

**Analytical system for
carbon stable isotope
measurements**

A. Zuiderweg et al.

This discussion paper is/has been under review for the journal Atmospheric Measurement Techniques (AMT). Please refer to the corresponding final paper in AMT if available.

Analytical system for carbon stable isotope measurements of light non-methane hydrocarbons

A. Zuiderweg, R. Holzinger, and T. Röckmann

Atmospheric Physics and Chemistry Group, Institute for Marine and Atmospheric research
Utrecht, Utrecht University, Utrecht, The Netherlands

Received: 14 December 2010 – Accepted: 23 December 2010 – Published: 11 January 2011

Correspondence to: A. Zuiderweg (azuider@gmail.com)

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

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Abstract

Isotope analysis can be a useful tool in constraining the budgets (sources and sinks) of atmospheric trace species and is increasingly applied for organic constituents. This may be useful in particular for investigating the oxidative capacity of the atmosphere and studying long-range.

We present setup, testing and initial results from a new automated system for carbon stable isotope ratio measurements on C₂ to C₆ atmospheric hydrocarbons. The inlet system is flexible and allows analysis of trace gases from medium size to very large ambient air samples (5–300 L) without loss of compounds of interest.

The first application of this system was the analysis of ambient air during a short campaign in August 2009 in Utrecht, the Netherlands. Results obtained agree well with previous research, but highlight the complex diurnal behavior of hydrocarbons in an urban environment.

1 Introduction

A significant amount of the total reactive carbon input (estimated as near 1150 Tg/y, Guenther et al., 1995) to the atmosphere consists of non-methane hydrocarbons (NMHCs). These are emitted to the atmosphere through many processes, both natural as a product of vegetative growth, decay and natural combustion of plant material, and anthropogenic including biomass burning for energy or heating, fossil fuel combustion, and industrial processes. These hydrocarbons play important roles in atmospheric chemistry contributing to the production of tropospheric ozone and resultant photochemical pollution, the formation of aerosol particles, and the oxidative capacity of the atmosphere (Warneck, 1988; Seinfeld and Pandis, 1998; Goldstein and Galbally, 2007).

The light NMHC, consisting of compounds with 2 to 7 carbon atoms (C₂ to C₇), account for the vast majority of anthropogenic emissions to the troposphere. Acetylene,

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



ethylene, and propene originate primarily from combustion processes such as fossil fuel combustion and biomass burning; alkanes mainly stem from natural gas leakage and petroleum product evaporation, with significant transportation sources as well; and aromatic compounds mainly from transportation sources and solvent evaporation. Oxidative processes provide the atmospheric removal mechanism of NMHC compounds, mainly through reaction with OH*, which is by far the dominant process (Conny and Currie 1996):



Where R* stands for any alkyl radical remaining after hydrogen abstraction from the hydrocarbon RH. Other removal reactions include NO₃, Cl, or O₃ as the first step (Warneck, 1988; Seinfeld and Pandis, 1998; Brenninkmeijer, 2009).

The rare stable isotope of carbon, ¹³C, has an average natural abundance of approximately 1.1%. As the presence of ¹³C atoms in a molecule typically reduces its reactivity, small deviations from the planetary ¹³C/¹²C ratio can be observed. This information provides a tool to improve the understanding of hydrocarbon atmospheric processing. Isotopically lighter molecules usually react faster than isotopically heavier ones. The ratio of the two rate coefficients of the different isotopologues is known as a kinetic isotope effect (KIE) and the fractionation constant, ε, is defined as

$$\varepsilon = (\text{KIE} - 1) = \left(\frac{k_{12}}{k_{13}} - 1 \right) \quad (2)$$

Note that in many publications a fractionation constant α is defined as:

$$\alpha = \frac{k_{13}}{k_{12}} = \frac{1}{(\varepsilon + 1)} \quad (3)$$

and values have to be converted accordingly.

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The production and removal processes of compounds can thus change the stable isotope ratio, which is expressed as

$$\delta^{13}\text{C} = \left[\frac{([\text{}^{13}\text{C}]/[\text{}^{12}\text{C}])_{\text{sample}}}{([\text{}^{13}\text{C}]/[\text{}^{12}\text{C}])_{\text{standard}}} - 1 \right] \quad (4)$$

where measurements are referenced against a standard carbon isotopic ratio, usually VPDB (Vienna Pee Dee Belemnite). Measurements of $\delta^{13}\text{C}$ and KIE are commonly multiplied by 1000‰ for readability purposes (Goldstein and Shaw, 2003; Brenninkmeijer, 2009).

In the case of light non-methane hydrocarbons, the relatively short lifetime of these compounds in the atmosphere, from mere hours to tens of days, gives the possibility of utilizing emissions as tracers of transport and aging in the atmosphere by observing the isotopic ratio (Rudolph et al., 1981, 2002; Goldstein and Shaw, 2003; Redeker et al., 2007).

Development of the coupled gas chromatography – (combustion interface) – isotope mass spectrometer, as pioneered by Matthews and Hayes (1978) for CO_2 and N_2 isotope work, substantially improved upon earlier techniques based on dual-inlet isotope ratio mass spectrometers by greatly reducing necessary sample size and eliminating the need to extract individual compounds from a sample, which is a difficult and time-consuming task. This breakthrough allowed significant research work into the stable isotopic ratios of carbon, nitrogen, oxygen and hydrogen containing compounds in the atmosphere.

Development of instrumentation able to accomplish compound specific measurement of carbon isotope ratios of NMHC is somewhat newer (Rudolph et al., 1997; Goldstein and Shaw, 2003; Brenninkmeijer, 2009). Rudolph et al. (1997) developed the first instrument capable of compound specific carbon stable isotope ratio analysis measurements of multiple NMHCs. This instrument was initially used for observing carbon isotope ratios of emissions from biomass burning and transportation related

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

sources, and urban environment atmospheric samples. The observance of the magnitude of the kinetic isotope effect in hydrocarbon reactions with OH* and O₃ was also undertaken in subsequent research with this instrument (Rudolph et al., 1997, 2002; Iannone et al., 2003; Anderson et al., 2004).

5 The availability of such measurements allowed the subsequent development and application of the so-called isotopic hydrocarbon clock approach, which is expressed as follows (Rudolph and Czuba, 2000):

$$\delta_Z = t_{av} \cdot {}^{OH}k_Z \cdot [OH] \cdot {}^{OH}KIE_Z + {}^0\delta_Z \quad (5)$$

10 where δ_Z is the measured isotopic ratio of a compound Z, t_{av} the average age of the air mass, ${}^{OH}k_Z$ the rate of reaction of the compound with OH*, [OH] the concentration of OH*, ${}^{OH}KIE_Z$ the KIE in the reaction of compound Z with OH*, and ${}^0\delta_Z$ the source isotope ratio of compound Z; it may also be further extended by adding terms representing reactions with e.g. O₃ or Cl. This approach can improve estimates of compound age compared to previous efforts, which relied on ratios of mixing ratios of two compounds emitted at the same time (Rudolph and Czuba, 2000).

15 Other applications of similar instruments that have been subsequently derived include measurements of NMHC $\delta^{13}C$ in urban, marine and coastal atmospheres and over the North Pacific and East Asia to evaluate atmospheric transport and air mass age (Tsunogai et al., 1999; Saito et al., 2000, 2009; Nara et al., 2007); of NMHC from biomass burning (Czapiewski et al., 2002; Nara et al., 2006); with some extension, measurements of halocarbons and NMHC (Archbold et al., 2005; Redeker et al., 2007) and specific measurement of chloromethane from plants and its atmospheric budget (Bill et al., 2002; Harper et al., 2003; Keppler et al., 2005).

20 Here we present a new instrument that is capable of high-precision measurements of NMHC carbon stable isotope ratios. It has the unique capacity of being able to process very high volume samples, such as those necessary for carbon stable isotope measurements of NMHC from very clean samples (e.g. stratospheric) and the flexibility of accepting samples from many other sources. The system is constructed

Analytical system for carbon stable isotope measurementsA. Zuiderweg et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

to analyze $\delta^{13}\text{C}$ of non-methane hydrocarbons from C_2 to C_6 , halocarbons, including methyl chloride, and CFCs of samples of varying origin.

2 Experimental

2.1 System description and procedure

2.1.1 The preconcentration system

The pre-concentration system (Fig. 1) is largely based on well established cryotrapping techniques and allows for stable isotope analysis of a variety of different samples. To allow the sampling of large volume samples, it is necessary to initially utilize large diameter cryotrap and progressively cryofocus to smaller volumes prior to GC injection. Cryogenic traps, when implemented properly, do not create isotopic fractionation (Archbold et al., 2005; Redeker et al., 2006). The following parts of the pre-concentration system are described below: (i) the primary cryogenic sampling trap (referred to as SAMP trap); (ii) the separation column to separate CO_2 from the NMHCs (referred to as SEP column); (iii) the W-shaped cryogenic recovery trap (REC trap); and the final cryogenic focusing trap (FOC trap).

The SAMP trap is a 0.3 m \times 4 mm ID stainless-steel tube filled with 100/120 mesh glass-bead packing material, capable of at least 100 standard mL/min (standard conditions are 0 °C, 1 bar) flow rates without loss. Typically this trap was operated at a flow of 50 standard mL/min, which was maintained by a MKS thermal mass flow-controller. A dual-head rotary pump draws the sample through the cryotrap, and provides removal of bulk gases (mainly N_2 and O_2). Desorption of any sample on the trap is accomplished by heating it to 120 °C within 1 min after extraction.

The particular design feature of the pre-concentration system is the method of CO_2 removal. Whereas other systems (Rudolph et al., 1997; Tsunogai et al., 1999; Archbold et al., 2005) rely on chemical removal of any CO_2 employing Carbosorb, Ascari-

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



11 or other sodium hydroxide-on-silica beads, here GC-based removal has been chosen. CO₂ must be removed before IRMS analysis can occur, because the target compounds are oxidized to CO₂ for isotope analysis. To ensure effectively separation for large samples or samples with high CO₂ content, we designed the SEP column as a non-chemical removal method, utilizing a GC packed column (Supelco PoraPAK Q, 3 m×4 mm). This material allows CO₂ to elute first and thus be vented, while retaining desired NMHC compounds.

Figure 2 displays a total ion abundance chromatogram demonstrating the separation properties of this column under room temperature and standard He flow rates of 70 mL/min, utilizing a 200 mL 50:50 CO₂/natural gas testing mix and a quadrupole mass spectrometer as a detector. Natural gas has a widely varying composition, but generally contains significant amounts of nitrogen, CO₂, and higher hydrocarbons (e.g. ethane, propane) in addition to methane (Škrbić and Zlatković, 1983; Milton et al., 2010). The injected mixture of natural gas and CO₂ as chosen here represents a test of separation column performance of a very demanding sample introduced on the system, representing the CO₂ content of approximately 300 L of ambient air. Figure 2 shows that at 10 min after injection on column the bulk of methane, remnant nitrogen (peak A), and CO₂ (peak B) have eluted while ethane and other hydrocarbons (peak C) are still on the SEP column. The system procedure thus reverses the flow through the column after 10 min (any CO₂ having been vented) to retrieve the compounds of interest from the column at a reduced flow rate (11.2 standard mL/min). During recovery, the column is heated to and kept at 120 °C over a period of 40 min.

It was tested that the presence of the SEP column has no significant effect on δ¹³C measurements of the selected hydrocarbons. These tests consisted of 10 measurements of calibration gas in two configurations: (i) with liquid nitrogen traps (LN₂) only (i.e. the SEP column removed) and (ii) with the system in standard configuration, respectively. Table 1 shows that the means and standard deviations are nearly identical for the hydrocarbons. However, there is a consistent shift (−2‰) for methyl chloride, which has to be corrected for. A similar effect was noted in Archbold et al. (2005), for

chemical removal and adsorbance traps. The cause of this shift is as yet unexplained.

Before the sample material is recovered on the REC trap, any small remnant CO₂ and any H₂O is removed in a small glass reactor containing Ascarite II and Mg(ClO₄)₂. The REC trap is a 0.5 m×2.5 mm ID W-shaped stainless steel cryotrap immersed in liquid nitrogen containing 100/120 mesh glass beads. After the recovery time of 40 min, the REC trap is heated to 100 °C, thereby releasing the sample over the course of 5 min at 4.1 mL/min to the FOC trap, a 0.3 m×0.25 mm ID stainless steel-jacketed capillary cryotrap. Sample injection into the GC occurs by extracting and heating the FOC trap to a temperature of over 100 °C within 30 s, at a flow rate of 2.1 mL/min.

2.1.2 GC separation, combustion and detection

Gas chromatographic separation is done on a 52.5 m×0.25 mm Varian PoraPLOT Q GC column in a HP 5890 GC. The column is maintained at 40 °C for 10 min, thereafter being heated at a rate of 12 °C/min to 240 °C. This temperature is maintained for 35 min, giving a total run time of 65 min. When not in use, the GC oven is maintained at 150 °C.

The effluent from the GC column is roughly split 1:1 between a quadrupole mass spectrometer (HP5970) for identification of the compounds, and the remainder sent to a ThermoFinnigan Delta⁺ XP IRMS by way of a platinum-copper-nickel ceramic combustor (maintained at 900 °C and restored daily with O₂), a nafion drier, and an open-split interface {Röckmann, 2003 #2132}. IRMS δ¹³C drift is monitored through direct injection of CO₂ via the open-split as a working standard. The carbon stable isotope ratio of this CO₂ has been calibrated as -34.0‰ ± 0.1 vs. VPDB by Rijksuniversiteit Groningen, The Netherlands. Mixing ratios are calculated from the IRMS peak area measurements of each peak in the chromatogram, relative to peak areas from the calibration gas. Mixing ratios of compounds not contained in the calibration gas were estimated by extrapolation based on the number of carbon atoms in the molecules of the species in question and can therefore contain a larger systematic error. δ¹³C values are calculated from the individual ion signals of the IRMS, integrated per trace

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



(m/z 44, 45, 46; automatic peak detection under normal operation, manual evaluation if necessary), and mathematically corrected for ^{17}O through the ISODAT isotope ratio analysis package, utilizing the correction from Santrock et al. (1985).

2.1.3 Ambient air sampling unit

As an addition to the basic system described above, a high-flow sampling unit was developed allowing ambient air sampling at rates of up to 1 L/min. The unit is set up as an auxiliary 2-stage cryogenic trapping system consisting of a large diameter stainless steel water trap and a 0.5 m \times 1.27 cm glass bead (80/100 mesh) filled stainless steel U-trap (Fig. 3). The water trap, designed and constructed of 2.54 cm tubular stainless steel with large diameter Swagelok fittings and 0.32 cm stainless steel lines, is immersed in liquid nitrogen, permitting any water vapor to be frozen out of the sample gas passed through it. The internal volume of this trap is approximately 100 mL.

Sampling proceeds as follows: both traps are immersed in liquid nitrogen while ultra pure synthetic air (78/22 N_2/O_2) is drawn through the system at 50 mL/min by a dual head high-flow rotary pump downstream of the traps. The use of a pump keeps pressure inside the traps low at all times to prevent the condensation of oxygen. Once both traps are at temperature (approximately 2 min), the synthetic air supply is closed, the ambient sample line valve is opened, flow rates are increased to 0.5–1 L/min and sampling begins. Following the sampling of the desired volume, the flow rate is reduced to 50 mL/min, the sampling valve is closed, and synthetic air is reintroduced. Then the pump valve is closed and the valve to the preconcentration system is opened and the traps are extracted from the liquid nitrogen in turn: first the water trap is removed and left to warm in laboratory ambient air for 5 min to reduce pressure effects from rapid warm up of such a large volume. Then it is inserted in a warm water bath at 40 °C to release adsorbed volatiles, while retaining water in liquid form at the bottom of the trap. The liberated volatiles are transferred to the large diameter U trap over 5 min. This trap is then extracted from the liquid nitrogen and allowed to warm in ambient laboratory

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



air over 5 min, and is subsequently heated out under a 500 °C air stream for 5 min to transfer all sampled compounds to the analysis system by the synthetic air carrier gas.

2.2 Performance and stability

For calibration, a 9-compound reference gas (AiR Environmental, inc.) is used as the primary working standard. Of the compounds in this gas, 4 are monitored in test and calibration runs at the start and end of each measuring day, and during night (automated), namely ethane (206 ppb), propane (103 ppb), methyl chloride (103 ppb) and benzene (103 ppb). Calibration runs with the standard were done with varying volumes, either 50, 100, or 200 mL, to ensure a range of peak areas similar to results in sample measurements and to test for non-linearity effects.

The $\delta^{13}\text{C}$ values of propane, methyl chloride, and benzene in the working standard were established utilizing the method described in Fisseha et al. (2009), at the Forschungszentrum Jülich, Germany, to be -34.8 ± 0.4 , -48.7 ± 0.4 , and $-28.1 \pm 0.3\%$ vs. VPDB, respectively. Due to incapability, no independent measurement of ethane was achieved. However, calibration results of the other tested gases and the reference CO_2 give high confidence that our estimate of $-28.6 \pm 0.4\%$ vs. VPDB is valid for ethane. These calibration results agree (± 0.3 to 0.8% , depending on compound) with all measurements of these compounds obtained by our system when calibrated against the aforementioned injected CO_2 , and taking into account the shift in methyl chloride.

It was observed that, if the peak area of a given eluted compound was maintained above 0.5 V s, IRMS nonlinearity is not a factor that needs to be corrected for, as for the compounds reported here it does not occur at peak areas above 0.5 V s.

To illustrate the time stability of the system in the current configuration (since May 2009), in Fig. 4a,b time series plots of $\delta^{13}\text{C}$ (‰) and system sensitivity of standard measurements are presented, respectively. Sensitivity (V s/ng C) shows some variability, which is expected as the emission of the filament in the IRMS is variable over time, but this is taken into account by referencing against the aforementioned reference

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



gas. Repeatability of mixing ratio measurements is evaluated to be less than $\pm 5\%$ for all compounds. Figure 4a illustrates also a drift of $\delta^{13}\text{C}$ in the system over the selected period. In order to correct for drift in $\delta^{13}\text{C}$, detrending is accomplished by observing weekly averages as compared to long-term calibration measurement means.

To evaluate the overall precision of the system a series of Gaussian-fitted histograms of $\delta^{13}\text{C}$ for the compounds measured in the standard gas are provided in Fig. 5a–d, with a bin size of 0.1‰, outliers greater than 3σ rejected. For ethane, propane and benzene the $1-\sigma$ error was below 0.5‰ for all volumes tested. For methyl chloride, the standard deviation is $\sim 0.8\%$ for all tested volumes. Likewise, the reproducibility for other compounds was tested by introducing a different standard gas, containing 20 to 50 ppb each of acetylene, ethylene, propylene and C_4 and C_5 saturated hydrocarbons. The results of stability evaluations of these compounds are broadly similar to those of the primary working standard. Table 2 summarizes $1-\sigma$ error of all tested compounds.

3 First results

To demonstrate the measurement capabilities of this instrument, we present the results of a 48-h measurement campaign of selected non-methane hydrocarbons undertaken over 4–6 August 2009. Samples were taken from an ambient air inlet located $\sim 20\text{ m a.g.l.}$ at $52^\circ 05' 14'' \text{ N}$, $5^\circ 09' 57'' \text{ E}$. The sampling location is within 500 m to a high traffic highway, and is located in our laboratory on the Utrecht University campus, in a semi-urban environment. Thus, an abundance of local sources, dominated by traffic emissions, can be expected for hydrocarbons. Atmospheric conditions at the time of the campaign were characterized by warm stable summer weather. During this period, high surface pressure was located above the North Sea. The sample days were similar meteorologically, with clear skies, light winds, and high temperatures near 30°C . At night, temperatures decreased to near 20°C and the winds became near calm (ECMWF, 2010; KNMI, 2010).

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



The samples were taken and processed in situ using the aforementioned ambient sampling subsystem, with 20 L samples (sampling rate 0.5 L/min) taken at approximately 2-h intervals (excepting necessary calibration of the instrument) and processed immediately. The 20 L sample size was chosen to assure IRMS peak areas of >0.5 V s for the light saturated hydrocarbons.

3.1 Mixing ratio

Broadly, mixing ratios are in line with what may be expected for an urban environment (e.g., Seinfeld and Pandis, 1998), although for some compounds, especially the light alkanes, quite high mixing ratios of several ppb were measured. Mixing ratio measurements (Fig. 6a–j and Table 3) show a clear diurnal cycle, which corresponds very well to patterns of urban activity. Each compound has a peak in the morning hours, minimum values in the afternoon, and elevated values at night (an exception is *n*-pentane, where minima occur at night).

The unsaturated compounds in particular (acetylene, ethylene, propylene; Fig. 6a, b and d, respectively), which generally stem from combustion processes, show very similar traces, although ethylene displays slightly more variability, (see also Table 3). The diurnal cycle patterns during this period agree well with morning vehicular traffic intensity; heavy congestion on local highways is common in the periods from 07:00 to 09:00. The afternoon-evening (16:00 to 18:00) peak of traffic, though generally less intense than that of the morning but still notable, is not clearly observed in the data. This is likely due to the short lifetime of these compounds: OH* oxidation during daytime may be responsible for the afternoon minimum in mixing ratio and nightly buildup, as OH* mixing ratios have a strong diurnal cycle related to sunlight. This is likely enough to suppress the afternoon traffic peak.

Ethane (Fig. 6c) also displays a clear diurnal cycle, but in contrast to the above compounds has peaks in mixing ratio during the night and early morning, far earlier than other compounds. As mentioned previously, the prevailing meteorological conditions of nearby high surface pressure caused (near) calm winds during night, leading

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Analytical system for carbon stable isotope measurementsA. Zuiderweg et al.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

to a suppression of mixing and a decrease in the boundary layer height as shown by ECMWF ERA Interim reanalysis maps at 03:00 UTC on both days (ECMWF, 2010; KNMI, 2010). This loss of mixing would then allow the buildup of continuously emitted gasses. Presuming that the main urban source of ethane is leakage of natural gas, local leakage could cause such an increase of mixing ratio. The observed rate of increase of ethane over the sample days in the period of 19:00 to 05:00 approaches 0.6 ppb per hour, which is considerable. The daytime decrease may be similarly ascribed to the increase in mixing and consequent dilution; the oxidation of ethane by OH* occurs, but the light alkanes are relatively long-lived and not significantly removed on these timescales.

The change in mixing during daytime and nighttime can help to explain the afternoon decrease and nighttime buildup in mixing ratio of all alkanes measured, with the exception of *n*-pentane (Fig. 6h). Beside the common morning mixing ratio peak, this compound differs from others measured in that there is little evidence of a rapid daytime decrease of mixing ratio, especially on 6 August. This implies different dominating sources during this period, which are not as affected by the increase in mixing during the day, suggesting that the source is not local. According to Goldstein and Shaw (2003), a significant source of C₅ to C₁₀ alkanes and aromatics can be found in industrial emissions, but as there is little industry in the region of the measurement site this cannot explain these elevated afternoon and evening measurements of *n*-pentane directly. However, supporting evidence for a distinct and non-local source can be found in the stable isotope measurements of this compound, of which discussion follows.

Isopentane, hexane, and benzene (Fig. 6g,i, and j) show profiles similar to the unsaturated hydrocarbons mentioned above, and some of the alkanes, pointing to transportation-related sources.

3.2 Carbon stable isotope composition

Figure 7a–j shows $\delta^{13}\text{C}$ measurements over the sampling period. In general, $\delta^{13}\text{C}$ averages over the 48-h period (Table 4) agree well with published values from studies

of urban air, despite the large variations, especially in unsaturated compounds. Acetylene (Fig. 7a), for example, has a large daily variation (maximum of 5‰ and minimum of -15‰), but its mean over the entire period is -9.1‰, which falls well in the urban range of $-8 \pm 4\%$ as reported in Goldstein and Shaw (2003). The maximum observed in acetylene is more enriched than previous measurements reported in urban environments, but is not unreasonable, as Redeker et al. (2005) reported for daytime values in summer.

Ethylene (Fig. 7b), which shows a very well defined diurnal cycle with minima near -30‰ in the early morning hours and maxima near -5‰ during the afternoon (24 h mean -17‰), agrees with expected mean values for C₂ to C₅ alkenes ($-22 \pm 8\%$, Goldstein and Shaw, 2003), as does propylene (Fig. 7d), which shows a mean of -21.1‰. The large diurnal variation in ethylene, as seen here, can be expected for such a reactive compound with a high KIE (18.6‰, Anderson et al., 2003), strong fractionation during the daylight hours occurs (Goldstein and Shaw, 2003), and this can be seen in Table 4 (periods 2 and 3). Further, utilizing the isotopic clock parameterization (Eq. 5, Rudolph and Czuba, 2000) provides additional support for this: assuming that the nighttime $\delta^{13}\text{C}$ value (mean -27‰) and daytime value (mean -10‰) represent the unoxidized ($^0\delta_{\text{C}_2\text{H}_4}$) and oxidized ($\delta_{\text{C}_2\text{H}_4}$) isotope ratios of ethylene, respectively, a value for $^{\text{OH}}\text{KIE}_{\text{C}_2\text{H}_4}$ of 18.6‰ (Anderson et al., 2003) and $^{\text{OH}}k_{\text{C}_2\text{H}_4} = 7.9 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ (at 296 K, Atkinson et al., 2006), it is calculated that $[\text{OH}^*]$ required for causing this fractionation reaches $3.6 \times 10^6 \text{ molecules cm}^{-3}$ for a 9 h atmospheric processing time. This OH* concentration is within the range for summer tropospheric conditions (e.g., Lu and Khalil, 1991).

Ethane (Fig. 7c), is more enriched than higher alkanes, because of its differing source from natural gas, the ethane in which is known to be relatively enriched. The other alkanes originate mainly from combustion processes (Goldstein and Shaw, 2003). The mean $\delta^{13}\text{C}$ of ethane was measured to be $-24.5 \pm 0.6\%$ for the entire period. Tsunogai et al. (1999) reported values between -28 to -22‰ in urban and marine locations. There is almost no diurnal variation in our measurements (with the exception

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of a slight depletion during the period of highest mixing ratio values, in the morning), which is also reasonable to expect for the most stable and longest-lived non-methane hydrocarbon.

The $\delta^{13}\text{C}$ of the C_3 to C_6 alkanes measured also show little diurnal variation and mean values of -27 to -30‰ . Previously reported measurements indicated $-27 \pm 2.5\text{‰}$ (Rudolph et al., 2002; Goldstein and Shaw, 2003). The presence of a single very depleted point (-45‰) in measurements of hexane is notable, but this outlier may be due to an unidentified experimental problem. Apart from this point, standard deviations for these compounds also correspond well to previous results. Benzene also fits well to previous measurements despite some apparent high morning variability: mean $-26.2 \pm 2.3\text{‰}$, compared to literature values of $-27 \pm 2\text{‰}$ (Goldstein and Shaw, 2003).

3.3 Source signatures

A common tool for atmospheric isotope research to decipher sources is the Keeling plot analysis, which was first developed for the analysis of stable carbon isotopes of carbon dioxide (Keeling, 1958). This involves correlating $\delta^{13}\text{C}$ against the inverse of the mixing ratio, and linearly fitting the result. The y -intercept of this fit then indicates the isotopic composition of the contaminating source that mixes into background air. This procedure is based on a few assumptions: (1) there should be only one source and a stable reservoir into which it is being diluted; (2) the compound concerned should be (relatively) non-reactive; and (3) the $\delta^{13}\text{C}$ and inverse mixing ratio should be well-correlated; lest the values calculated become unclear and unreliable (Keeling, 1958). In our dataset, the Keeling plot analysis works well for ethylene, n -butane, and n -pentane (Fig. 8a–c). The isotope source signatures determined this way are given in Table 5. Other measured compounds are not included because of small isotopic variation or low correlation, indicating that the above conditions are violated.

For ethylene (Fig. 8a) the source signatures derived from this analysis agree well with engine emission measurements (Rudolph et al., 2002; Goldstein and Shaw, 2003).

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



It should be noted that in the case of ethylene the slope in the Keeling plot is rather caused by reaction kinetics (KIE of the ethylene OH reaction) than by diluting emissions into a pool with background isotope signatures.

Where there are good correlations for fairly non-reactive compounds, the values can be instructive with respect to mixing. For example, in *n*-butane (Fig. 8b), a mixing effect is seen; higher mixing ratios are clearly associated with more enriched $\delta^{13}\text{C}$; distinctly different isotopic ratio values are indicated for lower mixing ratios. In periods 3 and 4 good correlations allow determining source signatures of -25.4 and -24.5 , respectively, in agreement with the literature ($-27 \pm 2.5\%$, Goldstein and Shaw, 2003) for fossil fuel combustion.

In *n*-pentane (Fig. 8c), there is a strong departure in source signature values in Table 5 period 3: here a strongly correlated source signature of -23.9% occurs, as compared to more depleted values at other times. This would lend support to the speculation that there is a distinct isotopically different emission occurring at this time as discussed above for the mixing ratios.

4 Conclusions

We have presented a NMHC carbon stable isotope analysis system capable of high-resolution measurements of many compounds from a large variety of sample sources with small measurement errors (1% vs. VPDB or less). In particular, the capability to process high volume atmospheric allows examination of samples with large quantities of bulk gases and CO_2 , without loss of any compounds of interest, and with a short processing time as well. As the first results demonstrate, $\delta^{13}\text{C}$ values measured during a 48 h ambient air measurement campaign agree well with previous research, while highlighting the complex diurnal behavior of hydrocarbons in an urban environment. This on the one hand demonstrates reliable operation of the system and on the other opens the doorway to exciting future measurements.

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Acknowledgement. We would like to thank Henk Jansen, of Rijksuniversiteit Groningen, The Netherlands, for calibration of the CO₂ reference standard; and Iulia Gensch, of Forschungszentrum Jülich, Germany, for calibration of the NMHC working standard.

References

- 5 Anderson, R. S., Huang, L., Iannone, R., Thompson, A. E., and Rudolph, J.: Carbon kinetic isotope effects in the gas phase reactions of light alkanes and ethene with the OH radical at 296 ± 4 K, *J. Phys. Chem. A*, 108, 11537–11544, doi:10.1021/jp0472008, 2004.
- Archbold, M. E., Redeker, K. R., Davis, S., Elliot, T., and Kalin, R. M.: A method for carbon stable isotope analysis of methyl halides and chlorofluorocarbons at pptv concentrations, *Rapid Commun. Mass Sp.*, 19, 337–340, doi:10.1002/rcm.17, 2005.
- 10 Atkinson, R., Baulch, D. L., Cox, R. A., Crowley, J. N., Hampson, R. F., Hynes, R. G., Jenkin, M. E., Rossi, M. J., Troe, J., and IUPAC Subcommittee: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species, *Atmos. Chem. Phys.*, 6, 3625–4055, doi:10.5194/acp-6-3625-2006, 2006.
- 15 Bill, M., Rhew, R. C., Weiss, R. F., and Goldstein, A. H.: Carbon isotope ratios of methyl bromide and methyl chloride emitted from a coastal salt marsh, *Geophys. Res. Lett.*, 29, 4, 4 pp., doi:10.1029/2001GL012946, 2002.
- Brenninkmeijer, C. A. M.: Applications of stable isotope analysis to atmospheric trace gas budgets, *Eur. Phys. J. C*, 1, 137–148, doi:10.1140/epjconf/e2009-00915-x, 2009.
- 20 Czapiewski, K. V., Czuba, E., Huang, L., Ernst, D., Norman, A. L., Koppmann, R., and Rudolph, J.: Isotopic composition of non-methane hydrocarbons in emissions from biomass burning, *J. Atmos. Chem.*, 43, 45–60, 2002.
- Conny, J. M. and Currie, L. A.: The isotopic characterization of methane, non-methane hydrocarbons and formaldehyde in the troposphere, *J. Atmos. Environ.*, 30, 4, 621–638, 1996.
- 25 European Center for Medium Range Weather Forecasting (ECMWF): ERA Interim Reanalysis for period 4–6 August 2009, accessed 24 October 2010, available at: http://data-portal.ecmwf.int/data/d/interim_daily/, 2010.
- Fisseha, R., Spahn, H., Wegener, R., Hohaus, T., Brasse, G., Wissel, H., Tillmann, R., Wahner, A., Koppmann, R., and Kiendler-Scharr, A.: Stable carbon isotope composition

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



of secondary organic aerosol from β -pinene oxidation, *J. Geophys. Res.*, 114, D02304, doi:10.1029/2008JD011326, 2009.

Iannone, R., Anderson, R. S., Rudolph, J., Huang, L., and Ernst, D.: The carbon kinetic isotope effects of ozone-alkene reactions in the gasphase and the impact of ozone reactions on the stable carbon isotope ratios of alkenes in the atmosphere. *Geophys. Res. Lett.*, 30(13), 1684–1688, doi:10.1029/2003GL017221, 2003.

Iannone, R., Koppmann, R., and Rudolph, J.: $^{12}\text{C}/^{13}\text{C}$ kinetic isotope effects of the gas-phase reactions of isoprene, methacrolein, and methyl vinyl ketone with OH radicals, *J. Atmos. Environ.*, 43, 3103–3110, doi:10.1016/j.atmosenv.2009.03.006, 2009.

Johnson, M. S., Feilberg, K. L., von Hessberg, P., and Nielsen, O. J.: Isotopic processes in atmospheric chemistry, *Chem. Soc. Rev.*, 31, 313–323, doi:10.1039/b108011n, 2002.

Goldstein, A. H. and Galbally, I. E.: Known and unexplored organic constituents in the Earth's atmosphere, *Environ. Sci. Technol.*, 41(5), 1514–1521, doi:10.1021/es072476p, 2007.

Goldstein, A. H. and Shaw, S. L.: Isotopes of volatile organic compounds: an emerging approach for studying atmospheric budgets and chemistry, *Chem. Rev.*, 103, 5025–5048, 2003.

Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global-model of natural volatile organic-compound emissions, *J. Geophys. Res.-Atmos.*, 100, 8873–8892, 1995.

Harper, D. B., Hamilton, J. T. G., Ducrocq, V., Kennedy, J. T., Downey, A., and Kalin, R. M.: The distinctive isotopic signature of plant-derived chloromethane: possible application in constraining the atmospheric chloromethane budget, *Chemosphere*, 52, 433–436, doi:10.1016/S0045-6535(03)00206-6, 2003.

Keeling, C. D.: The concentration and isotopic abundances of atmospheric carbon dioxide in rural areas, *Geochim. Cosmochim. Acta*, 13, 322–334, 1958.

Keppler, F., Harper, D. B., Röckmann, T., Moore, R. M., and Hamilton, J. T. G.: New insight into the atmospheric chloromethane budget gained using stable carbon isotope ratios, *Atmos. Chem. Phys.*, 5, 2403–2411, doi:10.5194/acp-5-2403-2005, 2005.

Koningklijk Nederlands Meteorologisch Instituut (KNMI): Archived weather analysis maps for 4–6 August 2009, accessed 24 October 2010, available at: <http://www.knmi.nl/klimatologie/daggegevens/weerkaarten/index.cgi>, 2010.

Liu, Y., Shao, M., Kuster, W. C., Goldan, P. D., Hualì, X., Lu, S., and De Gouw, J. A.: Source

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- identification of reactive hydrocarbons and oxygenated VOCs in the summertime in Beijing, *Environ. Sci. Technol.*, 43, 75–81, 2009.
- Lu, Y. and Khalil, M. A. K.: Tropospheric OH: model calculations of spatial, temporal, and secular variations, *Chemosphere*, 23, 397–444, 1991.
- 5 Matthews, D. M. and Hayes, J. M.: Isotope-ratio-monitoring gas chromatography-mass spectrometry, *Anal. Chem.*, 50, 11, 1465–1473, 1978.
- Meritt, D. A., Freeman, K. H., Ricci, M. P., Studley, S. A., and Hayes, J. M.: Performance and optimization of a combustion interface for isotope ratio monitoring gas chromatography/mass spectrometry, *Anal. Chem.*, 67, 2461–2473, 1995.
- 10 Milton, M. J. T., Harris, P. M., Brown, A. S., and Cowper, C. J.: Normalization of natural gas composition data measured by gas chromatography, *Meas. Sci. Technol.*, 20, 025101, doi:10.1088/0957-0233/20/2/025101, 2010.
- Nara, H., Nakagawa, F., and Yoshida, N.: Development of two-dimensional gas chromatography/isotope ratio mass spectrometry for the stable carbon isotopic analysis of C₂–C₅ non-methane hydrocarbons emitted from biomass burning, *Rapid Commun. Mass Sp.*, 20, 241–247, doi:10.1002/rcm.2302, 2006.
- 15 Nara, H., Toyoda, S., and Yoshida, N.: Measurements of stable carbon isotopic composition of ethane and propane over the Western North Pacific and Eastern Indian Ocean: a useful indicator of atmospheric transport process, *J. Atmos. Chem.*, 56, 293–314, doi:10.1007/s10874-006-9057-3, 2007.
- 20 Redeker, K. R., Davis, S., and Kalin, R. M.: Isotope values of atmospheric halocarbons and hydrocarbons from Irish urban, rural, and marine locations, *J. Geophys. Res.*, 112, D16307, doi:10.1029/2006JD007784, 2007.
- Rudolph, J. and Czuba, E.: On the use of isotopic composition measurements of volatile organic compounds to determine the “photochemical age” of an air mass, *Geophys. Res. Lett.*, 27, 23, 3865–3868, 2000.
- 25 Rudolph, J. and Ehhalt, D. H.: Measurements of C₂–C₅ hydrocarbons over the North Atlantic, *J. Geophys. Res.*, 86, C12, 11959–11964, 1981.
- Rudolph, J., Lowe, D. C., Martin, R. J., and Clarkson, T. S.: A novel method for compound specific determination of $\delta^{13}\text{C}$ in volatile organic compounds at ppt levels in ambient air, *Geophys. Res. Lett.*, 24(6), 659–662, 1997.
- 30 Rudolph, J., Czuba, E., Norman, A. L., Huang, L., and Ernst, D.: Stable carbon isotope composition of nonmethane hydrocarbons in emissions from transportation related sources and

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



- atmospheric observations in an urban atmosphere, *Atmos. Environ.*, 36, 1173–1181, 2002.
- Saito, T., Tsunogai, U., Kawamura, K., Nakatsuka, T., and Yoshida, N.: Stable carbon isotopic compositions of light hydrocarbons over the Western North Pacific and implication for their photochemical ages, *J. Geophys. Res.*, 107(D4), 4040, doi:10.1029/2000JD000127, 2002.
- 5 Saito, T., Kawamura, K., Tsunogai, U., Chen, T., Matsueda, H., Nakatsuka, T., Gamo, T., Uematsu, M., and Huebert, B. J.: Photochemical histories of nonmethane hydrocarbons inferred from their stable carbon isotope ratio measurements over east Asia, *J. Geophys. Res.*, 114, D11303, doi:10.1029/2008JD011388, 2009.
- Santrock, J., Studley, S. A., and Hayes, J. M.: Isotopic analyses based on the mass spectra of
- 10 carbon dioxide, *Anal. Chem.*, 57, 7, 1444–1448, doi:10.1021/ac00284a060, 1985.
- Seinfeld, J. H. and Pandis, S. N.: *Atmospheric Chemistry and Physics: from Air Pollution to Climate Change*, John Wiley and Sons, New York, 1326 pp., 1998.
- Škrbić, B. D. and Zlatković, M. J.: Simple method for the rapid analysis of natural gas by gas chromatography, *Chromatographia*, 17(1), 44–46, 1983.
- 15 Tsunogai, U. and Yoshida, N.: Carbon isotopic compositions of C₂–C₅ hydrocarbons and methyl chloride in urban, coastal, and maritime atmospheres over the Western North Pacific, *J. Geophys. Res.*, 104, D13, 16033–16039, 1999.
- Warneck, P.: *Chemistry of the Natural Atmosphere*, Academic Press, San Diego, CA, 757 pp., 1988.

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Table 1. Mean and standard deviation $\delta^{13}\text{C}$ (‰) for ethane, propane, methyl chloride, and benzene, without (LN_2 traps only), and with CO_2 separation column installed (Standard config.). $n=10$ for both sets of data.

Compound	LN_2 traps only mean $\delta^{13}\text{C}$	LN_2 traps only $\sigma\delta^{13}\text{C}$	Standard config mean $\delta^{13}\text{C}$	Standard config $\sigma\delta^{13}\text{C}$
Ethane	−28.4	0.33	−28.6	0.27
Propane	−34.6	0.49	−34.3	0.49
Methyl chloride	−46.4	0.69	−48.8	0.72
Benzene	−27.4	0.36	−27.5	0.39

[Title Page](#)
[Abstract](#)
[Introduction](#)
[Conclusions](#)
[References](#)
[Tables](#)
[Figures](#)
[Back](#)
[Close](#)
[Full Screen / Esc](#)
[Printer-friendly Version](#)
[Interactive Discussion](#)


Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Table 2. $1-\sigma$ standard deviations of $\delta^{13}\text{C}$ (‰) and IRMS Sensitivity (V s/ng C) for all compounds in the two calibration gases. For the compounds in the working standard the values represent ~ 9 months detrended long term accuracy levels; for the other compounds accuracy levels were determined from a series of 20 standard gas measurements over a period of 1 month.

Compound	$\delta^{13}\text{C}$ σ (‰)	Sensitivity σ (V s/ng C)
Primary NMHC working standard		
Ethane	0.294	0.0053
Propane	0.397	0.0063
MeCl	0.795	0.0058
Benzene	0.484	0.0083
Other tested compounds		
Acetylene	0.441	0.0062
Ethylene	0.716	0.010
Propylene	0.658	0.010
Isobutane	0.542	0.0097
Butane	0.476	0.0083
Isopentane	0.308	0.0095

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Table 3. Mean mixing ratio and sample standard deviation of all measurements and individual measurement periods of selected compounds in ambient air of samples taken during 48-h measurements, 6 to 8 August 2009. Periods are the same as those in Figs. 8–10.

Compound	Mean VMR all (ppb)	σ (ppb)	Mean VMR P1 (ppb)	σ (ppb)	Mean VMR P2 (ppb)	σ (ppb)	Mean VMR P3 (ppb)	σ (ppb)	Mean VMR P4 (ppb)	σ (ppb)
Acetylene	0.29	0.22	0.26	0.07	0.51	0.36	0.15	0.01	0.22	0.09
Ethylene	0.77	0.62	0.88	0.48	1.45	0.71	0.33	0.10	0.40	0.27
Ethane	3.09	2.23	4.52	2.43	3.98	2.68	1.41	0.69	2.14	1.03
Propylene	0.21	0.14	0.21	0.08	0.36	0.19	0.11	0.02	0.16	0.05
Propane	2.02	2.14	1.83	0.77	3.87	3.88	1.41	0.90	0.99	0.45
<i>n</i> -Butane	1.19	0.67	1.13	0.47	2.03	0.74	0.77	0.17	0.85	0.38
Isopentane	0.42	0.34	0.31	0.12	0.76	0.58	0.31	0.08	0.30	0.09
<i>n</i> -Pentane	0.45	0.27	0.23	0.10	0.61	0.31	0.43	0.30	0.55	0.17
Hexane	0.16	0.09	0.12	0.03	0.25	0.11	0.18	0.08	0.11	0.03
Benzene	0.20	0.11	0.24	0.07	0.27	0.21	0.12	0.03	0.17	0.06

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Table 4. Mean $\delta^{13}\text{C}$ (‰) vs. VPDB and sample standard deviation of all measurements and individual measurement periods of selected compounds. Samples and periods are the same as in Table 3.

Compound	Mean $\delta^{13}\text{C}$ (‰) all	σ (‰)	Mean $\delta^{13}\text{C}$ P1 (‰)	σ (‰)	Mean $\delta^{13}\text{C}$ P2 (‰)	σ (‰)	Mean $\delta^{13}\text{C}$ P3 (‰)	σ (‰)	Mean $\delta^{13}\text{C}$ P4 (‰)	σ (‰)
Acetylene	-9.1	4.4	-10.2	1.4	-10.2	4.8	-6.2	6.8	-9.6	2.8
Ethylene	-17.0	7.9	-23.3	3.2	-21.5	5.3	-9.1	4.2	-11.7	6.1
Ethane	-24.5	0.6	-24.1	0.5	-24.6	0.8	-24.6	0.8	-24.6	0.17
Propylene	-21.1	2.3	-21.7	1.3	-19.6	2.5	-20.3	2.5	-22.8	2.1
Propane	-27.9	1.7	-27.0	2.3	-27.8	1.4	-28.6	1.7	-28.3	1.1
<i>n</i> -Butane	-27.6	1.7	-27.0	1.4	-26.2	1.3	-29.3	1.3	-27.8	1.1
Isopentane	-29.0	0.6	-29.0	0.8	-29.0	0.6	-29.4	0.6	-28.9	0.3
<i>n</i> -Pentane	-27.0	1.6	-28.0	1.2	-28.2	0.9	-26.0	2.0	-25.8	0.4
Hexane	-30.4	3.7	-28.6	1.7	-32.1	7.4	-29.4	1.0	-30.7	1.0
Benzene	-26.2	2.3	-25.9	1.4	-26.8	5.1	-25.5	1.6	-26.7	0.2

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Table 5. Ethylene, *n*-butane and *n*-pentane source signature (SS, in ‰ vs. VPDB) and R^2 from the fits in Fig. 8 of all measurements and individual measurement periods of selected compounds. Samples and periods are the same as in Table 3.

Compound	SS All (‰)	R^2 All	SS P1 (‰)	R^2 P1	SS P2 (‰)	R^2 P2	SS P3 (‰)	R^2 P3	SS P4 (‰)	R^2 P4
Ethylene	-26.8	0.68	-29.8	0.76	-25.7	0.17	-12.6	0.04	-22.7	0.89
<i>n</i> -Butane	-24.7	0.52	-26	0.07	-24.7	0.29	-25.4	0.47	-24.5	0.98
<i>n</i> -Pentane	-25.9	0.22	-27	0.17	-27.8	0.08	-23.9	0.65	-26	0.03

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

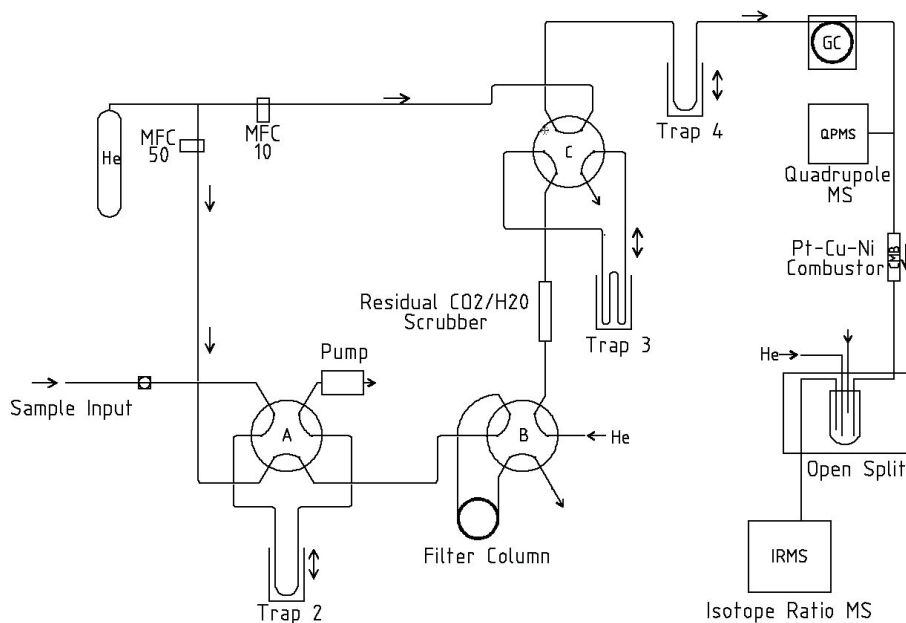


Fig. 1. System diagram. A, B, C indicate Valco 6-port valves; SAMP indicates 0.5 m×4 mm ID glass-bead (80/100 mesh) filled stainless steel cryotrap; REC indicates 0.7 m×2.5 mm ID glass-bead (80/100 mesh) filled stainless steel W-shaped recovery cryotrap, FOC indicates 0.5 m×0.25 mm stainless steel jacketed capillary focusing cryotrap. SEP indicates 3 m×4 mm ID PoraPAK Q (100/120 mesh) stainless steel packed separation column.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

**Analytical system for
carbon stable isotope
measurements**

A. Zuiderweg et al.

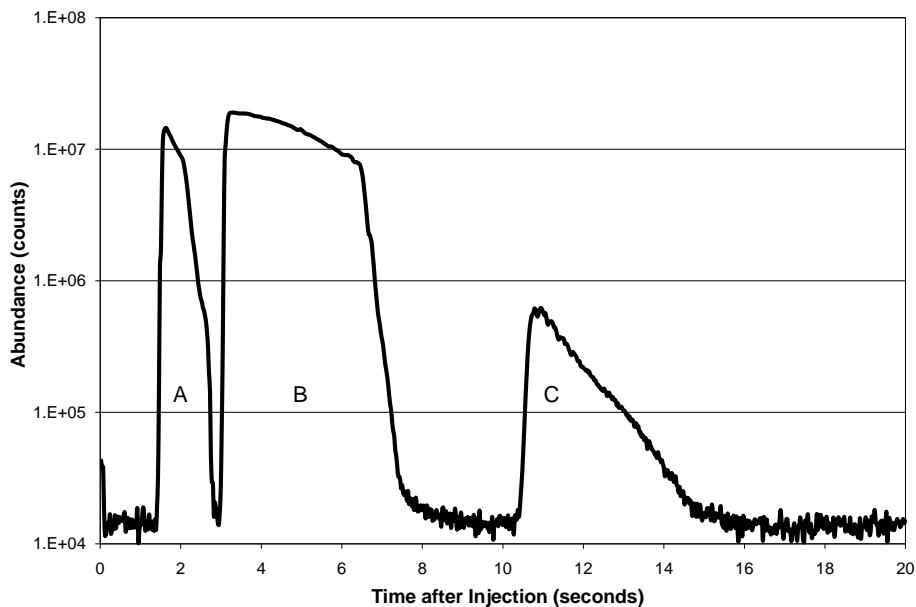


Fig. 2. GCMS results 3 m×4 mm ID PoraPAK Q (100/120 mesh) stainless steel packed separation column performance, total MS ion abundance vs. elution (after injection) time. Peaks A, B, and C are due to elution of methane and nitrogen, bulk carbon dioxide, and ethane and other hydrocarbons, respectively.

[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[⏪](#)[⏩](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

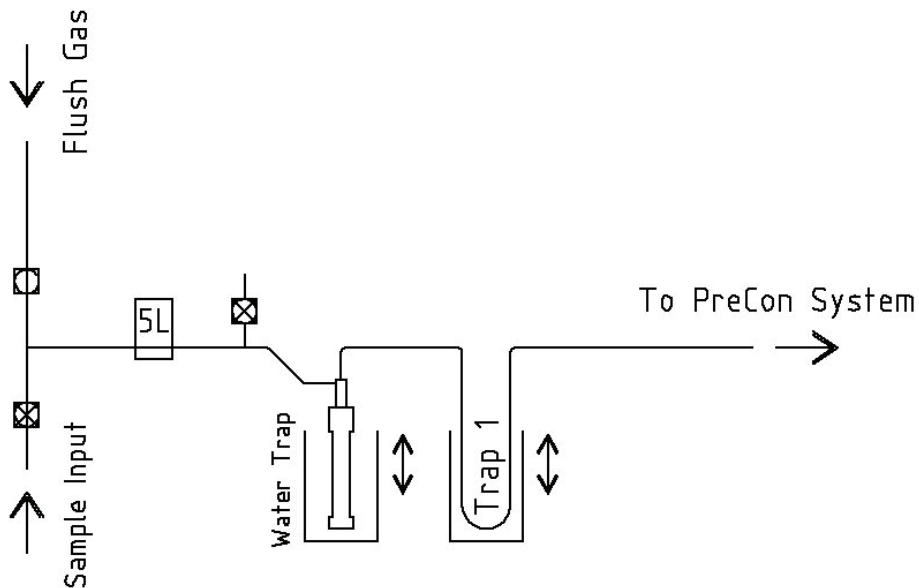


Fig. 3. Ambient air drying and trapping subsystem. The water trap is a large diameter (0.25 m × 2.54 cm) cryogenic stainless steel trap, trap 1 is a large diameter (0.5 m × 1.27 cm) glass-bead (80/100 mesh) filled stainless steel primary capture cryotrap. Flush gas may be He or synthetic air (78:22 N₂-O₂ mix). Flows are regulated by a 5 L/min capacity MKS instruments thermal mass flow controller. After extraction and drying, the contents of trap 1 can be flushed to the analytical system (Fig. 1).

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

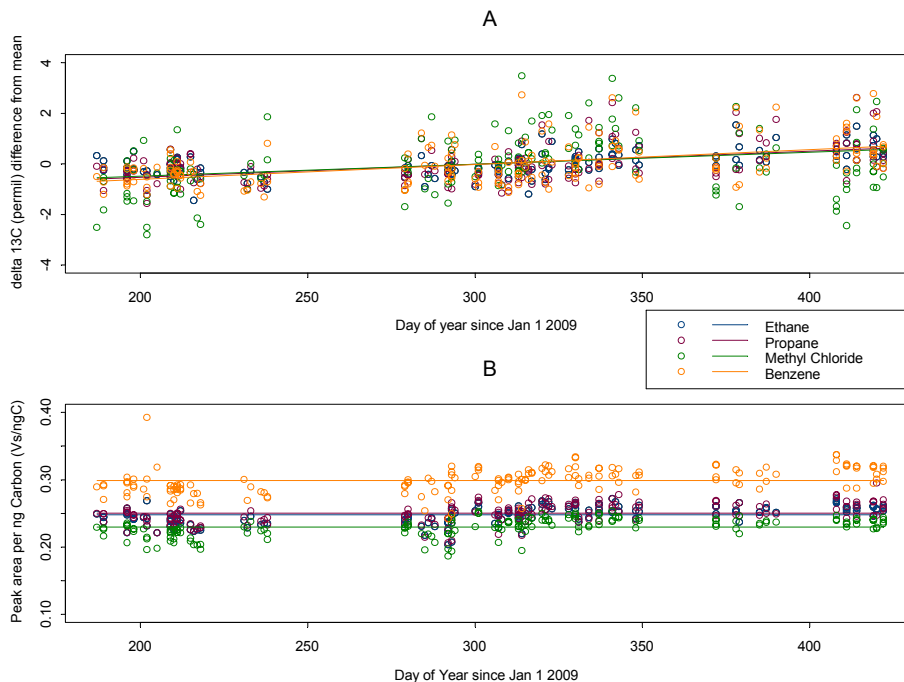


Fig. 4. Time-stability difference from mean of $\delta^{13}\text{C}$ (‰) and sensitivity (V/s/ngC) of the GC-MS-C-IRMS NMHC system tested with 4 compounds in Apel-Riemer (AiR Inc.) calibration gas, various volumes, respectively. Horizontal lines are plotted to make the long-term variability better visible.

A. Zuiderweg et al.

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

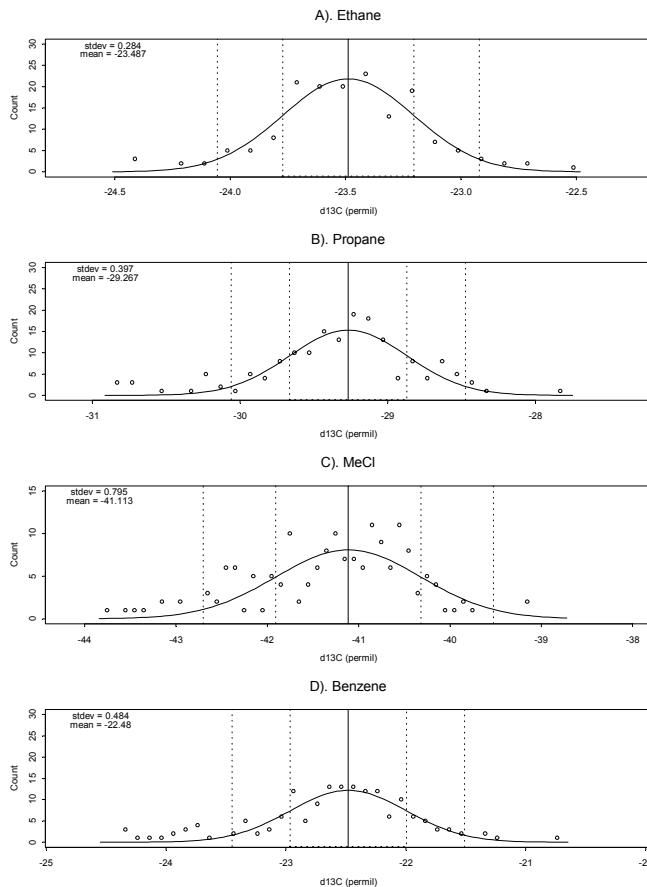


Fig. 5. Histograms of detrended $\delta^{13}\text{C}$ (‰) data, together with Gaussian fit for the Apel-Riemer (AiR) multicomponent NMHC calibration gas, including measurements of various volumes (50, 100, 200 mL) for peak area ranges comparable to measurements. Dashed lines indicate 1 and 2σ intervals. **(A)** ethane, **(B)** propane, **(C)** methyl chloride, **(D)** benzene.

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

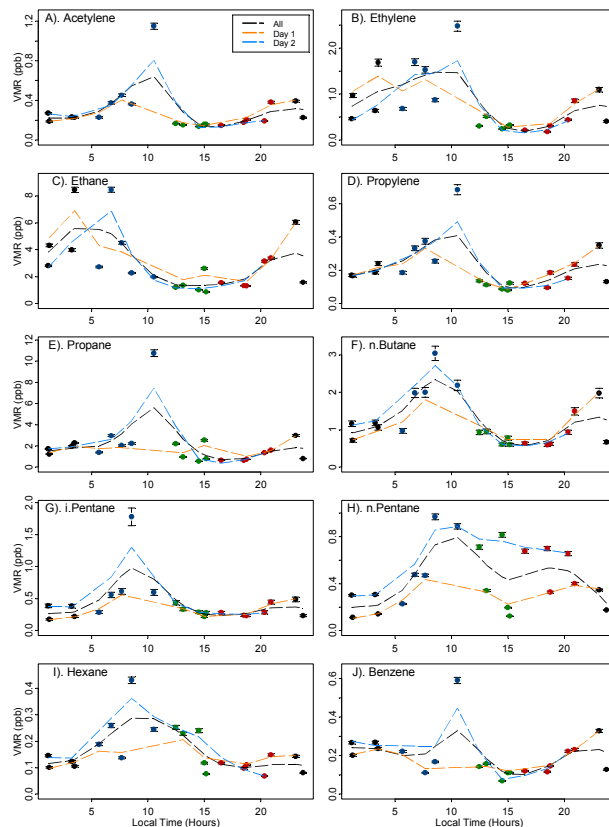


Fig. 6. Mixing ratios vs. time over 48-h (4–6 August 2009) period, overlapped on one diurnal cycle. **(A)** acetylene, **(B)** ethylene, **(C)** ethane, **(D)** propylene, **(E)** propane, **(F)** *n*-butane, **(G)** isopentane, **(H)** *n*-pentane, **(I)** hexane, **(J)** benzene. Error bars indicate the 5% accuracy levels. Period means in Table 3. Colors indicate time periods: P1 (black): 21:00–05:00; P2 (blue): 05:00–11:00; P3 (green): 11:00–15:30; P4 (red): 15:30–21:00; all times CEDT. Period codes correspond to those in Tables 3, 4, and 5.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



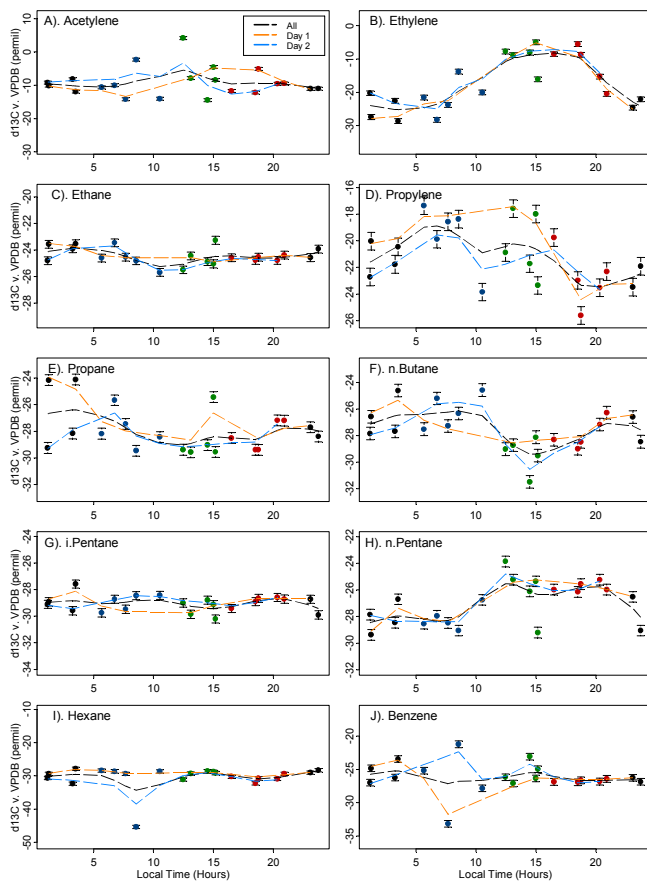


Fig. 7. Compound $\delta^{13}\text{C}$ (‰ vs. VPDB) vs. time (hours) over 48-h (4–6 August 2009) period, overlapped. Error bars indicate 1σ ranges. Letter codes identical to Fig. 6. Period means and standard deviations in Table 4.

Analytical system for carbon stable isotope measurements

A. Zuiderweg et al.

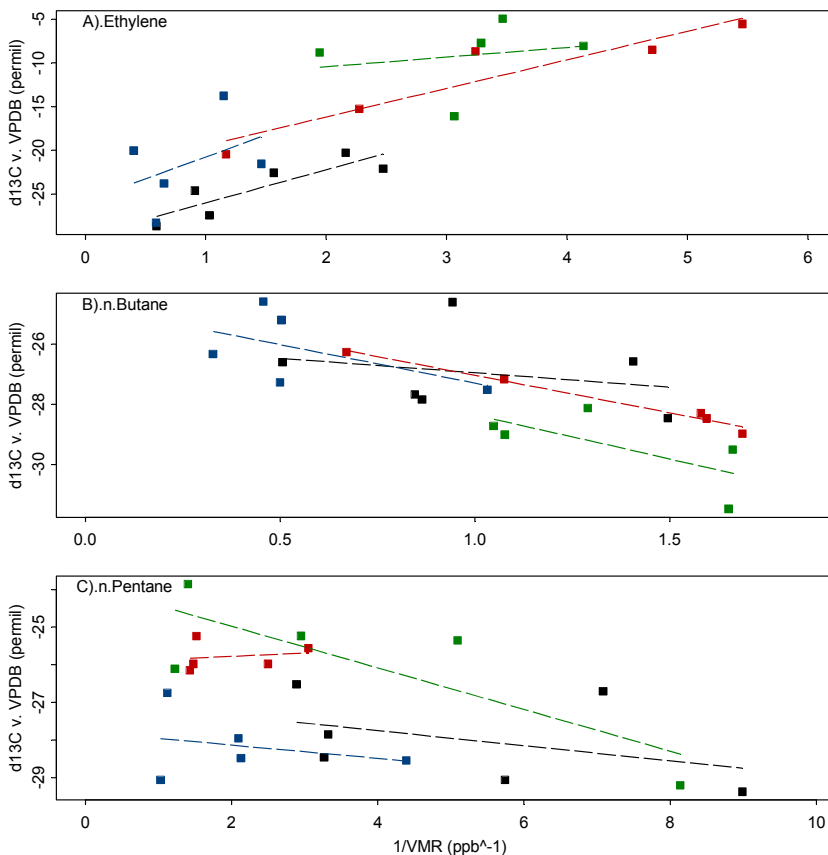


Fig. 8. Ethylene, *n*-butane, and *n*-pentane $\delta^{13}\text{C}$ (‰ vs. VPDB) plotted versus inverse mixing ratio (ppb^{-1}) over the 48-h (4–6 August 2009) period, with linear fits to points of each time period. Derived values for isotope source signatures are given in Table 5. Colors indicate periods as indicated in Figs. 6 and 7 and correspond to P1 through P4 in Tables 3, 4, and 5.