control (QC). The quality of NMHC measurement techniques employed by a number of laboratories throughout the world (including GAW/Hohenpeissenberg) has been assessed in several formal intercomparison experiments, most notably NOMHICE (Nonmethane Hydrocarbon Intercomparison Experiment [1,2]) and AMOHA (Accurate Measurements of Hydrocarbons in Air [17]).

By far the most widely used methods for NMHC measurements are based on preconcentration of NMHCs from sample air followed by gas chromatographic separation and subsequent detection with flame ionization detection (FID) (see recent reviews by Apel and co-workers [1,2], Rudolph [18], Cao and Hewitt [19], and Slemr et al. [17]). In quality

assurance one has to take into account the major causes of uncertainties in NMHC measurements, which may arise from (1) unreliable standards, (2) changes of the NMHC composition due to loss, contamination and chemical reactions in the measurement system, and (3) misidentification and erroneous quantification of peak areas resulting from peak overlap or bad baseline (noise and/or spikes, wander, offset or drift of baseline). The accuracy of NMHC measurements is difficult to assess experimentally, because multiple on-line measurements under identical atmospheric conditions involving different and independent methods are often impossible [2]: at most measurement sites, either a single analytical instrument, or a single canister sampling method is used. Therefore, both the measurement precision and accuracy for each compound should be individually determined, and as part of a quality control procedure the corresponding measurement technique should be intercompared with other NMHC measurement techniques, e.g., in formal projects such as NOMHICE [1,2] or AMOHA [17].

NMHC measurements are measured at the Meteorological Observatory Hohenpeissenberg (German Weather Service, 47°48'N, 11°02'E, 980 m above sea level) since 1995 as part of the GAW global station Zugspitze/Hohenpeissenberg. Atmospheric C₂–C₈ and C₅–C₁₂ hydrocarbon mixing ratios are automatically measured using two different on-line analytical techniques: (1) gas chromatography with flame ionization detection (GC–FID), and (2) GC–FID including ion trap mass spectrometry (GC–MS–FID), respectively. This paper will present in detail the GC–FID system. In accordance with stage 1 of the GAW-VOC program [16] ambient air mixing ratios of approximately 40 C₂–C₈ hydrocarbons (including alkanes, alkenes, dienes, and monocyclics) are measured at 13:00 CET on a regular daily basis. In addition, during intensive measurement campaigns air can be analyzed for up to 70 hydrocarbon compounds on a 80 min interval cycle. The quality assurance and quality control protocol applied at Hohenpeissenberg will also be presented here. In a detailed error analysis overall precision and accuracy estimates are derived for each compound based on the corresponding error contributions. Finally, we discuss our results obtained in NOMHICE, task 4 (E. Apel, personal communica-

tion, 1998), and in AMOHA, phase 3 [17] and present some results of ambient air NMHC measurements at Hohenpeissenberg.

2. Experimental

2.1. The Hohenpeissenberg C_2 – C_8 GC–FID system and measurement procedure

The on-line GC system for the measurement of C_2 – C_8 hydrocarbons in ambient air is shown schematically in Fig. 1. The main components of the system include a sample line, a permeation dryer, a cryogenic preconcentration unit, a GC (series 3600CX, Varian, Walnut Creek, CA, USA) equipped with an FID system, and multiport valves in a heated compartment. The system is fully automated and operated by Star Chromatography Workstation software (version 5.41, Varian) and has been extended by an external relays board (70 RCK 24, Grayhill, LaGrange, IL, USA) connected to a personal computer board (PC-DIO-24, National Instruments, Austin, TX, USA) for the operation of valves and programmable temperature controllers (Typ GR4896, Gräff, Troisdorf, Germany).

In on-line operation mode, ambient air is continuously flushed through a 10 m×4 cm I.D. glass tube (Duran, Schott Glaswerke, Mainz, Germany) at 1 m³ min⁻¹ using a fan installed at the downstream end of the tube (a similar air intake was used by Goldan et al. [20]). The air intake is at 10 m above ground level, which is comparable in height to the nearby tree canopies. Samples are transferred to the GC system from the center of the air inlet flow through a silica-lined stainless steel tube (1 m×1/8 in. O.D., Silcosteel, Restek, Bellefonte, PA, USA) at 30–50 cm³ min⁻¹, a stream selector valve (12 port, 423 K, VICI, Valco Europe, Schenkon, Switzerland), and a Nafion dryer (MD 5048 S, 1.25 m length in stainless steel tube, operated at 295 K, Permapure, Toms River, NJ, USA) (1 in.=2.54 cm). For the counter gas flow through the outer sheath tubing of the Nafion dryer we use ultrahigh purity nitrogen or helium (20 cm³ min⁻¹ at 20 kPa pressure). Under these conditions dew point temperatures in the sample air are reduced to below 241 K corresponding to less than 300 ppm (parts per million) water vapour.

Sample flow-rates are manually adjusted with a Nupro metal bellows needle valve (SS-4BMG, 403 K, Nupro, Willoughby, OH, USA). This type of

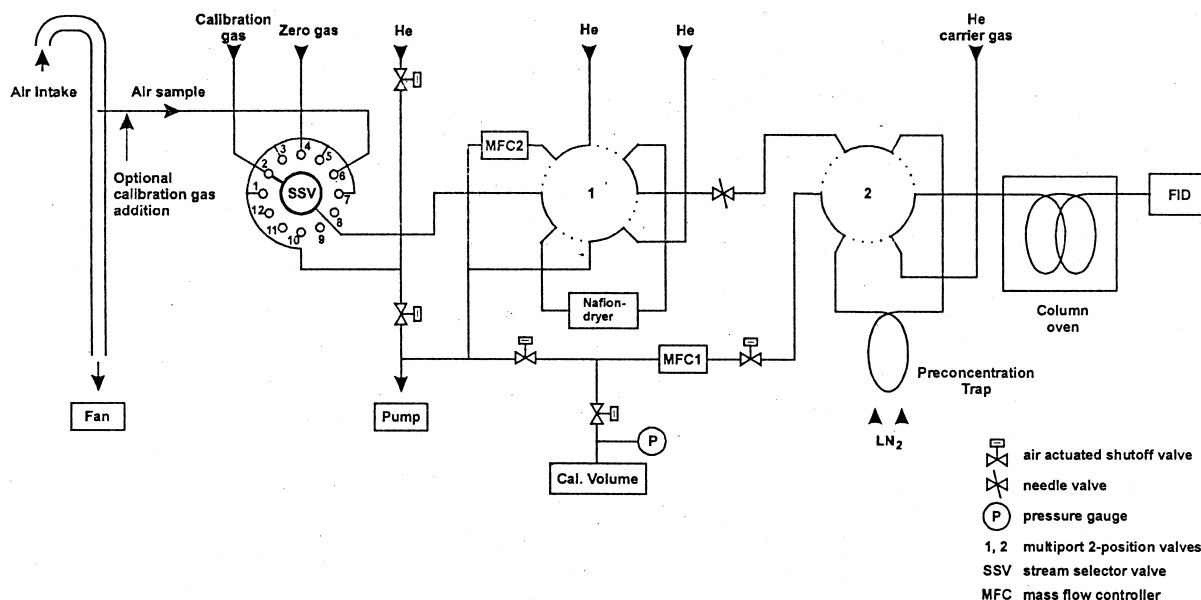


Fig. 1. Schematic of the analytical system for measurement of C_2 – C_8 hydrocarbons.

valve is used for two reasons: first, it consists entirely of stainless steel components assuring a relatively high degree of chemical inertness, and second, it restricts the pressure to less than 30 kPa in the downstream preconcentration trap. The preconcentration trap is a stainless steel tube (8 cm×1/8 in. O.D.×2.1 mm I.D.) filled with glass beads (sample preconcentration trap, SPT, Varian). It is cooled by liquid nitrogen (LN2) to 87±10 K. In order to reduce consumption of LN2, we have designed a cooling system allowing controlled immersion of the trap into LN2 based on previously described systems by Rudolph et al. [21] and Greenberg et al. [22]. NMHCs are quantitatively adsorbed to the glass bead surfaces of the trap while the main constituents of the sample air, N₂ and O₂, pass through the trap without condensation. The sampled volume is determined by measuring the corresponding increase in pressure in an evacuated stainless steel canister of 6 l volume using a capacitive pressure gauge (Baratron 626, MKS, Methuen, MA, USA) (see also Rudolph et al. [23]). The sample gas contacts only stainless steel surfaces in heated compartments (>400 K), the material of the rotors of the GC valves is Valcon E (VICI, Switzerland).

The trapped NMHC sample is thermally desorbed by direct current heating of the 1/8 in. tube to 503 K at a rate of 20 K s⁻¹ and injected onto a porous-layer open tubular (PLOT) column (Al₂O₃/KCl, 50 m×0.53 mm I.D., Chrompack, Middelburg, The Netherlands) with a helium carrier gas stream at 4.8 cm³ min⁻¹. The helium gas (99.999%, Messer Griesheim, Krefeld, Germany) is further purified at 210 K in a cartridge filled with activated charcoal and molecular sieve of 0.5 and 1.0 nm pore size, respectively. The GC column oven is heated after an initial isothermal phase (2 min at 313 K) in a first ramp at 4 K min⁻¹ to 345 K, and in a second ramp of 6 K min⁻¹ to the final temperature of 473 K, which is kept constant for 33.7 min. The column end extends into the FID system, which is operated at 523 K. The FID system is supplied by N₂ make-up gas at 30 cm³ min⁻¹, H₂ at 30 cm³ min⁻¹ (both 99.999%, Messer Griesheim), and 300 cm³ min⁻¹ compressed air, which is purified in a platinum catalyst cartridge at 723 K (Pt on Al₂O₃, H 5446, Hüls, Marl, Germany).

Four ports of the stream selector valve (SSV in

Fig. 1) are provided for gas calibration standards or samples from stainless steel canisters. To effectively flush the sample lines, the stream selector valve is connected at every second port to a line which can be switched between purge gas (helium) and a vacuum pump (see Fig. 1). For standard addition measurements, a T-connection is installed in the Silcosteel sample line at the glass tube port (Fig. 1).

A basic measurement cycle consists of taking an air sample (30 min) and analyzing the sample by GC-FID (65 min). A new cycle can be started every 80 min since in continuous operation a new sample is taken during the chromatographic analysis of the preceding sample. The sampling procedure starts with an initial flushing of the entire sample line including the Nafion dryer and valve 2 (Fig. 1) for 10 min with sample air at 20–50 cm³ min⁻¹. In this initial phase all surfaces are preconditioned to establish an adsorption–desorption equilibrium with the sample air. When canisters or calibration gas cylinders are connected, the corresponding connections are first helium leak tested and then evacuated and flushed with the sample gas several times. The trapping of a sample in the preconcentration trap takes 15 min (flow-rate: 50 cm³ min⁻¹; sample volume: 750 cm³) followed by a 1 min purge with ultrapure helium at 20 cm³ min⁻¹ at reduced pressure (about 20 kPa). After thermal desorption, the trap is conditioned at 503 K for 39 min. The preconcentration trap is cooled down to 87 K concurrently with the 10 min purge of the system for the following sample. Before a new sample is taken, the Nafion dryer is back-flushed with helium at 10 cm³ min⁻¹ for about 30 min. All operations are automated and visualized using LabView version 5.0 software (National Instruments).

Some results presented in this paper were obtained using earlier versions of the system, in particular this concerns the ozone removal experiments by NO titration (Section 3.2.2) and the NOMHICE results (Section 4.3). Briefly, experimental conditions different from the current set up were as follows: a GasPro GSC capillary column (60 m×0.32 mm I.D., ASTEC, Whippany, NJ, USA) was used with a polar precolumn (DB-Wax, 15 m×0.53 mm I.D., 1 μm film, J&W Scientific, Folsom, CA, USA). A CO₂ and a moisture trap, consisting of cartridges filled with Ascarite and Mg₂ClO₄, respectively (both filled

in 1/4 in. Silcosteel tubes of 10 cm length, held in place by silanized quartz wool plugs) were mounted in the sample line instead of the Nafion dryer. Prior to the glass sample line, a 1/4 in. Silcosteel tube of about 8 m length was used. It was flushed at 20 l min⁻¹, in the NO test at 2 l min⁻¹. Instead of the stream selector valve, we used a manifold (stainless steel, 1/4 in.) with four shut-off valves (SS-HK4, metal bellows, sealing tip Vespel, Nupro) installed in a heated compartment at 423 K.

2.2. Zero gas, calibration and reference gases, and standard addition measurements

In addition to daily measurements of ambient air, at least once every 2 weeks measurements of helium (zero gas), calibration gas, and two different reference gases are carried out. These measurements characterize the performance of the system and are used for blank peak area determination, calibration, and compound identification. Best reproducibilities were obtained, when the corresponding gas cylinders were permanently connected to pressure reducers (RB 200/1 3, AGA redline, Bottrop, Germany; or Model 6 regulator, Scott, Breda, The Netherlands) and Silcosteel transfer lines which were capped with shut-off valves. In this configuration, the internal surfaces were always in contact with the corresponding gas.

For calibration (see Section 2.4), a gas standard supplied by the National Physical Laboratory (NPL, Teddington, UK, purchased in 1998) is used containing 30 components in a passivated aluminum cylinder with mixing ratios between 1 and 11 ppb (Table 1, Fig. 2) and an accuracy of better than 1% (95% confidence) as certified by NPL at the time of dispatch. NPL expects the mixture to remain stable for a period of at least 2 years. Potentially unstable compounds are ethyne, isoprene, 1,3-butadiene, and the trimethyl benzenes. Before 1998, a 27-component calibration gas standard also prepared by NPL (purchased in 1995) was used with mixing ratios between approximately 10 and 100 ppb. For this mixture, accuracies were stated to be better than 5% with potential instabilities for the same compounds as listed above. The NPL gas standards and their accuracies are discussed in Section 4.1.

Compressed ambient air with relatively low mix-

ing ratios (few ppt to 2 ppb for the various NMHC) is used as reference gas (hereafter referred to as reference gas 1). The corresponding sample was taken on 1 February 1996 at the Hohenpeissenberg Observatory in rural background air. About 700 l of air were cryogenically trapped into an aluminum cylinder (10 l) immersed in LN₂. In addition, a second NMHC mixture (reference gas cylinder 2) of 70 compounds in the C₅–C₈ range was prepared at Hohenpeissenberg from hydrocarbon mixtures purchased from Supelco (“Alphagaz PIANO Calibration Standards”: PIANO paraffins, catalog No. 4-4585-U; PIANO isoparaffins, catalog No. 4-4586-U; PIANO olefins, catalog No. 4-4589-U; PIANO aromatics, catalog No. 4-4587-U; and PIANO naphthenes, catalog No. 4-4588-U, Supelco, Taufkirchen, Germany). The resulting mixing ratios in this reference gas 2 range approximately between 1 and 20 ppb with N₂ as buffer gas. Samples from this mixture are analyzed regularly to detect shifts in retention time and prevent peak misidentification, e.g., as a result of column aging, and to detect peak overlap.

In standard addition measurements we make use of the (NPL) calibration standard which is continuously added to ambient air samples at the standard addition port (see Fig. 1). Typically, a few cm³ min⁻¹ of the 27-component NPL mixture were added yielding mixing ratios of several ppb in the air intake line, i.e., at least one order of magnitude higher mixing ratios than ambient air levels for more than about 90% of the corresponding NMHC compounds. The peak areas were determined after the subtraction of peak areas of ambient air measurements performed before or after standard addition measurements. These standard addition measurements are used to characterize the GC system in various tests (see below) [24] which provide information on compound specific artifacts such as alkene losses due to reaction with ozone.

2.3. Peak integration, compound identification, and data processing

In a first step peaks are automatically integrated by a commercially available chromatography software (Star Chromatography Workstation, Varian). However, this procedure frequently produces wrong

Table 1
Mixing ratios and errors (95% confidence) of calibration gas measurements (30 component NPL mixture) based on 15 measurements^a

No. ^b	Compound	Mixing ratio (ppb)	Accuracy (%)	Precision (%)	Random error-contributions				Combined random error ^c (%)	Reproducibility ^c (%)	Calibration uncertainty (%)
					Integration	Blank	Volume	FID ^d			
1	Ethane	7.54	6.1	3.5	2.0	0.4	2.0	2.0	3.5	2.8	5.0
2	Ethene	11.82	5.9	3.1	2.0	0.7	2.0	2.0	3.5	2.3	5.0
3	Propane	2.85	6.4	4.0	2.0	2.0	2.0	2.0	4.0	2.8	5.0
4	Propene	7.45	8.0	6.2	2.0	0.3	2.0	2.0	3.5	5.9	5.0
5	<i>i</i> -Butane	3.34	6.1	3.5	2.0	0.0	2.0	2.0	3.5	2.9	5.0
6	Acetylene	9.85	15.7	4.5	2.0	0.0	2.0	2.0	3.5	4.0	15.0
7	<i>n</i> -Butane	2.88	6.4	4.0	2.0	0.0	2.0	2.0	3.5	3.4	5.0
8	<i>trans</i> -2-Butene	2.47	5.9	3.1	2.0	0.0	2.0	2.0	3.5	2.8	5.0
9	1-Butene	3.70	6.4	3.9	2.0	0.0	2.0	2.0	3.5	3.4	5.0
10	<i>i</i> -Butene	3.16	52.7	49.7	2.0	6.4	2.0	2.0	7.3	49.2	17.6
11	<i>cis</i> -2-Butene	2.64	5.8	2.9	2.0	0.0	2.0	2.0	3.5	1.8	5.0
12	2-Methylbutane	1.32	6.4	4.0	2.0	0.0	2.0	2.0	3.5	3.4	5.0
13	<i>n</i> -Pentane	2.94	5.8	2.9	2.0	0.0	2.0	2.0	3.5	2.0	5.0
14	Propyne	3.21	11.8	10.7	10.0	0.0	2.0	2.0	10.4	3.3	5.0
15	1,3-Butadiene	5.91	10.4	2.8	2.0	0.0	2.0	2.0	3.5	2.0	10.0
16	<i>trans</i> -2-Pentene	4.49	6.2	3.6	2.0	0.0	2.0	2.0	3.5	3.0	5.0
17	<i>cis</i> -2-Pentene	1.71	7.5	5.6	2.0	0.0	2.0	2.0	3.5	5.2	5.0
18	Cyclohexane	3.71	7.5	5.5	2.0	0.0	2.0	2.0	3.5	5.2	5.0
19	2-Methylpentane	3.53	14.8	13.5	10.0	0.0	2.0	2.0	10.4	8.9	6.0
20	3-Methylpentane	4.04	12.3	11.2	10.0	0.0	2.0	2.0	10.4	4.7	5.0
21	<i>n</i> -Hexane	1.96	9.9	8.5	2.0	0.0	2.0	2.0	3.5	8.3	5.0
22	Isoprene	2.05	10.9	4.4	2.0	0.0	2.0	2.0	3.5	3.9	10.0
23	<i>n</i> -Heptane	3.08	7.0	4.9	2.0	0.0	2.0	2.0	3.5	4.4	5.0
24	Benzene	3.81	6.1	3.4	2.0	0.7	2.0	2.0	3.5	2.7	5.0
25	Toluene	3.58	6.9	4.8	2.0	0.0	2.0	2.0	3.5	4.3	5.0
26	Ethylbenzene	1.97	8.7	7.2	2.0	0.0	2.0	2.0	3.5	6.8	5.0
27	<i>m</i> -Xylene	1.56	10.9	9.7	2.0	0.0	2.0	2.0	3.5	9.4	5.0
28	<i>o</i> -Xylene	1.11	11.0	9.8	2.0	0.0	2.0	2.0	3.5	9.5	5.0

^a Measurements of NPL standard were conducted within 1 month with volumes of about 110 ml each.

^b Numbers correspond to Fig. 2.

^c Reproducibility corresponds to 2×standard deviation of 15 measurements of standard gas.

^d FID refers to sensitivity changes of the FID system.

^e Gaussian propagation of random error contributions.

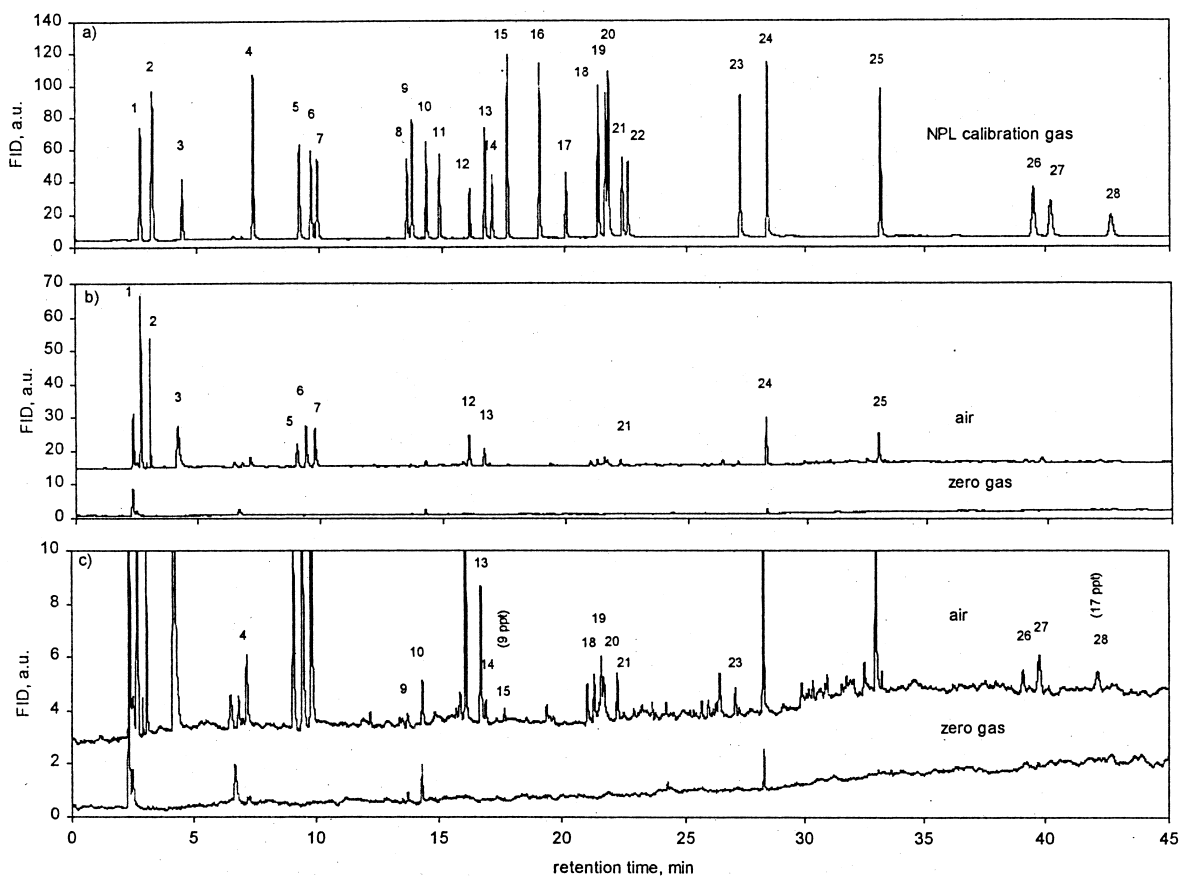


Fig. 2. FID chromatograms of (a) NPL calibration standard, (b) ambient air sample and zero-gas in full scale presentation, and (c) enlarged scale of (b). Numbers refer to peak identification presented in Table 1, for better orientation some mixing ratios are given in the figure, others are listed in Table 1.

results especially with respect to the quantification of overlapping or relatively small peaks. Peak overlap generally cannot be treated automatically, since small changes in separation or the relative sizes of the encountered peaks may cause substantial differences in the automatically determined results. Furthermore, in case of small peaks the noise of the detector signal may invoke a wrong baseline evaluation. Both effects may easily account for peak integration errors of up to a factor of 2. Thus, we check and correct the peak baselines and peak splitting in each chromatogram manually using standard tools of the chromatography software, e.g., baseline adjustment. However, some peak integration errors especially in case of overlapping peaks still remain. These are estimated and manually listed

during data reprocessing for later consideration in the total error assessment (Section 4.1).

Peak identification is based on retention times. Reference retention times are obtained from (a) measurements of pure substances and/or mixtures of a few selected compounds, (b) measurements of identification gas mixtures of known composition based on the FID C-response (see Section 2.4), and (c) literature references of the elution order [24–27]. The identification mixtures are either commercially supplied (Linde, Wiesbaden, Germany), or self-prepared gas mixtures (e.g., from Alphagaz PIANO calibration standards, see above). Further checks of correct identification have been performed during intercomparison experiments (NOMHICE, phases 4 and 5, E. Apel, personal communication, 1998;

AMOHA [17]). In data processing of each sample, up to 10 selected compound peaks evenly distributed over the chromatogram are identified. The reference retention times are consecutively adjusted to the retention times of the identified compounds using linear interpolation between the identified compounds. Finally, the adjusted reference retention times are used to identify the atmospheric NMHC peaks according to their retention times allowing a maximum tolerance of 2 s. Using this procedure, a table is generated from the raw data with all identified peaks and their retention time shifts compared to the reference retention times. This table is used as a first, manual check of the correct identification. This method was automated (Excel Visual Basic, Excel 97, Microsoft) and proved to be much easier to handle and more reliable than peak identification with the standard chromatography software, especially when a large number of compounds (about 70) must be identified.

Excel Visual Basic programs are also used for peak quantification and error assessment. The peak areas of the identified compounds of ambient air samples as well as of zero gas, calibration and reference gas are copied into different sheets of the same Excel workbook, peak integration errors are manually added where significant errors exist (see Section 4), and further error information concerning sample volume and detection limit is inserted. The program then calculates the mixing ratios, accuracy and precision for each compound and each measurement.

2.4. Quantification

Quantification of NMHC measurements in ambient air is based on a gas calibration standard (NPL) (Table 1) and the assumption of an approximately equal response per carbon number (C-response) of the FID for the alkanes, alkenes, cyclic and aromatic hydrocarbons (corresponding uncertainties are discussed in Section 4.1). This assumption is based on the “effective carbon number concept” (ECN) by Sternberg et al. [28], who demonstrated identical FID-response for carbon atoms in alkanes and aromatic compounds, 5% reduced response for carbon atoms with olefinic (double) bonds, and 30% enhanced response for those in acetylenic (triple)

bonds. In many investigations following this original study, approximately linear response of the FID (independent of the manufacturer and model) with the molecular mass or the number of carbon atoms per molecule for the above listed compound classes, were observed (e.g., Refs. [1,24,29–31]). Therefore, many investigators have determined hydrocarbon concentrations based on a particular standard compound (e.g., propane).

We calculate the mixing ratio m_i^s of a compound i in sample s according to:

$$m_i^s = \frac{K_i(A_i^s - A_i^b)}{V^s} \quad (1)$$

with K_i the calibration factor for compound i ; A_i^s the peak area of compound i in sample s ; A_i^b the mean peak area of compound i in blank runs b and V^s the volume of sample s .

The calibration factor for each compound, with the exception of acetylene, is calculated from the mean carbon response factor R and the number of carbon atoms per molecule N_i :

$$K_i = \frac{1}{RN_i} \quad (2)$$

The mean carbon response factor R is calculated as the arithmetic mean of all the compounds' response factors R_i obtained in multiple measurements using the corresponding calibration standards (index st):

$$R = \frac{1}{n} \sum_{i=1}^n R_i = \frac{1}{n} \sum_{i=1}^n \left(\frac{1}{k} \sum_{j=1}^k \frac{A_{i,j}^{st} - A_i^b}{n_i^{st} N_i V_j^{st}} \right) \quad (3)$$

with n the total number of compounds used for calibration; k the total number of calibration gas measurements (at least five per month) and j the running index of calibration gas measurement.

In the specific case of acetylene we calibrate directly from the NPL standard. For propyne we use Eq. (2) since direct calibration from NPL does not yield a significant difference.

2.5. Quality assurance and quality control

As part of the quality assurance procedure we have already discussed measurements of zero, calibration, and reference gases (Section 2.2), and details of peak identification and integration (Section

2.3). Additionally, the following procedures are carried out on a regular basis.

(1) The entire system is checked for leaks at least once every 3 months, or whenever potential gas leaks are identified from the chromatograms. For this we use a helium leak detector (UL 200, Leybold Vakuum, Cologne, Germany) and leaks exceeding $5 \cdot 10^{-7}$ kPa l s⁻¹ are removed.

(2) In frequent zero gas measurements blank values are determined and considered in quantification (Section 2.4) and error assessment (Section 4).

(3) The ECN response concept for FID [28] is used in standard measurements to check for systematic losses of individual compounds, and to check the stability of the detector (Section 3.2).

(4) Standard addition to ambient air samples is used to detect chemically or physically induced artifacts for conditions which are as close as possible to ambient air samples (Section 3.2).

(5) Contributions from various error sources are estimated or calculated for each compound and each measurement to assess overall precision and accuracy of the measurement of that compound.

In quality control we follow five major steps.

(1) To check for peak misidentification, retention times of groups of compounds with similar retention times (about 15 compounds each) are plotted versus the consecutive run number for sets of about 30 measurements each. In this procedure, parallel lines for the various compounds' retention times should show up and errors due to inconsistent peak identifications are easily detected.

(2) Occasionally occurring peak overlap is identified by plotting peak half widths as a function of the consecutive run numbers (similar to the procedure described before).

(3) Mixing ratios are checked for internal consistency by comparing the mixing ratios of compounds which are assumed to originate from similar sources, e.g., combustion sources. For this purpose the mixing ratios of groups of compounds are plotted (log-scale) against consecutive run number and checked for deviations in their relative abundance. In this approach, deviations from source patterns which are qualitatively not compatible with atmospheric decay are identified. This is a similar, but less detailed approach as has been recently described by Parrish et al. [5]. If such deviations are detected for restricted

measurement periods, the instrument log is checked for any indications of irregular operation. If such indications exist, all results of the respective compounds are rejected, if not, the respective errors are enlarged to include the expected mixing ratio levels in the 95% confidence intervals.

(4) The resulting mixing ratios are compared with the results from concurrent analyses with our second on-line GC–MS–FID system, and with results from intercomparison experiments (Section 4.3). If significant deviations are found exceeding the respective accuracy, the peak identification, integration, and potential peak overlap are carefully checked, and corrected if indications for errors exist.

The precision of our measurements is compared to the experimentally determined reproducibility from multiple measurements of a compressed reference air sample (Section 4.2).

3. Characterization of the analytical system

3.1. Chromatographic separation

FID chromatograms of a calibration gas run, an ambient air sample, and a helium blank are shown in Fig. 2. The peak identifications and mixing ratios are given in Tables 1 and 2 for selected compounds which are considered to be most important at Hohenpeissenberg with respect to abundance, reactivity, and toxicity. The zero gas shows small peaks of propene, *i*-butene, and benzene in a range corresponding to approximately 10 ppt in air samples and traces of other butenes. Occasionally, also ethene blanks corresponding to about 10 ppt have been observed.

Obviously, not all peaks in Fig. 2 are baseline separated. Peak overlap due to insufficient chromatographic separation represents a general problem in the analysis of complex NMHC mixtures and is one of the major error sources in peak quantification (see Section 4). To some extent this problem could be reduced by using a Nafion dryer which quantitatively removes polar VOCs like aldehydes, ketones and alcohols from the sample. This reduces the complexity of the mixture and the occurrence of broad, asymmetric peaks. However, of the 59 compounds listed in Table 2, still nine compounds are entirely

Table 2

List of analysed compounds, mixing ratios and measurement errors of the air sample shown in Fig. 2 (6 December 1999, 13:00 CET, 512 ml)

No. ^a	Compound	Retention time (min)	Mixing ratio (ppt)	Accuracy (ppt)	Precision (ppt)	Random error contributions ^b			Calibration uncertainty (%)
						Integr. (%)	Blank (%)	Reproducibility ^c (%)	
1	Ethane	2.678	1798	112	37	2.0	0.0	1.5	5.9
2	Ethene	3.147	602	42	18	2.0	1.0	1.1	6.2
3	Propane	4.229	809	55	22	2.0	0.0	2.7	6.2
	Cyclopropane	7.006	13	4	4	21.3	0.0	10.0	15.0
4	Propene	7.176	121	16	15	10.0	3.4	0.8	5.0
5	<i>i</i> -Butane	9.087	195	11	5	2.0	0.0	0.7	5.0
6	Acetylene	9.568	670	91	24	2.0	0.0	4.0	15.0
7	<i>n</i> -Butane	9.817	344	29	15	2.0	0.0	4.4	7.0
8	<i>trans</i> -2-Butene	13.534	7	6	6	89.3	0.0	1.2	5.0
9	1-Butene	13.737	14	13	13	50.0	38.3	2.1	5.0
10	<i>i</i> -Butene	14.329	12	45	45	50.0	182.2	5.0	7.5
11	<i>cis</i> -2-Butene	14.862	4	3	3	73.5	0.0	1.8	5.0
	Cyclopentane	15.862	23	15	14	60.0	0.0	10.0	15.0
12	2-Methylbutane	16.100	183	12	7	2.0	0.0	3.9	5.0
13	<i>n</i> -Pentane	16.719	107	10	9	2.0	0.0	7.9	5.0
14	Propyne	16.974	27	6	4	10.5	0.0	11.0	12.8
15	1,3-Butadiene	17.649	9	2	2	23.8	0.0	5.2	10.0
	3-Methylbutene-1	18.502	6	4	4	60.0	0.0	10.0	15.0
16	<i>trans</i> -2-Pentene	18.928	0	3	3			14.0	9.4
	2-Methylbutene-2	19.398	12	3	2	14.7	0.0	10.0	15.0
	1-Pentene	19.506	7	2	2	24.5	0.0	10.0	15.0
	2-Methylbutene-1	19.658	5	2	2	31.5	0.0	10.0	15.0
17	<i>cis</i> -2-Pentene	20.006	0	3	3			15.3	13.2
	Methylcyclopentane + 2,2-dimethylbutane	21.021	27	5	3	5.2	0.0	10.0	15.0
18	Cyclohexane	21.286	37	8	7	3.8	0.0	18.4	8.3
	2,3-Dimethylbutane	21.494	11	4	4	30.0	0.0	10.0	15.0
19	2-Methylpentane	21.585	46	15	12	10.0	0.0	23.5	18.5
20	3-Methylpentane	21.693	38	8	6	15.0	0.0	4.4	14.2
21	<i>n</i> -Hexane	22.233	32	7	7	20.0	0.0	5.5	5.0
22	Isoprene	22.490	5	2	2	37.0	0.0	12.1	10.0
	2-Methylpentene-2	23.662	7	2	2	20.7	0.0	10.0	15.0
	4-Methylpentene-1	23.796	3	2	2	50.0	0.0	10.0	15.0
	<i>trans</i> -2-Hexene	23.903	0	2	2			10.0	15.0
	1-Hexene	24.547	3	2	1	51.5	0.0	10.0	15.0
	<i>cis</i> -2-Hexene	24.873	0	2	2			10.0	15.0
	2,2-Dimethylpentane + 2,4-dimethylpentane	25.716	8	2	1	14.7	0.0	10.0	15.0
	Methylcyclohexane + 2,2,3-trimethylbutane	25.993	9	2	1	14.2	0.0	10.0	15.0
	3,3-Dimethylpentane + ethylcyclopentane	26.185	3	1	1	41.5	0.0	10.0	15.0
	2,3-Dimethylpentane + 3-ethylpentane	26.325	8	2	2	15.6	0.0	10.0	15.0
	3-Methylhexane + 2-methylhexane	26.481	35	7	4	5.0	0.0	10.0	15.0
23	<i>n</i> -Heptane	27.123	14	2	1	8.9	0.0	6.1	5.0
24	Benzene	28.277	177	24	22	2.0	5.0	7.2%	5.0
	4-Methylheptane + <i>n</i> -propylcyclopentane	30.723	8	3	3	25.0	0.0	20.0	20.0
	2-Methylheptane	30.922	6	2	2	20.0	0.0	20.0	20.0
	3-Methylheptane	31.012	11	4	3	20.0	0.0	20.0	20.0
	<i>n</i> -Octane	31.636	6	4	3	56.5	0.0	20.0	20.0
25	Toluene	33.039	136	16	15	5.0	2.0	8.4	5.0
	<i>n</i> -Nonane	37.761	0	1	1			30.0	20.0
26	Ethylbenzene	39.325	17	4	3	18.2	0.0	9.1	6.7
27	<i>p</i> -Xylene + <i>m</i> -xylene	40.061	37	6	6	8.4	0.0	13.4	5.0
28	<i>o</i> -Xylene	42.401	17	4	4	18.7	0.0	10.4	10.5

^a Numbers correspond to Fig. 2.

^b The various random error contributions are related to the mixing ratio (95 confidence, see Section 4, the error of the sample volume of 0.4 is not shown).

^c Reproducibility refers to 2 × standard deviation of multiple measurements of standards from the corresponding month.

overlapping with eight other identified compounds and one unidentified compound (expressed as sums in Table 2). Furthermore, about 20 peaks are not baseline separated from other peaks (enhanced integration errors in Table 2). However, of the 28 numbered peaks (Fig. 2 and Table 2) which are considered to represent the most important compounds and which are currently evaluated for the GAW program, only seven peaks are not baseline separated and show small peak overlap, corresponding to integration errors due to peak overlap of generally less than 20% (Tables 1 and 2; note that integration errors listed in Table 2 are often larger due to the very small peak areas of the specific sample air; see Section 4).

Peak separation is limited by the injection volume which results from the volume of the (cryo)-adsorption trap (effective geometric volume: 0.3 cm^3), and the amount of condensable compounds, mainly water vapour [typically 0.3 cm^3 (STP), after passing the Nafion dryer] and CO_2 (typically 0.3 cm^3 , STP). During desorption, heating from 87 K to initial column temperature (313 K) produces a volume increase of the carrier gas by a factor of more than 3 at a column head pressure of 270 kPa. Thus, a total column injection volume of effectively more than 3 cm^3 (STP) is produced. However, peak half widths are at a few seconds for a number of reasons. The compounds elute from the trap in the carrier gas stream during thermal desorption at various temperature stages. For example, ethane, ethene and acetylene elute from the trap before CO_2 and the majority of C_2 – C_6 NMHCs elute before water is completely desorbed. Furthermore, the carrier gas flow is reversed in direction compared to the sample flow, the glass beads prevent a good mixing in the entire trap volume, and a refocussing occurs on the column head for the higher boiling compounds. This all results in peak half widths between typically 1 s (ethene) and 4 s (C_4 – C_7 NMHCs), 6–10 s for the C_8 aromatics due to their elution in the final, isothermal phase (473 K), and 8 s for propane due to a CO_2 interference (Fig. 2). These peak half widths and the above mentioned peak separation are considered sufficient and a refocussing trap with small internal volume was not employed between preconcentration and column.

In addition to propane, also the C_4 hydrocarbon

peaks are broadened due to the presence of CO_2 . This was checked by comparison with standard addition measurements, in which a cartridge filled with Ascarite had been installed in the sample gas flow upstream of the Nafion dryer: using Ascarite, peaks were significantly sharper than without Ascarite, in the latter case sometimes the peaks of *trans*-2-butene and 1-butene even split into two or three peaks (Fig. 2). Artifacts due to CO_2 (in measurements without Ascarite) or Ascarite are not observed, neither in zero gas nor in standard addition measurements. In our current analytical system, CO_2 is not removed from air samples, since the poor peak shapes of C_3 and C_4 hydrocarbons cause only small errors in peak integration: only a few compounds elute within the corresponding retention time range and thus, peak separation is generally sufficient to overcome drawbacks due to bad peak shapes. Furthermore, the risk of contaminating the sample inlet system with NaOH as a consequence of improper reconditioning of the Ascarite between subsequent measurements can be avoided. This contamination may occur when sampled water vapour adsorbed on the Ascarite surface accumulates until NaOH–water droplets are formed which may then be transported in the sample gas stream.

In an earlier version of the analytical procedure, a GasPro GSC column ($60 \text{ m} \times 0.32 \text{ mm}$ I.D., Astec) was used but was then replaced by the Al_2O_3 PLOT column since peak separation for the important compounds (Table 2) and the stability of retention times was not satisfactory. In particular, the retention of isoprene which in standard runs eluted between 3-methylpentane and *n*-hexane, decreased up to co-elution with 2-methylpentane, most likely due to enhanced water contents on the column. Furthermore, *i*-butane and *i*-pentane co-eluted with unknown compounds.

3.2. Specific tests

3.2.1. Recovery of hydrocarbons in standard gas measurements

With the expected similar C-response of the FID for all hydrocarbons except acetylene (Section 2.4), significant deviations from the mean C-response should be indicative for sample losses or contamination in the chromatographic system. Corresponding

analytical tests have been reported, e.g., by Donahue and Prinn [24] and Apel et al. [1]. In Fig. 3, carbon response factors R_i (Eq. (3)) for the various NMHCs of the calibration gas mixture (NPL) are presented with twice their standard deviations based on repeated measurements of the same standard gas mixture. All C-response factors are within 15% of the mean C-response factor (R , Eq. (3)); they are within 6% of the mean if acetylene, *i*-butene, 1,3-butadiene, 2-methylpentane, isoprene and the trimethylbenzenes are excluded. The 2-sigma scatter for the various compounds is below 10%, on average 5%, if *i*-butene and the trimethylbenzenes are not considered. In general, the standard deviations are systematically higher for the higher boiling compounds, i.e., the C_8 and C_9 aromatics.

For a more detailed analysis, data obtained under five different conditions with respect to the set-up of the sampling line are shown in Fig. 4. The conditions referred to as (1) and (2) represent reduced pressure

conditions in the sample line including the Nafion dryer since no needle valve was used in this set-up and the flow was restricted by a low pressure setting of the pressure regulator. Under all conditions shown, the acetylene C-response factor is systematically higher by $(14 \pm 3)\%$ than the mean for all compounds. The observed deviation is in the range of previously reported acetylene response factors of 1.3 [28], 1.07 [29], and 1.2 [1]. The corresponding C-response factors for the trimethylbenzenes are lower compared to the mean by approximately 10%, which in view of the relatively lower reproducibility most likely resulted from adsorptive losses. Deviations in both directions of the mean were observed for *i*-butene. These will be discussed in the next section. No baseline separation was found for 2- and 3-methylpentane and due to asymmetric peak shapes the area of 2-methylpentane is slightly underestimated whereas that of 3-methylpentane is overestimated. The dienes (1,3-butadiene and isoprene) have

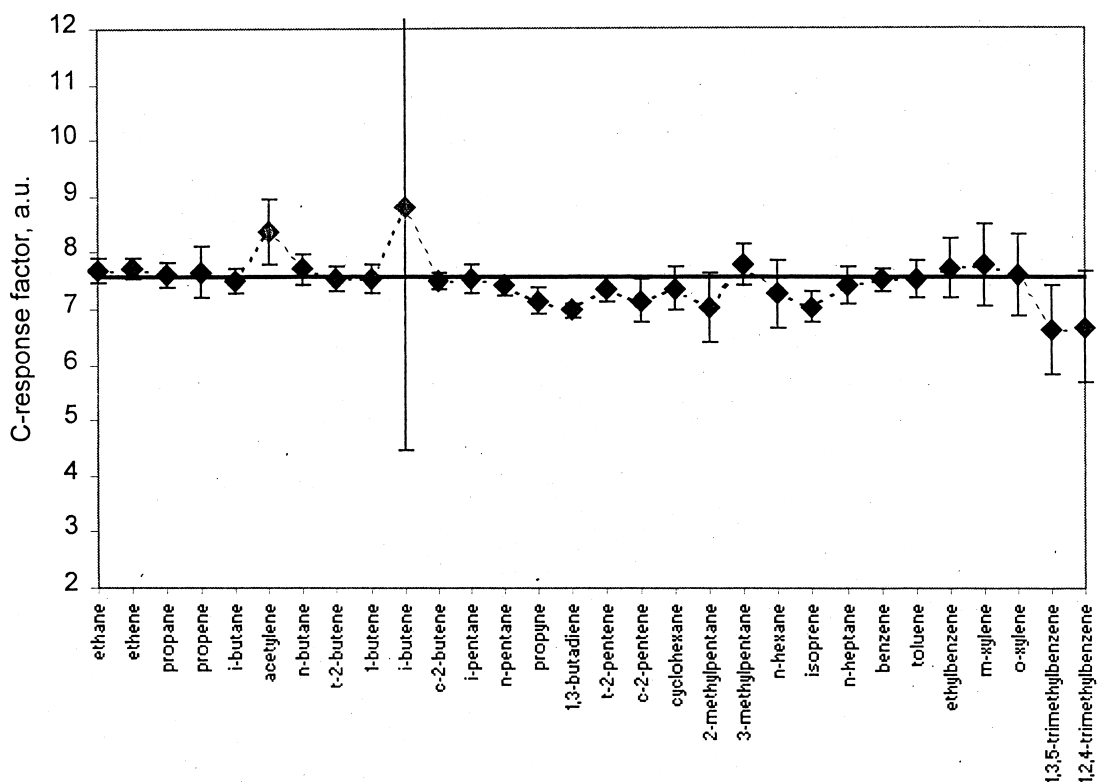


Fig. 3. FID C-response factors (see text) for the 30 NPL standard compounds. The symbols represent arithmetic means from 14 measurements in a 1-month period (November 1998), the bars show the 2-sigma scatter of the data.

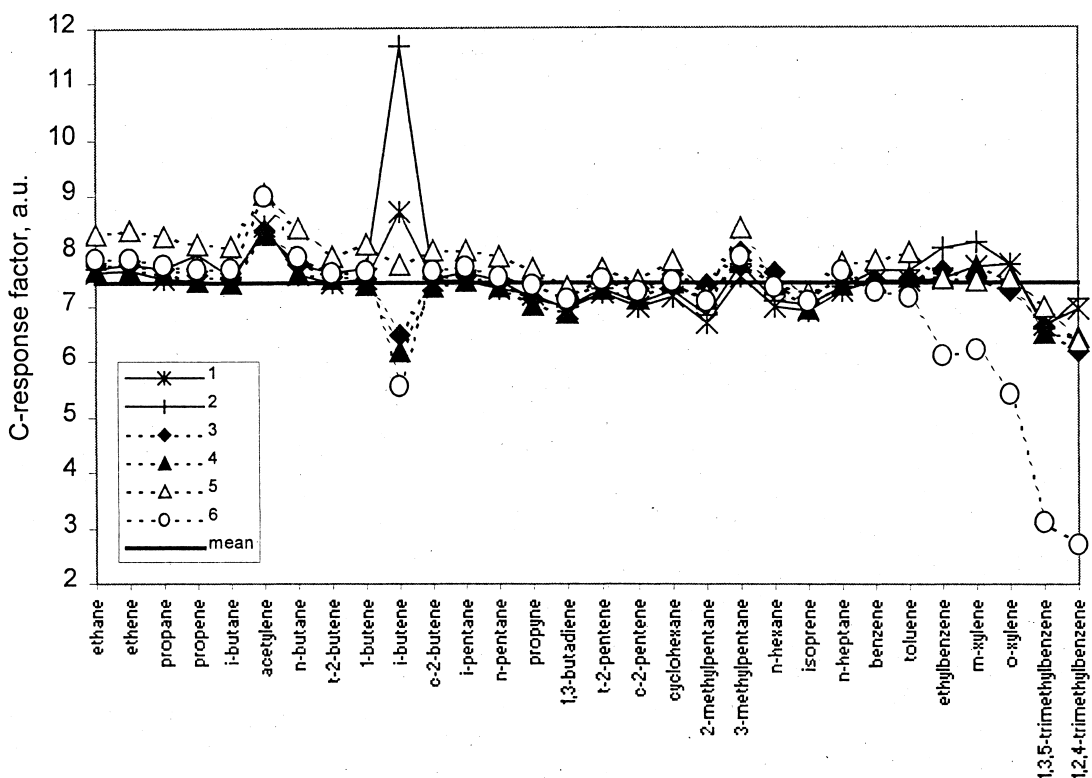


Fig. 4. FID C-response factors for various data series with different experimental conditions each with respect to the gas flow scheme as presented in Fig. 1: (1) Nafion dryer, flow control by reduced pressure of pressure regulator on NPL standard cylinder, (2) same as (1) but with an additional piece of stainless steel tubing (0.8 m \times 1/4 in. O.D., heated at 403 K), (3) Nafion dryer and Nupro needle valve, slight overpressure in the Nafion dryer, (4) same as in (3) but additionally with manifold including Nupro shut-off valves and about 0.5 m stainless steel tubing (1/4 in.) all heated at 423 K, (5) no Nafion dryer, stream selector valve and needle valve; the higher FID C-response in this series is due to modified FID gas flows, (6) same as in (4) but no flow restrictor upstream of the preconcentration trap and additional Silcosteel tubing (see text), "mean" refers to the arithmetic mean of series (1)–(4) for the C₂–C₇ hydrocarbons except for acetylene, *i*-butene, 2- and 3-methylpentane.

C-response factors which are lower by about 8% compared to the mean, possibly because of their lower effective carbon numbers [28], or losses in the cylinder (R. Partridge, H. D'Souza, National Physical Laboratory, UK, personal communication, 1998).

The data series (1) to (5) indicate no artifacts resulting from potential interaction of the sample gas with surfaces of heated stainless steel, or metal bellow valves. The data series (6) in Fig. 4 represents an example for a deviation from the mean C-response factor concept: The C₈ and C₉ aromatics show substantially reduced response factors with high scatter of ± 20 –30%. In this data series, we used a previous version of the instrument and

experimental conditions were different in two aspects from the conditions in other experiments: (1) an additional piece of unheated Silcosteel line (1 m \times 1/16 in. O.D.) was added to the sample line, and 2. no flow restrictor in the carrier gas line upstream from the preconcentration trap was used. Under these conditions it is very likely that during thermal desorption the expanding gas volume transported parts of the hydrocarbon sample upstream towards the pneumatics section where the hydrocarbons may have come into contact with cold wall surfaces of the carrier gas line. Hence, the least volatile compounds, i.e., the C₈ and C₉ aromatics, may have partially been adsorbed at these surfaces.

The preceding discussion has shown that our

analytical system generally is conservative with respect to measurements of synthetic standards, since the NMHCs investigated cover a wide range of reactivity and volatility. Thus, quantification as presented in Section 2.4 based on a mean C-response factor for the C₂–C₈ hydrocarbons (except for acetylene) is warranted by our results and experience. As shown below, corresponding uncertainties are typically less than 10%. The mean C-response factor is calculated from the C₂–C₈ hydrocarbons except for acetylene, *i*-butene, 1,3-butadiene, isoprene, 2- and 3-methylpentane and the C₈–C₉ aromatics. The latter compounds were not considered since they would increase the error of the mean C-response factor due to the reasons discussed earlier. However, deviations from the mean C-response factor and poor reproducibility in the mea-

surement of these compounds are included in the total error estimates (Section 4).

3.2.2. Ozone interference

Alkenes are highly reactive towards ozone, and without ozone scrubbing, substantial loss rates for the alkenes (up to about 50%) can be expected in the cryogenic preconcentration and thermal desorption processes [32–34]. Various methods have been proposed for ozone removal in the sample line (see review by Helmig [34]). In our system we tested the use of NO for titrating O₃ (e.g., Refs. [34–36]) and of heated stainless steel tubing [33] in standard addition measurements.

In Table 3 the relative change in the C-response factors R_i due to the addition of NO (250 ppm NO in N₂) is shown for standard addition measurements. In

Table 3
Relative changes in standard addition measurements due to adding NO at 600 ppb^a (bold type indicates significant differences)

	Relative difference ^b	2 σ uncertainty ^c
Ethane	0.09	0.21
Ethene	0.18	0.27
Acetylene	-0.12	0.62
Propane	-1.59	3.76
Propene	0.01	0.01
<i>i</i> -Butane	-0.19	0.39
<i>n</i> -Butane	-0.07	0.12
1-Butene	0.26	0.23
<i>trans</i>-2-Butene + 1,3-butadiene	0.54	0.07
<i>cis</i>-2-Butene	0.33	0.06
2-Methylbutane	-0.01	0.03
<i>n</i> -Pentane	-0.04	0.02
<i>trans</i>-2-Pentene	0.63	0.21
<i>cis</i>-2-Pentene	0.74	0.11
2-Methylpentane + 3-Methylpentane + isoprene	0.12	0.10
Isoprene (calculated) ^d	0.47	0.57
<i>n</i> -Hexane	0.02	0.01
<i>n</i> -Heptane	0.02	0.02
Benzene	0.00	0.03
Toluene	0.07	0.04
Ethylbenzene	0.13	0.13
<i>m</i> -Xylene	0.11	0.17
<i>o</i> -Xylene	0.14	0.16

^a Three measurements of ambient air+NPL standard and four measurements of ambient air+NPL standard+NO were compared.

^b (standard addition)–(standard addition+NO)/mean of all standard addition measurements.

^c The errors of the mean values with and without NO addition were determined and combined 2 σ uncertainties (95 confidence) were calculated using Gaussian error propagation.

^d Isoprene areas were calculated from the sum of 2- and 3-methylpentane and isoprene areas by assuming unchanged peak areas of 2- and 3-methylpentane due to NO induced reactions.

these tests, a previous configuration of the system as described in Section 2.1 was used. NO was added at the air intake at $5 \text{ cm}^3 \text{ min}^{-1}$ to yield 600 ppb in the sample air; ambient ozone mixing ratios were 50–70 ppb. For these conditions, it was calculated that more than 95% of the ozone are chemically destroyed before sample preconcentration. Significant losses were observed for 1-butene, the sum of *trans*-2-butene and 1,3-butadiene (not sufficiently separated on the GasPro GSC column), *cis*-2-butene, and *cis*-2-pentene and *trans*-2-pentene. Isoprene was also

reduced, however, due to co-elution with 2- and 3-methylpentane the reduction was not significant on the 95% level. Taking into account the uncertainties of the NMHC measurements and of NMHC chemical reaction rate constants, the observed relative losses of the reactive alkenes would in principle be consistent with OH or NO_3 chemistry [37].

In the present experimental set-up (Section 2.1) we use heated stainless steel tubing at 403 K to destroy ozone similar to Koppmann et al. [33]. In standard addition measurements with 40–60 ppb ozone, no interferences for the reactive alkenes were observed. Fig. 5 shows the ratios of C-response factors which have been calculated from pure 27-component NPL standard divided by standard addition measurements (see Section 2). The bars in Fig. 5 show the 2-sigma reproducibilities of the respective ratios. Differences exceeding the 2-sigma level were observed for ethane, ethene and acetylene. For these compounds, peak areas in ambient air samples are typically in the range of 20–50% of the peak areas in standard addition measurements. Therefore we assume that for these three compounds changes in ambient air mixing ratios have most likely been the reason for the observed difference in Fig. 5. Overall, deviations between standard addition and pure standard measurements are smaller than 10% for all compounds, and below 5% for the reactive C_3 – C_5 alkenes. Thus, ozone is efficiently removed by the heated stainless steel surfaces of tubing and valves without any detectable interference for the C_2 – C_8 hydrocarbons routinely measured at Hohenpeissenberg.

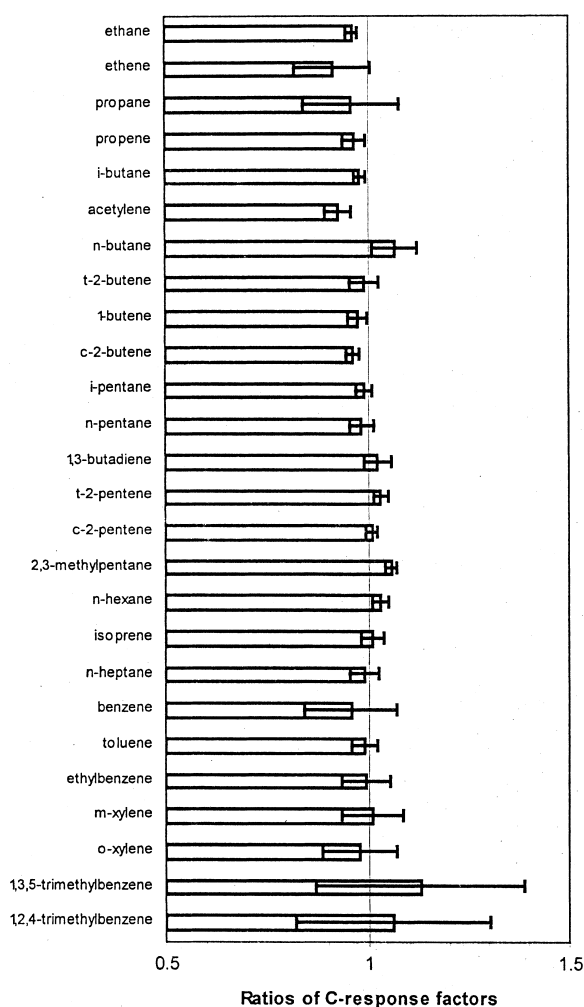


Fig. 5. Ratios of the C-response factors obtained in measurements of a pure standard mixture relative to standard addition to ambient air with 40–60 ppb ozone (27-component NPL standard). The bars correspond to the 2-sigma scatter of the ratios.

3.2.3. Water vapour removal and Nafion artifacts

In a previous version of the sample inlet system, water vapour was removed from the sample air by a $\text{Mg}(\text{ClO}_4)_2$ trap heated to 343 K, episodically to 383 K. However, this trap also caused significant losses of isoprene (30–80%). Furthermore, significant losses of heavier compounds (C_7 – C_9) were detected. The losses of C_7 – C_9 hydrocarbons increased with decreasing temperature of the trap. Based on these experiences, $\text{Mg}(\text{ClO}_4)_2$ was subsequently replaced by a Nafion dryer.

FID C-response factors (R_i) do not differ significantly whether a Nafion dryer was used or not (Fig. 4), except for *i*-butene. In a measurement series

without Nafion dryer (series 5 in Fig. 4), *i*-butene response is comparable to other hydrocarbons. However, at sampling conditions with reduced pressure in the Nafion dryer, the *i*-butene peak areas are enhanced and at higher than ambient pressures they are reduced. A Nafion artifact for *i*-butene has also been observed by Mowrer and Lindskog [25], and Donahue and Prinn [24]. Gong and Demerjian [38] reported losses and rearrangements of some alkenes on Nafion dryers after thermal regeneration. In our system, no thermal regeneration is applied during routine operation. However, after the Nafion dryer had been purged for 3 weeks continuously with helium, the first measurements of dry NPL standard consistently showed indications for alkene rearrangement on the membrane: the *trans*-2-butene and *trans*-2-pentene peaks were both enhanced by up to 15% whereas 1-butene, *cis*-2-butene, *cis*-2-pentene and isoprene peaks were reduced by less than 10% each. Furthermore, small artifact peaks of 2-methylbutene-2 and 1-pentene were produced. Therefore we conclude that the Nafion membrane may be activated by thermal regeneration or excessive purging with dry inert gas, and consequently a rearrangement of some alkenes may occur.

In zero gas measurements, contaminant peaks of propene, *trans*-2-butene, *i*-butene, and *cis*-2-butene were observed when a Nafion dryer was used. In measurements of very clean ambient air (Fig. 2 and Table 2), peak areas of these compounds were comparable to the blank values, corresponding to less than 10 ppt (several 10 ppt in case of *i*-butene). Thus, no indications for a possible ozone-Nafion artifact yielding enhanced alkene concentrations were found. However, it appeared that light alkenes are desorbed from the Nafion membrane. The presence of alkenes in blank gas measurements could not be eliminated by thermal regeneration of the Nafion dryer at 343 K for several days under a steady purge flow of He or N₂. In contrast, blank values of *i*-butene were enhanced in the first measurements subsequent to the conditioning and slowly decreased to levels comparable to those before the heat treatment. However, using purified compressed air (Section 2.1, FID flame gas, absolute humidity of 0.3%) instead of N₂ during thermal regeneration (343 K) and during the consecutive purge phase of more than 2 h, the alkene blank values could be reduced.

Furthermore, no alkene rearrangement was observed in subsequent standard gas measurements. This conditioning procedure is currently tested in our long term measurement program.

For all 30 compounds of the NPL-mix, measurements of “dry” calibration gas standards showed no significant differences to standard addition measurements (“wet”) when a Nafion dryer was employed (Fig. 5).

4. Error assessment

In this section, we first will present our routine assessment of measurement precision and accuracy. As outlined in the Introduction, a complete error estimation of on-line GC analysis is problematic. In order to check the reliability of the assessed uncertainties, these are compared to corresponding reproducibilities of reference gas measurements (Section 4.2) and results obtained in recent inter-comparison experiments (Section 4.3).

4.1. Determination of accuracy and precision

Based on Eqs. (1)–(3), the following errors are assessed by propagation of the respective individual errors in each measurement and for each compound: errors of the calibration factor, the peak area of each compound in sample and blank measurements, and the sample volume.

The calibration factor is determined from the arithmetic mean (R) of the compounds' C-response factors (R_i). The error of the mean is typically 1–2%, which, however, is only part of the total error. The major contributions are due to (a) the uncertainty of assuming a uniform C-response of the FID system and (b) the accuracy assumed for the 30-component NPL standard. As shown in Section 3.2.1, we observed deviations from the mean C-response factor of less than 6% for most compounds (Section 3.2.1). In a recent paper, Apel et al. [2] reported agreement between gravimetric standards from NIST, NPL, Environment Canada, and NCAR of better than $\pm 10\%$ for most compounds. Consequently, as a reasonable estimate of the error of each compounds' calibration factor we choose the maximum of the relative deviation of the compounds' C-response

factor from the mean and 5%, which approximately corresponds to the 1σ -range of these relative deviations. These numbers are higher than 1% (2-sigma) accuracy stated by NPL for the standard at the time of dispatch. However, with regard to potential systematic changes, which may arise from minor instabilities of the NPL standard and interaction of calibration gas compounds with the used gas cylinder valve, pressure regulator, transfer line, and analytical system, the uncertainties of the calibration factors are necessarily higher than those stated for the standard by NPL. Changes in the relative abundance of the various compounds in measurements of the NPL-standard were at an insignificant level of less than a few percent over a period of 2 years, if acetylene and *i*-butene are not considered for the reasons given above. For those compounds not included in the 30-component NPL standard, accuracies of 15–20% were assumed (“calibration uncertainty” in Tables 1 and 2).

For small peaks (typically below 100 ppt), the peak area integration (“integration” error in Tables 1 and 2) is generally limited by the detection limit, for large peaks by the reproducibility of the integration (2%). The detection limit was determined by multiple integration of the same small peaks with variations of the baseline within 2-sigma of the baseline noise. Corresponding standard deviations were used to calculate an averaged 2-sigma detection limit. However, peak overlap or bad baseline in parts of the chromatogram can be the major contribution to peak integration error. To assess the error due to peak overlap, artificial peaks with asymmetric peak shapes were superimposed and the peak areas were determined for “split peak” integration using the chromatographic software. The relative deviations from the “true” values were determined for different types of peak overlap, and were considered as peak area errors. If blank peak areas occur, mean blank areas for the respective compounds are subtracted from the corresponding sample peak areas. The error (“blank” in Tables 1 and 2) corresponds to the 2-sigma scatter of the blank peak areas. With these derived integration and blank errors, detection limits for ambient air samples (750 cm³) are below 3 ppt for most compounds and below 20 ppt for those compounds with blank peak areas.

The sample volume is determined by pressure

increase in an evacuated reference volume. Since calibration and sample measurement procedures refer to the same reference volume, the uncertainty of the volume is cancelled out in the error estimate. The pressure gauge is regularly calibrated against a laboratory reference gauge. From the manufacturer’s accuracy given for the pressure gauge, the volume error is generally less than 1% of the overall error, for small sample volumes (50 cm³) it is up to 3%.

In Tables 1 and 2 the various error contributions (relative to the determined mixing ratios) are listed for the ambient air sample and NPL standard mixture, respectively, presented in Fig. 2. Also, in Table 1 a 2% error of the FID sensitivity (“FID”) was included representing possible temporal changes in FID sensitivity. This estimate was derived from variations of mean C-response factors in various standard measurements. With error propagation applied to integration, blank, volume and FID errors, “combined random errors” of typically 4% for NPL measurements are obtained which should be comparably large as the observed reproducibility of NPL measurements (“reproducibility” in Tables 1 and 2). However, these reproducibilities are larger for some compounds, especially *i*-butene and the C₈-aromatics, than the calculated “combined random errors”. These worse reproducibilities are attributed to deviations from an adsorption/desorption equilibrium on the internal surfaces which may result from too short purge intervals prior to sampling, or from small changes in pressure from the initial purging period to the subsequent sampling. Consequently, the reproducibility was included in the accuracy and precision estimates. For compounds not present in the 30 component NPL standard, slightly worse reproducibilities as for comparable NPL compounds were assumed. For example, a 10% reproducibility was ascribed to 1-pentene with respect to measured reproducibilities of about 3% for *trans*- and *cis*-2-pentene (Table 2). The reproducibility values for NPL measurements already include the uncertainty of peak area integration, blank peak areas, FID sensitivity, and sample volume. Consequently, the integration error for large peaks (see above) was excluded from the error propagation. In contrast to standard measurements, peak areas are generally much smaller in ambient air measurements and also smaller sample volumes may occasionally be used.

Thus, in ambient air measurements, error contributions due to “integration”, “blanks”, and “volume” have to be considered in addition to the above defined reproducibility since uncertainties of the latter parameters may contribute substantially more to the overall precision and accuracy than the reproducibility of standard measurements. In Table 2 error contributions from peak integration and blank errors are substantially larger than 10% for some compounds, occasionally even exceeding 50%. These large errors result from either substantial peak overlap, or mixing ratios close to the detection limit, in particular when unstable blank peak areas are encountered.

4.2. Verification of the determined precision

In Fig. 6 the precision calculated for the measurements of reference gas 1 (compressed ambient air from Hohenpeissenberg) is compared to the experimentally determined reproducibility (2-sigma standard deviation) of nine consecutive measurements. In contrast to on-line measurements, highly reactive constituents, e.g., free radicals and ozone, are not present, and water vapour concentration is much lower corresponding to the total pressure of $7 \cdot 10^6$ Pa in the cylinder. Furthermore, potentially

interfering peaks are constant in size and by this do not enhance the measured variability.

For most compounds with mixing ratios above 10 ppt, precision and reproducibility are below 20%, and in general, the estimated precision is comparable to the measured reproducibility within less than 10%. Significant deviations between precision and reproducibility are indicated by numbers 1–4 in Fig. 6. Acetylene (1) could not be reproducibly measured in the 30-component NPL standard (14% precision). This is due to changing response and reproducibility of acetylene over periods of weeks for the respective NPL standard. In contrast, the reproducibility (95% confidence) is better than $\pm 3\%$ in measurements of reference gas 1, and also of the 27-component NPL standard purchased in 1995. Therefore, for acetylene we use the reproducibility of 3% for error assessment. *n*-Hexane (2) co-elutes with an unknown compound which is occasionally detectable as a shoulder on the *n*-hexane peak. This unknown peak is always smaller than *n*-hexane and we conservatively estimated an uncertainty of 40% for *n*-hexane measurements. For the reasons outlined above, e.g., constant peak area of the interfering compound in reference air, the reproducibility of 7% is much better than the estimated precision. Propene (3) and *trans*-2-butene (4) both showed unusual high blank values in the corresponding measurement period (September 2000) with a 2-sigma scatter corresponding to 31 and 24 ppt, respectively, which were most probably due to changes concerning the Nafion dryer in that period. In the measurement series of the reference gas 1 which was conducted on a single day, a much better reproducibility was observed. Typically, blank values and the corresponding 2-sigma scatter of propene and *trans*-2-butene are at or below 5 ppt, which would result in precisions comparable to the observed reproducibilities.

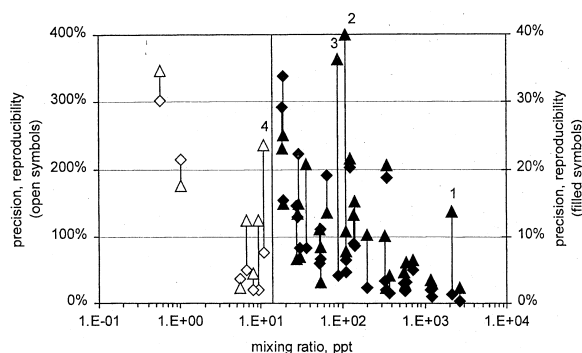


Fig. 6. Comparison of the estimated precision (triangle) and measured reproducibility (diamonds) for 39 compounds obtained from nine consecutive measurements of reference air 1. For each compound, precision and reproducibility (connected by a vertical line) are shown as a function of the compound's mixing ratio. A second y-axis was used for compounds with mixing ratios higher than 15 ppt (filled symbols, right axis), numbers indicate selected compounds: acetylene (1), *n*-hexane (2), propene (3), and *i*-butene (4) (see text).

4.3. Verification of the determined accuracy

Results obtained from formal intercomparison measurements of different working groups are used to assess the accuracy of C_2 - C_8 hydrocarbon measurements. However, it must be kept in mind that only the accuracy with respect to the specific test mixture used in the intercomparison is evaluated which is not generally assumable for the whole range

Table 4
DWD^a results of a compressed air sample obtained in phase 3 of the AMOHA intercomparison experiment (see text for details)

	Results DWD (ppb)	Accuracy DWD (%)	Reference (ppb)	Standard deviation reference (%)	Error reference ^b (%)	Deviation DWD-reference (%)	Combined uncertainty ^c (%)
Ethane	3.148	5	2.920	23	14	8	15
Propane	0.905	5	0.875	9	5	3	7
<i>n</i> -Butane	0.758	5	0.755	7	4	0	7
<i>i</i> -Butane	0.590	5	0.590	8	5	0	7
<i>n</i> -Pentane	0.350	5	0.355	10	6	-1	8
2-Methylbutane	1.087	5	1.090	6	4	0	6
2-Methylpentane	0.282	15	0.340	7	5	-17	16
3-Methylpentane	0.195	12	0.200	11	8	-3	15
<i>n</i> -Hexane	0.148	23	0.160	18	10	-8	25
<i>n</i> -Heptane	0.077	6	0.090	28	17	-14	18
Ethene	14.226	5	13.430	10	6	6	8
Propene	0.719	5	0.745	8	5	-4	7
<i>i</i> -Butene	0.484	19	0.390	23	14	24	24
1-Butene	0.259	5	0.260	10	6	-1	8
<i>trans</i> -2-Butene	0.243	12	0.230	11	7	6	13
<i>cis</i> -2-Butene	0.179	6	0.180	10	6	0	8
<i>trans</i> -2-Pentene	0.095	5	0.100	118	71	-5	71
<i>cis</i>-2-Pentene	0.052	6	0.060	15	9	-13	10
1,3-Butadiene	0.178	10	0.170	14	8	5	13
Isoprene	0.051	10	0.050	116	77	2	78
Ethyne	24.828	15	24.240	4	3	2	15
Propyne	0.203	16	0.210	16	10	-3	19
Cyclohexane	0.059	6	0.070	38	23	-16	24
Benzene	1.384	6	1.415	9	5	-2	8
Toluene	1.222	5	1.315	9	5	-7	7
Ethylbenzene	0.213	5	0.230	8	5	-7	7
<i>p,m</i> -Xylene	0.680	5	0.710	11	7	-4	9
<i>o</i> -Xylene	0.279	6	0.280	8	5	0	8

Bold type indicates compounds with deviations exceeding the combined uncertainties.

^a DWD: Deutscher Wetterdienst (German Weather Service).

^b 2-Sigma error of the mean of the results of the participating laboratories, after the highest and lowest results had been discarded.

^c Calculated from the accuracy of DWD results and the error of the median assuming independent errors.

of possible chemical compositions in ambient air. Furthermore, reference concentrations in whole air intercomparison samples are also subject to errors, which makes it difficult to assess the corresponding accuracy.

During the intercomparison experiment NOMHICE (organized by the National Centre for Atmospheric Research, NCAR, Boulder, CO, USA [1,2]), we participated in phases 4 and 5 with an earlier version of the instrument. Basically, a $\text{Mg}(\text{ClO}_4)_2$ moisture trap which caused losses of the higher boiling compounds, and a GasPro GSC column were used (see Section 2.1). In NOMHICE phases 4 and 5, canister samples of compressed ambient air were used as test gases, with mixing ratios above 100 ppt for most C_2 – C_6 hydrocarbons (range: 10 ppt–10 ppb) in phase 4, and lower mixing ratios in phase 5 (range: few ppt–2 ppb). Our C_2 – C_6 hydrocarbon results of phase 4 generally agreed with the NCAR results (Apel, personal communication, 1998) better than about 10%, which was generally in the range of our estimated accuracies. Deviations larger than 15% occurred for two out of 11 compounds (ethene and benzene). For ethene, this resulted from insufficient separation from ethane. No explanation could be found in the case of benzene. The results obtained for propene, 1-butene and 1-pentene are not included in this evaluation since these compounds were unstable in the canisters. However, our measured mixing ratios were consistently in the range between the upper and lower limit measured by NCAR. During NOMHICE phase 5, our results again agreed with respect to the majority of the C_2 – C_6 compounds better than 20% or 10 ppt (E. Apel, personal communication, 1998). The C_3 – C_5 alkane results, however, were higher by less than 40% than the mixing ratios measured by NCAR except for *i*-butane and *i*-pentane which were higher by factors of 3 and 8, respectively. With the earlier version of the instrument used in NOMHICE (see above), co-elution of *i*-butane and *i*-pentane (Section 3.1) with unidentified compounds, most probably polar compounds, was frequently observed and is considered to be the reason for this deviation.

In contrast to the NOMHICE experiment, in which all participants used their own calibration gases, in the European intercomparison experiment AMOHA (Accurate Measurements Of Hydrocarbons in Air) all laboratories were asked to use the same NPL cali-

bration gas mixture circulated with the test cylinders. Here we will compare our results (DWD) obtained with our own quantification and error assessment methods as described in Sections 2.4 and 4.1 to the AMOHA reference values (Table 4) for a compressed air sample measured in AMOHA phase 3 [17]. The accuracy estimated for our measurements (five replicates) is compared in Table 4 to the deviation from the reference value, which corresponds to the median of the results obtained from all 15 participants.

The results obtained by the various working groups were all close to the respective median values (standard deviations were about 10%, only for six compounds they were >20%; Table 4). As a first approximation, we assume that the uncertainty of the reference value can be described by the error of the mean after excluding the highest and the lowest value. Deviations between our results and the reference values were generally well below 10%. Only the results of 2-methylpentane, *n*-heptane, *i*-butene, *cis*-2-pentene, and cyclohexane showed deviations of up to 24%. If the combined uncertainties (Table 4) are considered, only two deviations exceeded the uncertainties by a few percent. In the case of *cis*-2-pentene (13% deviation versus 10% uncertainty) this may have resulted from additional uncertainties in the reference value at the low mixing ratio of 50–60 ppt. For 2-methylpentane (17% deviation versus 16% uncertainty) our mixing ratio has an accuracy of 15% mainly due to partial peak overlap with 3-methylpentane and 2,3-dimethylbutane. For *i*-butene (24% versus a combined uncertainty of 24%) both, our accuracy estimate (19%) and the error of the reference value (14%), are fairly large and indicate problems in the measurement of this alkene which may at least partially arise from the use of Nafion dryers (see above). For all other compounds, the deviations were found to be lower, in most cases substantially lower than the uncertainty range. Thus, the accuracies calculated for our measurements can fully account for the deviations between our results and the reference values of the AMOHA intercomparison.

5. On-line NMHC measurements at Hohenpeissenberg

Annual cycles of ethane, benzene, and 1-pentene

are presented in Fig. 7 as an example for the long term measurements of NMHC at Hohenpeissenberg. All three NMHC are predominantly of anthropogenic origin and are removed from the atmosphere by chemical reactions, mainly with hydroxyl radicals (OH). Mixing ratios differ by orders of magnitude between these compounds with highest values observed for ethane (up to a few ppb), followed by benzene (about 50–500 ppt) and 1-pentene (detection limit of 2–20 ppt). The error bars correspond to the respective accuracies (2σ). In the chosen logarithmic presentation, the length of the error bars are larger for the compounds with lower mixing ratios. In some months, e.g., August and October, the errors in the benzene measurements were enhanced due to local contamination sources. In these months the contaminations were most probably caused by emissions due to the dismantling of a fuel oil tank in a building 20 m off from the air intake of the sample line.

Ethane and benzene show similar annual cycles with maxima in winter and minima in summer. However, two substantial differences (apart from the different mixing ratio levels, see above) can be recognized: (1) the scatter in the data is lower for ethane; and (2) the annual cycle which can be approximated by a sine function for ethane is shifted against the benzene cycle by about 2 months later.

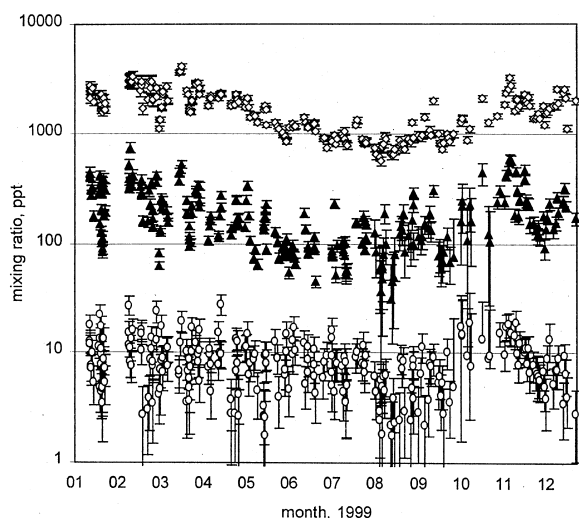


Fig. 7. Mixing ratios of ethane (open diamonds), benzene (filled triangles), and 1-pentene (open circles) with corresponding error bars (accuracy) for the year 1999. Most samples were obtained at midday (13:00 CET).

For both ethane and benzene, the relative scatter in the data is higher in winter than in summer. In contrast, 1-pentene data do not show a significant annual cycle. The observed differences in the data series of the three compounds presented here are, in first approximation, a result of their substantially different atmospheric lifetimes: ethane is the longest lived NMHC with lifetimes of approximately 3 months in winter, and 1 month in summer which are due to much lower OH radical concentrations in winter (on average about $0.5 \cdot 10^6$ molecules cm^{-3}) than in summer (about $1.5 \cdot 10^6$ molecules cm^{-3}). Benzene and 1-pentene have lifetimes in winter of 19 days (summer: 6 days) and 11 h (summer: 4 h), respectively. Due to the relatively long residence time of ethane in the lower troposphere a substantial background level can accumulate, thereby smoothing out the potential impact of local and regional ethane sources in the data record. Furthermore, ethane follows the OH annual cycle with a lag interval which is determined by its atmospheric life time. Finally, due to the latitudinal distributions of both ethane sources and OH concentrations, a considerable latitudinal gradient for ethane develops in winter whereas it is almost evenly distributed in summer [40]. Consequently, long range transport from different areas of the northern hemisphere contributes to relatively higher variations in ethane mixing ratios in winter than in summer. Benzene shows principally similar, but less pronounced features than ethane due to its relatively shorter life time. In contrast, 1-pentene is so short lived that it exclusively originates from sources in the vicinity of the measurement site and no background concentrations can build up. Therefore, the scatter in 1-pentene mixing ratios is largest. No significant seasonal variations are detected. A possible explanation would be that for relatively short lived compounds the measured mixing ratios are preferentially determined by transport and dilution and not by chemical lifetime.

6. Conclusions

A new on-line GC system for automated measurements of C_2 – C_8 hydrocarbons has been presented and the high quality performance of the system for measurements in the lower ppt range as required for the long term GAW measurement program has been

demonstrated. The system components were thoroughly tested for potential artifacts by a detailed quality assurance protocol including (a) the FID effective carbon number response concept [28] and (b) standard addition measurements. With respect to (a), the FID area response is approximately proportional to the volume mixing ratio and the number of carbon atoms per molecule for all NMHCs except for those with triple bonds. Observed deviations from this proportionality were used as indications for artifact processes in the GC system including the sample line. The components and/or processes that caused these artifacts could be identified. In standard addition measurements, a few percent of a multi-component NMHC standard in the 10–100 ppb range were continuously added to the ambient air sample flow. By this procedure, possible artifacts due to interaction of hydrocarbons with components of ambient air, such as ozone, water vapour, or free radicals can be simulated and quantitatively assessed. Based on our experience and results we agree with Donahue and Prinn [24] in concluding that the standard addition method is the only way one can rigorously demonstrate whether or to what extent on-line GC systems are free of sampling artifacts.

Our present GC system shows no significant deviations from a uniform carbon number response for all compounds studied except for *i*-butene and acetylene. For acetylene, the FID carbon response is higher by 14% which is expected due to the triple bond. For *i*-butene both higher and lower C-response factors compared to the mean factor were observed which could be attributed to adsorption and desorption effects in the Nafion dryer, respectively. Furthermore, adsorption and desorption effects caused slightly worse reproducibilities in standard measurements of the higher boiling C₈ and C₉ aromatics (2 σ of 7–15%) which could not be further reduced by, e.g., enhanced temperatures in the sample line. Instead, they may result from artifact processes in the standard cylinder and/or the corresponding pressure regulator. Also, episodically observed unusually low reproducibility of acetylene measurements (e.g., 14%) using one of the calibration gas cylinders by NPL pointed towards a problem in this 30-component mixture (dispatched in 1998), since reproducibilities of acetylene measurements from other cylinders were much better, typically at 3%.

Chemical interferences due to ozone were not detectable when effective ozone destruction on heated stainless steel surfaces was employed in the sample line. An alternative approach using NO titration of ozone in the sample line resulted in significant losses of the more reactive alkenes. No indications for chemical interferences of air samples with materials of the sample line were observed.

Some alkenes in the C₃–C₄ range showed artifact blanks caused by the Nafion dryer. These compounds were observed in zero gas measurements at mixing ratios corresponding to about 10 ppt comparable to the lowest concentrations measured in ambient air samples. Chemical changes in the Nafion dryer as a consequence of thermal conditioning prior to each run, as reported by Gong and Demerjian [38], were not observed since the Nafion dryer is kept at room temperature in routine operation. A Mg(ClO₄)₂ trap was tested for water removal but produced substantial losses of isoprene and C₇–C₉ compounds even when it was heated to temperatures up to 383 K.

A routine QA/QC procedure is applied based on regular measurements of standards, blanks, and reference gases containing complex NMHC mixtures. Deviations from a uniform carbon response, unusually low reproducibilities in standard or reference gas runs, the occurrence of unusual peak areas in blank runs and changes in the chromatograms of the reference gases are considered to be indications for irregular operation of the analytical system. When such deviations are observed, the system is carefully checked until the responsible causes are identified and eliminated.

A procedure for error estimation has been developed which is routinely applied to our ambient air measurements. Error estimates provide the final data quality attribute in determining the potential deviation from the true mixing ratio. The present error assessment procedure combines the estimates of all quantified error contributions for each component in each measurement. Total error estimates derived by this approach can be used as weighting factors in subsequent data interpretation, for example, in source attributions using chemical mass balance [39]. We showed a specific approach to check the reliability of the calculated precision and accuracy. The precision was shown to be consistent with the experimentally determined reproducibility from multiple measure-

ment of a compressed ambient air reference sample. The assessed accuracy agreed with the deviation of our results from reference values obtained in the recent international hydrocarbon intercomparison experiments NOMHICE and AMOHA.

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