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Comprehensive two-dimensional gas chromatography (GC×GC) measurements of volatile organic compounds in the atmosphere

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Abstract. During the MINOS campaign in August 2001 comprehensive two-dimensional gas chromatography (GC×GC) was applied to the in situ measurements of atmospheric volatile organic compounds (VOCs) at the Finokalia ground station, Crete. The measurement system employs a thermal desorption unit for on-line sampling and injection, and a GC×GC separation system equipped with a flame ionization detector (FID) for detection. The system was optimized to resolve $C_7 - C_{14}$ organic components. Two-dimensional chromatograms from measurements of Finokalia air samples show several hundred well-separated peaks. To facilitate peak identification, cartridge samples collected at Finokalia were analyzed using the same GC×GC system coupled with a time-of-flight mass spectrometer (TOF-MS). The resulting mass spectra were deconvoluted and compared to spectra from a database for tentative peak identification. About 650 peaks have been identified in the two-dimensional plane, with significant signal/noise ratios (>100) and high spectra similarities (>800). By comparing observed retention indices with those found in the literature, 235 of the identifications have been confirmed. 150 of the confirmed compounds show up in the $C_7 - C_{14}$ range of the chromatogram from the in situ measurement. However, at least as many peaks remain unidentified. For quantification of the GC×GC measurements, peak volumes of measured compounds have been integrated and externally calibrated using a standard gas mixture.

1 Introduction

Depending on their physical and chemical properties, volatile organic compounds (VOCs) play a wide variety of important roles in the atmosphere. Reactive hydrocarbons and their intermediate products have been recognized as precur-

sors of tropospheric O_3, organic acids, and organic aerosols (Fehsenfeld et al., 1992; Andreae and Crutzen, 1997; Limbeck and Puxbaum, 1999; Krivácsy et al., 2001; O'Dowd et al., 2002). If present at a high concentration in the boundary layer, O_3 is toxic for humans and vegetation. Some VOCs themselves, especially those from anthropogenic sources, endanger human health directly (Mohanmed et al., 2002). Organic acids contribute to the acidification of precipitation, while some organic species may form aerosols which as potential cloud condensation nuclei can affect weather and climate (Andreae and Crutzen, 1997; Krivácsy et al., 2001). Long-lived VOCs can be transported to remote areas, where they may influence chemical and physical properties of the remote atmosphere. Some VOCs, particularly halocarbons, have very long lifetimes, so that they may be transported into the stratosphere and act there as destroyers of stratospheric O_3 (WMO, 1994). Many halocarbons are strong greenhouse gases as well (IPCC, 2001). For the aforementioned reasons, the accurate measurement of volatile organic components in ambient air is an important aspect of atmospheric science.

Gas chromatography (GC), in combination with flame ionization detection (FID) or mass spectrometry (MS), has been used in many studies to measure atmospheric VOCs (e.g. Helmig et al., 1996; Rappenglück et al., 1998; Wedel et al., 1998). However, conventional GC often fails to separate components in complex samples to a satisfactory degree, being limited by the separation power of a single column. Severe peak overlap in single-column chromatography causes difficulties in identification and inaccuracy in quantification. Peak overlapping has another consequence for air analysis. Due to the strong differences in abundance between components, a large number of components with relatively lower mixing ratios may be completely masked by the enhanced baseline, so that they are not visible on the conventional chromatograms (Lewis et al., 2000). These components can be very reactive ozone precursors, intermediate products of photochemical reactions, tracers of specific processes and hence

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**Table 1.** GC×GC parameters and conditions

First Column	DB-5, 30 m long, 0.25 mm I.D., 1 μm film ((5%-Phenyl)-methylpolysiloxane) 50°C to 200°C at 2.5°C min^{-1}
Second Column	Carbowax, 1 m long, 0.1 mm I.D., 0.1 μm film (polyethylene glycol) 30°C to 180°C at 2.5°C min^{-1}
Modulator	Jet-cooled and -heated Cold jet tubes I.D. 2.7 mm, axial distance between cold jets 7.8 mm Hot jet tubes I.D. 4.2 mm, axial distance between hot jets 8.2 mm Cold jet flows 10 l min^{-1} N$_2$, hot jet flows 70 l min^{-1} N$_2$ Modulation time 6 s, upstream pulse duration 0.3 s, downstream pulse duration 0.3 s, pulse delay 0.4 s
Carrier Gas	Helium (99.9999%, filtered using water, hydrocarbon and oxygen traps), 276.8 kPa

of interest for atmospheric chemists. Even though their individual abundances are low, quantification of these species may be of importance for understanding atmospheric processes such as ozone formation.

Since its invention just over a decade ago, the novel technique of comprehensive two-dimensional gas chromatography (GC×GC) has been developed to separate and analyze complex samples, such as, petroleum, flavors, and environmental samples. This technique employs two coupled columns of different selectivity and subjects the entire sample to a two-dimensional separation. Effluent from the first column is modulated to produce sharp chemical pulses, which are rapidly separated on the second column. A separation plane is produced by the two orthogonal retention time axes for both columns. Usually, the first column contains a non-polar stationary phase, and the second column a polar stationary phase. This combination allows components to be independently separated, first according to their volatility, and then according to their polarity. In comparison to conventional single-column gas chromatography, GC×GC has a much higher peak capacity, because the entire plane of a GC×GC chromatogram can be used for separation. Other advantages of GC×GC include enhanced sensitivity due to analyte refocusing, true background around resolved peaks, more reliable identification due to two retention times and due to well ordered bands of compound groups (Phillips and Xu, 1995; Phillips and Beens, 1999; Schomburg, 1995; Beens et al., 1998, 2000; Kinghorn and Marriott, 1998; Bertsch, 1999, 2000).

The key element in a GC×GC system is the modulator, which compresses segments of the effluent from the primary column and re-injects them onto the secondary column. Different types of modulator have been designed and shown to be capable of making GC×GC measurements. In their pioneer work, Liu and Phillips (1991) and Phillips and Xu (1995) used an on-column two-stage thermal modulator,

which is heated by a resistive film painted onto the capillary surface and cooled by ambient air. This modulator is difficult to operate and has only a short lifetime. A similar thermal modulator using a wire, instead of the painted film, has higher durability, but sluggish thermal response (de Geus et al., 1997). A more robust thermal modulator using a rotating heated sweeper showed good performance; however, the operation temperature of the GC oven must be about 100°C lower than the maximum allowed temperature of the stationary phase in the modulation capillary (Phillips et al., 1999). Instead of using heating, Kinghorn and Marriott (1998b) developed a modulator using cooling. This modulator regularly traps and releases solutes from the first column by moving a cryogenic trap back and forth along the second column. While achieving good performance, the prototype of this modulator showed problems with ice build-up, which were overcome in modified designs (Kinghorn et al., 2000; Beens et al., 2001b). Both the heated sweeper technique and the moving cryogenic trap technique have a common drawback, i.e. frequent breakage of capillaries by moving parts in the system. More recent development of the modulation technique is the jet-cooled modulator, which uses no moving parts. Adapted from the jet-cooled thermal modulator (Ledford and Billesbach, 2000), a jet-cooled/heated modulator was reported by Ledford (2000). The modulator employs two cold and two hot nitrogen jets that are pulsed to alternately cool and heat two spots at the front end of the second column for focusing and remobilizing analytes eluting from the first column. While this type of modulator allows excellent modulation of compounds even as volatile as methane, use of liquid nitrogen is limited by its availability and requires bulky facilities for storage and insulation. A practical solution has already been demonstrated by Beens et al. (2001a), who used a CO$_2$-cooled jet modulator and obtained sharp (about 30 ms) second-dimension peaks.
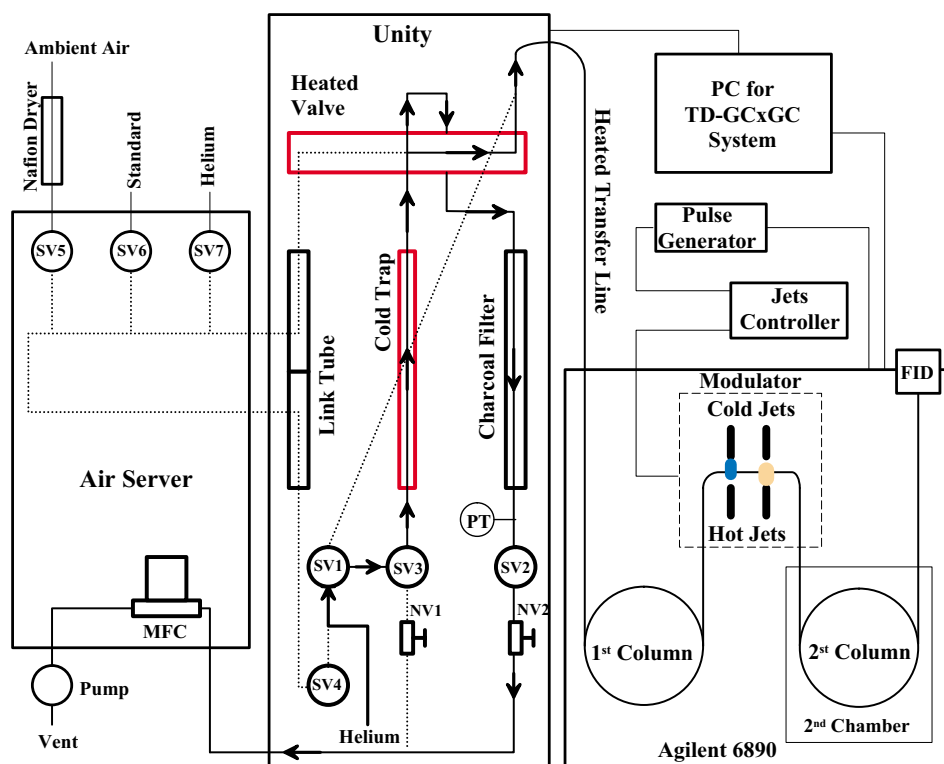
Fig. 1. Schematic of the thermal desorber-GC×GC-FID system. The left part shows an air server that contains a sampling manifold and a mass flow controller (MFC). A Nafion dryer can be used for removing moisture from ambient air. The middle part shows the thermal desorber in the trap desorption step. The arrows give flow directions of carrier gas (helium). During on-line sampling the carrier gas flows in the reversed direction. The solid and dotted lines show flow-paths with and without gas flow, respectively. SV, NV, PT, and MFC represent solenoid valve, needle valve, pressure transducer, and mass flow controller, respectively. The right part shows the GC×GC system with its controlling units. In the real design, the hot jets tubes are orthogonal to the cold jets tubes.

Apart from the thermal modulators, valve-based modulators can also be used to make GC×GC measurements (Bruckner et al., 1998; Fraga et al., 2000; Johnson et al., 2002). However, the valve-based modulators send only a part of the effluent from the first column to the second column because they use the so-called heart-cutting technique. Therefore, use of the valve-based modulation technique is limited to relatively concentrated samples.

The GC×GC technique is now beginning to be applied to a wide variety of complex sample measurements. The potential of GC×GC to ambient air measurements was first demonstrated by Lewis et al. (2000). It was shown that some 550 individual components could be separated in urban air. In this study we have applied GC×GC to the in situ measurements of VOCs at a more remote site, approximately days transport time from sources. This paper describes the instrumental set-up as well as the identification and quantification techniques. An atmospheric chemistry analysis and interpretation of the quantitative data are given in a separate paper (Xu et al., 2003).

2 Experimental

2.1 Site

The in situ measurements were performed during the Mediterranean INtensive Oxidant Study (MINOS) project in August 2001 (summarized by Lelieveld et al., 2002). Atmospheric VOCs were observed at Finokalia, Crete, a ground-based station (35°19′ N, 25°40′ E; 130 m a.s.l.) established by the University of Crete. Crete is located roughly in the middle of the Eastern Mediterranean, about 400 to 1000 km away from the coasts of Greece and Turkey. The wind was steady and northerly throughout the campaign. The 7.4 m s^{-1} average windspeed corresponds to a transport time of 0.5–1 d from continental coastal sources to measurement point.

2.2 GC×GC System

The measurement system used for the in situ observation is depicted schematically in Fig. 1. The whole system consists of a flow controller and a thermal desorber (both from

Markes International, Pontyclun, UK), and a gas chromatograph (GC6890, Agilent, Wilmington, DE, USA), equipped with a flame ionization detector (FID) and jet-modulated GC×GC parts (Zoex, Lincoln, NE, USA). The sampling and desorption control software (Markes International, Pontyclun, UK) and ChemStation (Agilent, Wilmington, DE, USA) installed on a personal computer controlled the sampling/thermal desorption system and the GC, respectively. For the GC×GC modulation, a homemade multipurpose device (V25) was used as a pulse generator, which can be easily synchronized with the GC. The main benefit of such synchronization is that the second-dimension retention times do not drift randomly and consistent geometries can be achieved from run to run.

The thermal desorber can be set either to the on-line mode or to the 2-stage desorption mode. In the on-line mode ambient air is drawn through a link tube and collected directly onto the cold trap (quartz, 12 mm, 2 mm I.D.) of the thermal desorber and analyzed immediately after the sampling (for more details, see Sect. 2.3). The cold trap contains two beds of sorbent, i.e. Tenax TA and Carbograph, supported by quartz wool. The sorbent beds of the cold trap are cooled by a 2-stage Peltier cell. A minimum of $-10°C$ in ambient temperature as high as $30°C$ can be reached. If set to the 2-stage desorption mode, the thermal desorber can transfer volatile compounds from a sample tube into the cold trap for focusing and subsequent injection. In this case, the link tube is replaced by the sample tube (for more details, see Sect. 2.4). A split flow is used during the desorption and the injection. The discharged flow is filtered using a charcoal filter of the same size as the sample tube. The front and rear ends of the sample tube (or the link tube in the case of on-line sampling), the cold trap, and the charcoal filter are connected through adapters to the solenoid valves and to the heated valve ($200°C$), respectively. All connections are sealed using Viton O-rings. PTFE filters are inserted into the adapters to prevent particles from being carried into the valves. Two needle valves and a mass flow controller are used to measure and control the desorption and split flows.

A DB-5 column (Agilent, Waldbronn, Germany) and a Carbowax column (Quadrex, Woodbridge, CT, USA) are used as the first- and the second-dimension columns, respectively. Detailed column parameters and operation conditions are listed in Table 1. Roughly 1 m of the first column is used as the transfer line from the thermal desorber to the GC. This transfer line is protected by a heated sleeve (PTFE tubing covered with silicone foam rubber insulation). The sleeve temperature is set to $200°C$ to ensure no retention of compounds of interest in the transfer line.

A jet-cooled and -heated modulator is used for the GC×GC modulation. The modulator consists of two cold jet tubes installed in an evacuated outer casing and two hot jet tubes. Both cold jet tubes lie parallel to each other as do the hot jet tubes, but the cold jet tubes are orthogonal to the hot jet tubes. Both cold jets and hot jets are nitrogen gas from a Dewar (120 l, max. 4 bar, Linde, Dortmund, Germany), with the cold jet gas being conductively cooled by passing it through copper tubing coiled in a cryogenic trap (liquid N_2) and the hot jets being heated by a heater at the tube outlet. More details about the modulator are given in Table 1.

No extra modulation tube is used. Modulation is performed on the second column, at a distance of about 10 cm from the connection with the first column. The middle segment (about 75cm) of the second column is housed in a separate chamber, which can be heated and cooled independently. The end segments (about 25 cm) of the column are exposed to the air bath in the main oven of the GC.

2.3 In situ Measurement

During the in situ measurements the sampling system was set to its on-line mode. The on-line measurement includes five steps, i.e. leak test, link tube purging, on-line sampling, trap purging, and injection. During the leak test every part of the flow-path of the thermal desorber is pressure tested, without heat or carrier gas flow. The pressure is measured by a pressure transducer. If the measured pressure drops more than 5% in 30 s, the leak test fails, and the other steps are not conducted. If the leak test is passed, the sampling system is purged using sample gas at a rate of 50 ml min^{-1} for 4 min, with no gas flowing through the cold trap. After the purging the ambient air (or helium in the case of the blank measurement) is sampled directly onto the cold trap. The sampling flow is usually set to 50ml min^{-1}. A Nafion dryer connected to the air server can be used to continuously remove water vapor in the air sample stream. However, Nafion dryers can partially remove some VOCs as well, especially the oxygenated hydrocarbons. For this reason, the dryer was off-line for most of the time during the campaign. To avoid trapping significant amounts of water, the trapping temperature of the cold trap was set to $10°C$, which was adequate for the targeted $C_7 - C_{14}$ compounds. The sampling took 60 or 80 min, corresponding to a sample volume of 3 or 4 l. After the sampling the cold trap was purged using helium for 4 min, and heated to $250°C$ in less than 5 s and held at this temperature for 5 min to inject the focused compounds. During the injection, the direction of the flow through the cold trap is reversed from that during sampling (see Fig. 1), so that heavier compounds on the Tenax bed (rear) have no contact with the stronger sorbent Carbograph (front). The flow from the cold trap was split, with 2.5 ml min^{-1} being directed to the GC and 5 ml min^{-1} to the charcoal filter.

Chromatographic signals from the in situ measurements were detected by the FID attached to the GC. The data acquisition frequency was set to 100 Hz, which was high enough for the measurements, allowing 10 points per peak even for those with small peak widths. FIDs have proven to be robust detectors capable of high frequency data acquisition necessary for GC×GC measurements. Since the response factor of the FID depends mainly on the carbon number of
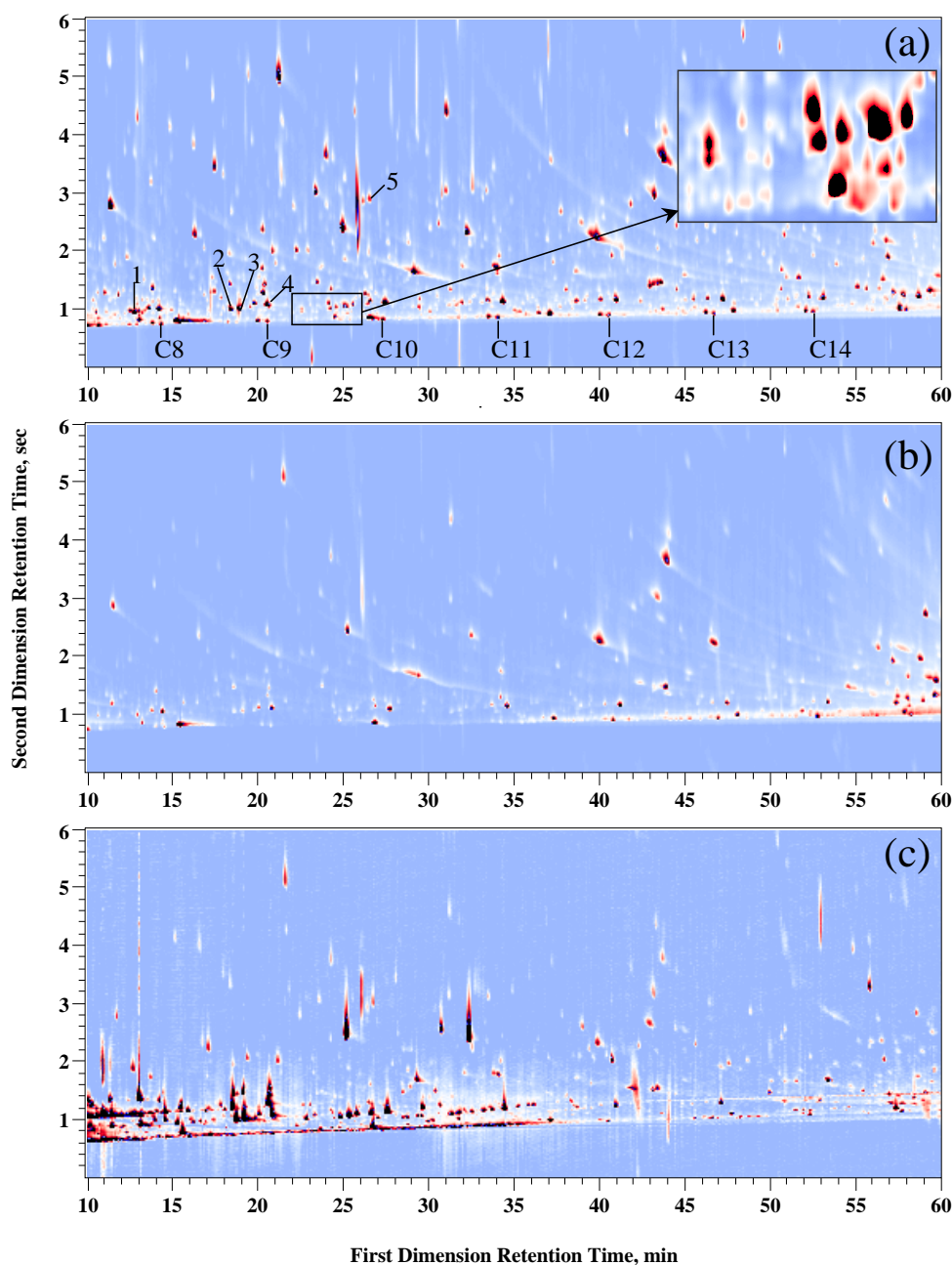
Fig. 2. Example GC×GC chromatograms. **(a)** and **(b)** are FID chromatograms from the MINOS field measurements of an air sample and a blank sample, respectively. **(c)** is a TIC chromatogram from the GC×GC-TOF-MS analysis of a cartridge sample collected at Finokalia, Crete, during the MINOS campaign.

compounds, the peaks of compounds for which no standard is available, can be calibrated relative to other compound of the same carbon number. This advantage becomes more significant when all isolated peaks should be quantified, as is intended in ambient air studies. For identification, cartridge samples were collected at Finokalia and analyzed in the laboratory with a time-of-flight mass spectrometer (TOF-MS) as described in the following section.

2.4 Laboratory GC×GC-TOF-MS Measurement

In addition to the on-line measurements, several cartridge samples were collected using sample tubes with DiffLok caps (Markes International, Pontyclun, UK). The sample tubes (Silcosteel, 89mm, 5 mm I.D.) are packed in sequence of increasing retention capacity with Tenax TA, Carbopack B, and Carboxen 1000, effectively trapping VOCs down to

propane. Ambient air was drawn through the tubes at 100 ml min^{-1} for one or two hours using a calibrated air pump (FL-1001, CHEMATEC, Roskilde, Denmark). After sampling, the tubes were stored in an isolated box for 3 months before analysis.

The analysis of the cartridge samples was performed on the same thermal desorption and GC×GC system under the same conditions as in the on-line measurements. For the detection a TOF-MS (Pegasus II, LECO, St Joseph, MI, USA) was used. A transfer line (ca. 20 cm) was used to connect the second column of the GC×GC system and the TOF-MS. The TOF-MS was controlled by another personal computer. Spectra with a mass range of m/z 35–300 were collected and stored at a rate of 100 Hz. A detailed description of this system is given elsewhere (Dallüge et al., 2002b).

To analyze a cartridge sample, the sample tube was positioned in the desorption oven (i.e. the link tube position in Fig. 1). A leak test was done, without heating the desorption oven. After a successful leak test, the sample tube was purged using helium at a rate of 50 ml min^{-1} for 4 min to remove moisture and oxygen, with no carrier gas flowing through the cold trap. After the purging the sample tube was heated to 280°C at 20°C s^{-1} and held at this temperature for 5 min to desorb the organic compounds. During the desorption the cold trap was set to -10°C to focus compounds from the cartridge sample. The desorption and split flows were set to 10 ml min^{-1} and 5 ml min^{-1}, respectively. After the desorption the cold trap was purged and heated to inject the focused compounds as in on-line measurements.

3 Results and Discussion

3.1 GC×GC Chromatograms

Figure 2 shows three example GC×GC chromatograms. Figures 2a and 2b are typical ambient air and blank chromatograms from the in situ measurements using GC×GC-FID. Figure 2c is a total ion count (TIC) chromatogram from the GC×GC-TOF-MS analysis of a cartridge air sample collected at Finokalia, Crete, during the MINOS campaign. The dark spots with white boundary are the major peaks, while the red and white spots are the medium and small peaks, respectively. At first glance, there seem to be roughly two hundred peaks on the in situ air sample chromatogram (Fig. 2a), but the peak density is actually much higher. There are a lot of small peaks, especially in the lower bands, as can be seen in the insert of Fig. 2a. Including the small peaks, there are approximately 30 peaks in the small area of the chromatogram. The total number of peaks may be well above 500.

Under the aforementioned conditions, the optimum separation range is between 10 min and 55 min, corresponding roughly to $C_7 - C_{14}$ n-alkanes. In the first 10 min the separation is bad because of overloading and eluting temperatures that are too high for the very volatile species. Therefore, data from that retention range are not shown in the figure. The lower right-hand corner of the separation area is usually crowded with peaks of heavy compounds that are believed to originate from column bleeding or artifacts from other parts of the system. The long tailing peaks, the so-called "flying comets", are also believed to be caused by system artifacts, e.g. degradation products of stationary phases and sorbents. They elute from the first column above certain temperatures and produce consecutive peaks of which the retention time in the second dimension shifts towards t=0 as the oven temperature rises. These artifact peaks affect the quantification of peaks overlapping on them and removal of these tailing peaks should be one of the tasks in future system improvements.

In comparison with some GC×GC chromatograms in the literature (e.g. Beens et al., 2000; Ledford and Billesbach, 2000), the peaks on the chromatogram shown in Fig. 2 seems less ordered. This is not caused by the conditions used for the analysis, but rather a result of the different nature of an air sample compared with petrochemical samples. As will be discussed in Sect. 3.3, atmospheric VOCs cover many classes of compounds. Some of the compounds may come from anthropogenic emissions associated with fossil fuel use. Other airborne compounds are photoproducts, biogenic in origin, or products from industries unrelated to fuel processing. Hence a wider range of compounds can be expected in the air. The differences in polarity between different classes of compounds can be large or small, depending on degree of oxidation. The situation is further complicated by different degree of branching and by compounds with two or more functional groups. As a consequence, distinct bands tend to be masked by compounds that are scattered between the bands. Nevertheless, some bands are still visible, for example, the lowermost alkane band and the bands of aromatic hydrocarbons. These aid orientation considerably over 1D GC.

There are several peaks below the alkane band. These peaks are so-called "wrap-arounds". Because of higher polarity, the retention times of some compounds are longer than the modulation period, so that they elute during the second or third period after being injected onto the second column. Wrap-arounds, if overlapping other peaks, may affect the quantification. They can be removed by using a longer modulation period. On the other hand, a longer modulation period leads to a lower resolution on the first column. In this work a modulation period of 6 s is used as a compromise.

The chromatogram of the blank sample (Fig. 2b) contains much fewer peaks than that of the air sample. However, it is not as clean as expected. Besides the column bleeding and sorbent degradation, slight contaminations on the O-rings, filters, etc., of the thermal desorber, may have been responsible for the peaks in the blank chromatogram. After the MINOS campaign the thermal desorber was cleaned by the manufacturer. The blank level has been improved significantly since then.

Table 2. Compounds tentatively identified by TOF-MS and confirmed by RI comparison

Compound	1st R.T. (min)	2nd R.T. (sec)	Similarity[a]	Observed RI	Literature RI	Reference[b]	Found in field measurements
Acyclic alkanes							
Pentane	4.5	4.31	929	500.0			
2,2-Dimethylbutane	5.0	4.67	871	526.3	528.5	1	
2,3-Dimethylbutane	5.6	1.03	890	557.9	558.7	2	
3-Methylpentane	6.0	1.04	903	579.0	578.6	1	
Hexane	6.4	1.04	943	600.0			
2,2-Dimethylpentane	7.0	1.53	827	618.2	620.5	1	
2,4-Dimethylpentane	7.1	1.05	884	621.2	625.8	1	
2,2,3-Trimethylbutane	7.4	1.05	933	630.3	631.4	1	
3,3-Dimethylpentane	8.1	0.66	899	651.5	650.5	1	
2-Methylhexane	8.5	0.72	913	663.6	662.9	1	
3-Methylhexane	8.8	0.76	930	672.7	672.2	1	
2,3-Dimethylpentane	8.9	1.08	862	675.8	665.0	1	
Heptane	9.7	0.73	910	700.0			y
2,4-Dimethylhexane	11.1	1.11	880	729.2	731.7	1	y
2,3-Dimethylhexane	12.5	1.13	935	758.3	757.9	1	y
3-Ethyl-2-methylpentane	12.6	1.15	859	760.4	759.7	1	y
2-Methylheptane	12.7	1.14	914	762.5	764.1	1	y
4-Methylheptane	12.8	1.14	944	764.6	765.6	1	y
3-Methylheptane	13.1	1.14	931	770.8	772.1	1	y
3-Ethylhexane	13.2	1.14	934	772.9	775.0	1	y
Octane	14.5	1.18	849	800.0			y
2,4-Dimethylheptane	15.9	1.18	934	822.2	823.1	1	y
4-Methyloctane	18.5	0.78	951	863.5	863.7	1	y
3-Methyloctane	19.0	0.80	916	871.4	871.4	1	y
2,4,6-Trimethylheptane	19.2	0.80	837	874.6	874.5	2	
Nonane	20.8	0.81	942	900.0			y
2,6-Dimethyloctane	23.0	0.85	827	933.3	921.6	1	y
3-Ethyl-2-methylheptane	23.6	0.85	839	942.4	951.2	1	y
4-Ethyloctane	24.5	0.86	832	956.1	965.0	1	
4-Methylnonane	24.9	0.85	880	962.1	961.6	1	y
3-Methylnonane	25.5	0.87	884	971.2	970.5	1	y
2,2,4,6,6-Pentamethylheptane	27.2	0.87	921	997.0	990.2	2	y
Decane	27.4	0.88	917	1000.0			y
Undecane	34.1	0.95	887	1100.0			y
2-Methylundecane	38.2	1.00	825	1165.1	1164.5	2	y
Dodecane	40.4	1.02	955	1200.0			y
Tridecane	46.5	1.08	950	1300.0			y
3-Methyltridecane	50.6	1.11	852	1371.9	1371.1	2	y
Tetradecane	52.2	1.14	960	1400.0			y
Cyclic alkanes							
t-1,2-Dimethylcyclopropane	4.8	3.55	879	515.8	503.0	3	
c-1,2-Dimethylcyclopropane	4.8	4.67	828	515.8	523.6	3	
Cyclopentane	5.7	2.79	846	563.2	566.5	4	
Ethylcyclobutane	7.3	0.64	870	627.3	628.4	3	
Methylcyclopentane	7.3	1.05	878	627.3	625.6	4	
t-1,3-Dimethylcyclopentane	9.2	3.17	826	684.8	687.9	5	
c-1,3-Dimethylcyclopentane	9.3	1.09	914	687.9	691.5	5	y
Isopropylcyclobutane	9.4	1.10	934	690.9	696.4	3	y
t-1,2-Dimethylcyclopentane	9.4	4.54	822	690.9	693.3	5	y
c-1,2-Dimethylcyclopentane	10.8	1.11	898	722.9	717.9	2	y

Table 2. Continued.

Compound	1st R.T. (min)	2nd R.T. (sec)	Similarity[a]	Observed RI	Literature RI	Reference[b]	Found in field measurements
Methylcyclohexane	10.9	1.12	944	725.0	718.1	2	y
Ethylcyclopentane	11.3	1.12	905	733.3	733.7	3	y
Norbornane	12.4	0.75	839	756.3	754.3	3	y
1,2,4-Trimethylcyclopentane	13.4	1.16	848	777.1	779.2	5	y
c-1,3-Dimethylcyclohexane	13.7	1.16	914	783.3	782.2	5	y
t-1,4-Dimethylcyclohexane	13.8	0.75	884	785.4	783.9	5	
c-1-Ethyl-2-methylcyclopentane	14.3	0.75	854	795.8	814.9	3	
t-1-Ethyl-3-methylcyclopentane	14.3	1.17	896	795.8	789.4	3	y
t-1,2-Dimethylcyclohexane	14.8	1.19	908	804.8	799.1	3	y
1,4-Dimethylcyclohexane	14.9	1.18	815	806.3	796.6	3	
$(1\alpha,2\alpha,3\beta)$-1,2,3-Trimethylcyclopentane	15.1	1.17	810	809.5	795.1	3	
c-1-Ethyl-2-methylcyclopentane	16.2	1.19	813	827.0	814.9	3	
c-1,2-Dimethylcyclohexane	16.7	1.21	894	834.9	821.7	3	
Ethylcyclohexane	16.9	1.20	938	838.1	829.0	3	
Propylcyclopentane	16.8	1.20	856	836.5	825.7	3	
1,1,4-Trimethylcyclohexane	17.2	1.21	824	842.9	834.8	3	
1,2,4-Trimethylcyclohexane	17.3	0.79	869	844.4	859.6	3	
1,2,3-Trimethylcyclohexane	19.7	0.81	829	882.5	872.1	2	
c-1-Ethyl-3-methylcyclohexane	20.4	0.82	910	893.7	885.6	3	y
c-1-Ethyl-4-methylcyclohexane	20.6	0.82	896	896.8	899.8	3	y
c-1-Ethyl-2-methylcyclohexane	21.8	0.85	878	915.2	912.2	3	y
Propylcyclohexane	23.2	0.85	840	936.4	929.2	2	y
c-Decahydronaphthalene	32.2	0.98	875	1071.6	1068.9	3	y
Acyclic alkenes							
(Z)-1,3-Pentadiene	4.7	1.03	869	510.5	529.8	3	
2-Methyl-2-butene	4.8	4.27	932	515.8	523.0	6	
1-Hexene	6.1	1.03	833	584.2	592.1	6	
2-Methyl-1-pentene	6.1	2.79	836	584.2	591.0	6	
(E,Z)-2,4-Hexadiene	7.6	0.69	845	636.4	651.1	6	
5-Methyl-1-hexene	7.7	1.06	811	639.4	659.3	6	
1-Heptene	9.4	0.17	880	690.9	691.9	6	
3-Heptene	10.1	1.12	823	708.3	703.9	6	
3-Methyl-1-heptene	12.0	1.12	837	747.9	757.2	3	
3-Methyleneheptane	13.4	1.16	838	777.1	787.1	3	
2-Methyl-1-heptene	13.9	0.75	858	787.5	783.9	6	
1-Octene	14.0	1.18	924	789.6	790.1	7	
(E)-2-Octene	14.4	1.17	827	797.9	807.2	6	
(E)-3-Octene	15.4	1.19	850	814.3	801.5	6	
t-4-Decene	27.0	0.87	841	993.9	991.4	5	
Diisoamylene	28.0	0.88	830	1009.0	998.2	3	
1-Tetradecene	51.7	1.14	920	1391.2	1392.3	7	y
Cyclic alkenes							
Methylenecyclohexane	11.7	1.15	801	741.7	754.1	8	
1-Methylcyclohexene	13.2	1.18	862	772.9	771.0	6	
4-Ethenylcyclohexene	16.9	1.29	817	838.1	833.0	8	
5-Ethylidene-bicyclo[2.2.1]hept-2-ene	22.2	0.94	940	921.2	922.6	8	y
α-Pinene	23.5	0.88	952	940.9	941.0	9	y
Camphene	24.7	0.92	822	959.1	953.0	9	y
3-Carene	28.7	0.96	881	1019.4	1034.0	10	
Limonene	29.9	1.01	924	1037.3	1039.1	7	y

Table 2. Continued.

Compound	1st R.T. (min)	2nd R.T. (sec)	Similarity[a]	Observed RI	Literature RI	Reference[b]	Found in field measurements
Aromatic hydrocarbons							
Benzene	8.4	1.28	981	660.6	660.1	7	
Toluene	13.1	0.96	946	770.8	767.6	7	y
Ethylbenzene	18.8	1.03	968	868.3	861.5	7	y
1,3/4-Dimethylbenzene	19.4	1.05	975	877.8	869.3	7	y
Phenylethyne	19.6	1.92	810	881.0	875.9	7	
Styrene	20.5	1.32	953	895.2	892.9	7	y
1,2-Dimethylbenzene	20.7	1.12	959	898.4	895.6	7	y
(1-Methylethyl)-benzene	22.8	1.05	971	930.3	919.0	11	y
2-Propenylbenzene	24.2	1.21	927	951.5	954.2	3	y
Propylbenzene	24.7	1.09	976	959.1	949.0	11	y
1-Ethyl-3-methylbenzene	25.3	1.10	960	968.2	962.6	2	y
1-Ethyl-4-methylbenzene	25.4	1.11	967	969.7	958.0	11	y
1,3,5-Trimethylbenzene	25.7	1.13	961	974.2	963.0	11	y
1-Ethyl-2-methylbenzene	26.6	1.15	971	987.9	975.0	11	y
α-Methylstyrene	26.6	1.31	893	987.9	980.0	7	y
1,2,4-Trimethylbenzene	27.4	1.17	960	1000.0	993.4	2	y
(2-Methylpropyl)-benzene	28.4	1.08	915	1014.9	1007.9	2	y
1-Methyl-3-(1-methylethyl)-benzene	29.2	1.11	950	1026.9	1023.1	2	y
1-Methyl-2-(1-methylethyl)-benzene	29.3	1.11	964	1028.4	1034.0	11	y
1,2,3-Trimethylbenzene	29.6	1.24	957	1032.8	1023.1	2	y
Indane	30.6	1.29	949	1047.8	1036.1	12	y
1,3-Diethylbenzene	31.1	1.14	955	1055.2	1052.6	3	y
1,2-Diethylbenzene	31.2	1.14	917	1056.7	1060.9	3	y
1-Methyl-3-propylbenzene	31.3	1.13	959	1058.2	1052.6	3	y
1,4-Diethylbenzene	32.1	1.17	929	1070.1	1051.0	11	y
1-Ethyl-2,4-dimethylbenzene	33.2	1.20	968	1086.6	1075.0	11	y
4-Ethyl-1,2-dimethylbenzene	33.6	1.21	971	1092.5	1086.7	3	y
1-Ethyl-2,3-dimethylbenzene	33.7	1.22	968	1094.0	1106.9	3	y
2-Ethyl-1,3-dimethylbenzene	34.1	1.24	849	1100.0	1090.5	3	y
1,2,4,5-Tetramethylbenzene	36.0	1.30	953	1130.2	1119.6	3	y
1,3-Diethyl-5-methylbenzene	37.3	1.20	863	1150.8	1142.6	3	
1,2,3,4-Tetrahydronaphthalene	39.1	1.42	904	1179.4	1166.3	2	
Naphthalene	40.6	2.06	975	1203.2	1186.9	12	y
2-Methylnaphthalene	47.5	1.99	945	1317.5	1310.0	11	y
Oxygenated aromatics							
Benzaldehyde	25.1	2.48	974	965.2	960.2	7	y
Phenol	26.0	3.10	956	978.8	979.9	7	y
Benzoic acid methyl ester	34.1	2.04	943	1100.0	1101.9	12	y
Benzofuran	27.8	2.00	933	1006.0	995.9	12	y
Benzeneacetaldehyde	30.7	2.58	956	1049.3	1053.0	10	y
Acetophenone	32.2	2.45	977	1071.6	1068.4	7	y
4-Methylbenzaldehyde	32.5	2.25	918	1076.1	1085.9	7	y
Acetic acid phenylmethyl ester	38.4	2.15	838	1168.3	1164.0	10	
α,α-Dimethylbenzenemethanol	33.4	3.16	926	1089.6	1089.1	3	y
1-(3-Methylphenyl)-ethanone	39.3	2.25	930	1182.5	1175.2	3	
1-(4-Ethylphenyl)-ethanone	44.9	2.06	854	1273.8	1282.2	3	
α-Oxobenzeneacetic acid methyl ester	48.5	4.27	864	1335.1	1325.3	3	

Table 2. Continued.

Compound	1st R.T. (min)	2nd R.T. (sec)	Similarity[a]	Observed RI	Literature RI	Reference[b]	Found in field measurements
Alcohols							
Isopropyl alcohol	4.8	0.88	945	515.8	522.2	3	
2-Methyl-2-propanol	5.0	0.82	929	526.3	527.8	3	
2-Butanol	6.5	1.09	878	603.0	589.5	3	
2-Methyl-1-propanol	7.1	1.40	885	621.2	610.0	11	y
1-Butanol	8.2	1.59	955	654.5	650.1	4	y
1-Pentanol	12.6	1.92	921	760.4	764.0	10	y
(S)-2,5-Dimethyl-2-hexanol	18.1	1.21	836	857.1	859.2	3	y
1-Hexanol	18.6	1.98	863	865.1	860.1	12	y
(E)-2-Hexen-1-ol	19.9	2.15	859	885.7	887.0	10	
(Z)-2-Hexen-1-ol	19.9	2.15	859	885.7	871.8	3	
3-Heptanol	20.3	1.48	837	892.1	883.4	13	y
1-Heptanol	25.2	1.93	879	966.7	966.7	12	y
1-Octen-3-ol	25.9	1.82	825	977.3	982.0	3	
1-Octanol	32.0	1.84	910	1068.7	1067.9	12	y
1-Nonanol	38.6	1.76	805	1171.4	1169.2	12	y
1-Decanol	44.9	1.71	855	1273.8	1269.9	12	y
1-Undecanol	50.7	1.69	916	1373.7	1371.1	12	y
Aldehydes							
2-Methyl-2-propenal	5.8	0.79	936	568.4	575.8	3	
Butanal	6.2	0.78	956	589.5	573.6	7	
Pentanal	9.4	1.34	863	690.9	696.0	7	y
2-Methylpentanal	11.9	0.91	821	745.8	747.8	3	y
2-Methyl-2-pentenal	12.6	1.01	838	760.4	760.8	3	y
3-Methyl-2-butenal	13.7	1.53	801	783.3	800.5	3	y
Hexanal	14.5	1.02	922	800.0	799.4	7	y
(E)-2-Hexenal	17.7	1.37	901	850.8	854.0	10	y
2-Ethylhexanal	24.4	1.07	911	954.5	963.1	3	y
(Z)-2-Heptenal	24.5	1.43	855	956.1	957.0	10	y
Octanal	27.6	1.17	932	1003.0	1003.8	14	y
(E)-2-Octenal	31.3	1.44	856	1058.2	1060.0	10	y
Nonanal	34.3	1.24	956	1103.2	1103.3	7	y
(E)-2-Nonenal	38.4	1.29	801	1168.3	1167.5	3	
Decanal	40.8	1.28	948	1206.6	1207.0	7	y
Undecanal	47.0	1.33	967	1308.8	1309.7	7	y
Ketones							
2-Butanone	6.3	0.81	933	594.7	600.5	7	
2-Pentanone	9.1	0.91	902	681.8	689.0	15	y
Methyl isobutyl ketone	11.3	1.37	958	733.3	722.1	13	y
2-Methyl-3-pentanone	12.0	0.91	893	747.9	742.0	3	y
3-Methyl-2-pentanone	12.1	0.93	920	750.0	749.6	3	y
3-Hexanone	13.7	0.97	926	783.3	767.6	13	y
2-Hexanone	13.9	1.04	941	787.5	798.0	15	y
Cyclopentanone	14.2	1.36	965	793.8	788.9	3	y
2-Cyclopenten-1-one	16.7	2.37	803	834.9	822.4	3	y
3-Ethyl-2-pentanone	16.9	1.01	907	838.1	838.8	3	
2-Methylcyclopentanone	17.2	1.25	897	842.9	836.0	15	y
3-Methyl-2-hexanone	17.3	1.04	908	844.4	842.9	3	y
4-Methyl-2-hexanone	17.4	1.05	850	846.0	847.0	3	y
3-Methylcyclopentanone	17.5	1.32	874	847.6	855.8	3	

Table 2. Continued.

Compound	1st R.T. (min)	2nd R.T. (sec)	Similarity[a]	Observed RI	Literature RI	Reference[b]	Found in field measurements
(R)-(+)-3-Methylcyclopentanone	17.5	1.32	832	847.6	849.7	3	
3-Heptanone	19.8	1.08	974	884.1	869.2	13	y
2-Heptanone	20.0	1.14	953	887.3	890.0	15	y
Cyclohexanone	20.6	1.46	974	896.8	890.8	12	y
2-Methyl-2-cyclopenten-1-one	21.3	1.86	854	907.6	926.4	3	
2,2,4,4-Tetramethyl-3-pentanone	21.9	0.95	854	916.7	910.3	3	
1-Cyclopentylethanone	23.0	1.29	933	933.3	919.2	3	y
4-Methyl-2-heptanone	23.2	1.12	958	936.4	920.7	3	y
1-Octen-3-one	25.9	1.27	893	977.3	979.0	10	y
6-Methyl-5-hepten-2-one	26.4	1.34	906	984.8	985.3	7	y
2-Octanone	26.7	1.21	948	989.4	999.0	10	y
2-Nonanone	33.4	1.25	913	1089.6	1090.0	11	y
(1R)-(+)-Norinone	37.4	1.63	862	1152.4	1155.1	3	y
2-Decanone	40.0	1.30	955	1193.7	1196.5	3	y
2-Undecanone	46.1	1.34	906	1293.4	1292.2	12	y
Esters							
Acetic acid methyl ester	5.0	0.72	941	526.3	511.0	11	
Ethyl acetate	6.7	1.20	806	609.1	612.0	15	
2-Methyl-2-propenoic acid methyl ester	10.2	0.94	872	710.4	696.0	11	
Nitriles							
2-Propenenitrile	4.9	1.48	964	521.1	511.1	3	
Propanenitrile	5.9	1.58	858	573.7	587.5	3	
Pentanenitrile	13.2	1.51	895	772.9	772.7	3	
Hexanenitrile	19.2	1.60	922	874.6	871.4	3	y
Benzonitrile	26.6	3.07	977	987.9	983.4	7	y
Octanenitrile	32.8	1.62	620	1080.6	1081.7	12	
Halogenated HCs							
1,1-Dichloroethene	4.9	0.66	938	521.1	511.0	7	
Dichloromethane	5.1	1.28	918	531.6	521.9	7	
1,1,1-Trichloroethane	7.8	1.17	950	642.4	645.1	7	y
Trichloroethylene	9.8	1.33	950	702.1	691.0	11	
1-Chloropentane	12.3	0.83	843	754.2	754.9	3	y
Tetrachloroethylene	15.5	1.32	881	815.9	811.3	7	y
Chlorobenzene	17.8	1.28	970	852.4	846.5	7	y
1-Chlorohexane	18.1	0.92	932	857.1	849.0	13	y
Tribromomethane	20.3	2.44	834	892.1	892.3	16	y
1,4-Dichlorobenzene	28.4	1.51	930	1014.9	1016.5	7	y
1,3-Dichlorobenzene	28.8	1.61	965	1020.9	1004.1	13	y
1,2-Dichlorobenzene	28.9	1.60	961	1022.4	1027.0	11	y

In spite of the issues mentioned above, the advantages of using GC×GC over conventional 1D GC are obvious. Many compounds that would overlap on a 1D GC chromatogram are well separated by GC×GC, as can be seen in Fig. 2a. This is especially important for the peaks of medium and small sizes since they otherwise would be masked by the enhanced baseline or major peaks of the 1D chromatogram. In addition, in the GC×GC measurement the artifact peaks, such as the long tailing peaks, influence only the peaks with which they coincide in both dimensions, not all peaks in the first dimension retention ranges that they cover, which would be the case in 1D GC.

The basic features of the TIC chromatogram (Fig. 2c) are similar to those of the FID chromatogram of the air sample (Fig. 2a), but there are some differences between both chromatograms. On the TIC chromatogram there seems to

Table 2. Continued.

Compound	1st R.T. (min)	2nd R.T. (sec)	Similarity[a]	Observed RI	Literature RI	Reference[b]	Found in field measurements
Miscellaneous							
Dimethyl disulfide	12.0	1.05	803	747.9	742.0	10	
3-Furaldehyde	16.5	4.06	877	831.7	829.0	9	y
4-Hydroxy-4-methyl-2-pentanone	17.1	2.26	921	841.3	842.0	11	y
2-n-Butylfuran	20.3	1.01	853	892.1	893.0	15	y
2-Butoxyethanol	21.1	2.05	932	904.5	890.0	11	y
1-(2-Furanyl)-ethanone	21.5	3.10	908	910.6	904.0	15	y
2-Pentylfuran	27.0	1.07	932	993.9	994.0	15	y
Eucalyptol	30.2	1.03	930	1041.8	1030.0	10	y
Benzothiazole	43.1	3.20	936	1244.3	1240.0	15	y

[a] Comparison of acquired spectra to NIST mass spectral library.

[b] Literature *RI*s from: (1) Yin et al. (2001); (2) Hayes and Pitzer (1985); (3) prediction using the method of Zenkevich (1998); (4) Haagen-Smit Laboratory (1997); (5) Laub and Purmell (1988); (6) Lubeck and Sutton (1984); (7) Helmig et al. (1996); (8) Bermejo et al. (1987); (9) Andrade et al. (2000); (10) flavornet http://www.nysaes.cornell.edu/flavornet/chem.html; (11) HSE (1997); (12) Rostad and Pereira (1986); (13) J&W Scientific, Solvent Retention Data, http://www.chem.agilent.com/cag/cabu/pdf/b-0292.pdf; (14) David et al. (2000); (15) Madruga and Mottram (1998); (16) Weber (1986)

be a band 0.4 s above the lowermost band (i.e. the alkane band). This is a result of double modulation caused probably by a disturbance to the temperature of the downstream cold spot when the upstream hot jet is fired. It seems that the double modulation only occurs in the measurements of relatively concentrated samples. No double modulation was observed in the in situ measurements because the samples were less concentrated. Except for the double modulation problem, the TIC chromatogram also shows a higher noise level than the FID chromatogram. Another difference is that many small peaks of polar compounds are not visible on the TIC chromatogram. Possible reasons for that are the loss of these compounds during storage and/or low sensitivity of TOF-MS to these compounds.

3.2 Identification

Cartridge samples of volatile organics in ambient air were measured using the thermal desorption-GC×GC-TOF-MS system. All conditions were as listed in Table 1, except for the carrier gas (helium) pressure, which was increased to 289.4 kPa to compensate the effect of the transfer line between the GC and the TOF-MS. Data from one of the cartridge samples were analyzed using the ChromaTOF software from LECO for tentative initial identification. The sample (see the chromatogram in Fig. 2c) was collected at Finokalia on the 12th of August 2001 between 00:35 and 2:35 local time. Since a big biomass burning plume influenced the site in the period from the 8th to the 12th of August 2001, the sample was expected to contain more components than samples from other periods.

The ChromaTOF software uses a deconvolution algorithm which mathematically separates partially co-eluting peaks. The first step in the identification process was mass spectral library matching of the deconvoluted peaks against the NIST library (NIST '98, National Institute of Standards and Technology, Gaithersburg, MD, USA). Because of less interference from the background and co-eluting compounds the higher spectral purity of the deconvoluted peaks makes the library matching more reliable. Detailed examples of this method are described in Dallüge et al. (2002a,b). To allow both narrow and broad peaks being recognized by the software, three data analyses were performed for expected peak widths of 100, 300 and 2000 ms. Results of the tentative identifications were reported in peak tables, containing compound name, formula, retention time, similarity, signal-to-noise ratio (S/N), etc. The retention times were corrected for the time difference between the start of the TOF-MS data acquisition and the start of the sample injection, and then converted to the first-dimension and second-dimension retention times based on the modulation period of 6 s.

Starting with tens of thousands of peaks recognized in the data processing, several rules were applied to reduce this set of peaks. First, all peaks with a mass-spectral match (i.e. similarity) lower than 800 were discarded. Next, a selection based on the S/N was made. An important factor regarding the S/N is on which basis it is calculated; in mass spectrometry one can either choose a selected-ion chromatogram or the total ion chromatogram. For the present processings the so-called "unique mass" was chosen to calculate the S/N. During the deconvolution process described shortly above, the algorithm looks for masses (m/z values) that distinguish the peak in hand from other co-eluting compounds

or background signals, and designates this as the "unique mass". One has to realize that the S/N value based on this m/z does not say anything about the intensity in the total ion chromatogram or comparable FID chromatogram because the selected m/z has a variable relative intensity within the mass spectrum in hand. However, the advantage of the method is that many small peaks can be recognized which are co-eluting with other compounds or are engulfed in the (chemical) noise of the total ion chromatogram. Arbitrarily, a minimal S/N of 100 for the unique mass was chosen to reduce the set of peaks further to about 650 peaks which were subjected to additional confirmation using retention indices.

Linear retention indices on the first column (DB-5) were calculated using

$$RI_x = 100 \left(\frac{RT_x - RT_n}{RT_{n+1} - RT_n} + n \right), \qquad (1)$$

where RI_x is the retention index of component x; n is the carbon number of the last n-alkane eluting before component x; RT_x, RT_n, and RT_{n+1} are the retention times of component x, the preceding n-alkane with carbon number n, and the next n-alkane with carbon number $n + 1$, respectively. The calculation was done for components eluting between pentane and tetradecane. Because the solutes from the first column are refocused in the GC×GC measurement, it is possible that the first-dimension retention times, i.e. the peak apices of the solutes, are shifted back or forth, relative to the retention times from a single-column separation. However, the shift should be less than one modulation period, i.e. 6 s, corresponding to an average error of 3.2 index unit (i.u.).

To verify the tentative identifications, the measured RI values were compared with literature RI values determined on appropriately similar stationary phases. RI values of some compounds are not included in the available literature. Therefore, the model of Zenkevich (1998) was used to predict RIs from the boiling points and taxonomic parameters of the compounds. Since the contemporary level of interlaboratory reproducibility of experimental RI determination is about 10 i.u. (Zenkevich, 1998), it seems reasonable to allow a disagreement of 20 i.u. between RIs from this work and those from the literature or from the prediction. If the index disagreement exceeded 20 i.u, the compound was considered not confirmed and therefore discarded from the table. In some cases, mainly arising from the three different data processing results put together, several peaks were recognized as the same compound which all complied with the rules. In these cases, the identification with the highest S/N was chosen; if the S/N made no clear distinction, the peak with the highest spectral similarity was selected.

Table 2 lists components that have been tentatively identified by the software and confirmed by the RI comparison. The compounds are classified as acyclic alkanes, cyclic alkanes, acyclic alkenes, cyclic alkenes, aromatic hydrocarbons, oxygenated aromatics, alcohols, aldehydes, ketones, esters,

nitriles, halogenated hydrocarbons, and miscellaneous. In total 235 compounds have been confirmed. More than half of the confirmed compounds are hydrocarbons, with alkanes, alkenes, and aromatic hydrocarbons contributing 31%, 10%, and 15%, respectively. Nearly one third of the compounds are oxygenated species, including alcohols, aldehydes, ketones, esters, and oxygenated aromatic compounds. Other compounds, such as nitriles, halogenated hydrocarbons, and some miscellaneous species, make only a small contribution to the total number of the confirmed compounds. Retention times in both dimensions are given.

Not all confirmed compounds in Table 2 show up on the GC×GC chromatograms from the field measurements. The main reasons for that are: (1) the identification has been based on the GC×GC-TOF-MS measurement of a cartridge sample that is more concentrated than the on-line samples for the field measurements; (2) the sensitivity of TOF-MS is different from that of FID; (3) some compounds may have entered the sample tube during storage. Of the 235 confirmed compounds, 150 show up in the optimized separation range (C_7-C_{14}) on the chromatograms from the in situ measurements, suggesting that they were present in the atmospheric boundary layer at Finokalia during the MINOS campaign. While most of the peaks are well separated, there are a few overlaps, even with GC×GC separation. The overlaps are mainly caused by structural isomers (e.g. p-xylene / m-xylene) in a few cases, also by quite different compounds having similar retention times on both columns (e.g. 1,2,4-trimethylbenzene / octanal). Some of the overlapping peaks may be resolved in the future by using different column combinations.

Although the identification based on mass spectrometry together with RIs results in a high level of confidence of correct identification, one should realize that in some cases there is no complete certainty. If several isomers of a compound exist that elute closely together and produce mutually similar spectra, there is a chance that the compound is identified as another isomer, and that the isomer is (erroneously) confirmed because of the similar RI values of the various isomers. In the results presented in Table 2 a typical class in which this might occur are the branched alkanes.

Although the GC×GC-TOF-MS measurement has led to the successful identification of 150 peaks (cf. above), the identification process is still being completed because about 500 peaks show up in the GC×GC-FID chromatogram with S/N>10. Some of these unknown peaks which are in the list of unconfirmed initial identifications, obviously are the best candidates for a continued search.

The presence in the atmosphere of the organic compounds listed in Table 2 is not surprising. In fact, most of the compounds have already been detected in previous observations at urban and remote sites mainly using GC-MS (e.g. Ciccioli et al., 1992, 1993; Helmig et al., 1996). Due to direct emissions of organic species from anthropogenic and biogenic sources and photochemical production of secondary organic

species, the lower atmosphere always contains a large number of VOCs, even in Antarctic (Ciccioli et al., 1996). Given the numerousness of atmospheric VOCs, nonselective detection, such as FID, is preferred for the simultaneous quantification of the VOCs. GC×GC-FID, which combines the high separation power of GC×GC with the universal nature and robustness of FID, is very suitable for the routine measurements of atmospheric VOCs.

3.3 Quantification

As in conventional GC, determination of peak sizes is necessary for quantifying the analytes of interest. Integration and chemometric analysis are the two commonly used methods to quantify the sizes of GC×GC peaks. The chemometric method utilizes the multivariate techniques, such as the generalized rank annihilation method (GRAM) (see e.g. Fraga et al., 2000). The accuracy, precision, and lower detection limit in the quantification can be improved using the GRAM method. Another advantage of using this method is the quantification of partially overlapped peaks. In spite of these advantages, the GRAM method is not used in this work, because the requirements for its successful use were not fully met. Under the conditions used in this work, the data density for the first column is lower than 4 points per peak for most peaks. Some peaks only cover 1 or 2 separation periods. Such small peaks cannot be reliably quantified by GRAM though it was able to analyze peaks with a data density down to 3 points per peak by appropriate interpolation and retention time correction (Fraga et al., 2001). In addition, some peaks do not show near symmetrical ellipse boundaries, suggesting that the data matrix does not fit a bilinear structure, on which the GRAM analysis relies. Instead of chemometric analysis, integration and subsequent calibration have been done for some well resolved n-alkane and aromatic compounds, which are contained in the standard mixture used in this study.

The integration of GC×GC peaks was done using integration software called Blob from the Zoex Corporation. Prior to the integration, chromatogram data (retention time and FID signal) collected by the ChemStation software are saved in files of comma separated values (CSV) format. The CSV files are then read by the Blob software. 2-D chromatograms with color-coded peaks are created automatically, based on the given numbers of the modulation periods and the data points of each period. Background signals can be subtracted from the chromatograms using the corresponding command. Peak (or blob) volumes are calculated, after the user draws polygons around the peaks of interest and types in peak names. Integration reports, containing peak names, apex positions, peak height, peak volumes, etc., can be created for samples chosen by the user. The software often finds two or more peaks within a polygon. In this case it integrates all peaks in the polygon and reports data of all peaks. Among the peaks within a polygon, there is usually a major one. The
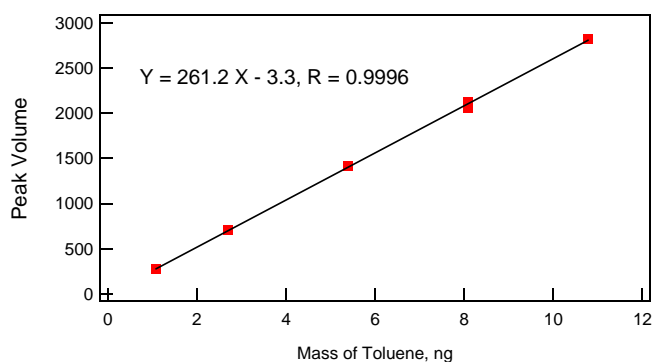
Fig. 3. Calibration curve for toluene. The mass of toluene was calculated from the sampled volume of the standard mixture and the mixing ratio of toluene in the mixture. The peak volume values were obtained using the integration software.

volume of the major peak is usually more than one order of magnitude larger than those of the minor ones. Therefore, the major peaks found in different polygons are considered to be the peaks of interest. The volumes of the major peaks are used for the concentration calculations.

While the software can integrate well-resolved medium or large peaks, it is not able to integrate some small peaks. The color tables available in the software cannot make the small peaks visible on the chromatogram, even if the color scale is reduced. In addition, the software cannot automatically integrate all GC×GC peaks that it finds on a chromatogram, but relies on polygons drawn by the user. If more than several tens of peaks need to be integrated simultaneously, drawing polygons is not only time-consuming and laborious, but it can lead to loss of overview and hence wrong positioning of polygons. These are major issues that need to be addressed in the future development of the integration software.

External calibrations were made to obtain masses of individual components in the samples. A standard gas mixture (Apel-Riemer Environmental, Denver, CO, USA) was used for the calibrations. The standard contains 74 $C_2 - C_{11}$ hydrocarbons in nitrogen, with mixing ratios ranging from 0.14 to 12.35 ppbv. Multipoint measurements of standard were made in the laboratory using the same sampling and analysis methods as in the field. Fig. 3 shows an example of calibration curves. The peak volume of toluene, as integrated using the Blob software, shows a linear dependence on the mass of toluene. The regression coefficient is close to unity, suggesting that the linearity of the relationship between the peak volume and the mass is very good. This was also found to be true for the other calibrated components (R^2 from 0.9832 to 0.9998). The good linear correlation between the peak volume and the mass of analytes suggests, that while providing strong separation power, GC×GC is also a competent technique for quantitative measurements, as shown by Beens et al. (1998).

During the MINOS campaign calibrations were made approximately once every five days. Only two-point calibrations were made, so as not to detract from the measurement frequency of atmospheric VOCs. The mixing ratio of any analyte in the ambient air sample x was calculated as

$$C_x = \frac{(\gamma_x - \gamma_b)V_s}{(\gamma_s - \gamma_b)V_x}C_s, \tag{2}$$

where C_x and C_s are the mixing ratio of the analyte in the air sample and the standard sample, respectively; γ_x, γ_s, and γ_b are peak volumes of the analyte corresponding to the air sample, the standard sample, and the blank sample, respectively; V_x and V_s are the volumes of the air sample and the standard sample, respectively. Blank levels were observed approximately once every three days, by simulating the air sampling using helium, i.e. passing helium through the air sample pathway in the air server and in the thermal desorber (see Fig. 1), and analyzing VOCs focused in the cold trap.

The accuracy of the measurements depends on the systematic errors of the peak integration, the sample volumes, and the standard. The integration error depends on the peak size and its relative contribution is small for the middle and large peaks. The error in the volume determination is about 1%. The error of the standard concentrations is 2%. Therefore, the accuracy is estimated to be about 5% for the already quantified compounds. The precisions for 20 quantified hydrocarbons range from 5% to 28%, as estimated from the relative (1σ) standard deviations of the compounds in the field calibrations.

The detection limit of the GC×GC method is theoretically much better than that of the 1D GC method since the modulation makes the peaks sharper and the baseline cleaner. In this study the enhancement of the peak height by the GC×GC modulation is estimated to be 20–60 times, based on the peak width for most isolated peaks (0.1–0.3 s) and the modulation period (6s). Even if the baseline were as noisy as that of the 1D GC, the detection limit would have been improved 20–60 fold. However, for some compounds this improvement was not practically reached during the MINOS campaign, because the blank levels and their variations were relatively high. The situation was significantly improved during the second half of the campaign after changing the cold trap and one of the filters of the thermal desorber. Therefore, the detection limit is estimated separately for the first and second half of the campaign, based on the (2σ) standard deviation of the blank values. The detection limit was between 0.2 and 35 pptv in the first half of the campaign and between 0.2 and 12 pptv in the second half of the campaign. The detection limit can be further improved by obtaining a cleaner sampling and injection system.

As an example of quantitative results, Table 3 lists the mixing ratios and LODs of some compounds found in an on-line measurement during the MINOS campaign. The peak positions of these compounds are marked on the chromatogram

Table 3. Mixing ratios and LODs (pptv) of selected compounds in an air sample measured during the MINOS campaign. The chromatogram of the sample is shown in Fig. 2a.

Peak No.	Compound	Mixing ratio	LOD[a]
1	Toluene	130	15
2	Ethylbenzene	22	9
3	p-/m-Xylene (co-elution)	33	17
4	o-Xylene	48	21
5	Benzonitrile[b]	6	

[a] Estimated for the first half of the campaign
[b] Calibrated using toluene standards and response factors from Katritzky et al. (1994).

shown in Fig. 2a. Toluene, ethylbenzene, and xylenes are important aromatic compounds. These compounds are released into the atmosphere mainly through the use of gasoline and solutions containing them. Biomass burning also emits certain amounts of these compounds. In polluted areas the mixing ratios of these compounds are usually at the ppb level, while in remote areas they decrease significantly, due to the dilution and photochemical degradation during the transport (Greenberg et al., 1996; Rappenglück et al., 1998). The mixing ratios of the aromatic hydrocarbons listed in Table 3 coincides with the remoteness of the Finokalia site. On the other hand, they also suggest that the anthropogenic impact on the air chemistry at the site may still be important, considering the high reactivity of the compounds. More detailed analysis and interpretation of the hydrocarbon data are presented in Xu et al. (2003).

One of the interesting results of this study is the complete separation of benzonitrile from the other compounds. If conventional capillary GC had been used, benzonitrile would not have been detected, because it would have been completely masked by a column bleed compound with the same first-dimension retention time as that of benzonitrile. The peak of this interfering compound, eluting just before decane in the lowest band in Fig. 2a, is usually two orders of magnitude higher than that of benzonitrile. The TOF-MS software has identified the compound as octamethylcyclotetrasiloxane, but it has not yet been confirmed. Benzonitrile is used as a solvent and chemical intermediate in the pharmaceutical, dyestuffs and rubber industries (US National Toxicology Program, http://ntp-server.niehs.nih.gov). Except for the industrial sources, biomass burning also emits benzonitrile (Lutes and Kariher, 1996; Friedli et al., 2001). Reaction with OH radical is probably the main sink for atmospheric benzonitrile. The OH lifetime of benzonitrile is about 10 days. Less is known about the atmospheric budget of this compound. Since no benzonitrile standard was available for the present work, benzonitrile peaks were indirectly calibrated using toluene standards and the FID response factors

for toluene (1.17) and benzonitrile (0.91) (Katritzky et al., 1994). The mixing ratio of benzonitrile was lower than 5 pptv for most of the time during the campaign, but increased significantly during the biomass burning events. A comparison of benzonitrile data with acetonitrile data from the PTR-MS measurements (Salisbury et al., 2003) shows a positive correlation (R=0.3, n=81) between benzonitrile and acetonitrile, a marker of biomass burning. More studies are necessary to estimate the source and sink strengths of benzonitrile and to know the role and usefulness of this compounds in atmospheric chemistry.

4 Conclusions

The novel GC×GC technique provides very high peak capacity and enhanced sensitivity, hence is an ideal tool for the simultaneous measurements of atmospheric VOCs. During the MINOS campaign the technique was successfully applied to the in situ measurement of atmospheric VOCs at the Finokalia ground station. GC×GC chromatograms from the measurements show hundreds of peaks, suggesting that even at the remote site ambient air is a very complex mixture which cannot be separated to a satisfactory degree by conventional GC. Indeed VOC concentrations determined by 1D-GC methods from highly complex samples such as biomass burning must be viewed with caution (Andreae and Merlet, 2001) because of the number of potential interferences seen here in ambient air. Multidimensional separation techniques, such as GC×GC, appear inevitable if atmospheric VOCs should be simultaneously measured to a detailed extent.

A 3-dimensional system coupling a GC×GC system with a TOF-MS was used for the identification of compounds in the air samples collected at Finokalia. About 650 identified two-dimensional peaks show significant S/N ratios (>100) and high spectra similarities (>800). So far, 235 of the identifications have been confirmed by an independent identification method, i.e. the retention index comparison. Of the 235 confirmed compounds, 150 show up in the $C_7 - C_{14}$ range on the chromatogram from the in situ measurement. However, at least as many peaks are still unknown. To identify these unknown peaks is one of the future tasks.

Quantification of GC×GC measurements is rather simple once the peak volumes are reliably integrated. For effective integration of hundreds of 2-D peaks the integration software has to be improved significantly. The accuracy and precision of the GC×GC-FID measurements in this work is comparable to conventional GC-FID measurements. Because of higher blank values the detection limit for some hydrocarbons did not show significant improvement over conventional GC, although the sensitivity of the GC×GC system is about 20–60 times higher than that of conventional GC. A very clean sampling and injection system is required to really achieve the low detection limits that the GC×GC technique can provide.

References

Andrade, E. H. A., Maia, J. G. S., and Zoghbi, M. d. G. B.: Aroma volatile constituents of Brazilian varieties, J. Food. Comp. Anal., 13, 27–33, 2000.

Andreae, M. O. and Crutzen, P. J.: Atmospheric aerosols: Biogeochemical sources and role in atmospheric chemistry, Science, 276, 1052–1058, 1997.

Andreae, M. O. and Merlet, P.: Emission of trace gases and aerosols from biomass burning, Global Biogeochem. Cycles, 15, 955–966, 2001.

Beens, J., Boelens, H., Tijssen, R., and Blomberg, J.: Quantitative aspects of comprehensive two-dimensional gas chromatography (GC×GC), J. High Resol. Chromatogr., 21, 47–54, 1998.

Beens, J., Blomberg, J., and Schoenmakers, P. J.: Proper tuning of comprehensive two-dimensional gas chromatography (GC×GC) to optimise the separation of complex oil fractions, J. High Resol. Chromatogr., 23, 182–188, 2000.

Beens, J., Adahchour, M., Vreuls, J. J., van Altena, K., and Brinkman, U. A. Th.: A simple, non-moving modulation interface for comprehensive two-dimensional gas chromatography (GC×GC), J. High Resol. Chromatogr., 919, 127–132, 2001a.

Beens, J., Dallüge, J., Adahchour, M., Vreuls, J. J., and Brinkman, U. A. Th.: Moving cryogenic modulator for the comprehensive two-dimensional gas chromatography (GC×GC) of surface water contaminants, J. Microcol. Sep., 13, 134–140, 2001b.

Bermejo, J., Blanco, C. G., Diez, M. A., and Guillén, M. D.: Kováts retention indices of selected mono and polycyclic olefins, J. High Resol. Chromatogr., 10, 461–463, 1987.

Bertsch, W.: Two-dimensional gas chromatography. Concepts, instrumentation, and applications – Part 1: Fundamentals, conventional two-dimension gas chromatography, selected applications, J. High Resol. Chromatogr., 22, 647–665, 1999.

Bertsch, W.: Two-dimensional gas chromatography. Concepts, instrumentation, and applications – Part 2: Comprehensive two-dimensional gas chromatography, J. High Resol. Chromatogr., 23, 167–181, 2000.

Bruckner, C. A., Prazen, B. J., and Synovec, R. E.: Comprehensive two-dimensional high-speed gas chromatography with chemometric analysis, Anal. Chem., 70, 2796–2804, 1998.

Ciccioli, P., Cecinato, A., Brancaleoni, E., Frattoni, M., and Liberti, A.: Use of carbon adsorption traps combined with high resolution gas chromatography-mass spectrometry for the analysis of polar and non-polar C_4-C_{14} hydrocarbons involved in photochemical smog formation, J. High Res. Chromatogr., 15, 75-84, 1992.

Ciccioli, P., Brancaleoni, E., Cecinato, A., and Sparapani, R.: Identification and determination of biogenic and anthropogenic

volatile organic compounds in forest areas of Northern and Southern Europe and a remote site of the Himalaya region by high-resolution gas chromatography-mass spectrometry, J. Chromatogr., 643, 55-69, 1993.

Ciccioli, P., Cecinato, A., Brancaleoni, E., Frattoni, M., Bruner, F., and Maione, M.: Occurrence of oxygenated volatile organic compounds (VOC) in Antarctica, Int. J. Environ. Anal. Chem., 55, 245-253, 1996.

Dallüge, J., van Rijn, M., Beens, J., Vreuls, R. J. J., and Brinkman, U. A. Th.: Comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometric detection applied to the dermination of pesticides in food extracts, J. Chromatogr. A, 965, 207–217, 2002a.

Dallüge, J., van Stee, L. L. P., Xu, X., Williams, J., Beens, J., Vreuls, R. J. J., and Brinkman, U. A. Th.: Unravelling the composition of very complex samples by comprehensive gas chromatography coupled to time-of-flight mass spectrometry: Cigarette smoke, J. Chromatogr. A, 974, 169–184, 2002b.

David, F., Scanlan, F., and Sandra, P.: Retention time locking in flavor analysis, presented at the 23rd International Symposium on Capillary Chromatography, 5–10 June, 2000, Riva del Garda, Italy, 2000.

de Geus, H.-J., de Boer, J., and Brinkman, U. A. Th.: Development of a thermal desorption modulator for gas chromatography, J. Chromatogr. A, 767, 137–152, 1997.

Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A. B., Hewitt, C. N., Lamb, B., Liu, S., Trainer, M., Westberg, H., and Zimmerman, P.: Emissions of volatile organic compounds from vegetation and implications for atmospheric chemistry, Global Biogeochem., 6(4), 389–430, 1992.

Fraga, C. G., Prazen, B. J., and Synovec, R. E.: Enhancing the limit of detection for comprehensive two-dimensional gas chromatography (GC×GC) using bilinear chemometric analysis, J. High Resol. Chromatogr., 23, 215–224, 2000.

Fraga, C. G., Prazen, B. J., and Synovec, R. E.: Objective data alignment and chemometric analysis of comprehensive two-dimensional separation with run-to-run peak shifting on both dimensions, Anal. Chem., 73, 5833–5840, 2001.

Friedli, H. R., Atlas, E., Stroud, V. R., Giovanni, L., Campos, T., and Radke, L. F.: Volatile organic trace gases emitted from North American wildfires, Global Biogeochem. Cycles, 15, 435–452, 2001.

Greenberg, J. P., Helmig, D., and Zimmerman, P. R.: Seasonal measurements of nonmethane hydrocarbons and carbon monoxide at the Mauna Loa Observatory during the Mauna Loa Observatory Photochemistry Experiment 2, J. Geophys. Res., 101, 14 581–14 598, 1996.

Haagen-Smit Laboratory: Procedure for the detailed hydrocarbon analysis of gasolines by single column high efficiency (capillary) column gas chromatography, Tech. Rep. SOP NO. MLD 118, Revision NO. I.I, Air Resource Board, California Environmental Protection Agency, 1997.

Hayes, P. C. and Pitzer, E. W.: Disengaging solutes in shale- and petroleum-derived jet fuels by altering GC programmed temperature rates, J. High Resol. Chromatogr., 8, 230–242, 1985.

Helmig, D., Pollock, W., Greenberg, J., and Zimmerman, P.: Gas chromatography mass spectrometry analysis of volatile organic trace gases at Mauna Loa Observatory, Hawaii, J. Geophys. Res., 101, 14 697–14 710, 1996.

HSE, Laboratory method using diffusive samplers, solvent desorption and gas chromatography, in Volatile organic compounds in air, 88, HSE Books, Suffolk, UK, 1997.

IPCC, Climate Change 2001: The Scientific Basis, Cambridge University Press, Cambridge, 2001.

Johnson, K. J., Prazen, B. J., Olund, R. K., and Synovec, R. E.: GC×GC temperature programming requirements to produce bilinear data for chemometric analysis, J. Sep. Sci., 25, 297–303, 2002.

Katritzky, A. R., Ignatchenko, E. S., Barcock, R. A., Lobanov, V. S., and Karelson, M.: Prediction of gas chromatographic retention times and response factors using a general quantitative structure-property relationship treatment, Anal. Chem., 66, 1799–1807, 1994.

Kinghorn, R. M. and Marriott, P. J.: Enhancement of signal-to-noise ratios in capillary gas chromatography by using a longitudinally modulated cryogenic system, J. High Resol. Chromatogr., 21, 32–38, 1998a.

Kinghorn, R. M. and Marriott, P. J.: Comprehensive two-dimensional gas chromatography using a modulating cryogenic trap, J. High Resol. Chromatogr., 21, 620–622, 1998b.

Kinghorn, R. M., Marriott, P. J., and Dawes, P. A.: Design and implementation of comprehensive gas chromatography with cryogenic modulation, J. High Resol. Chromatogr., 23, 245–252, 2000.

Krivácsy, Z., Gelencser, A., Mészáros, G. E., Molnár, A., Hoffer, A., Mészáros, T., Sárvári, Z., Temesi, D., Varga, B., Baltensperger, U., Nyeki, S., and Weingartner, E.: Study on the chemical character of water soluble organic compounds in fine atmospheric aerosol at the Jungfraujoch, J. Atmos. Chem., 39, 235–259, 2001.

Laub, R. J. and Purmell, J. H.: Specific retention volumes, retention indices, and family-plot regressions of aliphatic, alicyclic, and aromatic hydrocarbon solutes with OV-101 poly (dimethylsiloxane) stationary phase, J. High Resol. Chromatogr., 11, 649–660, 1988.

Ledford, Jr. E. B.: Recent advances in GC×GC, presented at the 23rd International Symposium on Capillary Chromatography, 5–10 June, 2000, Riva del Garda, Italy, 2000.

Ledford, Jr. E. B. and Billesbach, C.: Jet-cooled thermal modulator for comprehensive multidimensional gas chromatography, J. High Resol. Chromatogr., 23, 202–204, 2000.

Lelieveld, J., Berresheim, H., Borrmann, S., Crutzen, P. J., Dentener, F. J., Fischer, H., Feichter, J., Flatau, P., Heland, J., Holzinger, R., Kormann, R., Lawrence, M. B., Levin, Z., Markowicz, K., Mihalopoulos, N., Minikin, A., Ramanthan, V., de Reus, M., Roelofs, G. J., Scheeren, H. A., Sciare, J., Schlager, H., Schulz, M., Siegmund, P., Steil, B., Stephanou, E. G., Stier, P., Traub, M., Warneke, C., Williams, J., and Ziereis, H.: Global air pollution crossroads over the Mediterranean, Science, 298, 794–799, 2002.

Lewis, A. C., Carslaw, N., Marriott, P. J., Kinghorn, R. M., Morrison, P., Lee, A. L., Bartle, K. D., and Pilling, M. J.: A larger pool of ozone-forming carbon compounds in urban atmospheres, Nature, 405, 778–781, 2000.

Limbeck, A. and Puxbaum, H.: Organic acids in continental background aerosols, Atmos. Environ., 33, 1847–1852, 1999.

Liu, Z. and Phillips, J. B.: Comprehensive two-dimensional gas chromatography using an on-column thermal desorption modu-

lator interface, J. Chromatogr. Sci., 29, 227–231, 1991.

Lubeck, A. J. and Sutton, D. L.: Kovats retention indices of selected olefins on bonded phase fused silica capillaries, J. High Resol. Chromatogr., 7, 542–544, 1984.

Lutes, C. C. and Kariher, P. H.: Evaluation of emissions from the open burning of land-cleaning debris, final report, Tech. Rep. EPA-600/R-96-128, U.S. Environmental Protection Agency, Research Triangle Park, NC, USA, 1996.

Madruga, M. S. and Mottram, D. S.: The effect of pH on the formation of volatile compounds produced by heating a model system containing 5'-lmp and cysteine, J. Baz. Chem. Soc., 9, 261–271, 1998.

Mohanmed, M. F., Kang, D., and Aneja, V. P.: Volatile organic compounds in some urban locations in United States, Chemosphere, 47, 863–882, 2002.

O'Dowd, C., Aalto, D. P., Hämeri, K., Kulmala, M., and Hoffmann, T.: Atmospheric particles from organic vapours, Nature, 416, 497, 2002.

Phillips, J. B. and Beens, J.: Comprehensive two-dimensional gas chromatography: a hyphenated method with strong coupling between the two dimensions, J. Chromatogr. A, 856, 331–347, 1999.

Phillips, J. B. and Xu, J.: Comprehensive multi-dimensional gas chromatography, J. Chromatogr. A, 703, 327–334, 1995.

Phillips, J. B., Gaines, R. B., Blomberg, J., van der Wielen, F. W. M., Dimandja, J.-M., Green, V., Granger, J., Patterson, D., Racovalis, L., de Geus, H.-J., de Boer, J., Haglund, P., Lipsky, J., Sinha, V., and Ledford, Jr. E. L.: A robust thermal modulator for comprehensive two-dimensional gas chromatography, J. High Resol. Chromatogr., 22, 3–10, 1999.

Rappenglück, B., Fabian, P., Kalabokas, P., Viras, L. G., and Ziomas, I. C.: Quasi-continuous measurements of non-methane hydrocarbons (NMHC) in the Greater Athens Area during MEDCAPHOT-TRACE, Atmos. Environ., 32, 2103–2121, 1998.

Rostad, C. E. and Pereira, W. E.: Kovats and Lee retention indices determined by gas chromatography/mass spectrometry for organic compounds of environmental interest, J. High Resol. Chromatogr., 9, 328–334, 1986.

Salisbury, G., Williams, J., Holzinger, R., Gros, V., Mihalopoulos, N., Vrekoussis, M., Sarda-Estéve, R., Berresheim, H., von Kuhlmann, R., Lawrence, M., and Lelieveld, J.: Ground-based PTR-MS measurements of reactive organic compounds during the MINOS campaign in Crete, July–August 2001, Atmos. Chem. Phys. Discuss., 3, 911–948, 2003.

Schomburg, G.: Two-dimensional gas chromatography: principles, instrumentation, methods, J. Chromatogr. A, 703, 309–325, 1995.

Weber, L.: Utilization of the Sadtler standard RI system in micropollution analysis, J. High Resol. Chromatogr., 9, 446–451, 1986.

Wedel, A., Müller, K.-P., Ratte, M., and Rudolph, J.: Measurements of volatile organic compounds (VOC) during POPCORN 1994: Applying a new on-line GC-MS-Technique, J. Atmos. Chem., 31, 73–103, 1998.

WMO: Scientific assessment of ozone depletion: 1994, Global Ozone Research and Monitoring Project, World Meteorological Organization, Report No. 37, Geneva, 1994.

Xu, X., Williams, J., Plass-Dülmer, C., Berresheim, H., Salisbury, G., Lange, L., and Lelieveld, J.: GC×GC measurements of C_7-C_{11} aromatic and n-alkane hydrocarbons on Crete, in air from Eastern Europe during the MINOS Campaign, Atmos. Chem. Phys. Discuss., 3, 1477-1513, 2003. 2003.

Yin, C., Guo, W., Lin, T., Liu, S., Fu, R., Pan, Z., and Wang, L.: Application of wavelet neural network to the prediction of gas chromatographic retention indices of alkanes, J. Chinese Chem. Soc., 48, 739–749, 2001.

Zenkevich, I. G.: Reciprocally unambiguous conformity between GC retention indices and boiling points within two- and multi-dimensional taxonomic groups of organic compounds, J. High Resol. Chromatogr., 21, 565–568, 1998.