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~~ organic ~~Compounds~~ 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 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_3 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).

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 Clemitshawb, 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; Rudolph et al., 2003; Rudolph, 2007; Stein and Rudolph, 2007).

Measuring the isotope composition of VOC in the atmosphere is challenging due to the high precision and accuracy necessary to derive meaningful information. Rudolph et al. (1997) published a method for compound specific determination of the stable carbon isotopic composition for atmospheric VOC at sub-ppbV levels. The uncertainty of measured isotope ratios was close to 0.5 ‰, and Rudolph et al. (1997) suggested that further improvements in method may allow a precision close to 0.1 ‰. Within several years different research groups published results of stable carbon isotope measurements for a variety of atmospheric VOC (Anderson et al., 2004; Czapiewski et al., 2002; Iannone et al., 2003; Iannone et al., 2005; Irei et al., 2006; Norman et al., 1999; Rogers and Savard, 1999; Rudolph et al., 2002; Rudolph et al., 2003; Smallwood et al., 2002; Thompson et al., 2003). Nevertheless, the number of publications on isotopic composition measurements and their application is still quite limited due to the need for elaborate and expensive experimental techniques and challenging data interpretation (Eckstaedt et al., 2011; Fisseha et al., 2009; Giebel et al., 2010; Iannone et al., 2005; Iannone et al., 2009, 2010; Irei et al., 2006; Li et al., 2010; Moukhtar et al., 2011). An overview of existing techniques to measure stable carbon isotope ratios of VOC is given in a recent paper (Gensch et al., 2014).

Most of the online techniques used for measurements of the stable carbon isotope composition include a combination of a combustion interface (CI), a gas chromatograph (GC) and an isotope ratio mass spectrometer (IRMS) (Matthews and Hayes, 1978). In addition, for

gaseous compounds, sample purification, pre-concentration and separation steps are frequently added (Anderson et al., 2003; Czapiewski et al., 2002; Rudolph et al., 2002; Iannone et al., 2007; Iannone et al., 2010; Redeker et al., 2007). While VOC analysis by GC-IRMS is well established, collection of ambient VOC for the isotope analysis is challenging. One of the requirements for accurate GC-IRMS measurements is sufficient mass, which is usually 3 ng to 5 ng of carbon for each analysed VOC (Goldstein and Shaw, 2003; Rudolph, 2007; Thompson, 2003). Consequently, compounds that are present at low pptV levels need to be extracted from 30 L of air or more. Many of the currently reported stable carbon isotope ratio data for ambient VOC were obtained using whole air sampling in stainless steel canisters, which is adequate when 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; Rudolph et al., 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;Eckstaedt et al., 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.

2. Materials and method

2.1 Overview

Ambient VOC were analysed for concentration and isotope ratios ($\delta^{13}C$) using the following steps (1) collection onto adsorbent packed cartridges, (2) thermal desorption of VOC in a furnace at 553 K in a flow of high purity helium, (3) a two-stage preconcentration, (4)

chromatographic separation, (5) combustion to CO_2 and H_2O in a furnace at 1173 K, (6) analysis of the CO_2 isotopologues by Isotope Ratio Mass Spectrometry (IRMS).

2.2 Sampling

Selective VOC sampling from volumes between 20 L and 80 L of ambient air was done on adsorbent filled cartridges. The cartridges were made by filling stainless steel tubes of 13 cm to 15 cm in length and 1/4" OD (approximately 5 mm ID) (Swagelok, Canada), with 1 g (±0.2 g) of Carboxene 569 (Supelco Inc., Bellefonte, USA). To keep the adsorbent in place both ends were plugged with 0.3 g (±0.1 g) of quartz wool (Restek, USA). Both ends of the tubes were equipped with 1/4" stainless steel Swagelok nuts, which were closed with 1/4" stainless steel caps during storage and transportation.

Cartridges were cleaned at temperatures between 523 K and 573 K in a furnace while continuously purging them with a flow of 160 mL min^{-1} to 200 mL min^{-1} of pure helium for at least 24 hours. Used cartridges were cleaned for 12 hours to 24 hours. Cleaned cartridges were capped and stored at room temperature in closed glass containers. Some of the cleaned cartridges were analysed without sampling to determine blank values, as well as the influence of storage, transport and possible material degradation during use.

For sampling, one end of the sampling cartridge was connected to a 1/4" OD stainless steel inlet line (Swagelok, Canada) and the other end to a mass flow controller with a flow totalizer, and a pump. To prevent physical damage, the sampling equipment was placed inside a temperature controlled housing. The sampling flow rate was varied between 10 mL min^{-1} and 50 mL min^{-1}, depending on the required sampling time and volume. Typically the sampled air volume ranged from 30 L 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 mL min^{-1} and 80 mL min^{-1}. A range of conditions were tested to identify optimum conditions. The flow rate of the carrier gas was varied from 30 mL min^{-1} to 100 mL min^{-1}, the desorption temperature from 523K to 623 K, and the desorption time from 10 min 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) similar in design to the method described by Rudolph et al. (1997). It contained two cryogenic traps: one (Trap 1) is a U-shaped 1/8" OD stainless steel tube filled with glass beads (60/80 mesh, Chromatographic Specialties Inc., Canada); the other (Trap 2), consisted of a 15 cm long piece of 1/32" DB-1 capillary column placed in a 1/16" OD stainless steel tube. The GC column was connected with a Valco zero volume connector (VICI, USA) to a 1/32" stainless steel tube that was attached to a six-port valve. The heating of transfer lines and the valve were individually temperature controlled using temperature sensors (Quick disconnect thermocouple assembly with 12" and 18" length and 1/16" diameter 304 stainless steel probes (Omega, USA)) and were constantly maintained at 473 K. For cooling, Trap 1 was immersed in liquid nitrogen (10 cm to 13 cm deep), and Trap 2 was cooled by a liquid nitrogen flow that was controlled by a solenoid valve.

The two-position six-port valve was used to direct the gas and sample flow either through Trap 1 (Position A) or bypassing it (Position B). At the start of the analysis sequence the six-port valve was set to Position B and the cartridge was flushed with pure helium for five minutes. At the same time Trap 1 was cooled to 97 K. During desorption, the valve was set to Position A and desorbed VOC were transferred in a flow of helium to Trap 1, where they were adsorbed on the glass beads. At the end of this stage, Trap 2 was cooled to 97 K and the valve was rotated back to Position B, directing the GC carrier gas through rapidly heated Trap 1 (423K) to Trap 2. After seven minutes, Trap 2 was flash-heated to 493 K by applying approximately 2.5 V to the 1/16" OD stainless steel tube for seven minutes, injecting the VOC into the GC column. For testing purposes, temperatures of the traps were varied between 93 K and 123 K for trapping and 393 K and 513 K for desorption.

2.3.3 Gas chromatographic separation and VOC combustion

The separation was performed in a HP5890 Series II gas chromatograph equipped with a DB-1 column (100 m, 0.25 mm ID, 0.5 µm film thickness). The VOC were focused on the head of the column at 298 K for ten min, then the oven was heated at 2 K min^{-1} to 323 K followed by heating at 3K min^{-1} to 363 K and then at 10 K min^{-1} to 403 K. The column temperature was then maintained at 403 K for ten minutes. At the end of each analysis the oven temperature was

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

6   The combustion interface consisted of a 1/4" ceramic tube (0.5 mm ID, 44 cm length)
7 with copper, nickel and platinum wires inside. Helium containing traces of oxygen was added as
8 a makeup gas at the inlet of the furnace to prevent peak tailing and to provide oxygen. During
9 analysis the interface was kept at 1223 K, and CuO and NiO formed on the wire surfaces
10 converted VOC into CO_2 and H_2O. The oxide layers on the Cu and Ni wires were regenerated
11 every night by flushing the furnace and adjacent tubing with the He-O_2 mixture while reducing
12 the interface temperature to 823 K. A flow restrictor split (Fig. 1) was used in an open split
13 configuration to direct between 10 % and 20 % of the flow through a Nafion Dryer (25 cm, 0.6
14 mm ID, 0.8 mm OD) into the IRMS.

15

16 **2.4 Isotope ratio mass spectrometry and $\delta^{13}C$ determination**

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18   CO_2 was analysed by IRMS (GV Instruments, Manchester, UK) by detection of m/z 44,
19 45 and 46. The isotope ratios ^{45}R and ^{46}R were determined from the peak areas (A) for the

20 individual m/z ratios as described by Rudolph (2007): $^{45}R = \dfrac{A\left[^{45}CO_2\right]}{A\left[^{44}CO_2\right]}$ and $^{46}R = \dfrac{A\left[^{46}CO_2\right]}{A\left[^{44}CO_2\right]}$

21

22 ^{46}R was used for correction of the ^{45}R for the contribution from $^{12}C^{16}O^{17}O$ (Craig, 1957;
Santrock et al., 1985).

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

29   Throughout the run, reference CO_2, calibrated relative to the V-PDB (Vienna Peedee
30 Belemnite) standard was introduced several times directly into the IRMS in pulses of 20 s to 40 s
31 duration. Between three and five reference gas injections were made while the pneumatic valve
32 was open and the flow from the GC column was directed to the FID at the beginning and at the
33 end of each run. Between four and seven injections were made between peaks during the
34 chromatographic separation while the flow from the GC column was directed to the combustion
35 interface and IRMS.

36

37 **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 ng cm^{-3} to 0.7 µg cm^{-3} (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_2 was cryogenically separated, extracted and later analysed by IRMS, using a dual-inlet system, to determine their $\delta^{13}C$ 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 $\delta^{13}C$ 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 of the test mixtures. Accuracy of isotope ratio measurements was tested by comparing $\delta^{13}C$ values determined online for the test mixtures and offline for the individual VOC.

> **Comment [A1]:** *replace 'd' by 'δ'(=delta)*

3. Results and discussion

The components of the sampling and analysis system were tested under different operational conditions. Here, the most important results of the optimization and validation tests are presented and discussed.

3.1 Reproducibility, accuracy and linearity of the TSPS-GC-IRMS system

Performance assessment of the TSPS was based on injections of gaseous mixtures directly into the TSPS. On average, the relative standard deviation (RSD, %) of peak areas from repeat measurements (>10 repeats) was 5.3 %, with 4 % for alkanes and 6 % for aromatic compounds. For all targeted compounds, calibration curves were constructed with intercepts for regression set to zero, in most of the linear regression analysis the correlation coefficient (R^2 value) was >0.99. The intercept was set to zero since intercepts in linear regressions allowing non-zero intercepts did not significantly differ from zero. An example of a calibration curve is shown in Fig. 2. The sensitivity of the GC-IRMS measurements was in the range of (1.2 to 3.4) × 10^{10} ions ng^{-1} carbon.

Figure 3 shows the measured $\delta^{13}C$ values as function of sample mass for aromatic VOC and n-alkanes, also shown are the $\delta^{13}C$ values from the offline analysis of bulk VOC. The standard deviation for repeat measurements of online $\delta^{13}C$ was mostly lower than 0.3 ‰, on average 0.2 ‰ for >10 ng of alkanes and 0.3 ‰ for >1 ng of aromatics. Generally the standard deviation was lower for higher masses. For masses exceeding 5 ng, the measured $\delta^{13}C$ values were independent of sample mass, but for lower masses, the measured values systematically decreased with decreasing mass. The only exception was the combined measurement of p-xylene and m-xylene, where the decrease in measured $\delta^{13}C$ is already significant at sample masses below 10 ng. This is most likely due to the necessity 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 ng to 5 ng per compound 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.

No certified standards or equivalent internationally accepted reference mixtures suitable for tests of the accuracy of isotope ratio measurement of atmospheric VOC are available and consequently the accuracy tests had to be conducted using mixtures prepared in-house. In the case of good agreement between GC-IRMS analysis and the isotope ratio of the test mixtures this gives confidence in the accuracy of the GC-IRMS measurements. However, in case of a systematic discrepancy between off-line and GC-IRMS results this makes it difficult to identify the source of bias. While isotope fractionation during sampling on the adsorbent cartridges can be ruled out since the isotope ratios obtained from direct analysis of the test mixtures agreed with isotope ratios determined from samples of the test mixtures collected on adsorbent cartridges, uncertainty in the carbon isotope ratio of the test mixture as well as biased GC-IRMS isotope ratio measurements are possible explanations.

Error in the $\delta^{13}C$ in the test mixture can be due to loss or contamination during preparation of the mixture or error in the off-line $\delta^{13}C$ determination for the bulk n-alkanes. Since the mixtures were not prepared for the purpose of calibrating concentration measurements it is not possible to exclude or verify the existence of losses or contaminations from comparison of peak areas or calibration curves. The uncertainty of conventional dual-inlet $\delta^{13}C$ measurements in carbon dioxide is much lower than the observed discrepancy in the n-alkane carbon isotope ratios. However, incomplete oxidation of n-alkanes during the off-line combustion of the bulk n-alkanes could result in significant carbon isotope fractionation. Since n-alkanes are less reactive than benzene and alkylbenzenes, this would be consistent with the absence of bias for aromatic VOC.

Bias in the GC-IRMS analysis can be caused by contamination or losses during adsorption or desorption of VOC in the TSPS, problems in the chromatographic separation such as peak tailing or baseline drift, and incomplete oxidation in the combustion interface. A

significant impact from contamination or artifacts can be ruled out since this would result in a decrease of bias for high sample masses, which is not found (Figure 3). Although in principle none of the other explanations can be ruled out, there is no direct evidence which would support them. The good reproducibility of the measured n-alkane carbon isotope ratios would require that any loss in the TSPS would be highly reproducible, which is unlikely and the tests of the TSPS showed no indication for significant loss of n-alkanes in the TSPS. Except for n-pentane there also is no indication for problems due to chromatographic separation, peak shape, or baseline drift for n-alkanes. Due to the higher chemical stability of n-alkanes incomplete oxidation in the combustion interface could result in isotope fractionation for n-alkanes without influencing the results for aromatic VOC, although this would require inverse isotope effects for the catalytic oxidation of n-alkanes in order to explain the bias towards higher carbon isotope ratios.

3.2 Cartridge tests

The VOC masses observed for analysis of blank cartridges using desorption temperatures in the range of 474 K to 573 K are listed in Table 1 together with their standard deviations and the resulting 3σ 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 temperatures ranging from 295 K to 590 K showed no or only marginal signals. As can be seen from Table 1, the blank values were small compared to typical VOC masses in ambient samples. For the typical sample volume of 30 L the detection limits correspond to mixing ratios in the range of 3 pptV to 15 pptV.

Optimum desorption conditions were determined by analysing cartridges loaded with approximately 30 ng to 60 ng of VOC using the gaseous test mixtures. Desorption times, temperatures and flow rates were varied (Table 2). A flow rate of 50 mL to 80 mL was used for most of the tests. Lower desorption temperatures and shorter desorption times (Table 2) resulted in poor recovery of compounds of low volatility. However, the option of using very high temperatures is limited since a prolonged exposure to high temperatures may result in a degradation of the cartridge materials. Since recovery was, within the uncertainty of the measurements, quantitative at 553 K and 40 min, these conditions were chosen as standard desorption conditions. Table 3 shows the average recovery and its reproducibility for the chosen standard conditions.

Sampling efficiency tests using two cartridges in series showed that for sample volumes of up to 80 L, the second cartridge only contained between 2 % and 5 % of the mass found on the first cartridge. These masses often were close to or below the detection limits and therefore only provide an upper limit for breakthrough during sampling.

Capped sample-containing cartridges could be stored both at room temperature for a short period and in a freezer for longer time with no significant loss of VOC (Fig. 4). Generally the change in mass during storage is less than 10 %. Similarly, the isotopic fractionation during storage was less than 0.3 ‰ (Fig. 5). The masses of VOC loaded for these tests were in the range of 25 ng to 75 ng (Table 3).

3.3 Ambient measurements

The newly developed method was applied in an ambient air quality field study in 2009 to 2010 (Kornilova et al., 2013) at Egbert, a semi-rural location in Southern Ontario. Details about the sampling site can be found in Kornilova et al., 2013. This paper also contains a detailed discussion of the use of the measured VOC carbon isotope ratios to quantitatively evaluate photochemical VOC processing. Therefore, the discussion here will be limited to aspects related to performance of the analytical method.

Example chromatograms for the test mixture and an ambient sample are provided in Fig. 6. For ambient samples, it was found that n-pentane was subject to substantial peak overlap, which prevents reliable peak evaluation. Therefore, to minimize the risk of contamination of the combustion interface and the IRMS, monitoring the column effluent by IRMS started with hexane. Otherwise all target compounds were well separated with the exception of p-xylene and m-xylene, which were integrated as one peak. It should be noted that the change in time window of monitoring the column effluent changes the retention times, especially for peaks eluting early in the time window which is monitored by the IRMS. This is the result of a small counter pressure at the end of the separation column which results from the gas-flow that is used to prevent the column effluent from entering the combustion interface and the resulting lower pressure difference between the head and the end of the separation column.

For most of the samples the peaks for n-octane, n-nonane, and n-decane corresponded to masses below the lower limit of the linear range and for these compounds the number of available data points is too small to allow calculation of meaningful averages. Problems with peak evaluation due to small peak areas were not limited to the C_8-C_{10} n-alkanes, but occurred less frequently for aromatic VOC. The total number of samples that could be analysed for $\delta^{13}C$ was 50 and the number of $\delta^{13}C$ measurements available ranges from 46 for benzene to 26 for hexane.

Table 4 gives an overview for concentrations and $\delta^{13}C$. A comparison between measured $\delta^{13}C$ and $\delta^{13}C$ of typical urban VOC emissions, which are also included in Table 7, shows that the measured $\delta^{13}C$ values generally are heavier than those of typical emissions. This is expected since photochemical processing will typically result in enrichment of ^{13}C (Rudolph et al., 2002; Rudolph and Czuba, 2000). The only exception is hexane; here the lower end of the $\delta^{13}C$ values are about 1.4 ‰ lower than the $\delta^{13}C$ values of urban emissions, which is outside of the uncertainty range of known urban emissions and the measurement precision. The possible bias of

Comment [A2]: R2: *Can you comment on the apparent positive artifacts for n-hexane and benzene recovery with storage?*

Comment [A3]: Do we need to discuss this? These would be pure speculations, not sure if they are valid here.

n-hexane online measurements cannot explain this difference since a correction for a possible bias derived from the difference between online and offline results (Fig. 3) would result in an even larger difference, sometimes exceeding 3 ‰. This suggests the existence of a local or regional n-hexane source with a $\delta^{13}C$ value lower than typical urban emissions. The existence of a substantial unidentified regional n-hexane source is consistent with n-hexane mixing ratios which are often high compared to that of other VOC. It should be 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 $\delta^{13}C$ was not possible.

Due to the relatively high sample mass needed for $\delta^{13}C$ measurement by GC-IRMS bias due to the problem of reliable evaluation of $\delta^{13}C$ 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 $\delta^{13}C$. Figure 7 shows the dependence between measured $\delta^{13}C$ and concentration for benzene and p,m-xylene. Compared to the $\delta^{13}C$ values of emissions, the samples are enriched in $\delta^{13}C$ to various degrees. The number of samples substantially enriched in $\delta^{13}C$ 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 $\delta^{13}C$ value for the lowest ten concentrations is -23.1 ‰ ± 0.1 ‰ (error of mean) for benzene and -22.9 ‰ ± 0.9 ‰ for p,m-xylene, which indicates a substantial difference to the average for all measurements, which is -25.2 ‰ ± 0.1 ‰ and -25.4 ‰ ± 0.5 ‰ for benzene and toluene, respectively. This is a strong indication that limitations in making precise $\delta^{13}C$ measurements at very low mixing ratios can bias the average measured $\delta^{13}C$ 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 Gensch 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 methods is the sampling and VOC enrichment procedure. This is not surprising since the analysis of VOC carbon isotope ratios requires enrichment of VOC from large sample volumes, which is technically challenging and may require substantial logistic effort in field studies.

1   In principle, the lower limit of mixing ratios for which meaningful VOC carbon isotope
2 ratios can be conducted depends on the sample volume that can be used. This volume typically
3 ranges from several litres for whole air sampling to several hundred litres or more for cryogenic
4 sampling (Gensch et al., 2014 and references therein). With sample volumes of up to 80 L, the
5 method developed in this work allows collection of significantly larger samples than methods
6 using whole air sampling, but not for the extremely large sample volumes that can be used by
7 some cryogenic methods (Bahlmann et al., 2011; Bill et al., 2004; Iannone et al., 2007).
8 However, the adsorptive sampling method described in this paper requires less expensive
9 instrumentation than cryogenic sampling and can be conducted in the field with instrumentation
10 that is similar in requirements (electrical power, weight, storage, shipment) to whole air sampling
11 in pressurized containers.

12   While adsorptive sampling as described in this paper allows use of larger air sample
13 volumes than whole air sampling, it has some other limitations. Each sample can only be
14 analysed once, this can be a problem in cases where the mixing ratios in the sampled air is highly
15 variable or the range of mixing ratios expected is unknown, such as in many emission studies.
16 Due to the limited dynamic range of IRMS measurements, sampled VOC masses may be outside
17 of the dynamic range and thus lost. Whole air samples, in principle, allow repeat runs of the
18 same sample using different volumes or IRMS settings. This is very useful for samples with high
19 VOC concentrations, but of limited value for very low concentrations since existing methods for
20 whole air sampling do not provide sufficient sample volume for several measurements at sub-
21 ppbV levels.

22   Collection of whole air samples typically requires less time than adsorptive or cryogenic
23 sampling. This can be a significant advantage if sampling time is limited, for example in airplane
24 based sampling. On the other hand, adsorptive sampling can easily provide samples that are
25 integrated over long time periods. For example, our study at Egbert used 24 hour sampling
26 periods, which allows determination of representative averages without the necessity to collect
27 and analyse an extremely large number of samples. Finally, adsorptive sampling is not suitable
28 for collection of VOC with very high volatility such as C_2 or C_3 hydrocarbons.

29   The reproducibility of isotope ratio measurements for our newly developed method is
30 better than 0.5 ‰, similar to that of other state-of-the-art methods for measurement of $\delta^{13}C$ in
31 ambient VOC (Czapiewski et al., 2002; Eckstaedt et al., 2012; Kawashima and Murakami, 2014;
32 Rudolph et al., 1997; Saito et al., 2009; Turner et al., 2006; Wintel et al., 2013), however the
33 lower limit of concentrations for which this precision can be achieved is significantly lower than
34 that achieved by these other methods.

35   Tests of accuracy for $\delta^{13}C$ measurements of aromatic VOC demonstrate that there is no
36 detectable bias, similar to the findings in several other studies (Czapiewski et al., 2002;
37 Eckstaedt et al., 2012; Rudolph et al., 1997; Saito et al., 2009). However, for n-alkanes the GC-
38 IRMS results differ from the offline values for bulk material used to prepare test mixtures by
39 approximately 2 ‰. Unfortunately there are not many published tests of the accuracy of $\delta^{13}C$

measurements for C_6 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 $\delta^{13}C$ 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 $\delta^{13}C$ 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 concentration 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_5 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.

Tests of the accuracy of carbon isotope ratio measurements of n-alkanes showed a bias of approximately 2 ‰ between the isotope ratio of test mixtures prepared in-house and GC-IRMS measurements. It was not possible to identify if this is due to uncertainty in the isotope ratio of the test mixture or bias of GC-IRMS measurements. Nevertheless, this demonstrates the importance of testing the accuracy of GC-IRMS measurements of atmospheric VOC. Unfortunately the number of published comparisons between artificial VOC mixtures with known isotope ratios and GC-IRMS measurements is limited, a consequence of the substantial resources and effort required to prepare test mixtures with known isotope ratios and the unavailability of certified or otherwise well characterised reference mixtures suitable for such tests. This supports the necessity for creating reference materials for isotope ratio analysis of organic compounds in the atmosphere as pointed out by Gensch et al. (2014).

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 $\delta^{13}C$ for VOC at low mixing ratios therefore will bias the $\delta^{13}C$ observations towards

the source composition and therefore underestimate the role of chemical processing, which results in enrichment of ^{13}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 ± 0.2) g of carboxene and 0.2 g to 0.5 g of quartz wool.

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

[a] SD: Standard deviation calculated from at least 4 repeat measurements.

[b] 3σ detection limit (DL).

[c] average calculated from 50 ambient samples.

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

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

[a] Results are based on one measurement.

Table 3. Average recoveries[a] of VOC sampled on cartridges for desorption at 553 K for 40 min at (60 to 80) mL min^{-1} carrier gas flow rate.

Compounds	Mass of loaded VOC (ng)	Average Recovery[b] %	SD[c] of delta values ‰
Benzene	25	112 ± 2^c	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

[a] Values were not blank corrected.
[b] Based on 3 to 4 measurements.
[c] SD: Standard deviation.

Table 4. Concentrations and delta values determined from ambient samples collected at Egbert.

Compound	Concentrations (ppbV) (ambient)			$\delta^{13}C_{ambient}$ (‰)			$\delta^{13}C_{source}$ (‰)[a]	
	Median	10th percentile	90th percentile	Median	10th percentile	90th percentile	Average	SD[b]
n-Hexane	1.53	0.61	5.18	-27.0	-28.1	-24.0	-26.7	0.4
Benzene	0.10	0.05	0.24	-25.6	-27.9	-22.2	-28.0	1.1
n-Heptane	0.40	0.14	1.80	-24.2	-26.1	-21.7	-26.4	1.1
Toluene	0.13	0.06	0.25	-24.8	-26.7	-22.5	-27.6	0.6
Ethylbenzene	0.02	0.01	0.06	-23.9	-27.5	-18.6	-27.7	0.4
p,m-Xylene	0.03	0.01	0.11	-23.8	-27.7	-19.8	-27.4	0.5
o-Xylene	0.01	0.004	0.03	-23.5	-26.2	-20.7	-27.2	0.1

[a] Stable carbon isotope composition of the sources based on Rudolph et al. (2002).

[b] SD: Standard deviation

Figure Captions

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

Fig. 2. Calibration curve for toluene (based on TSPS-GC-IRMS measurements, slope = $1.46\times10^{10} \pm 0.03\times10^{10}$ ions ng^{-1}, R^2= 0.997)

Fig.3. Plot of δ^{13}C values versus injected mass measured online using TSPS-GC-IRMS. Dashed lines are the reference (offline) δ^{13}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.

Fig. 4. Impact of storage on sample recovery for storage of 1 to 2 weeks at ambient temperatures (diamonds) and 6 to 7 months in a freezer (circles). The recovered masses are given relative to samples analysed immediately after sampling. Both storage tests used the same reference values. Values used are the average of 3 to 4 measurements and the error bars show the variability of results for analysis after storage. Masses loaded range from 25 ng to 75 ng. Values were not corrected for blanks.

Fig. 5. Change in δ^{13}C of VOC collected on cartridges during storage for 1 to 2 weeks at ambient temperatures (diamonds) and 6 to 7 months in a freezer (circles). The differences are given relative to the δ^{13}C values of samples analysed without storage. Both storage tests used the same reference values. Values used are the average of 3 to 4 measurements and the error bars show the variability of results for analysis after storage. Masses loaded range from 25 ng to 75 ng. Values were not corrected for blanks.

Fig.6. Chromatogram obtained by GC-IRMS for a test mixture with 11 compounds (A) and an ambient sample (~~bottom~~B). Rectangular peaks are reference CO_2 signals and peaks numbered from 1 to 11 correspond to n-pentane, n-hexane, benzene, n-heptane, toluene, n-octane, ethylbenzene, p,m-xylene, o-xylene, n-nonane and n-decane.

Fig. 7. Mixing ratio versus stable carbon isotope ratio plots for samples collected at Egbert. The range (average ± σ) of isotope ratios reported by Rudolph et al. (2002) for urban sources are shown as dashed lines.
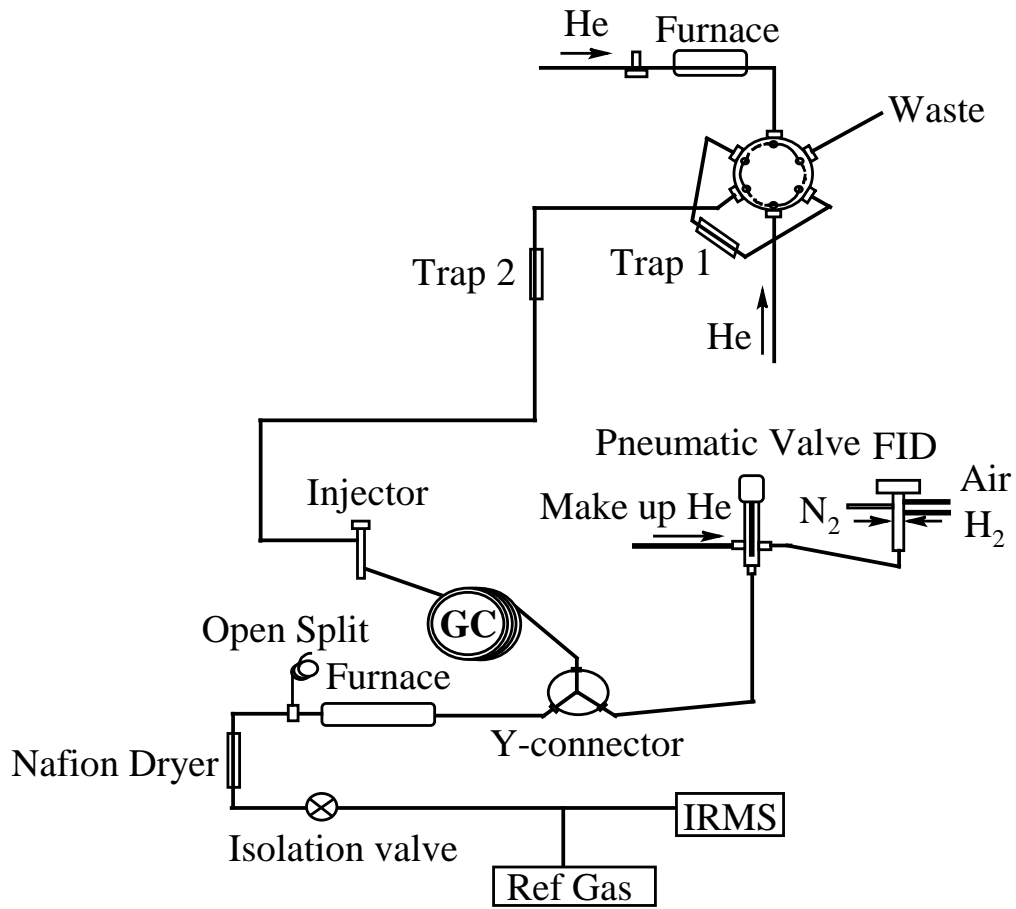
He   Furnace

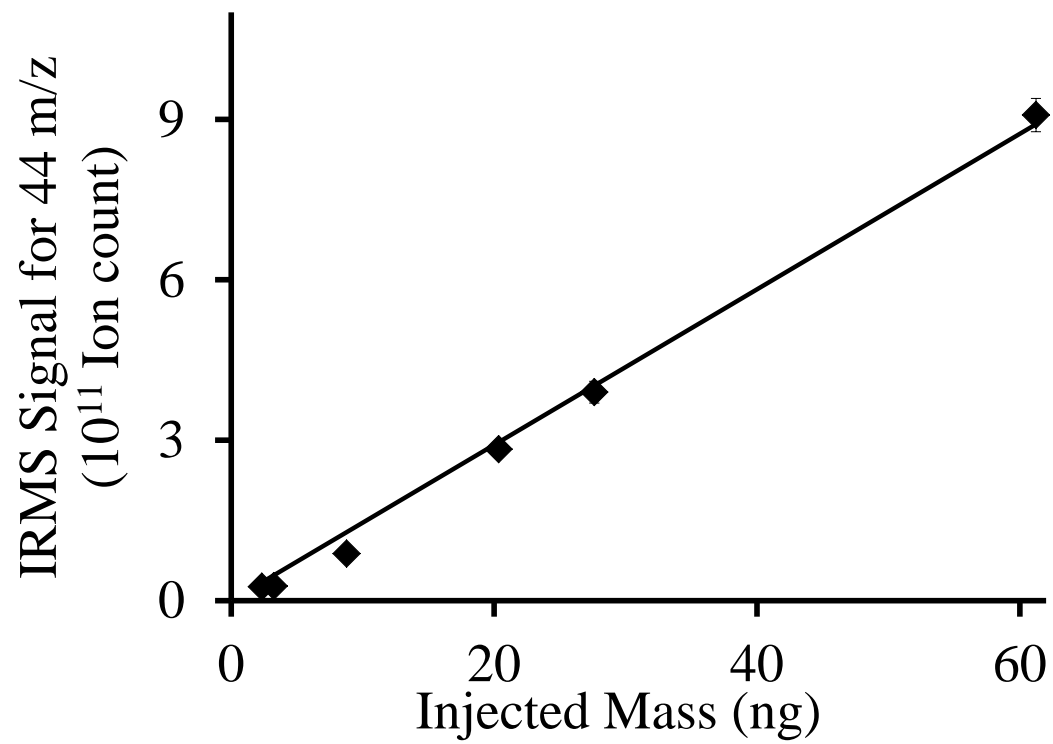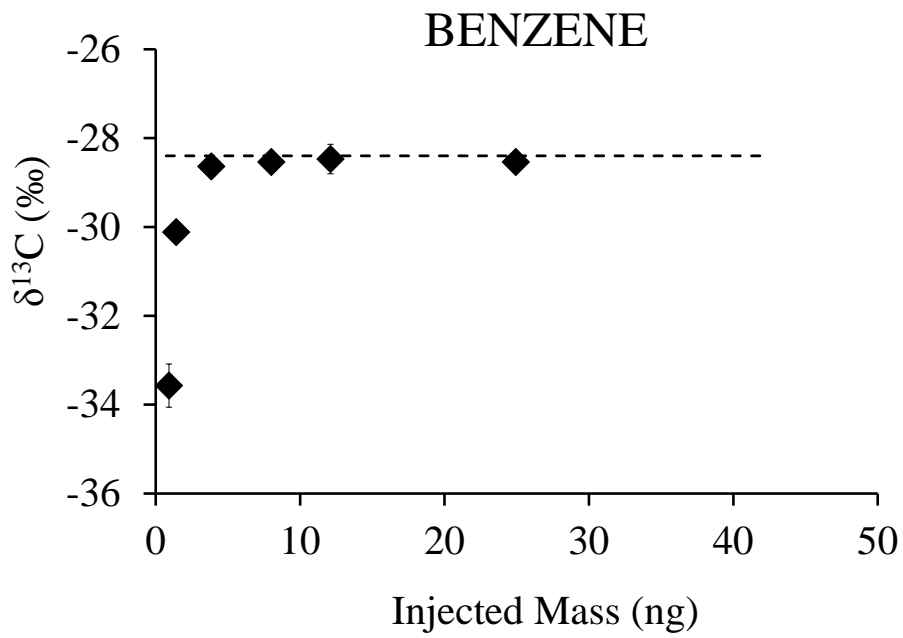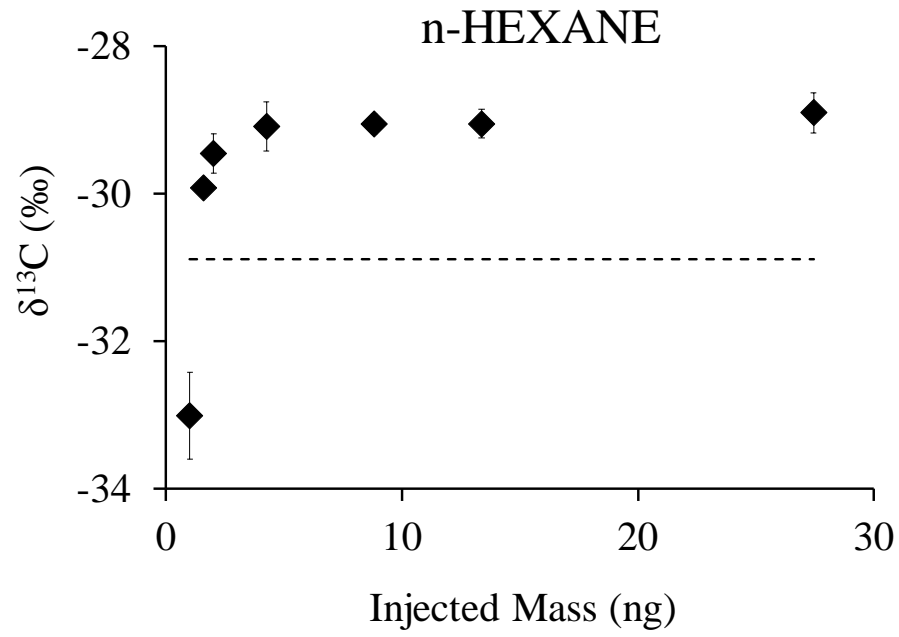Waste

Trap 2   Trap 1

He

Pneumatic Valve FID

Injector

Make up He N_2 Air H_2

GC

Open Split

Furnace

Nafion Dryer

Y-connector

Isolation valve

IRMS

Ref Gas

Fig. 1

Fig. 2

n-HEXANE

δ¹³C (‰)

Injected Mass (ng)

BENZENE

δ¹³C (‰)

Injected Mass (ng)

n-HEPTANE

TOLUENE

ETHYLBENZENE

P,M-XYLENE
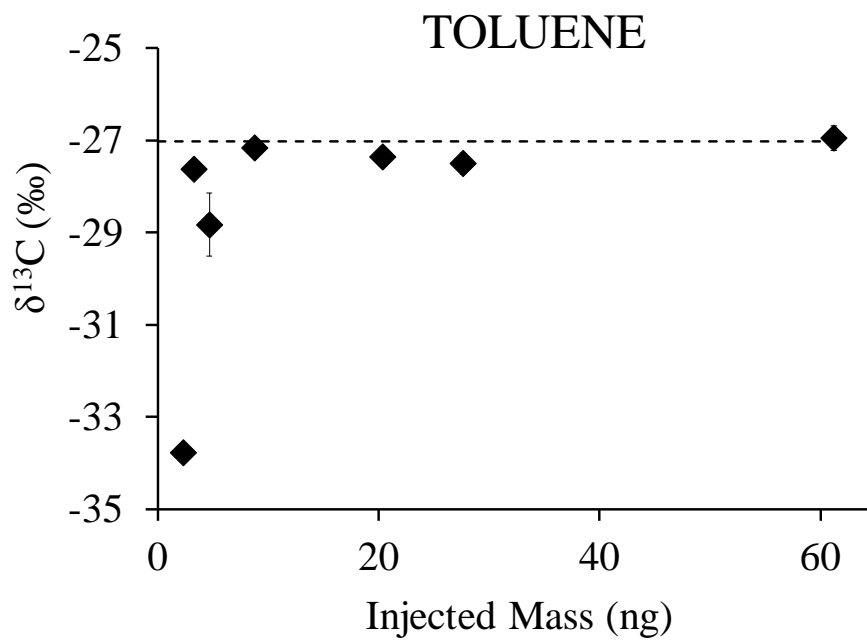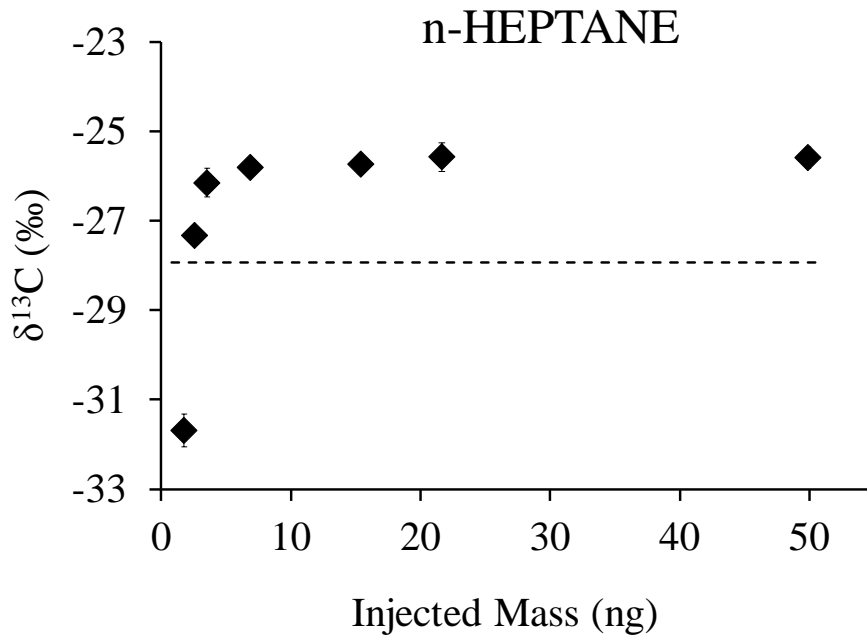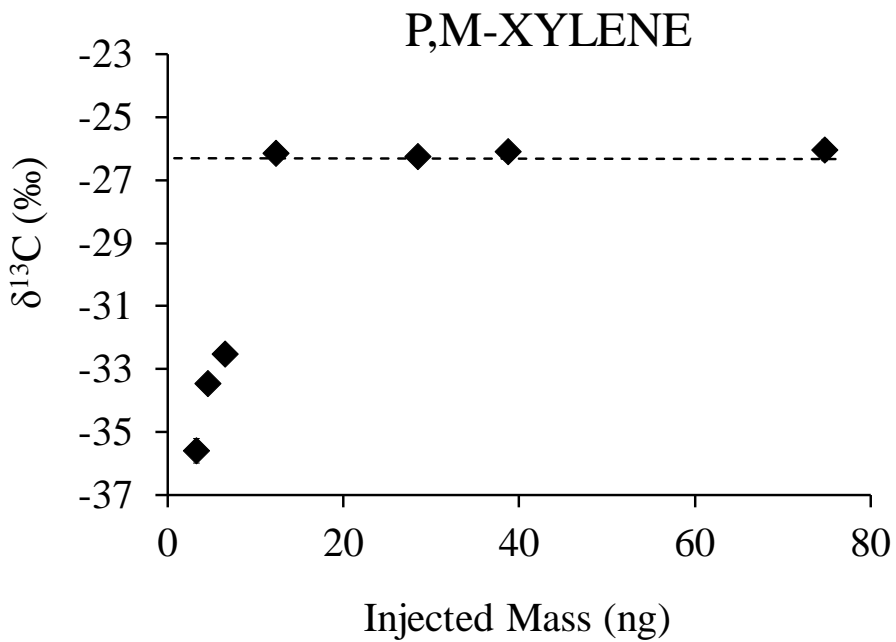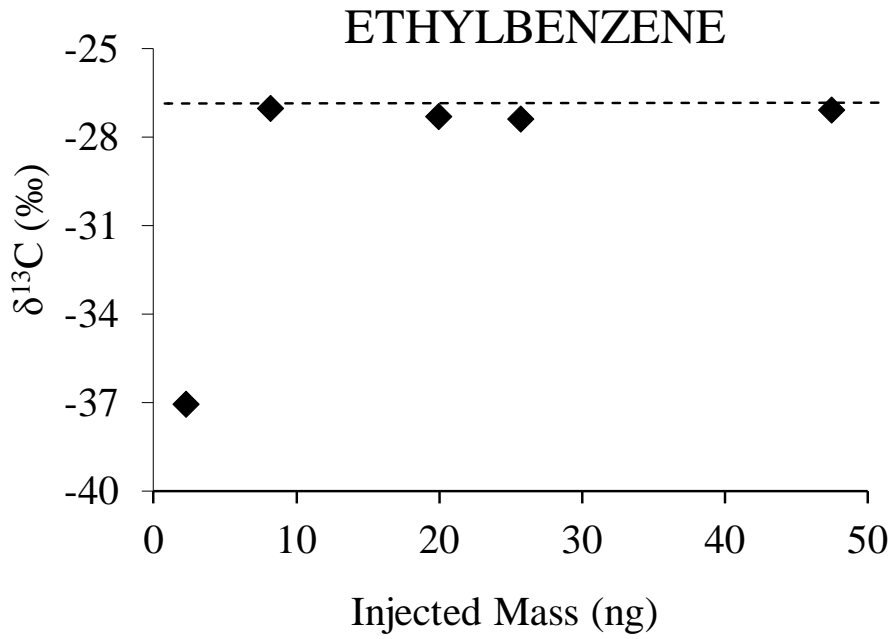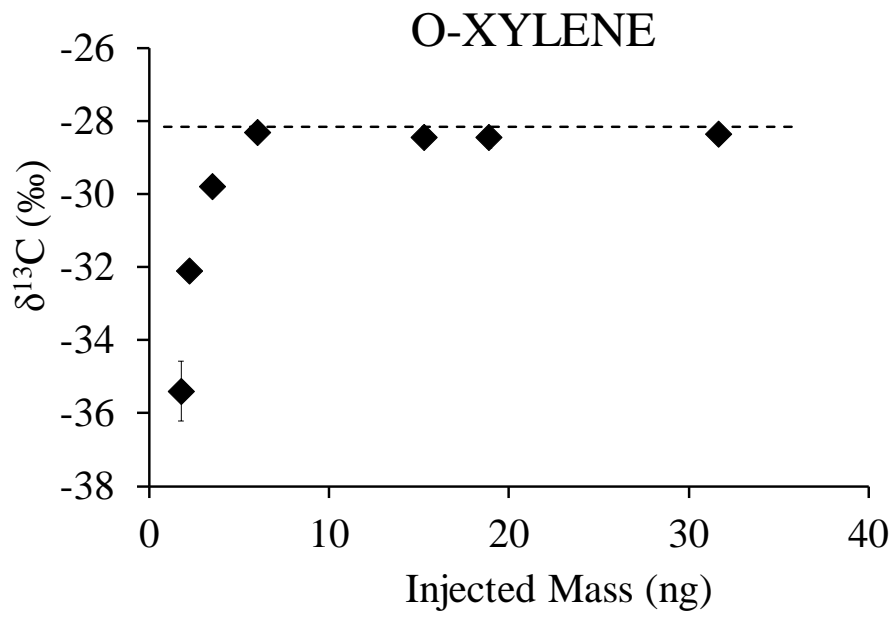
Fig. 3

Fig. 4

Fig. 5

A

B

Fig. 6

Fig. 7