



**A method for stable carbon isotope ratio and concentration measurements**

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# A method for stable carbon isotope ratio and concentration measurements of ambient aromatic hydrocarbons

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## Abstract

A technique for compound specific analysis of stable carbon isotope ratios and concentration of ambient volatile organic compounds (VOC) is presented. It is based on selective VOC sampling onto adsorbent filled cartridges by passing large volumes of air (up to 80 L) through the cartridge. The hydrocarbons are recovered by thermal desorption followed by two step cryogenic trapping and then are separated by gas chromatography in the laboratory. Once separated, individual VOC are subjected to online oxidation in a combustion interface and isotope ratio analysis by isotope ratio mass spectrometry. The method allows measurements of stable carbon isotope ratios of ambient aromatic VOC present in low pptV to ppbV levels with an accuracy of typically better than 0.5%. The precision of concentration measurements is better than 10%. Examples of measurements conducted as part of a joint Environment Canada-York University (EC-YU) measurement campaign at a semi-rural location demonstrate that the ability to make accurate measurements in air with low VOC mixing ratios is important to avoid bias from an over-representation of samples that are strongly impacted by recent emissions.

## 1 Introduction

Volatile Organic Compounds (VOC) comprise an important class of atmospheric pollutants emitted in large quantities from anthropogenic and biogenic sources (Atkinson, 2000; Guenther et al., 2000; Niedojadlo et al., 2008; Piccot et al., 1992; Rudolph, 2002; Sawyer et al., 2000). While their atmospheric mixing ratios are mostly in the ranges of pptV to ppbV, these compounds play an important role in tropospheric chemical processes (Atkinson, 2000; Jordan, 2009; Kleinman et al., 2003). Aromatic VOC are important constituents of urban and rural air masses (Forstener et al., 1997; Lurmann and Main, 1992). These compounds, mostly originating from fossil fuel use, are found in evaporated gasoline, fuels and solvents, vehicle exhaust and many

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5 other anthropogenic-related emissions (Hurley et al., 2001; Jang and Kamens, 2001; Reimann and Lewis, 2007). A large fraction of urban VOC are composed of aromatic compounds, up to 60 to 75 % of which are benzene, toluene, ethylbenzene, and 1,2,4-trimethylbenzene (Jang and Kamens, 2001; Smith et al., 1998). The atmospheric oxidation of these aromatics by reaction with OH and NO<sub>3</sub> can result in formation of ozone as well as oxygenated and nitrated products that can contribute to the formation of secondary organic aerosol (SOA) (Forstener and Flagan, 1997; Jang and Kamens, 2001).

10 In the atmosphere, VOC undergo various chemical and physical processes that lead to their transformation, removal, transport and re-distribution (Atkinson, 2000; Helmig et al., 2008; Jenkin and Clemitshaw, 2000; Parrish et al., 2007). The majority of the presently used methods use concentration measurements as an indicator of photochemical processing of VOC. However, since mixing of air parcels of different origin is a complex and dynamic process, use of concentration alone as a marker for photochemical processing is problematic (Parrish et al., 2007). The interpretation of the results is quite challenging due to the complexity of atmospheric processing and mixing, and thus many conclusions are made based on a substantial number of assumptions (de Gouw et al., 2005; Gelencsér et al., 1997; Jobson et al., 1998). The change in relative composition of the ambient samples is considered to be a better indicator of chemical processing, since the concentration ratios are less affected by physical mixing and dilution (Honrath et al., 2008; Kleinman et al., 2003; McKeen and Liu, 1993; McKeen et al., 1996; Parrish et al., 2007; Roberts et al., 1984; Rudolph and Johnen, 1990), but still requires several assumptions about the history of the studied air mass. It was recently shown that the use of the stable carbon isotope ratios of VOC requires very few and easily tested assumptions and therefore is more useful in providing insights into photochemical transformation and mixing of VOC in ambient air (Goldstein and Shaw, 2003; Roberts et al., 1984; Rudolph and Czuba, 2000; Rudolph et al., 2002, 2003; Rudolph, 2007; Stein and Rudolph, 2007).



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measuring VOC at ppbV and high pptV mixing ratios such as for source studies or polluted areas (Czapiewski et al., 2002; Redeker et al., 2007; Rudolph et al., 1997, 2002; Saito et al., 2002). However, collecting whole air samples with the large volumes required for measurement of isotope ratios for VOC mixing ratios well below one ppbV is technically challenging (Wintel et al., 2013).

Cryogenic sampling has been used to collect VOC from very large volumes of air (Bill et al., 2004; Iannone et al., 2007; Zuiderweg et al., 2011) but the technical and logistical challenges for field sampling are substantial. Selective sampling on adsorbent cartridges is a widely used inexpensive method for measurement of VOC concentrations and has recently been applied to collect VOC samples for isotope ratio analysis (Eckstaedt et al., 2011, 2012). However, this sampling technique suffered from substantial sample breakthrough problems for volumes exceeding 3 L. Although it was shown that breakthrough did not significantly impact isotope ratios, the relatively low breakthrough volume substantially restricts the useable sample volume. Furthermore, breakthrough would seriously affect the ability to measure concentrations and isotope ratios in the same sample.

In this article a method for the sampling and isotope ratio analysis of ambient VOC from large air volumes is presented. It is based on selective sampling of atmospheric compounds onto cartridges filled with an adsorbent (Carboxene 569). Thermal desorption of VOC from the cartridges is followed by two-step cryogenic trapping, separation by GC and online analysis by IRMS. Various validation tests were conducted and the results will be discussed. A brief overview of results from measurements at two locations with different levels of atmospheric pollution will be given.



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between 10 and 50 mL min<sup>-1</sup>, depending on the required sampling time and volume. Typically the sampled air volume ranged from 30 to 50 L. For sampling under conditions of very high humidity, a stainless steel water trap was added to the sampling line. The water trap was cooled by a Portable Ice Machine (Polar by Greenway, USA) to approximately 290 K. Condensed water was removed from the trap at regular intervals, depending on sampling flow rate and ambient humidity, using a removable plug at the bottom of the trap.

Trapping efficiency of Carboxene 569 was tested by sampling ambient air through two cartridges connected in series. Stability of VOC sampled on cartridges was tested by loading cartridges with test mixtures and analyzing them after storage at room temperature or in the freezer.

## 2.3 Sample processing

### 2.3.1 VOC desorption

VOC were extracted from the cartridges by thermal desorption. The cartridge was connected to a helium supply line on one end and to a preconcentration system on the other by 1/16" OD heated SS tubing. During desorption the cartridge was placed in the center of a temperature controlled 30 cm long ceramic furnace (Omega, USA). Standard conditions for cartridge analysis were 555 K for 40 min with a carrier gas flow rate between 60 and 80 mL min<sup>-1</sup>. A range of conditions were tested to identify optimum conditions. The flow rate of the carrier gas was varied from 30 to 100 mL min<sup>-1</sup>, the desorption temperature from 523 to 623 K, and the desorption time from 10 to 50 min.

### 2.3.2 Two stage preconcentration

Desorbed VOC were cryogenically trapped from the helium gas flow using a custom build two-stage preconcentration system (TSPS) (Fig. 1). It contained two cryogenic



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analysis the oven temperature was raised to 473 K and kept at this temperature for ten to twenty minutes. Helium was used as carrier gas with the flow rate controlled by an electronic pressure controller (EPC) at approximately  $2 \text{ mL min}^{-1}$ . Once separated in the GC column, the column effluent was directed either to the FID or the combustion interface by opening or closing a pneumatic valve as shown in Fig. 1.

The combustion interface consisted of a  $1/4''$  ceramic tube (0.5 mm ID, 44 cm length) with copper, nickel and platinum wires inside. Helium containing traces of oxygen was added as a makeup gas at the inlet of the furnace to prevent peak tailing and to provide oxygen. During analysis the interface was kept at 1223 K, and CuO and NiO formed on the wire surfaces converted VOC into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The oxide layers on the Cu and Ni wires were regenerated every night by flushing the furnace and adjacent tubing with the He- $\text{O}_2$  mixture while reducing the interface temperature to 823 K. A flow restrictor split (Fig. 1) was used in an open split configuration to direct between 10 and 20 % of the flow through a Nafion Dryer (25 cm, 0.6 mm ID, 0.8 mm OD) into the IRMS.

### 2.4 Isotope ratio mass spectrometry and $\delta^{13}\text{C}$ determination

$\text{CO}_2$  was analysed by IRMS (GV Instruments, Manchester, UK) by detection of  $m/z$  44, 45 and 46. The isotope ratios  $^{45}\text{R}$  and  $^{46}\text{R}$  were determined from the peak areas (A) for the individual  $m/z$  ratios as described by Rudolph (2007):  $^{45}\text{R} = \frac{A[^{45}\text{CO}_2]}{A[^{44}\text{CO}_2]}$  and  $^{46}\text{R} = \frac{A[^{46}\text{CO}_2]}{A[^{44}\text{CO}_2]}$ .  $^{46}\text{R}$  was used for correction of the  $^{45}\text{R}$  for the contribution from  $^{12}\text{C}^{16}\text{O}^{17}\text{O}$  (Craig, 1957; Santrock et al., 1985).

Peak integration was done manually using a method similar to that described by Rudolph et al. (1997). To minimize bias due to the manual definition of peak boundaries, each peak was integrated ten times with start and end points varying every time by 0.1 s. This allowed verifying that averaged delta values were not significantly biased by the choice of peak boundaries. All target VOC, except p- and m-xylene, were

completely separated. Due to their partial overlap the peaks for p- and m-xylene were integrated together.

Throughout the run, reference CO<sub>2</sub>, calibrated relative to the V-PDB (Vienna Peedee Belemnite) standard was introduced several times directly into the IRMS in pulses of 20 to 40 s duration. Between three and five reference gas injections were made while the pneumatic valve was open and the flow from the GC column was directed to the FID at the beginning and at the end of each run. Between four and seven injections were made between peaks during the chromatographic separation while the flow from the GC column was directed to the combustion interface and IRMS.

## 2.5 Validation tests

Gaseous test mixtures of target VOC were prepared in stainless steel canisters with VOC mixing ratios in the ppbV to ppmV range by injecting known quantities of pure VOC and diluting with helium. The VOC concentration in these test mixtures ranged from 0.1 ngcm<sup>-3</sup> to 0.7 µgcm<sup>-3</sup> (15 ppbV to 1.7 ppmV). All mixtures were quantified using a standard mixture of VOC (ppbV levels) provided by the National Research Council of Canada (NRC). VOC used to prepare gaseous mixtures, were individually combusted at high temperatures in vacuum sealed tubes containing CuO. The resulting CO<sub>2</sub> was cryogenically separated, extracted and later analysed by IRMS, using a dual-inlet system, to determine their δ<sup>13</sup>C values. These offline isotope ratios were: benzene -28.40 ± 0.02 ‰, toluene -27.02 ± 0.07 ‰, ethylbenzene -26.84 ‰, p-xylene -25.69 ± 0.05 ‰, m-xylene -26.92 ‰ and o-xylene -28.16 ± 0.07 ‰. Standard deviations for ethylbenzene and m-xylene cannot be given since repeat measurements are not available. These mixtures were used for calibration as well as determination of the accuracy of the δ<sup>13</sup>C measurements.

A number of tests were conducted to optimize and evaluate the accuracy and reproducibility of the method. Operation conditions and instrument performance were tested weekly using mixtures with known composition and isotope ratios. Precision of the system was determined by the reproducibility of peak areas from repeat measurements

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of a wider time window for integration of the two overlapping peaks and the resulting greater impact of baseline drift and baseline noise.

For aromatic VOC offline and online values usually agreed for masses of more than 3 to 5 ng compound<sup>-1</sup> within the uncertainty of the measurements (Fig. 3), however there was a significant bias towards lower delta values for smaller masses. For alkanes a significant difference between offline and online data was observed, even though both offline and online tests displayed good reproducibility, with uncertainties well below the observed difference. One possibility is isotopic fractionation of n-alkanes that might have taken place inside the stainless steel canisters where the mixtures were stored. Since <sup>12</sup>C containing molecules are more reactive compared to <sup>13</sup>C molecules, it is expected that any loss of n-alkanes with time will result in enrichment of <sup>13</sup>C. Another possible explanation for the bias between offline and online is incomplete oxidation during offline combustion. This also would result in a decrease of the isotope ratio in the CO<sub>2</sub> formed, since <sup>12</sup>C containing VOC will oxidize more readily than <sup>13</sup>C containing VOC. Aromatic VOC are more readily oxidized than n-alkanes, therefore incomplete oxidation will be less likely to be relevant for benzene and alkylbenzenes. Incomplete oxidation in the combustion interface is a less likely reason for the discrepancy between online and offline  $\delta^{13}\text{C}$  for n-alkanes. Incomplete combustion in the interface should result in <sup>13</sup>C depletion in the formed CO<sub>2</sub>, which was not observed. Furthermore, the very good reproducibility of both mass and  $\delta^{13}\text{C}$  measurements does not suggest any problem for the efficiency of the combustion interface.

### 3.2 Cartridge tests

The VOC masses observed for analysis of blank cartridges using desorption temperatures in the range of 474 to 573 K are listed in Table 1 together with their SDs and the resulting 3 $\sigma$  detection limit. For comparison, the averages of masses of VOC collected in ambient samples are also given. Tests of individual components of the cartridges showed that the main source of the blanks was Carboxene 569. Stainless steel tubes did not produce any contamination; tests of cartridges containing only quartz wool at

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noted that the results for n-hexane may be biased towards samples at the higher end of mixing ratios due to the significant number of samples for which reliable evaluation of  $\delta^{13}\text{C}$  was not possible.

Due to the relatively high sample mass needed for  $\delta^{13}\text{C}$  measurement by GC-IRMS bias due to the problem of reliable evaluation of  $\delta^{13}\text{C}$  in samples with low concentrations is a potentially significant problem. To evaluate this in more detail, we use results for aromatic VOC where between 80 and 90% of the samples could be analysed for  $\delta^{13}\text{C}$ . Figure 7 shows the dependence between measured  $\delta^{13}\text{C}$  and concentration for benzene and p, m-xylene. Compared to the  $\delta^{13}\text{C}$  values of emissions, the samples are enriched in  $\delta^{13}\text{C}$  to various degrees. The number of samples substantially enriched in  $\delta^{13}\text{C}$  is higher at low mixing ratios than at high mixing ratios. Although no statistically significant overall trend can be determined due to the substantial seemingly random variability of the data, the mean  $\delta^{13}\text{C}$  value for the lowest ten concentrations is  $-23.1 \pm 0.1\text{‰}$  (error of mean) for benzene and  $-22.9 \pm 0.9\text{‰}$  for p, m-xylene, which indicates a substantial difference to the average for all measurements, which is  $-25.2 \pm 0.1\text{‰}$  and  $-25.4 \pm 0.5\text{‰}$  for benzene and toluene, respectively. This is a strong indication that limitations in making precise  $\delta^{13}\text{C}$  measurements at very low mixing ratios can bias the average measured  $\delta^{13}\text{C}$  towards lower values. The origin of such bias is easily understood, air with higher mixing ratios of VOC is more likely to have been subjected to significant recent emissions than clean air.

### 3.4 Comparison with existing methods

Due to the complexity of the existing methods used for sampling and measurements of stable carbon isotope compositions of ambient VOC, the number of publications on method development and ambient measurements and their interpretation is still quite limited. An overview of existing methods has been given in a recent paper by Gen-  
sch et al. (2014). All methods for ambient measurements and emission studies use GC-IRMS for analysis of sampled VOC, although often details of the chromatographic separation and combustion interface differ. The main difference between the meth-

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ily provide samples that are integrated over long time periods. For example, our study at Egbert used 24 h sampling periods, which allows determination of representative averages without the necessity to collect and analyse an extremely large number of samples. Finally, adsorptive sampling is not suitable for collection of VOC with very high volatility such as C<sub>2</sub> or C<sub>3</sub> hydrocarbons.

The reproducibility of isotope ratio measurements for our newly developed method is better than 0.5‰, similar to that of other state-of-the-art methods for measurement of δ<sup>13</sup>C in ambient VOC (Czapiewski et al., 2002; Eckstaedt et al., 2012; Kawashima and Murakami, 2014; Rudolph et al., 1997; Saito et al., 2009; Turner et al., 2006; Wintel et al., 2013), however the lower limit of concentrations for which this precision can be achieved is significantly lower than that achieved by these other methods.

Tests of accuracy for δ<sup>13</sup>C measurements of aromatic VOC demonstrate that there is no detectable bias, similar to the findings in several other studies (Czapiewski et al., 2002; Eckstaedt et al., 2012; Rudolph et al., 1997; Saito et al., 2009). However, for n-alkanes the GC-IRMS results differ from the offline values for bulk material used to prepare test mixtures by approximately 2‰. Unfortunately there are not many published tests of the accuracy of δ<sup>13</sup>C measurements for C<sub>6</sub> and heavier n-alkanes in air. Rudolph (2007) summarized results from similar sets of comparisons, which included a wide range of n-alkanes and concluded that in most cases offline and online δ<sup>13</sup>C values agree within the uncertainty of the GC-IRMS measurement. However, in a few cases differences in the range of 1‰ were observed, although these differences were statistically not significant.

#### 4 Summary and conclusions

The newly developed method for analysis of atmospheric VOC allows measurement of δ<sup>13</sup>C of light aromatic hydrocarbons with an accuracy and precision of better than 0.5‰ for mixing ratios in the lowest pptV range. For n-alkanes a similar precision could be achieved, but a systematic bias of up to 2‰ is possible. The precision of con-

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centration measurements is estimated to be better than 10%. Sampling is done with inexpensive equipment suitable for field work and samples can be stored for more than one week under ambient conditions and at least six months in a freezer without detectable sample degradation. This allows transport and storage of samples with little logistic effort. Overall, these performance characteristics are a significant improvement over that of other currently available methods.

The methodology has been specifically developed and tested for the purpose of accurate measurement of light aromatic hydrocarbons, but this does not exclude its use for analysis of other VOC. Tests demonstrated that breakthrough of heavier than C<sub>5</sub> VOC is negligible for up to 80 L of air, but since no tests have been conducted for larger volumes, collection of VOC from even larger volumes may be possible with no or little modification of the sampling cartridges.

The measurements conducted over a semi-rural area demonstrate the importance of accurate measurements at low mixing ratios to avoid bias and lack of representativeness of the measurements. Higher mixing ratios often are the result of substantial impact of nearby sources and therefore have carbon isotope ratios close to the isotopic composition of emissions. Inability to measure  $\delta^{13}\text{C}$  for VOC at low mixing ratios therefore will bias the  $\delta^{13}\text{C}$  observations towards the source composition and therefore underestimate the role of chemical processing, which results in enrichment of  $^{13}\text{C}$ .

Overall, the simplicity and affordability of the developed sampling and sample processing system is a valuable step towards the possibility of a wider application of stable carbon isotope measurements in studies of ambient VOC. However, it should be noted that GC-IRMS instrumentation is still demanding and expensive. Nevertheless, due to the option to collect VOC from large volumes of air that results in larger sample masses, the need for highly sensitive GC-IRMS instrumentation might not be critical. This is an important step towards establishing VOC isotope ratio measurements as a standard technique in atmospheric chemistry.

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**Table 1.** Averages of background signals for cartridges containing ( $1 \pm 0.2$ ) g of carboxene and 0.2 to 0.5 g of quartz wool.

Compound	Blank $\pm$ SD <sup>a</sup> (ng)	DL <sup>b</sup> (ng)	Average mass per ambient cartridge (ng) <sup>c</sup>
n-Hexane	$0.2 \pm 0.3$	1.0	146
Benzene	$0.7 \pm 0.5$	1.5	16
n-Heptane	$1.1 \pm 0.1$	0.3	64
Toluene	$0.2 \pm 0.1$	0.4	61
Ethylbenzene	$0.2 \pm 0.2$	0.6	7
p, m-Xylene	$0.2 \pm 0.2$	0.5	17
o-Xylene	$0.2 \pm 0.1$	0.4	5

<sup>a</sup> SD: SD calculated from at least 4 repeat measurements.

<sup>b</sup>  $3\sigma$  detection limit (DL).

<sup>c</sup> average calculated from 50 ambient samples.

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**Table 2.** Recoveries of VOC (%) under different desorption conditions (samples were analysed with GC-FID or GC-IRMS)\*.

Test#	1	2	3	4	5	6	7	8
Duration (min)	15	15	15	20	25	30	30	40
Temperature (K)	523	553	573	673	573	573	583	553
Flow rate (mL/min)	55	53	54	78	58	58	53	60
n-Hexane	70	107	164	102	106	104	102	102
Benzene	73	105	148	104	106	105	108	113
n-Heptane	39	93	102	99	96	97	96	100
Toluene	43	96	110	103	100	100	102	103
Ethylbenzene	29	74	77	86	87	86	87	90
p, m-Xylene	24	65	67	82	90	87	97	95
o-Xylene	25	68	64	81	85	84	92	94

\* Results are based on one measurement.

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**Table 3.** Average recoveries<sup>a</sup> of VOC sampled on cartridges for desorption at 553 K for 40 min at (60 to 80) mL min<sup>-1</sup> carrier gas flow rate.

Compounds	Mass of loaded VOC (ng)	Average Recovery <sup>b</sup> ±SD (%)	SD of delta values (‰)
Benzene	25	112 ± 2	0.6
Heptane	50	93 ± 9	0.7
Toluene	60	102 ± 14	0.6
Ethylbenzene	50	84 ± 13	0.3
p, m-Xylene	75	99 ± 20	0.6
o-Xylene	35	94 ± 5	0.5

<sup>a</sup> Values were not blank corrected.

<sup>b</sup> Based on 3 to 4 measurements.

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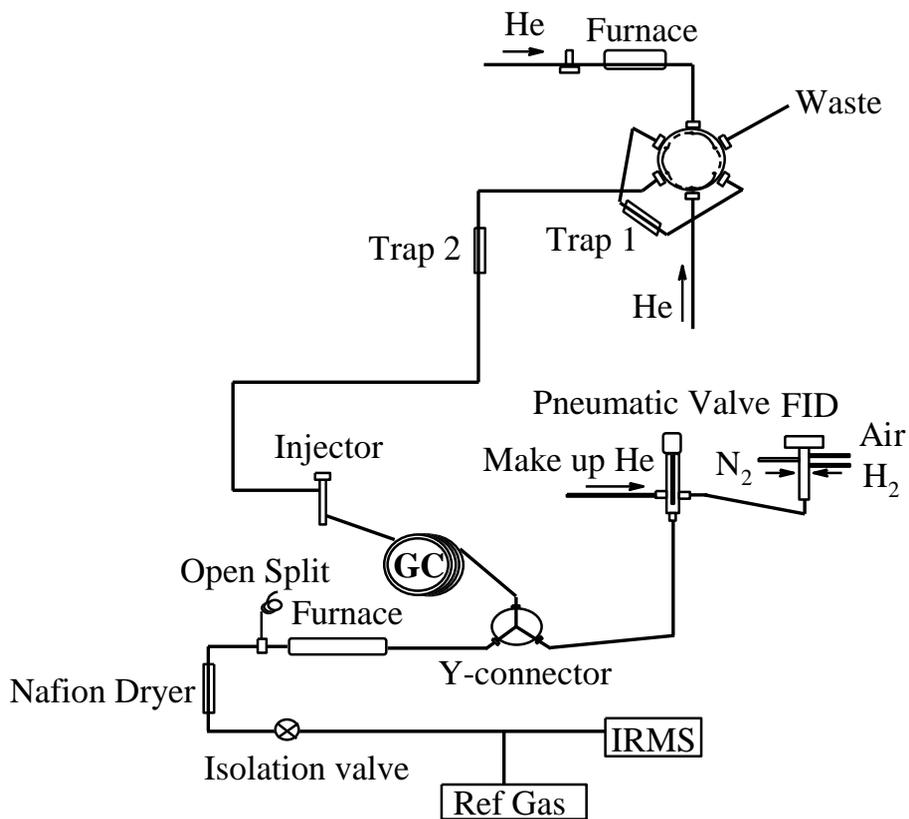
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**Figure 1.** Schematic diagram of the Two Stage Preconcentration System (TSPS).

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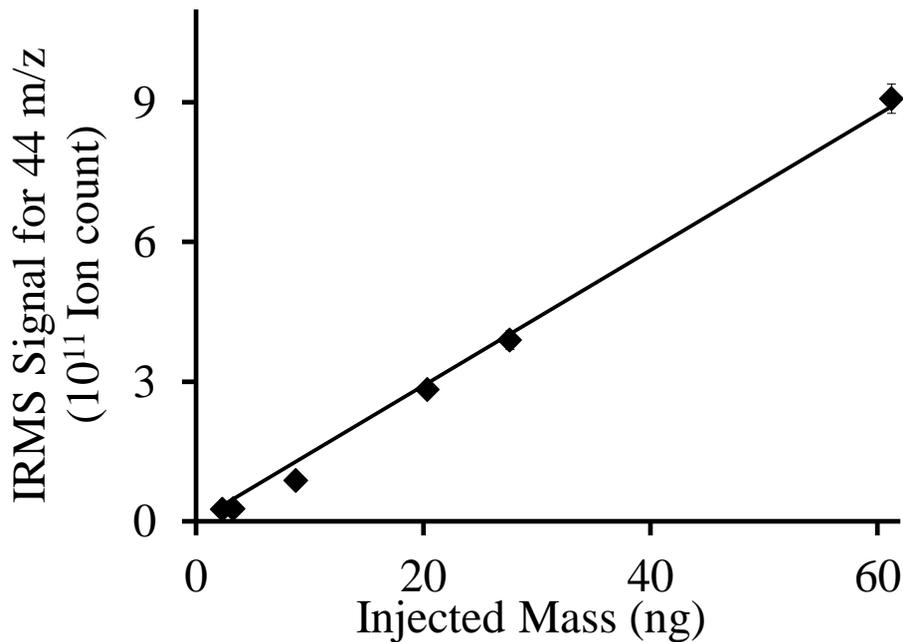
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**Figure 2.** Calibration curve for toluene (based on TSPS-GC-IRMS measurements, slope =  $1.46 \times 10^{10} \pm 0.03 \times 10^{10}$  ions  $\text{ng}^{-1}$ ,  $R^2 = 0.997$ ).

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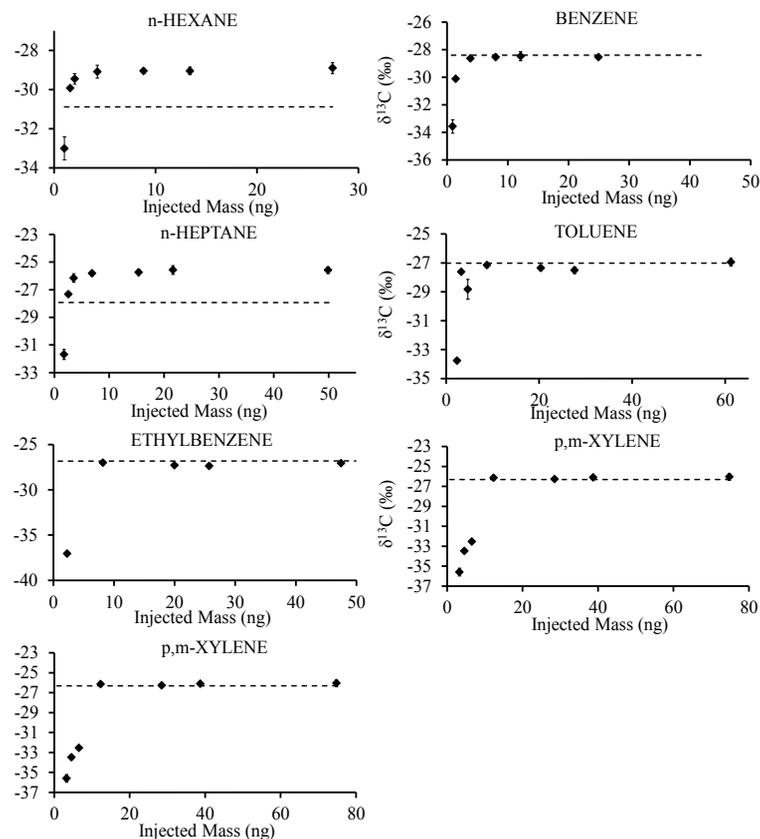
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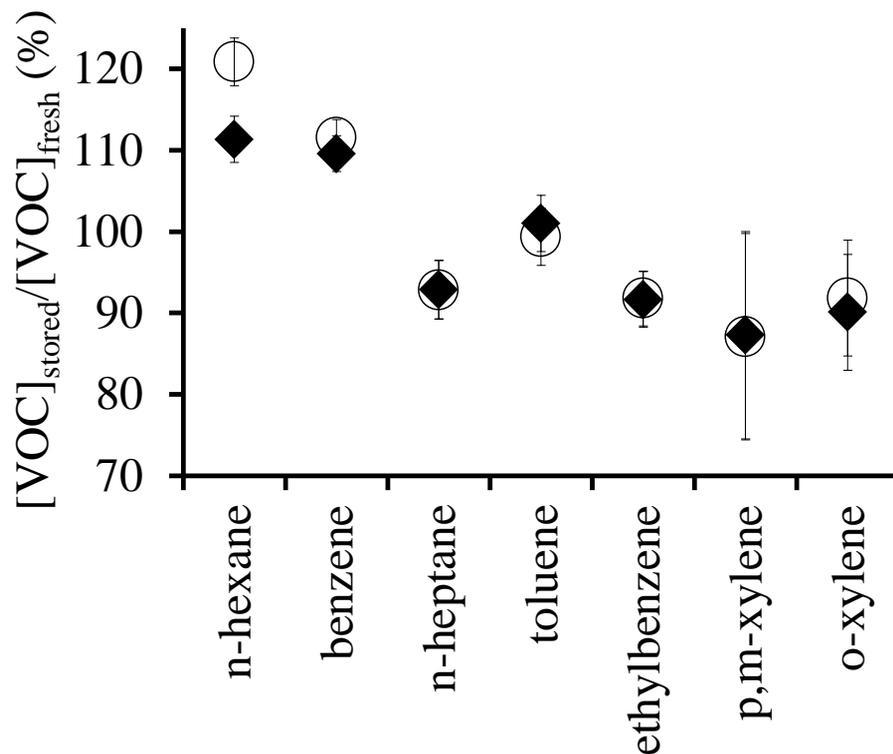
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**Figure 3.** Plot of  $\delta^{13}\text{C}$  values vs. injected mass measured online using TSPS-GC-IRMS. Dashed lines are the reference (offline)  $\delta^{13}\text{C}$  values. For p, m-xylene the average of the p-xylene and m-xylene offline values is given since the mixtures contained equal masses of both xylenes.

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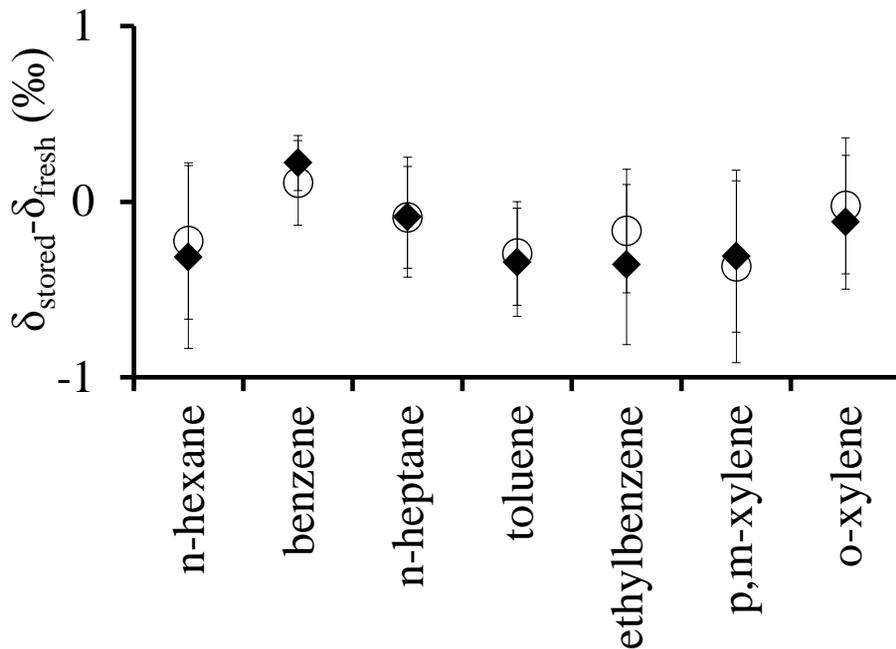
**Figure 4.** Impact of storage on sample recovery for storage of 1 to 2 weeks at ambient temperatures and 6 to 7 months in a freezer. The recovered masses are given relative to samples analysed immediately after sampling. Values used are the average of 3 to 4 measurements. Masses loaded range from 25 to 75 ng. Values were not corrected for blanks.

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**Figure 5.** Change in  $\delta^{13}\text{C}$  of VOC collected on cartridges during storage for 1 to 2 weeks at ambient temperatures and 6 to 7 months in a freezer. The differences are given relative to the  $\delta^{13}\text{C}$  values of samples analysed without storage. Values used are the average of 3 to 4 measurements.

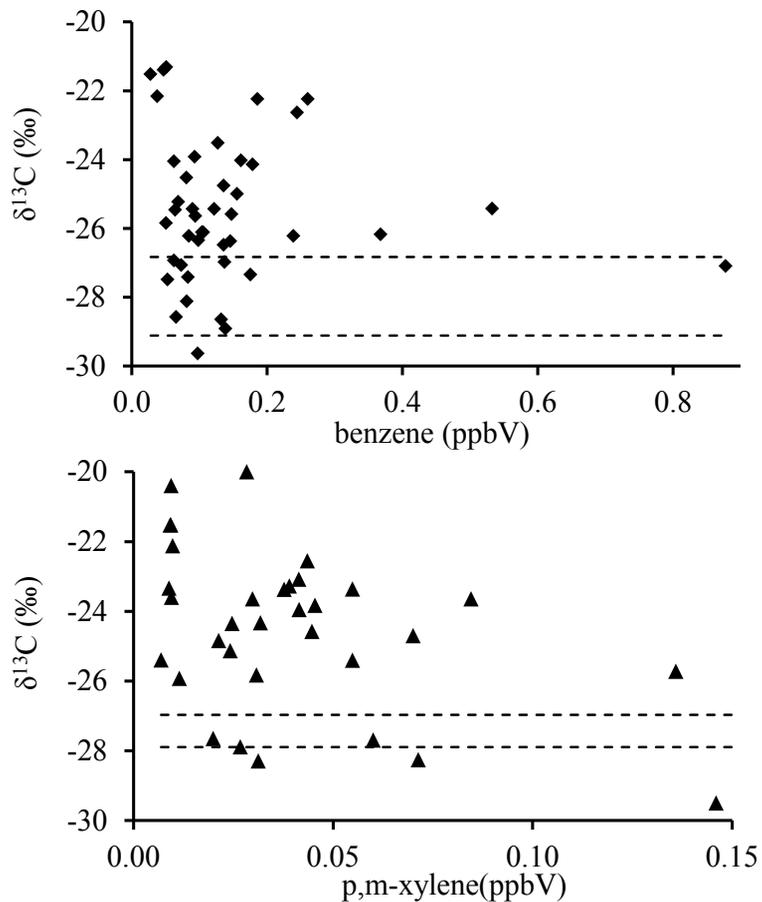
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**Figure 7.** Mixing ratio vs. stable carbon isotope ratio plots for samples collected at Egbert. The range (average  $\pm \sigma$ ) of isotope ratios reported by Rudolph et al. (2002) for urban sources are shown as dashed lines.

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