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A novel method for compound specific determination of δ13C in volatile organic compounds at ppt levels in ambient air

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Abstract. A novel method for the compound specific determination of $\delta^{13}C$ in VOC is presented. It combines a cryogenic preconcentration procedure with gas chromatographic separation, on-line combustion and isotope ratio mass spectrometry. The method allows the determination of $\delta^{13}C$ values of VOC at sub ppb levels with a precision of 0.5‰. The procedure is suitable for routine operation. The accuracy of the method is of the same quality as the reproducibility of the measurements. The first ever measurements of $\delta^{13}C$ in selected VOC in clean air are presented and compared with data from samples of contaminated air. The variability in the $\delta^{13}C$ values of atmospheric VOC is much larger than the accuracy and precision of the measuring method. Hence the technique will be a very valuable tool to complement concentration measurements of VOC and to improve our understanding of the processes governing the distribution of VOC in the atmosphere.

Introduction

Volatile organic compounds (VOC) play an important role in the chemistry of the atmosphere. There are many investigations of the sources, sinks, atmospheric transport, conversion reactions and distributions of these compounds (cf. Müller, 1992, Rudolph 1995; Singh and Zimmerman, 1992; Kanakidou et al., 1991; Fehsenfeld et al., 1992; and references therein). It has been demonstrated that measurements of the distributions of VOC can be used to study and understand key atmospheric processes (Rudolph and Johnen, 1990; Rudolph 1995, Rudolph et al., 1996; Parrish et al., 1992; McKeen et al. 1990; Jobson et al., 1994; McKenna et al., 1995). However, the interpretation of atmospheric distributions of VOC is seldom straightforward, often ambiguous, and the conclusions drawn may be controversial (Finnlayson Pitts, 1993; Parrish et al., 1993; McKeen and Liu, 1993).

For a few atmospheric trace gases e.g. CO_2, CO, CH_4, concentration measurements have been complemented by determinations of their isotopic composition. Such information has provided additional constraints on budgets and removal mechanisms (Francey et al., 1995, Lowe et al, 1994, Brenninkmeijer et al, 1995). However, for atmospheric VOC other than methane, very few measurements of isotopic composition are available (Conny and Currie, 1996).

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Measurements of the stable isotopic composition of the more abundant atmospheric trace gases are made by isotope ratio mass spectrometry (IRMS) in dual inlet mode. This requires large samples, e.g. for the precise determination of $\delta^{13}C$ in CO in southern hemisphere air at mixing ratios of 35-70 ppb, 400-800 liters of air are needed. The atmospheric mixing ratios of most VOC are generally in the range of several hundred ppt to a few ppb and even lower in clean background air. A measurement of $\delta^{13}C$ of atmospheric VOC using conventional IRMS dual inlet techniques would thus require enrichment of the VOC from several thousand liters of air.

The isotopic composition of atmospheric VOC will depend on the isotopic composition of various sources and kinetic fractionation occurring as a result of removal reactions (e.g. by OH-radicals). Hence it is essential that isotopic composition measurements are compound specific in order to obtain meaningful information. Because the atmosphere contains a complex mixture of numerous VOC, compound specific preparation of the amount of sample required for conventional dual inlet IRMS is extremely difficult.

In recent years a combination of capillary gas chromatography with on line combustion and IRMS has been developed which allows the determination of $\delta^{13}C$ in organic substances containing less than a nanogram of carbon. This technique, pioneered by Matthews and Hayes (1978), is often referred to as gas chromatography combustion isotope ratio mass spectrometry (GCC-IRMS). Very recently an excellent review of the technique has been published by Brand (1996).

In this paper a method is described which allows the application of GCC-IRMS to the compound specific determination of $\delta^{13}C$ in light non-methane hydrocarbons and chlormethane in the atmosphere at ppt levels. Several examples of measurements will be presented, which demonstrate that this method will provide valuable additional information on sources and sinks of VOC.

Experiment

The technique is based on the combination of (1) a two step cryofocussing technique developed for the determination of the concentration of light NMHCs in the background atmosphere, (2) gas chromatographic separation on a capillary column, (3) quantitative combustion of all separated VOC to CO_2 and (4) determination of $\delta^{13}C$ in the CO_2 resulting from each VOC species by IRMS. A schematic drawing of the experimental setup is shown in Figure 1.

The samples are collected in stainless steel canisters

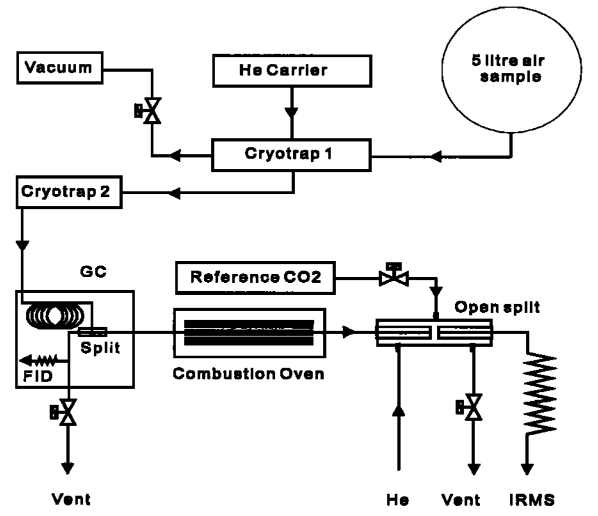

Figure 1. Schematic drawing of the instrumental setup for the compound specific isotope analysis of VOC in ambient air. The effluent of the column enters the micro combustion oven (Finnigan MAT, Bremen) of the GCC-IRMS system where the VOCs are oxidized to CO_2.

equipped with two metal bellows valves. For analysis, between 0.5 and 8 liters of air are cryogenically preconcentrated. In front of the preconcentration unit an adsorption trap, 25 cm long, 20 mm i.d., packed with 10/20 mesh Drierite (Alltech) and 12/20 mesh Carbosorb (BDH) is installed in the sample inlet line to remove water and carbon dioxide from the sample air. The preconcentration method and subsequent analysis follow closely the established procedures for NMHC measurements in ambient air (cf. Rudolph et al., 1989). The VOC are separated on a Poraplot column (30m, 0.32 mm i.d.). The flow rate for the separation is kept constant at 0.8 ml/min by a flow restrictor (2 m stainless steel capillary with 0.1 mm i.d.) and a pressure regulator. The gas chromatograph (HP 5890 series II) was maintained at 35°C for 10 minutes and then, depending on the desired separation, heated at a rate of 1-3°C/min to 150°C or 200°C. The effluent of the column enters the micro combustion oven of the GCC-IRMS system where the VOCs are oxidized to carbon dioxide and water. This oven consists of a ceramic tube of 25 cm length and 2 mm i.d. with single copper, nickel and platinum wires twisted together. The temperature of the combustion oven is kept constant at 960°C. The metal wires in the combustion furnace are reactivated at least once each day by passing pure oxygen through the ceramic tube for 1 hour. Details of the design, operation and performance of the combustion interface (Finnigan MAT) are described in a study by Merrit et al. (1995).

The gas leaving the combustion furnace enters an open split from where about 0.3 ml/min are transferred to the ion source of a Finnigan MAT 252 IRMS. A reference gas inlet allows the introduction of a very small flow of carbon dioxide with a known $\delta^{13}C$ content (-13.65‰ relative to PDB) for a defined period This was done for intervals of 20 s at least twice during each run at times where no chromatographic peaks were observed. Masses 44 ($^{12}C^{16}O_2$), 45 ($^{13}C^{16}O_2$ and $^{12}C^{16}O^{17}O$) and 46 ($^{12}C^{16}O^{18}O$) are monitored simultaneously by the mass spectrometer and the data are stored on a Compaq 486/66 computer which operated the instrument. Thus for each chromatographic separation, chromatograms for three different masses are obtained. The chromatograms were evaluated with the standard ISODAT software supplied with the Finnigan MAT 252 instrument. The baseline and the peak boundaries were defined manually. The $\delta^{13}C$ values are calculated by the software from the peak areas for the different masses. A correction, following standard procedures, of the ^{17}O contribution to mass 45 is included in the calculations. The calculations are always made relative to the measurements of the reference gas included in the same chromatogram. In order to determine and reduce the effect of random noise in the chromatograms, between 3 and 15 slightly different settings of baseline and peak boundaries were used for the evaluation of each peak and the average of the $\delta^{13}C$ values was used.

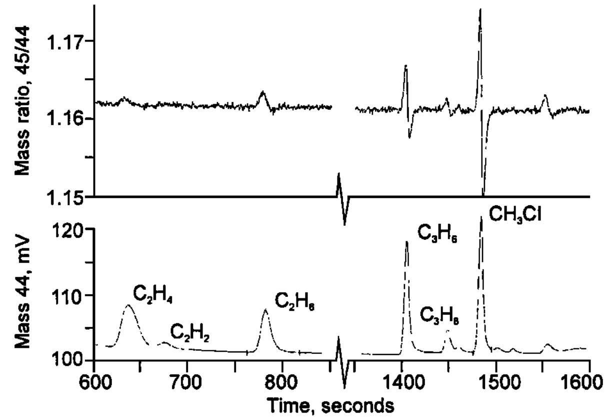

Figure 2. Chromatogram of an air sample (2 liters Southern Hemispheric air with VOC mixing ratios of 0.5 ppb or less for each compound). (a) Mass 44. (b) Ratio of masses 45 and 44.

The amount of substance in the samples was calculated from the peak areas for the mass chromatograms. Artificial mixtures of ethane and propane in air were used as external standards for quantification and as test gases to test the accuracy of the $\delta^{13}C$ determinations.

Two mixtures with 0.9 ppb and 11 ppb of ethane and chlormethane in hydrocarbon free air (Matheson) were prepared by two step static dilutions of the pure substances. The $\delta^{13}C$ values for the two substances were determined independently by passing mixtures with 5% of the pure substances in zero air over copper oxide at 900°C for oxidation. The carbon dioxide produced was collected at liquid nitrogen temperature, vacuum distilled and its $\delta^{13}C$ value determined by conventional dual inlet IRMS.

Results and discussion

An example of a chromatogram for mass 44 and the trace of the ratio of mass 45 and 44 is shown in Figure 2. The sharp in-

Table 1. Comparison of $\delta^{13}C$ in artificial mixtures determined by GCC-IRMS* with results of conventional dual inlet IRMS.

	Ethane		Chlormethane	
Method	Dual inlet	GCC-IRMS	Dual inlet	GCC-IRMS
Mean	-29.0	-28.3	-41.8	-41.9
Reproducibility		0.4		1.0
Error of mean	0.05	0.1	0.05	0.3

* From 11 measurements of mixtures with 0.9 ppb and 11 ppb, sample volumes between 0.5 and 2 liters. Results are ‰ rel. to PDB.

Table 2. Reproducibility of the Evaluation of $\delta^{13}C$ Measurements Determined From the Baseline Noise for Different Amounts of Sample.

Compound	Sample size (ng C)	Reproducibility (‰)[†]
Chlormethane	0.2	1.4
Ethane	0.5	1.4
Chlormethane	0.5	1.0
Chlormethane	1.0	0.7
Ethane	1.0	0.7
Ethane	2.0	0.3

crease in the mass 45/44 ratio marginally ahead of each peak at mass 44 and the often following sharp decrease is the result of the slightly lower retention time of the molecules containing a ^{13}C atom compared to those containing only ^{12}C. It should be noted that the baseline of the mass 45/44 ratio signal represents mainly the ^{13}C content of the column bleed. In Table 1 the results of the measurements of ethane and chlormethane in the artificial mixtures and of the pure substances are summarized. As can be seen, the agreement between the two methods is very good. For chlormethane the differences are well within the range of the estimated error of the GCC-IRMS measurements. For ethane the differences are somewhat larger, but with 0.7‰ still within reasonable limits. The reproducibility of the ethane measurements is significantly better (σ = 0.4‰), this points towards a small systematic error. However, this has no effect on the comparison between GCC-IRMS measurements; for example the measurements of the mixtures with 0.9 ppb and 11 ppb of ethane differ on average by less than 0.1‰.

The amount of sample used for the GCC-IRMS measurements listed in Table 1 was in the range of 0.3-6 ng carbon. It can be expected that for these small amounts of sample the noise of the signal will contribute substantially to the uncertainty of the measurements. In Table 2 the errors which result from the baseline noise are listed for $\delta^{13}C$ measurements of samples with different amounts of carbon. It is evident that the sample size is a key factor for the precision of the measurements. For sample sizes of less than about 1 ng C, the error resulting from baseline noise contributes substantially to the overall errors. It should be noted that, as a result of the open split interface only about 30% of sample is introduced into the mass spectrometer.

Table 3. Results From the Repeat Analysis of an Air Sample Collected in a Plume From Biomass Burning[#].

Compound[†]	$\delta^{13}C$ (‰)	Uncertainty (‰)	Sample amount (ng C)
Ethene	-24.4	0.6	37
Propene	-25.2	0.3	10
Ethane	-28.7	0.8	9.0
Acetylene	-13.0	1.6	8.0
2-Butene	-29.7	0.6	2.3
Propane	-27.7	0.2	2.1
1-Butene	-6.9	0.7	1.2
Chlormethane	-45.1	0.6	0.9
n-Butane	-25.4	0.9	0.8
n-Pentane	-28.0	0.4	0.4
i-Butene	-23.7	0.6	0.3
i-Pentane	-26.6	2.3	0.2
i-Butane	-30.3	3.6	0.1

[#] The biomass burnt was Manuka, a native New Zealand C-3 plant. Sample volume was 175 ml. The $\delta^{13}C$ values are relative to PDB.

[†] The compounds are sorted in the order of amount of substance.

The results presented above were derived for ideal chromatographic separations with only two peaks in the chromatograms. Table 3 shows the results of 3 repeat measurements of an air sample with a more complex composition (from biomass burning emissions). The results in Table 3 clearly indicate that the sample size is not the only factor which determines the precision of the $\delta^{13}C$ measurements. For substances which are not clearly separated or have broad peaks, e.g. the C_2 hydrocarbons, the variability is substantial, even for large samples. It is also possible that the measurements of the C_2 hydrocarbons are adversely affected by the tailing of the residual CO_2 and N_2O peak (see Figure 2). Apart from these exceptions, it seems that for sample sizes of 0.3 ng C or more, measurements with a precision of 0.5‰ or better are possible. On the average the standard deviation for all measurements, except the C_2 hydrocarbons and the substances where the sample size is less than 0.3 ng C, is 0.5‰. It is interesting that for n-alkanes the $\delta^{13}C$ values are comparable to the values expected for the parent material (-28‰), whereas for several other compounds the burning process causes strong isotope fractionations. In order to test the suitability of the method for the analysis of ambient air samples and to get an idea about the variability of the $\delta^{13}C$ values of light VOC in air we measured a few air samples with different pollution levels. The results are summarized in Table 4. For most of the compounds there are considerable variations in the $\delta^{13}C$ values between the different samples. With the exception of ethene and butane the differences are roughly 10‰, and in a few cases even higher. These variations are well above the errors of the measurements.

Summary and conclusions

The newly developed method allows the compound specific determination of the $\delta^{13}C$ values of VOC in air samples. The amount of sample needed is in the range of a fraction of a nanogram to a few nanograms. Even for atmospheric mixing

Table 4. Comparison of the $\delta^{13}C$ (‰, Relative to PDB) Values for Light VOC in Different Air Samples [#].

	Baring Head (3/96)[†]	Baring Head (7/ 95)[‡]	Greta Point (4/96)[#]	Mt Victoria Tunnel (4/96)[*]
Ethane	-22.0	-29.7	-27.3	-31.3
Ethene	-26.1		-27.6	-25.9
Propane	- 6.7		-26.5	-24.4
Propene	-28.7		-15.8	-23.1
n-Butane			-27.7	-25.7
i-Butane			-35.4	-27.6
2-Butene			-30.0	-22.2
Chlormethane	-43.5		-37.4	-21.9

[#] Sample volumes were between 5 and 10 liters.

[†] Clean air site at the southern end of the North Island of New Zealand. Mixing ratios for chlormethane were around 500 ppt, for ethane 150 ppt, for other NMHC below 100 ppt.

[‡] Ethane mixing ratio 250 ppt, other VOC not available.

[#] Moderately polluted site at the waterfront close to Wellington (New Zealand). VOC mixing ratios ranged around few hundred ppt.

[*] Connects Wellington city with some of the suburbs. VOC mixing ratios range from a few ppb (chlormethane) to 200 ppb (ethene).

ratios of less than 1 ppb sample sizes of around 10 liters of air are sufficient for measurements of δ^{13}C with a precision of about 0.5‰. Tests with artificial mixtures showed that the accuracy of the method is comparable with the precision.

The isotopic compositions of VOC in the atmosphere depend on the isotopic signature of the sources, the mixing of air from different sources and the isotopic fractionation processes occurring during atmospheric degradation of the VOC, mostly by reactions with OH-radicals or ozone. At present little is known about these processes. However, the variability of the δ^{13}C values between different air samples demonstrates that the magnitude of these effects by far exceeds the precision and accuracy of the measuring method. Thus it can be expected that compound specific measurements of the isotopic composition of atmospheric VOC will be a very valuable tool to improve our understanding of the sources, sinks and atmospheric distributions of VOC. Evidently, investigations of the isotopic signature of the relevant VOC sources as well as laboratory studies of isotopic fractionation processes resulting from the atmospheric degradation of VOC are needed to fully exploit this potential. This method allows routine δ^{13}C measurements with sufficient precision and accuracy. The technique is directly applicable to many C_2-C_5 VOC, and with minor modifications the δ^{13}C values of a broad range of atmospheric VOC can be determined by this method. Measurements of δ13C in atmospheric methane can be made with uncertainties well below 0.1 ‰ (cf. Lowe et al, 1994). It will need a considerable amount of further developments and substantial improvements until δ13C in atmospheric VOC can be measured with comparable quality. Nevertheless, the use of larger amounts of sample and improved peak evaluation algorithms will probably allow such measurements with a precision close to 0.1 ‰ in the near future.

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