



**Measurement of
stable hydrogen
isotopes in VOC**

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An analytical system for the measurement of stable hydrogen isotopes in ambient volatile organic compounds

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Received: 01 May 2015 – Accepted: 19 June 2015 – Published: 10 July 2015

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

Stable isotope measurements in atmospheric volatile organic compounds (VOC) are an excellent tool to analyse chemical and dynamical processes in the atmosphere. While up to now isotope studies of VOC in ambient air mainly focus on carbon isotopes, we herein present a new measurement system to investigate hydrogen isotope ratios in atmospheric VOC. This system consisting of a GC-P-IRMS (Gas Chromatography Pyrolysis Isotope Ratio Mass Spectrometer) and a preconcentration system was thoroughly characterised using a working standard. A precision of better than 9‰ (in δD) is achieved for n-pentane, 2-methyl-1,3-butadiene (isoprene), n-heptane, 4-methyl-pentane-2-one (4-methyl-2-pentanone), methylbenzene (toluene), n-octane, ethylbenzene, m/p-xylene, and 1,2,4-trimethylbenzene. A comparison with independent measurements via elemental analysis shows an accuracy of better than 9‰ for n-pentane, n-heptane, 4-methyl-2-pentanone, toluene, and n-octane. Above a compound specific minimum peak area the obtained δD values are constant within the standard deviations. In addition, a remarkable influence of the pyrolysis process on the isotope ratios is found and discussed. Reliable measurements are only possible if the ceramic tube used for the pyrolysis is sufficiently conditioned, i.e. the inner surface is covered with a carbon layer. It is essential to verify this conditioning regularly and to renew it if required. Furthermore, influences of a necessary H_3^+ correction and the pyrolysis temperature on the isotope ratios are discussed. Finally, the applicability to measure hydrogen isotope ratios in VOC at ambient levels is demonstrated with measurements of outside air on five different days in February and March 2015. The measured hydrogen isotope ratios range from -136 to -105 ‰ for n-pentane, from -86 to -63 ‰ for toluene, from -39 to -15 ‰ for ethylbenzene, from -99 to -68 ‰ for m/p-xylene, and from -45 to -34 ‰ for o-xylene.

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1 Introduction

Isotope effects in nature provide “fingerprints” of physical and chemical processes, which are often difficult to quantify. The ratios of stable isotopes in trace constituents in the atmosphere are altered in almost all processes they are involved in, such as chemical reactions, thermodynamic equilibration, diffusion, phase transitions, photolytic processes and isotope exchange reactions. The large variety of possible applications ranges from the reconstruction of past climates to the investigation of current physical and chemical processes in the atmosphere.

The application of isotope ratio studies in atmospheric VOC at ambient concentrations (ppbV and even pptV levels) is a relatively recent development (Rudolph et al., 1997). It opened the possibility to study isotopic signatures of ambient organic compounds, to investigate their sources, photochemical histories and residence times (C₂-C₈ hydrocarbons, aromatics, methyl halides, CFC and 2-methyl-1,3-butadiene (isoprene)) (Tsunogai et al., 1999; Saito et al., 2002; Rudolph et al., 2002, 2003; Thompson, 2003; Archbold, 2005; Saito et al., 2009; Redeker et al., 2007). Goldstein and Shaw (2003) and Gensch et al. (2014) reviewed available information on stable carbon isotope ratios of VOC and the possibility of using isotope ratio measurements to study atmospheric budgets of VOC. The applications in atmospheric chemistry were reviewed by Brenninkmeijer et al. (2003). Measurements of stable isotope ratios in VOC allow to investigate physical and chemical processes on a wide range of temporal and spatial scales (micro scale processes, exchange processes between different atmospheric regions, both horizontally and vertically, large-scale transport processes and interdependencies between different compartments of the Earth system). Such studies provide valuable information on the dominant processes on these scales, since VOC have highly variable atmospheric lifetimes (hours to months) and different sources (biogenic, anthropogenic, chemical reactions in the atmosphere) (Rudolph, 2007). Furthermore, VOC are useful tracers to investigate reactions that are not directly accessible to current measurement techniques or as probes to “visualise” transport and mix-

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ing processes (also in case of rapid mixing) in the atmosphere or across atmospheric boundaries.

However, to our knowledge up to now all studies concerning ambient VOC concentrated on carbon isotope ratios. In principle, the investigation of isotope ratios of other elements can further improve our understanding of atmospheric processes by adding additional pieces of information. Measurements of D/H would be especially promising. Hydrogen isotope effects will be more pronounced than carbon isotope effects because of the larger mass ratio of D/H than that of $^{13}\text{C}/^{12}\text{C}$ leading to larger kinetic isotope effects (KIE) of hydrogen compared to carbon (Iannone et al., 2004, 2005; Gensch et al., 2014).

Owing to the much lower isotope abundances of D (0.015 ‰; De Bièvre et al., 1984) compared to ^{13}C (1.1 ‰; De Bièvre et al., 1984), significant larger sample volumes (~200 L, instead of ~20 L for carbon) are needed to obtain adequate signal-to-noise ratios in the Isotope Ratio Mass Spectrometer. Regarding the expected δD values of atmospheric VOC (−250 to −140 ‰) based on published studies of source rocks, crude oil, sediments, plant waxes, and aerosol particles (Xiong et al., 2005; Liu et al., 2006; Yeh and Epstein, 1981; Duan et al., 2011; Bi et al., 2005; Yamamoto and Kawamura, 2010) and the few known KIEs (~10 to ~100 ‰; Iannone et al., 2004, 2005), stable hydrogen isotope ratios should at least be measured with a precision (in terms of δ -values) of 10–20 ‰ to identify isotope effects. For measurements of hydrogen isotope ratios in atmospheric VOC at ambient concentrations the currently available sample preparation techniques have to be modified to allow the analysis of large volume whole air samples. Furthermore, it has to be ensured that the analysis can be done with sufficient sensitivity and precision to identify changes in hydrogen isotope ratios occurring in atmospheric processes.

Recently, two studies were published using both $\delta^{13}\text{C}$ and δD measurements of selected VOC under specific conditions (von Eckstaedt et al., 2011a, b). The authors applied a GC-P-IRMS (Gas Chromatograph Pyrolysis Isotope Ratio Mass Spectrometer) to investigate stable isotope ratios in emissions from biomass combustion, the exhaust

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from diesel and petrol cars, and from an aluminium industry stack. They obtained δD values for a variety of VOC, but obviously at rather high concentrations compared to atmospheric conditions. Their δD values ranged from -280 to $+30$ ‰. Another very recent study concerning benzene and methylbenzene (toluene) emissions from cars (Kikuchi and Kawashima, 2013) obtained δD values in these compounds ranging from -159.5 to -25.6 and -59.2 to -19.3 ‰, respectively. They compared their source measurements with ambient samples taken at a roadside. Here they found δD values of -174.4 to -74.9 and -134.7 to -35.0 ‰ for benzene and toluene, respectively, which indicates an impact of the sources to the ambient values. These measurements seem to be the only available δD values of VOC in ambient air so far. Another study on ambient VOC is reported by Rice and Quay (2009). However, their study solely focusses on formaldehyde. These studies showed that it is generally possible to measure δD values of VOC with considerable precision. To our knowledge, there are no other measurements of stable hydrogen isotope ratios in atmospheric VOC reported up to now.

In this paper we describe a method for measurements of δD of atmospheric VOC based on a modification of existing methods for the measurement of $\delta^{13}C$ in atmospheric VOC (see Iannone et al., 2007; Wintel et al., 2013).

2 Experimental set up

Hydrogen isotope ratios were measured by a gas chromatograph pyrolysis isotope ratio mass spectrometer (GC-P-IRMS) in Continuous Flow mode. The system consists of four main components: (1) a preconcentration unit designed for high volume whole air samples, (2) a gas chromatograph coupled to a quadrupole mass spectrometer, (3) a pyrolysis unit, and (4) an isotope ratio mass spectrometer. Figure 1 schematically shows the setup of the GC-P-IRMS. The total analysis time for one measurement is 180 min for VOC preconcentrated from a volume of 50 L of air for the characterisation measurements.

2.1 Sample preparation

VOC are extracted from the air sample and preconcentrated using a specifically designed cryo focussing system (TDSG-L, Gerstel GmbH and Co.KG, Mühlheim a.d.R., Germany). It consists of two unpacked traps (traps 1+2), a Thermal Desorption System (TDS), followed by two further unpacked traps (traps 3+4) and finally a Cold Injection System (CIS) and a Cryo Trap System (CTS) (see Fig. 1). All traps as well as the TDS are stainless steel tubes with a length of 52.5 cm (ID 12 mm), of 30 cm (ID 12 mm) and of 11 cm (ID 5 mm) for the TDS, traps 1+2 and traps 3+4, respectively. The CIS consists of a glass liner (length 68 mm, ID 1.7 mm) packed with glass beads (60/80 mesh) and allows for cooling and heating at a high rate (12 K s^{-1}). The CTS is placed at the beginning (85 mm) of the first chromatographic column, located inside the GC oven. It allows for a rapid cooling and heating (12 K s^{-1}) of a 5 cm long section of the capillary. To avoid wall losses, the TDS and all traps are Sulfinert[®] coated (Restek GmbH, Bad Homburg, Germany). All temperatures are individually controlled by a combination of cooling by liquid nitrogen and electrical heating.

During the experiments, two different configurations of the TDS were tested. In the first configuration (A), the TDS was packed with glass beads (60/80 mesh), on which the VOC were cryogenically trapped. In this configuration TDS temperatures were set to 103 and 503 K for adsorption and desorption, respectively. In the second configuration (B) the VOC were extracted from the sample using Tenax[®]TA (Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany). In this configuration temperatures were set to 272 and 573 K for adsorption and desorption, respectively. The advantage of Tenax[®]TA is the very low break through volume for water and especially for CO₂ (Helmig and Vierling, 1995) and therefore it has widely been used for sampling atmospheric VOC (see for example Rudolph et al., 1990). This reduces significantly the amount of CO₂ in the preconcentrated sample, thus avoiding the CTS to freeze over which was frequently observed when VOC were preconcentrated on glass beads.

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In both configurations the sample is drawn through traps 1 and 2 and the TDS for 50 min with a mass flow of 1000 mL min^{-1} using a rotary pump. The sample volume can be altered by varying the time of the preconcentration step or the flow rate. The volume of the whole air sample for all characterisation measurements presented here was $\sim 50 \text{ L}$. Traps 1 and 2 are used to reduce water from the atmospheric samples at 253 K prior to preconcentrating the VOC on the adsorbent within the TDS at the respective adsorption temperature (depending on the packing material). Valves 1, 2 and 3 are in “enrichment position” at this step (cf. Fig. 1a). In configuration A, H_2O and CO_2 are also partially trapped because of the low TDS temperature, in configuration B CO_2 and most of H_2O are mainly exhausted with the bulk air. In the next step valve 2 is switched to “transfer position” to flush the TDS with helium for two minutes. After this, valves 1 and 3 are also switched to “transfer position” and the desorbed VOC pass through two additional traps (traps 3 and 4) to the CIS (cf. Fig. 1b). At that time the TDS is heated up to the respective desorption temperature (depending on the packing material) at a rate of 40 K min^{-1} . The VOC are desorbed for 20 min with a helium flow rate of 110 mL min^{-1} and focussed on the CIS at 103 K. Traps 3 and 4 are set to 243 K and used to further reduce H_2O following the preconcentration step (Thompson, 2003). To avoid any wall losses all transfer lines in the TDSG-L are held at 393 K. In a last focussing step the VOC are desorbed in a splitless mode from the CIS with a flow rate of 4 mL min^{-1} by heating it to 523 K at a rate of 12 K s^{-1} and trapped on the CTS at 103 K. After 3 min the VOC are desorbed by heating the CTS to 503 K at a rate of 12 K s^{-1} , which marks the start of the chromatographic separation.

During the chromatographic separation the preconcentration system is purged for 60 min with helium at a flow rate of 400 mL min^{-1} by switching valves 1 and 3 and heating all traps and transfer lines to 393 K (the TDS to 573 K). After the desorption of the VOC from the CTS the CIS is purged with helium by using the solvent vent mode of the GC. The helium used in the whole process is He 5.0 (Messer Industriegase GmbH, Bad Soden, Germany) purified by a Restek Super Clean[®] Gas Filter to better than He 6.0 (purity 99.9999 %).

2.2 Gas chromatographic separation

The VOC are separated by gas chromatography (GC 7890A, Agilent Technologies Inc., Santa Clara, CA, USA) using a two-column combination consisting of a non-polar Rtx[®]-1 (Restek GmbH) column (105 m, 0.32 mm ID, 3 µm df) followed by a midpolarity Crossbond[®] phase Rxi[®]-624Sil MS (Restek GmbH) column (60 m, 0.32 mm ID, 1.8 µm df) for additional separation during a single measurement. In the case of screening experiments to evaluate a newly developed technique this combination has the advantage to separate as many compounds as possible for the determination of stable isotope ratios. Using helium as carrier gas the initial GC temperature is 233 K (cooled with LN₂ and held isothermal for 12 min) and increased at a rate of 4 K min⁻¹ to a temperature of 473 K (held for 1 min). The oven temperature is then finally increased to 503 K at a rate of 20 K min⁻¹. The flow rate through the columns is kept constant at 4 mL min⁻¹ during the whole temperature program. Following separation, a minor part of the eluent is directed to the mass selective detector, the major part to the pyrolysis oven and the IRMS (split ratio approx. 1 : 9).

2.3 Mass selective detector

The mass selective detector (MSD, quadrupole mass analyser 5975C, Agilent Technologies Inc., Santa Clara, CA, USA) allows identification and quantification of the compounds. The MSD is operated at a measurement frequency of about 7 Hz and a mass range of 15–200 u. The quadrupole was kept at a temperature of 423 K, the source temperature was kept at 503 K. While the MSD is currently only used for identification during the characterisation measurements it will also be used to quantify substances when measuring unknown air samples in the future.

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2.4 Pyrolysis oven

In the pyrolysis oven (GC 5, Isoprime Ltd., Manchester, UK), the VOC are decomposed and the hydrogen atoms recombine to hydrogen molecules. During first tests, we used a quartz tube (ID ~ 0.5 mm) packed with chromium pellets, operated at 1273 K, for pyrolysis of the VOC. Because the quartz tube was blocked obviously with elemental carbon after only a few measurements, it was replaced by a ceramic tube (ID ~ 0.5 mm) which is operated at a temperature of 1723 K. This turned out to be the optimum temperature with respect to reproducible isotope ratio measurements (see Sect. 3.3.2). The resulting H₂ and HD molecules are then transferred to the (sector field) isotope ratio mass spectrometer (IRMS) via an open split and a 1 m deactivated fused silica capillary (0.1 mm ID). To maintain a constant flow through the pyrolysis oven and to avoid back diffusion, an additional helium flow (sample line helium) of approximately 1 mL min⁻¹ is added to the flow through the ceramic tube.

2.5 Isotope Ratio Mass Spectrometer

The isotope ratio measurements are performed with the Isoprime 100 Isotope Ratio Mass Spectrometer (IRMS, Isoprime Ltd.). After ionisation the ions pass through the electric and magnetic fields and are collected by Faraday cups. The resulting signals yield two chromatograms, one of H₂ (major signal) and one of HD (minor signal). From these data the δD values of the individual VOC are determined with respect to the H₂ reference gas (Air Liquide GmbH, Düsseldorf, Germany) with a δD of -261 ‰ vs. VSMOW (Vienna Standard Mean Ocean Water). The reference gas is connected to the IRMS via a reference gas injector box (Isoprime Ltd.) and a second open split. It allows supplying reference gas peaks at certain times. For this purpose a pneumatic valve controlled by the IRMS software is opened for 30 s for each reference gas peak.

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2.6 Determination of the δD values

The δD values are determined as follows. For each peak, major and minor signals are integrated automatically by the software IonVantage Continuous Flow Data Processing (CFDP v. 1.4.9.0), correcting for the H_3^+ contribution (also see Sect. 3.4) (Sessions et al., 2001a, b). If necessary, the integration parameters *peak start* and *peak end* are adjusted manually. Finally, for each peak the ratios of mass 3 (HD) to mass 2 (H_2) are calculated and converted to δD values w.r.t. VSMOW considering the reference gas D/H ratio by Eqs. (1) and (2), where $(\frac{D}{H})_{\text{sample}}$ and $(\frac{D}{H})_{\text{ref.}}$ are the calculated mass ratios of the sample peak and the reference gas peaks, respectively, and $\delta D_{\text{ref.-VSMOW}}$ is the known δD value of the reference gas w.r.t. VSMOW.

$$\delta D_{\text{raw}}[\text{‰}] = \frac{(\frac{D}{H})_{\text{sample}} - (\frac{D}{H})_{\text{ref.}}}{(\frac{D}{H})_{\text{ref.}}} \cdot 1000 \quad (1)$$

$$\delta D[\text{‰}] = \delta D_{\text{raw}} + \delta D_{\text{ref.-VSMOW}} + \frac{\delta D_{\text{raw}} \cdot \delta D_{\text{ref.-VSMOW}}}{1000} \quad (2)$$

2.7 Working standard

For the characterisation experiments a standard air sample with known VOC mixing and isotope ratios is needed. We prepared a laboratory standard (called VOC standard in the following) by injecting 16 VOC (see Table 1) from the liquid phase through a septum into a gas cylinder (Messer Industriegase GmbH), which was finally pressurised with N_2 to 60 bar. The final mixing ratios of the compounds range from 92 to 523 ppbV. As the mixing ratios of the VOC in this gas standard are much higher than ambient levels, the VOC standard is diluted with purified synthetic air (purity > 6.0) for every measurement to yield mixing ratios comparable to ambient air (about 1–10 ppbV). This is done with a dynamic dilution system (Hembeck, 2008) where the samples are additionally humidified (to a RH of about 48 % at room temperature). The pure compounds, which were used to prepare the VOC standard, have been analysed independently for

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δD via elemental analysis (EA) by Agroislab (Jülich, Germany). They injected about 1 to 2 μL of the liquid sample into their analytical system consisting of an element analyser (Eurovector 3000) combined with an IRMS (Micromass, Manchester, UK). Their combustion tube filled with nickel oxide and elemental chromium was operated at 1323 K. As internal laboratory standards three water samples covering the scale from 0 to -100‰ were used which were calibrated with IAEA-SMOW, IAEA-GISP and IAEA-SLAP.

Using the VOC standard mixture our analytical system was thoroughly tested, especially with respect to possible fractionation effects during sample preconcentration and analysis. In addition the measured δD values were compared to the results obtained by Agroislab.

3 Results of the characterisation experiments

The system as described above was characterised with respect to (1) the suitability of the adsorbent material in the TDS, (2) reproducibility, stability, and linearity, (3) an influence of the pyrolysis on the δD values, and (4) an influence of the H_3^+ correction on the δD values. All measurements described in the following were performed with the VOC standard diluted with purified synthetic air (dilution 1 : 76). An example of a typical chromatogram measured by the IRMS is shown in Fig. 2. At the beginning of each chromatogram 5 measurements of the reference gas were performed. At the end of each chromatogram the reference gas was measured again (2 peaks). Using the GC-program described above we are able to analyse 10 of the 16 compounds contained in the VOC standard for hydrogen isotope ratios. Methanol, acetone, pentanal, propanal, and hexanal cannot be analysed due to too small peak areas or to an influence by a water background at retention times lower than 3800 s. Moreover, no isotope values for benzene are presented because Tenax[®] TA produces a significant benzene background. This effect was already observed in previous studies (De Bortoli et al., 1992). With the exception of n-pentane and isoprene the peaks of all other compounds pre-

sented here were baseline separated with peak areas of 5 to 50 nAs (major signal) and can thus reliably be analysed. All results presented in the following are mean values calculated from a set of individual measurements. Furthermore, the standard deviations are calculated and corrected with the t factor considering Student's t distribution because of the limited number of individual data points.

3.1 Adsorbent material in the TDS

As stated above, two different configurations of the TDS were used. Initially, we used the TDS packed with glass beads (configuration A). However, when analysing ambient air, measurements using the TDS in this configuration are limited to a sample volume of about 30 L because of the high amount of CO₂ (at 400 ppmV this corresponds to 24 mg CO₂), which freezes out in the CIS and blocks the liner. As the D/H analysis of ambient VOC needs sample volumes of about 200 L (160 mg CO₂ at 400 ppmV) this configuration is no longer suitable for measurements of ambient air. Therefore, we changed the adsorbent material from glass-beads to Tenax[®]TA (configuration B). The δ D values of the VOC standard (CO₂-free) were determined in both configurations (Fig. 3). Although for some compounds (isoprene, n-heptane, xylenes) slight differences between both configurations were observed, there is a good agreement within the standard deviations. When evaluating the differences, it should be noted, that part of this deviation is obviously due to a change in the H₃⁺ factor by reason of a necessary renewal of the filament between both measurement series. Moreover, the standard deviations (size of the boxes) indicate that the measurements using Tenax[®]TA show a higher precision than those using glass beads. First test-measurements of ambient air (see Sect. 3.5) showed that using configuration B measurements of sample volumes up to 200 L are possible without difficulty.

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3.2 Reproducibility, stability, and linearity

Regarding reproducibility, stability, and linearity two cases have to be addressed. On the one hand stability and linearity of the IRMS are regularly controlled using the reference gas. On the other hand reproducibility and linearity of the complete measurement setup was verified using the VOC standard. In the case of stability tests of the IRMS 10 reference gas peaks are produced using the reference gas injector box and δD values are calculated for each peak. The standard deviation of these ten measurements is lower than 0.3‰ (in terms of δ -values). Linearity tests are performed by injecting the reference gas at different pressure levels resulting in different peak heights (0.3 to 5 nA in the major signal). The variation of the calculated δD values is lower than 0.4‰ nA⁻¹.

Following the verification that Tenax[®] TA is a suitable adsorbent the reproducibility and linearity of the complete system was verified by several individual measurements of the VOC standard.

In case of the reproducibility test, 18 individual measurements of the diluted VOC standard were performed. The obtained standard deviations in δD values are better than 2.5‰ for n-heptane, toluene, n-octane, and m/p-xylene, and better than 9‰ for all other compounds except o-xylene (12‰). These results show (at least for the compounds investigated) that the system is well suited to achieve the precision necessary to identify hydrogen isotopic effects in ambient VOC. Comparison of the mean δD values and the δD values obtained by the bulk analysis of the primary compounds by Agroisolab shows a perfect agreement within the standard deviations of our measurements and the uncertainties given by Agroisolab for n-pentane, 4-methyl-pentane-2-one (4-methyl-2-pentanone), toluene, and n-octane (Fig. 3 and Table 1). The differences between both mean values are lower than 5‰ for n-heptane, toluene, and n-octane and lower than 9‰ for n-pentane and 4-methyl-2-pentanone. A larger difference of 15 and 20‰ is only evident for 1,2,4-trimethylbenzene and isoprene, respectively. A direct comparison of δD values of the xylenes and ethylbenzene is not

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possible because only a mixture of these compounds was at our disposal. Thus, using EA, Agrosolab could only determine the bulk δD value of this mixture.

To identify possible non-linearity effects of the complete system the VOC standard was measured with different stages of dilution. From this measurement series we additionally derived the minimum required peak areas to obtain reproducible δD values. It turned out that reliable results regarding precision and accuracy as presented above can be achieved with dilutions of the VOC standard in synthetic air of 1 : 200 (yielding the minimum peak area) or lower. This corresponds to peak areas in the major signal of 1 to 20 nAs depending on the specific compound.

3.3 Influence of the pyrolysis system (ceramic tube) on the δD values

3.3.1 Carbon conditioning

During the pyrolysis of VOC, H_2 and HD are formed and elemental carbon is deposited on the inner surface of the pyrolysis tube. This carbon layer seems to be essential for an efficient production of H_2 and HD. According to the recommendation of the manufacturer (Isoprime) the ceramic tube has to be carbon-conditioned before the first use by flushing the tube with a light hydrocarbon in order to coat the inner surface with carbon. Following this first conditioning step, this carbon layer resulting from repeated measurements of VOC was said to be sufficient to sustain the conditioning of the pyrolysis tube. The first conditioning was performed using propane added to the sample line helium but in contrast to the recommendation, the conditioning seems to decline very rapidly with increasing number of measurements. Our results show that the carbon layer resulting from repeated measurements of VOC seems to be insufficient to maintain the conditioning of the pyrolysis tube. As a result, considerable fluctuations in the δD values occur indicating a significant influence of the status of the pyrolysis tube. Figure 4 shows three measurement series using n-octane as an example. As can be seen, after a certain number of measurements a noticeable “step” in the δD values occurs towards significantly lower δD values. This “step” is observed for all measured

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compounds. After a re-conditioning of the tube all measured δD values are at the same level as before. It appears that the durability of the conditioning depends on the number of measurements rather than on time. When conditioning the ceramic tube for 5, 10, and 20 min, the “step” in δD values arises after 6, 10, and 20 measurements, respectively. The δD values before the “step” fit obviously quite well to the results of the bulk analysis by Agrolislab. Furthermore, the standard deviations of the δD values of all analysed compounds increase significantly after the “step” (in the case of n-octane from 1.3‰ before to 19.8‰ after the “step”). For these reasons, we consider the δD values before the “step” to be more reliable. The increasing standard deviation in δD after the “step” is shown in Fig. 3 using the example of n-octane. The grey box represents the results of the reproducibility experiments with a well conditioned tube, the orange box represents results measured after the “step” was observed. As a consequence, regular measurements of the VOC standard are essential not only for calibration purposes, but also to verify the conditioning of the pyrolysis tube when measuring unknown air samples.

Our observations are in contrast to the observations reported by Brass and Röckmann (2010). They state that an extensive carbon conditioning may even have a negative effect on the formation of H_2 and repeated measurements of VOC are sufficient to condition the pyrolysis tube. The reason for this obviously different behaviour may be due to the different pyrolysis tubes used (silica vs. aluminium oxide). In any case, these details should be subject of further investigations.

Brass and Röckmann (2010) also report on the influence of H_2O on the pyrolysis of methane. Our results confirm this observation. When measuring ambient air the “step” in δD values is observed much earlier (after only 4 measurements, when conditioning for 20 min.) most probably due to a higher amount of water entering the system and the ceramic tube. A possible process reducing the carbon layer is that oxygen atoms from water molecules react with the carbon to CO and CO_2 . Because H_2O is also a source of protonation and can lead to an increase in H_3^+ formation, we therefore changed the chromatographic method to avoid that any H_2O enters the pyrolysis oven. It turned out

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that the conditioning is sustained for much more measurements when applying this method.

Kornexl et al. (1999) report on reactions of oxygen from the ceramic tube with sample compounds because of an oxygen self-diffusion in Al_2O_3 . If these reactions affect the abundance of H_2 and HD, this could be an explanation of the observed variation in δD values when the carbon layer is degrading. Another source of oxygen, which is unavoidable when analysing ambient VOC, is the presence of oxygenated compounds. However, due to the low amount of these compounds, this effect may be of minor importance, but still has to be verified in the future.

In order to get an impression of the carbon layer we inspected the surface condition of parts of a used ceramic tube at different positions (outside and inside the heated area) using a Scanning Electron Microscope (SEM). The part of the tube located outside of the hot area shows the typical structure of a more or less clean Al_2O_3 surface (cf. Fig. 5a). The part located inside the hot area shows a different texture indicating a carbon layer covering the Al_2O_3 surface. However, also some of the carbon seems to have been deposited in soot-like structures which obviously do not cover the ceramic surface completely (cf. Fig. 5b). At present, we do not have a definite interpretation of the pictures. The pictures show, however, that the carbon layer is either not as uniform as expected or changes dramatically during the use of the pyrolysis tube.

3.3.2 Pyrolysis temperature

A further source for errors in the stable isotope ratios of hydrogen in VOC is the potential formation of methane during the pyrolysis process. Burgoyne and Hayes (1998) report on the formation of methane as an intermediate product in the pyrolysis of VOC depending on the pyrolysis temperature. They investigated the methane formation during the pyrolysis of propane and showed that formation of methane starts at a temperature of about 530 K, peaks at about 700 K and stops at temperatures above 1100 K. A methane production would directly affect the ratio of D/H and thus distort the stable isotope ratios of the investigated VOC. Furthermore, methane is a source for protona-

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tion. Any methane getting in the ion source of the IRMS may lead to higher H_3^+ production, which again influences the calculated isotope ratios (Brand, 2004). Therefore, we determined the optimum temperature for the pyrolysis process to allow for a quantitative conversion of the hydrogen atoms of the VOC to H_2 with a specific measurement series.

Because the recommended temperature for the pyrolysis process in the ceramic tube (Al_2O_3) is 1723 K, we performed measurements at pyrolysis temperatures of 1173, 1273, 1473 and 1723 K, respectively. Temperatures were not set to values higher than 1723 K to avoid operating the oven too close to its maximum temperature of 1773 K. In this measurement series H_2 and HD signals were measured and δD values were derived. In a second step the IRMS was tuned to the mass of CH_4 to measure the methane signal at the temperatures given above. The results are shown in Fig. 6 using a normalisation for better comparison. For each compound the peak areas at all temperatures are summarised to a total peak area. For each compound and each temperature the corresponding peak area is normalised to this total peak area. The grey (CH_4) and blue (H_2) bars cover the range of results for all measured compounds including their standard deviations. As a specific example, the values of n-octane are presented as black squares. The methane signal peaks in the temperature range between 1173 and 1273 K, whereas the H_2 signal has a maximum in the temperature range between 1673 and 1723 K. Thus, our results are very similar to those obtained by Burgoyne and Hayes (1998). At 1723 K the methane signal was below the lower limit of detection. Below 1173 K no H_2 is produced and thus no H_2 signal is detectable. Furthermore, at a pyrolysis temperature of 1723 K the δD values of all compounds are very stable with the standard deviations presented above.

3.4 Influence of H_3^+ on δD values

H_3^+ ions are formed in the ion source of the IRMS by collision of H_2^+ ions with H_2 molecules (Sessions et al., 2001b). Because H_3^+ ions have the same mass to charge

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ratio as HD ions they increase the minor signal. As mentioned above the software package automatically corrects for the H_3^+ contribution using a H_3^+ factor. This factor is determined by a method similar to the stability and linearity tests of the IRMS described above. Four reference gas peaks at different pressure levels are measured and the amount of H_3^+ is calculated by comparing both the minor and major signals at these pressure levels. As the formation of H_3^+ in the ion source depends on the pressure of H_2 , the contribution of H_3^+ ions to the HD signal can be determined by comparing the increase in both signals with increasing pressure of the reference gas. One of the basic requirements is that this factor is stable (variation of only 0.1). During the measurement series reported here the determined H_3^+ factor ranged from 5.1 to 5.7 and thus was not as constant as expected. To analyse to what extent the δD values were affected by this variation when using CFDP, the same measurement series was analysed using H_3^+ factors of 5.0, 5.3 and 5.8. As can be seen from Fig. 7, δD values change with larger H_3^+ factors, because a larger factor means that a larger part of the mass 3 signal is assumed to originate from H_3^+ ions. Thus, the ratios of D/H become smaller and consequently the δD values change depending on the size and corrections of the reference gas and sample signals (cf. Eq. 1). The use of the different H_3^+ factors results in differences in the mean δD values from 2‰ (n-octane) to 10‰ (m/p-xylene), which is slightly larger than the standard deviations presented above. Thus, this influence has to be taken into account when considering uncertainties.

3.5 First test measurements of ambient air

Applying the new chromatographic method in order to avoid any water getting into the pyrolysis oven and with regular verifications of the conditioning of the ceramic tube, first test measurements of ambient air have been performed. For these test measurements ambient air was sampled on five different days in February and March 2015 from outside the institute's building through a PFA tube connected to the sample inlet of the TDSG-L. The university campus is located in the center of Wuppertal and one of the major sources of VOC is obviously vehicle exhaust. Focussing on the com-

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pounds contained in the VOC standard, the required peak areas in ambient air can be achieved with sample volumes of 200 L at least for n-pentane, toluene, ethylbenzene, and o- and m/p-xylene. Regarding the required peak areas, six measurements were selected and further analysed using the same method as for the characterisation measurements. The obtained δD values range from -136 to -105 ‰ for n-pentane, from -86 to -63 ‰ for toluene, from -39 to -15 ‰ for ethylbenzene, from -99 to -68 ‰ for m/p-xylene, and from -45 to -34 ‰ for o-xylene. It should be noted that these δD values result from a sampling time of 145 min per measurement. As mentioned before, to our knowledge the only other published δD values of atmospheric VOC at ambient levels were reported by Kikuchi and Kawashima (2013). They measured δD values in benzene and toluene in roadside air ranging from -174.4 to -74.9 ‰ and from -134.7 to -35.0 ‰, respectively. Compared to their results our δD values of toluene fit into the range given by Kikuchi and Kawashima (2013). The smaller range of our results may be attributed to different sources and production processes of the fuel used in Japan and Europe. We can further compare our results to the measurements of toluene, ethylbenzene, m-xylene, and o-xylene in car emissions by von Eckstaedt et al. (2011a). They measured δD values of different VOC in diesel and petrol car emissions. Their results for diesel car emissions are (-3 ± 8) , (-70 ± 14) , and (-49 ± 12) ‰ for toluene, m-xylene, and o-xylene, respectively. The results for petrol car emissions are (-65 ± 3) , (-47 ± 4) , (-61 ± 3) , and (-48 ± 4) ‰ for toluene, ethylbenzene, m-xylene, and o-xylene, respectively. Our δD values of toluene (-86 to -63 ‰), ethylbenzene (-39 to -15 ‰) and the xylenes (-99 to -68 ‰ for m/p-xylene and -45 to -34 ‰ for o-xylene) are comparable to the results of this source study, confirming that emissions from vehicle exhaust dominated the composition of our samples. In summary, our first measurements demonstrate the suitability of our instrumental setup for the measurements of δD values of VOC at ambient conditions.

4 Summary and outlook

We set up and successfully characterised a new measurement system consisting of a GC-P-IRMS and a preconcentration system to measure D/H ratios in atmospheric VOC at ambient levels. Using a standard gas mixture the system was characterised concerning reproducibility and linearity. The obtained standard deviations calculated from 18 individual measurements are < 9‰ in δD values for n-pentane, 1,2,4-trimethylbenzene, 4-methyl-2-pentanone, ethylbenzene, and isoprene and even ≤ 2.5 ‰ for n-heptane, toluene, n-octane, and m/p-xylene. Thus, this system is suitable to identify ambient hydrogen isotopic effects. In addition, a comparison with results obtained by elemental analysis of the pure compounds shows a perfect agreement within our standard deviations for n-pentane, toluene, 4-methyl-2-pentanone and n-octane. Moreover, linearity experiments showed that reproducible measurements of δD values are possible with IRMS major signals larger than a minimum peak area of 1 to 20 nAs (depending on the compound). Furthermore, a pyrolysis temperature of 1723 K was found to be suitable regarding sufficient H_2 and HD production as well as prevention of methane production which would affect the measured δD values. The characterisation measurements showed a considerable influence of the pyrolysis process on δD values. The ceramic tube (Al_2O_3) used for the pyrolysis process has to be regularly re-conditioned with a light hydrocarbon after a certain number of measurements to sustain a carbon layer on the inner surface of the tube. Otherwise considerable fluctuations in δD values occur. It is therefore necessary to verify the conditioning regularly with a working standard when measuring unknown air samples. Considering this effect, first test measurements of ambient air were performed demonstrating the applicability of the system when using Tenax[®] TA for VOC adsorption in the thermal desorption system of the preconcentration unit. With sample volumes of 200 L, which are necessary to achieve the required peak areas, the measured δD values range from –136 to –105‰ for n-pentane, from –86 to –63‰ for toluene, from –39 to –15‰ for ethylbenzene, from –99 to –68‰ for m/p-xylene, and from –45 to –34‰ for o-xylene.

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For prospective interpretation of ambient air measurements hydrogen kinetic isotope effects as well as model calculations concerning hydrogen isotope ratios are necessary. With a combination of stable hydrogen and stable carbon isotope ratios of atmospheric VOC it may then be possible to reduce uncertainties in stable isotope studies of atmospheric VOC.

Acknowledgements. Part of this work was funded by the German Sciences Foundation (DFG) under grant number KO 2340/4-1. We thank R. Kurtenbach and M. Gallus (chemistry department, atmospheric chemistry group, University of Wuppertal) for their help to prepare our working standard and for the measurements of the mixing ratios in this standard. We further thank D. Lützenkirchen-Hecht (physics department, condensed matter group, University of Wuppertal) for his assistance to take SEM pictures of the ceramic tube. We thank Agroisolab, Jülich, Germany, for their measurements of δD values in the VOC by elemental analysis.

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Table 1. Compounds contained in the VOC standard, volumes of the liquids injected into the gas cylinder and final mixing ratios. For comparison the hydrogen isotope ratios and standard deviations obtained by our GC-P-IRMS as well as the results of EA (Agroisolab) of the pure liquids are shown.

Compounds	volume in 10^{-3} mL	mixing ratio in ppb	δD in ‰	Agroisolab
Methanol	2.99	n/a		-123.2 ± 0.7
Acetone	5.42	n/a		-130.4 ± 1.2
n-Pentane	6.73	306 ± 19	-139.7 ± 7.6	-146.6 ± 1.3
n-Heptane	9.35	406 ± 34	-103.2 ± 2.1	-98.4 ± 1.1
Benzene	7.29	523 ± 41		-113.0 ± 1.0
Toluene	8.60	508 ± 42	-69.7 ± 2.5	-68.9 ± 0.5
1,2,4-Trimethylbenzene	11.21	373 ± 58	-43.1 ± 5.4	-64.0 ± 0.5
4-Methyl-2-pentanone	9.35	n/a	-186.5 ± 8.7	-178.1 ± 1.2
Xylenes + Ethylbenzene ^a	9.91			-83.8 ± 1.1
m/p-xylene		263 ± 15	-87.6 ± 2.2	
o-xylene		104 ± 11	-26.1 ± 12	
Ethylbenzene		92 ± 8	-46.9 ± 7.1	
Pentanal	8.04	n/a		-127.8 ± 0.7
Isoprene	6.36	401 ± 24	-123.1 ± 5.4	-102.8 ± 0.9
Propanal	5.42	n/a		-123.6 ± 0.9
Hexanal	9.35	n/a		-51.4 ± 0.7
n-octane	10.66	401 ± 24	-117.4 ± 1.3	-116.2 ± 0.9

^a Xylenes and ethylbenzene are one liquid mixture and thus only one δD value can be measured by EA.

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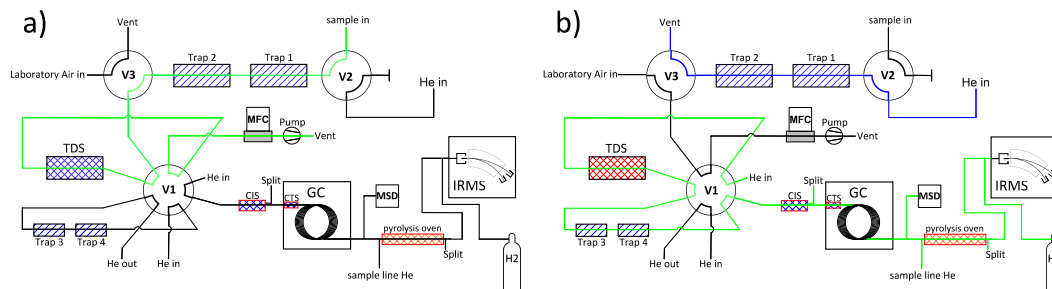


Figure 1. Schematic of the measurement system in enrichment mode (panel **a**): The sample volume is drawn through Traps 1 + 2 (reduction of water) and TDS, where the VOC are trapped. Sample gas stream is represented by the green line. System in transfer mode (panel **b**): The sample is desorbed from TDS through traps 3+4 (water reduction) to CIS and CTS for cryogenic focussing. After desorption from the CTS the VOC are chromatographically separated and detected in the MSD as well as in the IRMS after passing the pyrolysis oven. The sample gas stream is represented as green line, whereas the blue line shows a helium flow for purging the TDS and traps 1 + 2 after desorption. See text for more detail.

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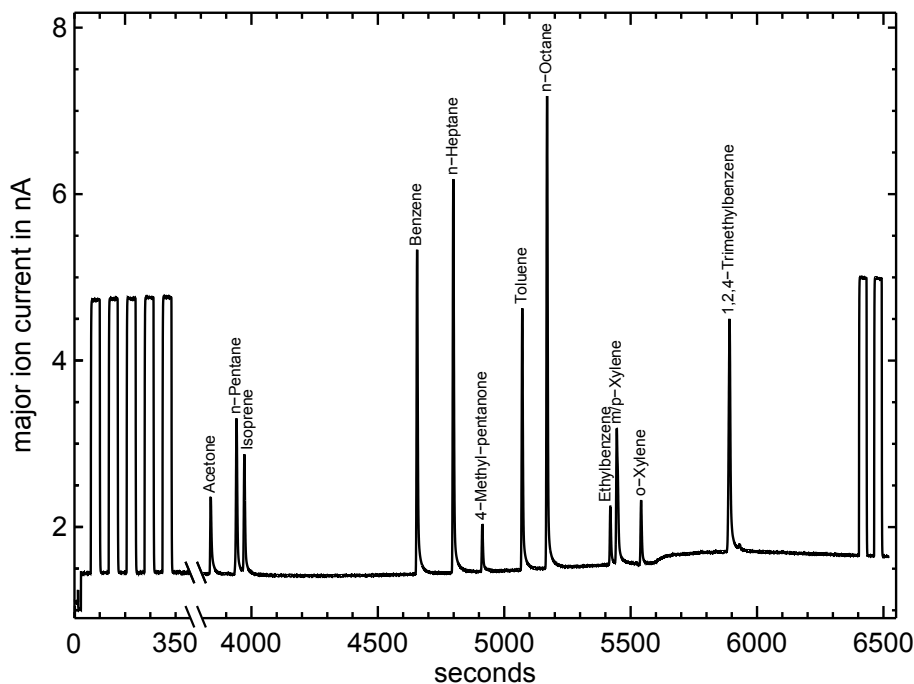


Figure 2. Example of an IRMS chromatogram (mass 2) of the VOC standard. Reference gas peaks are added at the beginning (5) and the end (2) of every chromatogram.

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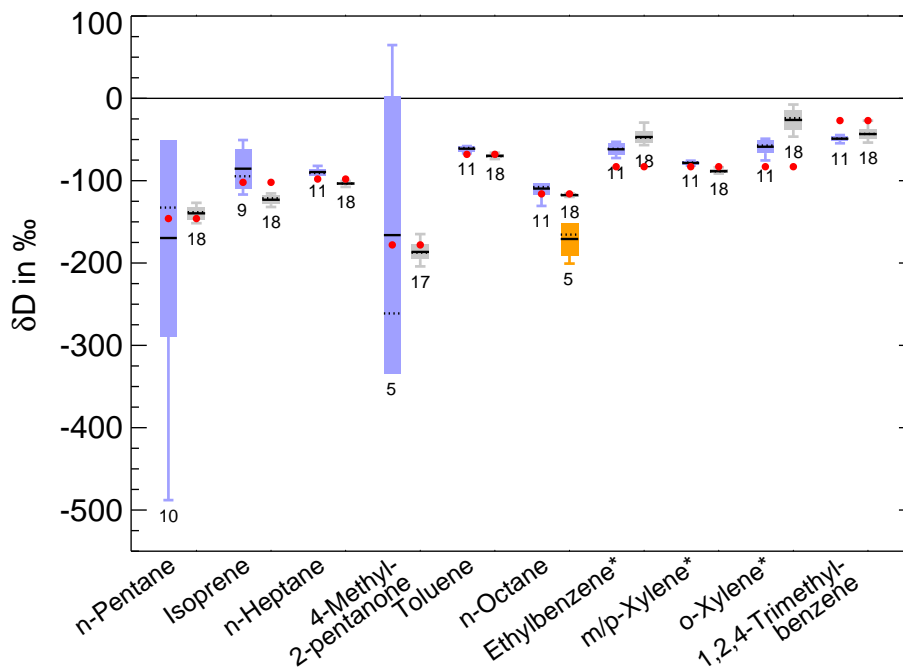


Figure 3. Compound-specific δD in different VOC adsorbed on glass-beads (blue boxes) and Tenax[®]TA (grey boxes), respectively. The size of each box represents the standard deviation, minimum and maximum values are indicated by the whiskers, solid and dashed black lines mark the mean and median value, respectively. The numbers below the boxes indicate the corresponding number of measurements. The values obtained by Agrosolab are represented as red dots. The orange box represents the mean value and standard deviation of δD of n-octane measured while a degrading of the conditioning of the ceramic tube in the pyrolysis oven is observed (see Sect. 3.3.1). *not comparable to the results of Agrosolab, see text for more detail.

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T. Meisehen et al.

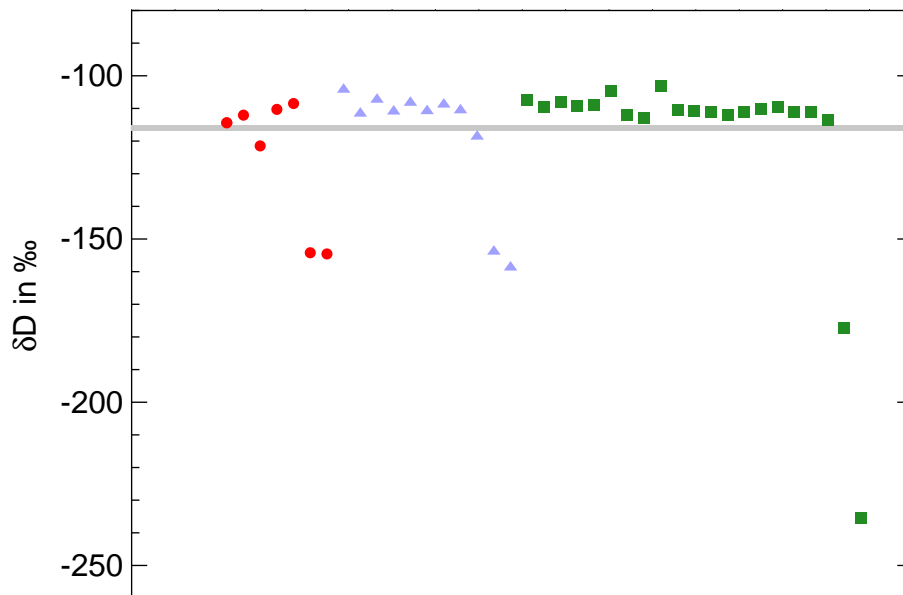


Figure 4. A “step” in δD values was apparent after 6 measurements, when the ceramic tube was conditioned for 5 min, after 10 measurements, when conditioned for 10 min and after 20 measurements, when conditioned for 20 min. The measurements after conditioning for 5 min are represented by red dots, measurements after conditioning for 10 min by blue triangles and measurements after 20 min by green squares. The grey bar shows the value obtained by EA (Agroisolab), where the thickness of the bar is equal to the uncertainty given by Agroisolab. This effect is observed for all measured substances and shown here for n-octane as an example.

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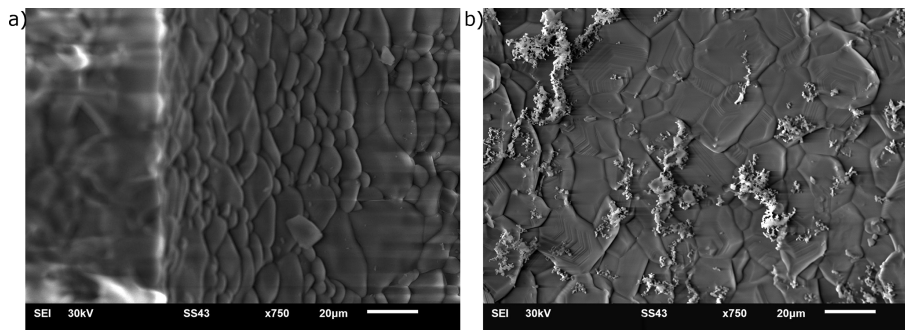


Figure 5. Scanning Electron Microscope (SEM) pictures of the inner surface of a ceramic tube at two different positions. **(a)** shows a part located outside of the hot area, where the typical structure of Al_2O_3 (ceramic) can be seen. **(b)** shows a part located inside the hot area (1723 K), where the ceramic is obviously partly covered with structures that might originate from carbon. Both pictures are taken with a magnification of 750.

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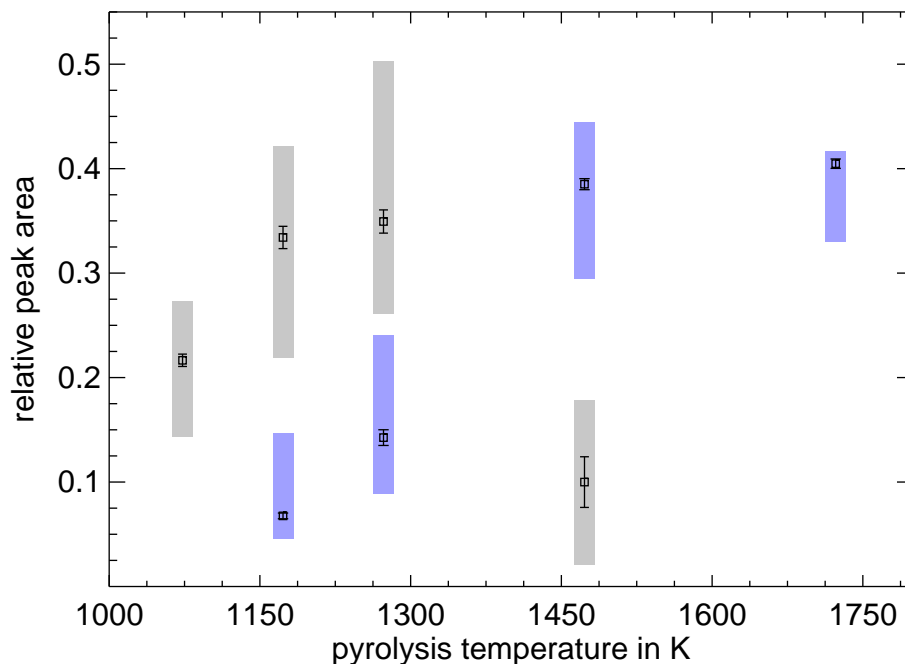


Figure 6. H_2 (blue bars) and CH_4 (grey bars) signals measured with the IRMS are shown in relative units for different pyrolysis temperatures. The bars represent results for all measured compounds including standard deviations. As an example results of n-octane are shown by black squares including standard deviation (error bars).

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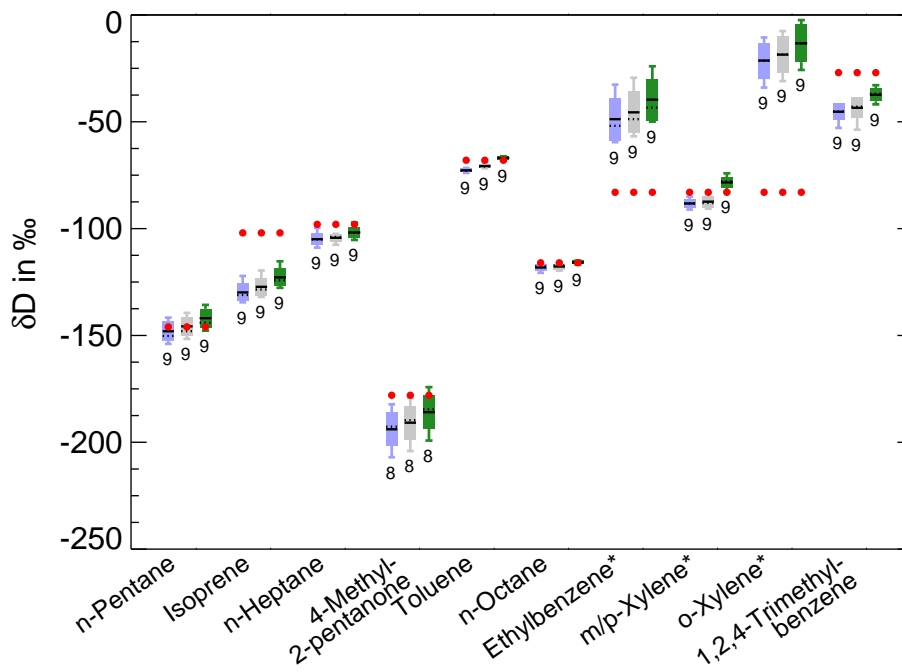


Figure 7. The same measurement series was analysed three times using H_3^+ factors of 5.0 (grey boxes), 5.3 (blue boxes) and 5.8 (green boxes). For comparison the results of EA (Agroisolab) are presented as red dots. The whisker plot is as in Fig. 3.*not comparable to the results of Agroisolab, see text for more detail.

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