Available online at www.sciencedirect.com

SCIENCE DIRECT®

International Journal of Mass Spectrometry 235 (2004) 255–262

International Journal of Mass Spectrometry

www.elsevier.com/locate/ijms

Synthetic isotope mixtures for the calibration of isotope amount ratio measurements of carbon

K. Russe*, S. Valkiers, P.D.P. Taylor

European Commission, Joint Research Centre, Institute for Reference Materials and Measurements, B-2440 Geel, Belgium

Received 4 May 2004; accepted 18 May 2004

Abstract

Synthetic isotope mixtures for the calibration of carbon isotope amount ratio measurements have been prepared by mixing carbon tetrafluoride highly enriched in ^{13}C with carbon tetrafluoride depleted in ^{13}C. Mixing procedures based on volumetry and gravimetry are described. The mixtures served as primary measurement standards for the calibration of isotope amount ratio measurements of the Isotopic Reference Materials PEF1, NBS22 and USGS24. Thus SI-traceable measurements of absolute carbon isotope amount ratios have been performed for the first time without any hypothesis needed for a correction of oxygen isotope abundances, such as is the case for measurements on carbon dioxide. As a result, "absolute" carbon isotope amount ratios determined via carbon tetrafluoride have smaller uncertainties than those published for carbon dioxide. From the measurements of the Reference Materials concerned, the absolute carbon isotope amount ratio of Vienna Pee Dee Belemnite (VPDB)—the hypothetical material upon which the scale for relative carbon isotope ratio measurements is based—was calculated to be $R_{13}(\mathrm{VPDB}) = (11\,101 \pm 16) \times 10^{-6}$.

Keywords: Absolute isotope amount ratio; Synthetic isotope mixture; Carbon tetrafluoride; Gas mass spectrometry; Isotopic reference material; Carbon isotopes

1. Introduction

Carbon isotope ratio measurements play an important role in many fields, such as geology, climate research and food authentication. Small differences in the isotopic composition of carbon can provide plenty of information, e.g. on ancient climatic conditions, identification of carbon dioxide sources, adulteration of juices or doping in sports. The current technique for carbon isotope ratio measurements is to convert the carbon into CO_2 and to compare the carbon isotope ratio of the unknown sample to that of a "known" reference using gas source mass spectrometry.

The major problem of such "differential" or "delta-"measurements is however, to ensure the comparability of results obtained in different laboratories over different moments in time. The most straightforward way would be to establish a direct link to the International System of Units, SI, by the measurement of so-called "absolute" carbon isotope amount ratios, i.e. performing SI-traceable measurements, preferably "primary", i.e. realising the definition of the SI-unit. Such measurements improve the comparability of measurement results via a much better traceability of these results to a much more stable metrological reference system. Only very few values for "absolute" carbon isotope amount ratios have been reported. They have relative combined uncertainties of 2.5×10^{-3} [1] and 5.3×10^{-3} [2], respectively. Compared to the precision of measurements relative to a standard ("delta"-measurements), which often is reported to be as good as 0.01‰, these uncertainties are far too large to be suitable for practical applications. To nevertheless ensure comparability of results, a common reference was established to which all measurements should be linked and which would, by definition, anchor the delta-scale.

Historically, the so-called PeeDee Belemnite (PDB) was agreed to be used as this common reference to define the zero-point of the carbon isotope "delta"-scale. However, PDB is virtually exhausted and no longer available. A "virtual" material, Vienna Pee Dee Belemnite (VPDB) was introduced as the new common reference and linked to the formerly used scale. A "real" VPDB-material thus does not

---

* Corresponding author. Tel.: +32 14 571 965; fax: +32 14 571 863.
E-mail address: katrin.russe@cec.eu.int (K. Russe).

1387-3806/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2004.05.007

exist and did never exist. To realise the connection of the historical PDB-scale and the currently applied VPDB-scale, a consensus value of $\delta^{13}C_{VPDB} = 1.95‰$ was assigned to the limestone material NBS19 [3]. Thus, today the comparability of carbon isotope ratio measurements depends on the quality (homogeneity, stability) and the availability of NBS19.

To overcome the current dependence on artefacts and consensus values, calibrated "absolute" measurements of carbon isotope amount ratios $R_{13} = n(^{13}C)/n(^{12}C)$ with sufficiently small uncertainties are needed.

Isotope ratio measurements can be called "absolute", when they are calibrated by means of synthetic isotope mixtures, the carbon isotope amount ratios of which are traceable to the International System of Units (SI). Synthetic isotope mixtures are usually prepared by gravimetry [4]. When establishing and maintaining an international system for measuring differences in isotope ratios in that way, not only the uncertainties of the various "delta"-measurements, but also the uncertainty on the "absolute" carbon isotope ratio of the material used to link results to the SI have to be considered. This latter uncertainty is mainly determined by the uncertainty associated with the synthetic isotope mixing. It is therefore crucial to prepare synthetic isotope mixtures with the smallest possible uncertainty.

Another major difficulty in establishing a link to the SI for carbon isotope amount ratio measurement results arises from the commonly applied conversion of carbon into CO_2. The conversion is straightforward and can be performed in automated procedures, but the introduction of two atoms of oxygen complicates the calculation of the carbon isotope ratios. Oxygen has three stable isotopes and shows rather large variations in its natural isotopic composition [5]. In addition to the carbon isotope ratio $R_{13} = n(^{13}C)/n(^{12}C)$ also the two oxygen isotope amount ratios $R_{17} = n(^{17}O)/n(^{16}O)$ and $R_{18} = n(^{18}O)/n(^{16}O)$ need to be known. In a typical mass spectrometric measurement process, only two ion current ratios can be measured with a sufficiently small uncertainty, making it necessary to introduce an assumption for the oxygen isotope ratios enabling to calculate the carbon isotope amount ratios [6,7].

Usually, Vienna Standard Mean Ocean Water (VSMOW) is used as reference for the oxygen correction, but the "absolute" value of R_{17}(VSMOW) is still subject to discussion [8]. This results in the uncertainties of the oxygen isotope ratios being the main contributions to the total combined uncertainty of any "absolute" carbon isotope amount ratio measured in carbon dioxide. In addition, the empirical oxygen correction introduces a break in the traceability chain to the SI, because it only relies on artefacts and non-metrological values.

Such problems can be avoided by converting, before the measurement, the carbon into CF_4 since fluorine is monoisotopic and will not complicate the mass spectrum.

This paper describes the process followed to obtain SI-traceable carbon isotope amount ratios through the CF_4-route. A gravimetric and a volumetric approach were applied to prepare synthetic isotope mixtures from two CF_4-gases, one enriched in ^{13}C and one depleted in ^{13}C. Several carbon isotopic reference samples were converted into CF_4 using a fluorination procedure described previously [9]. Ion current ratios $I(^{13}CF_3{}^+)/I(^{12}CF_3{}^+)$ from the CF_4 of the synthetic mixtures and the fluorinated samples were measured applying the "Avogadro measurement procedure" established and used frequently before [10,11]. SI-traceable "absolute" isotope amount ratios were obtained and a direct link between the VPDB-traceable "delta"-scale and the SI was established.

2. Theoretical considerations

In order to perform "absolute" isotope amount ratio measurements, a calibration by synthetic isotope mixtures is needed, the isotope amount ratios of which are traceable to the SI, in this case directly to the SI-unit "mole". This can be done by gravimetric mixing of pure isotopes or isotopically enriched materials of known isotopic composition. For the case of a mixture of $^{12}CF_4$ and $^{13}CF_4$, "absolute" carbon isotope amount ratios R_{13} can be obtained via a measurement model described by the following equation

$$R_{13} = \frac{n(^{13}CF_4)}{n(^{12}CF_4)} = \frac{[m(^{13}CF_4)/M(^{13}CF_4)]}{[m(^{12}CF_4)/M(^{12}CF_4)].}$$

M denotes the molar mass and m the mass of a component used. As the output quantity in this equation is a ratio of amounts, i.e. a ratio of numbers of entities (gas molecules) the result is traceable to the unit mole. In fact, both the numerator and the denominator are traceable to a number of entities and therefore a multiple of one entity. Such a method links the realisation of a unit directly to the definition of a unit and is therefore called a "primary method of measurement". Primary methods of measurement enable to constitute the first link in the traceability chain of the realisation of the unit. Thus, the traceability of the measurement results produced is straightforward and easy to understand.

When preparing gravimetric mixtures of gases, it is rather difficult (as compared to preparing mixtures of solids) to achieve a very small uncertainty because it is very much limited by the typically high tare weight of a gas ampoule relative to the small weight of the gas inside. To decrease the relative uncertainty of the gas weighing, the amount of gas needs to be large. However, as a consequence thereof, uncertainties due to small leaks might increase and the handling of high pressure might even become dangerous. Moreover, using large amounts of isotopically enriched gases is very costly.

Aiming at small uncertainties with smaller amounts of gas, a mixing procedure based on measurements of the pressure and volume of the different isotopically enriched gases presents an alternative (though a bit different from the conventional use of this term, this second approach is hereafter referred to as "volumetry"). According to the ideal gas law, the amount of gas n is related to the volume V, the pressure p and the temperature T by the equation $pV = nRT$, with R being the universal gas constant. Thus, for a mixture of $^{12}CF_4$ and $^{13}CF_4$, the carbon isotope ratio R_{13} can be obtained from the following equation

$$R_{13} = \frac{n(^{13}\mathrm{CF}_4)}{n(^{12}\mathrm{CF}_4)} = \left[\frac{p(^{13}\mathrm{CF}_4)}{p(^{12}\mathrm{CF}_4)}\right]\left[\frac{[V(^{13}\mathrm{CF}_4)}{V(^{12}\mathrm{CF}_4)}\right]\left[\frac{T(^{12}\mathrm{CF}_4)}{T(^{13}\mathrm{CF}_4)}\right],$$

provided CF_4 is behaving as an ideal gas. The behaviour of real gases is better described by the empirical 'van der Waals'-equation:

$$\left(p + a\frac{n^2}{V^2}\right)(V - nb) = nRT.$$

The $a(n/V)^2$-term accounts for long-range attractive forces and the b-term accounts for short range repulsive forces between the molecules of the gas. For $a = b = 0$, the 'van der Waals'-law reduces to the ideal gas law. The terms a and b are related to the temperature T_c, volume V_c and pressure p_c at the critical point by the equations

$$T_c = \frac{8}{27}\frac{a}{(Rb)}, \quad V_c = 3b \quad \text{and} \quad p_c = \frac{1}{27}\frac{a}{b^2}.$$

Using the critical constants for CF_4 [12] results in $a_{CF4} = (0.220 \pm 0.036)\ \mathrm{m^2\ Pa/mol^2}$ and $b_{CF4} = (4.67 \pm 0.38) \times 10^{-5}\ \mathrm{m^3/mol}$. Mixing the gases at pressures below 12 kPa would result in a correction of maximum 0.02% relative to the pressure as calculated via the ideal gas law. It might be discussed whether the empirical nature of the 'van der Waals'-correction for deviation from ideal gas behaviour introduces a break into the chain of traceability to the SI for carbon isotope ratio measurements. Anyhow, the correction has only a minor impact, because CF_4 shows close to ideal gas behaviour.

For the gravimetric as well as for the volumetric approach, the lowest uncertainty on the isotope amount ratio of a mixture is expected to be achieved for mixtures with a ratio close to unity. In that case, the amount ratio measurement is realised by a direct comparison of similar masses or similar pressures in a constant volume and preferably at a constant temperature. Many corrections, such as for buoyancy, non-ideal gas behaviour and some possible non-linearity of the scale or pressure sensor will be of similar magnitude for each of the components and will therefore cancel out within a small rest-uncertainty which must be evaluated. From a practical point of view, it is preferable to prepare mixtures with an isotopic composition close to that of the sample to be calibrated, i.e. close to the natural carbon isotopic composition ($R_{13} \approx 0.01$). In this work, mixtures with a carbon isotope ratio close to unity were prepared in order to be able to compare the gravimetric and the volumetric approach with smallest achievable uncertainty. Using the volumetric approach only, mixtures with an isotopic composition close to that of natural carbon were prepared with the intention to prove consistency within a wider range of isotopic compositions.

3. Experimental

3.1. Carbon tetrafluoride and carbon isotopic reference materials

For the preparation of the mixtures, CF_4 enriched in ^{13}C ('enriched CF_4') and CF_4 depleted in ^{13}C ('depleted CF_4') were used. Isotec Inc., USA supplied these gases with the following specifications:

- '*depleted CF*$_4$': "min 99.9 at.% ^{12}C", lot no. IM1657-1, initial amount: 22.85 L;
- '*enriched CF*$_4$': "min 99 at.% ^{13}C", lot no. TJ2508-1, initial amount: 1 L.

The amount-of-substance fraction of impurities in the enriched materials as determined by mass spectrometry is ~0.005% with the main impurities being H_2O, N_2, O_2, CO_2 and Ar.

For flushing the system to reduce memory effects as well as for preliminary tests, CF_4 with natural carbon isotopic composition ('natural CF_4', UHP, Messer Belgium S.A.) was used.

The following reference samples were converted into CF_4 by fluorination with elemental fluorine: NBS22 (paraffin oil), IAEA-CH-7 (PEF1, polyethylene) and USGS24 (graphite). All of them were supplied by IAEA, Vienna, Austria.

3.2. Experimental set-up

Fig. 1 shows a schematic drawing of the volumetric mixing line.

The line is made of 1/4-in. stainless steel tubes, Swagelok connections and Swagelok bellow valves with PCTFE stem tip (SS-4BK).

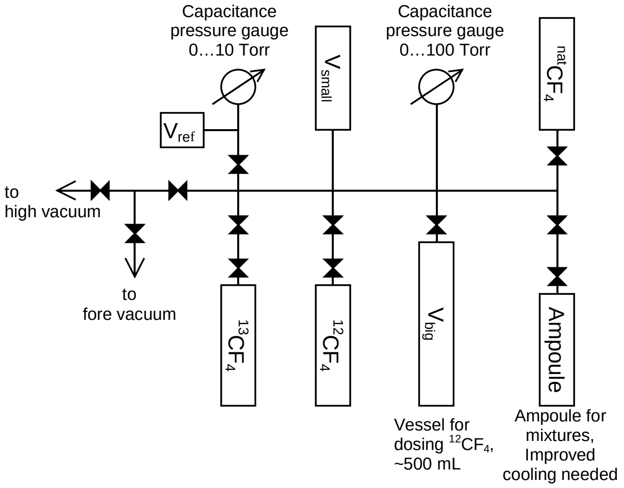

Fig. 1. Schematic drawing of the volumetric mixing line.

The line is connected to a two-stage rotary forevacuum pump (for pumping off gases until ∼1 Pa) and to a turbomolecular pump for high vacuum (to $\sim 10^{-5}$ Pa). It contains a connection to the sample ampoule, which can be cooled to 64 K using an improved cooling system [13]. Other connections are to a gas cylinder with ‘natural CF_4’ (for flushing the system) and to two gas-cylinders containing ‘enriched CF_4’ and ‘depleted CF_4’, respectively.

A capacitance diaphragm pressure gauge (CR90 ‘0–100 Torr’, Leybold Inficon, Germany) connected to a Leybold Inficon DM22 controller is used for pressure measurements. Since the pressure sensor itself is specified to have a higher resolution than can be displayed by the controller, the sensor is additionally connected to a multimeter (Hewlett-Packard 34401A) with a high-resolution readout of five significant digits.

The vacuum line contains two different gas cylinders, connected via a valve, which are intended for the preparation of gaseous synthetic isotope mixtures with natural carbon isotopic composition, i.e. $R_{13} = n(^{13}\mathrm{C})/n(^{12}\mathrm{C}) \approx 0.01$. The small cylinder has a volume V_{small} of about 50 mL (including the volume of the pressure gauge and the connection parts between the valves); the larger cylinder has a volume V_{big} of about 0.5 L. With this set-up, pressure measurements have to be performed only within a range of one order of magnitude, if the ‘enriched CF_4’ is dosed in V_{small} and the ‘depleted CF_4’ is dosed in $V_{\mathrm{total}} = V_{\mathrm{small}} + V_{\mathrm{big}}$. In comparison to pressure measurements performed over a range of two orders of magnitude, smaller uncertainties can be obtained. However, the volume ratio of V_{small} and V_{total} has to be known with the smallest possible uncertainty. Its measurement is described in Section 3.3.

To compensate for temperature changes, another capacitance diaphragm pressure gauge (CR90 ‘0–10 Torr’, Leybold Inficon) and a 50 mL stainless steel ampoule (V_{ref}) are connected to the vacuum line. V_{ref} is filled with CF_4 at a pressure of ∼1 kPa; the pressure is read using the second channel of the Leybold Inficon DM22 controller.

3.3. Volumetric mixing procedure

The ratio of the volumes V_{small} and V_{total} was measured by expanding a certain amount of gas from the small volume V_{small} to the total volume V_{total}. V_{small} was filled with CF_4 up to a pressure of ∼10 kPa and the pressure p was monitored during 20 min together with the pressure p_{ref} in the reference volume. (A stable ratio of p/p_{ref} indicates the absence of leaks or other effects such as adsorption and desorption.) Then the valve to the evacuated large volume V_{big} was opened and the pressure was monitored again during 20 min together with the pressure p_{ref}. The measurement was repeated several times before and after the preparation of the mixtures and at different ambient temperatures. The ratio of volumes as calculated from the ratio of pressures after correction for small discrepancies from ideal gas behaviour (using the “van der Waals” equation) was found to be $V_{\mathrm{small}}/V_{\mathrm{total}} = 0.106626$ (22).Before preparing a volumetric mixture, the line was evacuated to a pressure below 2×10^{-5} Pa and checked for leak-tightness. For mixtures with a targeted isotopic composition close to that of natural carbon, V_{small} was filled up to ∼1 kPa with ‘enriched CF_4’, for mixtures with a carbon isotope ratio of approximately one, V_{total} was filled to ∼10 kPa with ‘enriched CF_4’. After monitoring the pressure p together with the pressure p_{ref} in the reference volume during 20 min, the ‘enriched CF_4’ was transferred to the sample ampoule by cooling the ampoule down to below 66 K. Residual gases not condensable at 66 K were pumped off while monitoring the pressure difference. The amount-of-substance fraction of such residual gases was typical in the range of 0.0001. The line was flushed with ‘natural CF_4’. In a similar procedure as described for ‘enriched CF_4’, V_{total} was filled up to ∼10 kPa with ‘depleted CF_4’ and the gas was as well transferred to the sample ampoule.

The capacitance pressure gauges used for the preparation of the volumetric mixtures are specified to have a resolution of 0.0015% with respect to the full scale (F.S.), a temperature effect on the zero reading of 0.005% F.S./K and a temperature effect on the span of 0.1%/K of the reading. Based on these specifications, combined uncertainties u_{c} on the several pressure measurements were calculated. Taking also into account parameters such as the measurement of the isotopic composition of the enriched and depleted CF_4-gases and corrections for deviations from ideal gas behaviour, the uncertainties u_{c} obtainable with the procedure described above are in the range of 2×10^{-4} to 4×10^{-4} relative to the carbon isotope amount ratio. Fig. 2 shows the different contributions to the combined uncertainty of the carbon isotope amount ratio R_{13} of a volumetrically prepared mixture with natural carbon isotopic composition. The main contributions to the combined uncertainty of 4×10^{-4} relative to the carbon isotope amount ratio are the pressure measurement of the ‘enriched CF_4’ and the measurement of the ratio $V_{\mathrm{small}}/V_{\mathrm{total}}$.

In total, nine mixtures were prepared volumetrically. Two mixtures (mixtures A1 and A2) have a carbon iso-

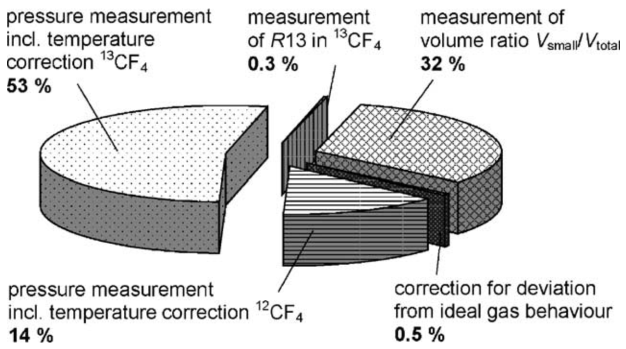

Fig. 2. Contributions to the combined uncertainty of 4×10^{-4} relative to the carbon isotope amount ratio R_{13} of a volumetrically prepared mixture with natural carbon isotopic composition (on the example of mixture B1).

tope amount ratio approximately equal to 1. Five mixtures (mixtures B1–B5) were targeted to cover the range of $R_{13} = 0.01056–0.01146$ or $\delta^{13}C_{VPDB} = -60‰$ to $+20‰$, with the absolute carbon isotope amount ratio of the mixture, R_{13}(mix), being linked to the $\delta^{13}C_{VPDB}$-value by the equation: $\delta^{13}C_{VPDB}$ (in ‰) $= [R_{13}(\text{mix})/R_{13}(\text{VPDB})\text{-}1]\cdot 1000$. For the calculations, the carbon isotope amount ratio of VPDB is assumed to be $R_{13}(\text{VPDB}) = 0.011\ 237\ 2$ [2], without taking into account any uncertainty on that value. In an approach independent from the measurement of the ratio of volumes $V_{\text{small}}/V_{\text{total}}$, one gas mixture (mixture C1) with a carbon isotope amount ratio of approximately 0.1 was prepared and a part of it was further diluted by a factor of ten to obtain the natural isotopic composition (mixture C2).

3.4. Gravimetric mixing procedure

Weighings were performed on a Mettler Toledo AX504 balance. This balance is specified to have a maximum load of 510 g, a readability and reproducibility of 0.1 mg, respectively, and a linearity of ±0.4 mg.

The ampoules, including the valve, used for the preparation of mixtures weighed approximately 380 g, whereas the mass of gas typically was around 250 mg. The high tare of the gas ampoule thus mainly limited the accuracy of the weighings of the gases. Particularly with regard to moisture adsorbed on the outer ampoule surface, reproducible weighing conditions were difficult to realise. To minimise errors related to the ampoule weighing as far as possible, all weighings were performed relative to a reference ampoule with similar shape and surface as the sample ampoule. Both ampoules were exposed to exactly the same conditions prior to weighing, i.e. after cleaning the outer surface with ethanol (to remove any contamination, e.g. fingerprints) the ampoules were dried at 350 K for about 12 h and were placed next to the balance to equilibrate with ambient conditions. Already after 2 h of equilibration the difference between ampoule and reference ampoule was constant within the readability of the balance (0.1 mg), whereas the reproducibility of weighings of a single ampoule was not better than 1 mg.

Also, the handling of the ampoule (e.g. screwing and unscrewing at the vacuum line) influenced its tare weight. A small decrease of the ampoule weight was observed, which might have been caused by abrasion of small metal pieces during screwing. To take this effect into account, the uncertainty on the ampoule tare weight is conservatively increased to 0.2 mg.

The gravimetric approach is intended to be used as an independent check for consistency of the volumetric procedure. Therefore the mixing procedure is the same as described for the volumetric approach, but with additional weighing steps after evacuating the ampoule, after the addition of 'enriched CF_4' and after the addition of 'depleted CF_4'.Using similar amounts of gases, the uncertainties obtainable for a mixture with an isotope ratio of unity are about five times larger for the gravimetric approach compared to those for the volumetric approach. With the relative uncertainties for gravimetrically prepared mixtures with natural carbon isotopic composition being even larger, it was decided to use only a mixture with a carbon isotope ratio close to unity (mixture A1) for the comparison of the two approaches.

3.5. Fluorination of carbon containing samples

Samples from three carbon isotopic reference materials, the graphite USGS24, the polyethylene foil PEF1 and the paraffin oil NBS22 were converted to CF_4 by fluorination with elemental fluorine. The conversion procedure is described in detail in reference [9]. For each fluorination, a sample containing ~300 μmol of carbon was weighed into a nickel crucible, placed in a nickel reactor and—after having evacuated air from the reactor—converted in a fourfold molar excess of high purity fluorine. The fluorination was performed at ~920 K for about 15 min. CF_4 was separated from excess fluorine by distillation at 66 K, using the same improved cooling system [13] as described in the section 'experimental set-up' in this paper. By-products such as C_2F_6 and C_3F_8 were removed using a CE instruments gas chromatograph, type 8000$^{\text{top}}$, with a 2.5 m long and 1/4 in. diameter column packed with silicagel, mesh 50/80. Since isotopic fractionation was observed due to the formation of by-products when fluorinating NBS22 and USGS24, the values given for these materials might be biased. However, this bias is estimated to be small compared to the uncertainty on the carbon isotope ratios in the synthetic mixtures.

3.6. Mass spectrometric measurements

All carbon isotope amount ratio measurements were performed using the "IRMM II Isotope Amount Comparator" and the "Avogadro measurement procedure" [10,11]. The instrument is a modified Finnigan MAT 271 gas mass spectrometer with electron impact ionisation and was designed particularly to perform highly accurate isotope amount ratio measurements on SiF_4 in the framework of the re-determination of the Avogadro constant. The "Avogadro measurement procedure" is based on a comparison of measured values with the theoretical progression of measurement as predicted by the kinetic gas model for the effusion of gases.

The measurement procedure is designed with the intention to make it completely transparent and fully understood. In the ideal case the measured ion current ratios could directly be converted into isotope amount ratios. The conversion factor K, which is defined to be the ratio of the "true" isotope amount ratio R, as derived from the preparation of a synthetic mixture, and the measured ion current ratio J would then expected to be unity.

For the isotope ratio measurements on CF_4 the ion currents on the fragments $^{12}CF_3^+$ at $m/z = 69$ and $^{13}CF_3^+$ at $m/z = 70$ were monitored sequentially using one faraday cup. Short-term fluctuations were eliminated by symmetrical scanning on the two peaks.

The isotopically enriched and depleted CF_4 starting materials, all prepared synthetic mixtures and the fluorinated graphite, polyethylene and oil samples were measured using exactly the same measurement protocol and measurement conditions. That way, the conversion factor K for measurements on CF_4 was determined from the synthetic mixtures and, in the same run, the ion current measurements of CF_4 from the fluorinated carbon isotopic reference materials were calibrated and thus converted into SI-traceable carbon isotope amount ratios.

4. Results and discussion

Uncertainties stated in this work were calculated according to the GUM [14], using the software GUM Workbench Pro 2.3.6 (Metrodata GmbH, Grenzach-Wyhlen, Germany).

Values given in brackets are combined standard uncertainties u_c and apply to the last digits of the given value. Expanded uncertainties U ($U = ku_c$) are given with a coverage factor $k = 2$ and are stated in the form 'value ± U'.

4.1. Calculation of conversion factor K for ion current measurements on the fragment CF_3^+

To calculate the carbon isotope amount ratio of the prepared mixtures of CF_4, the carbon isotope amount ratios of the isotopically enriched and depleted starting materials need to be determined accurately. However, to obtain these ratios from the mass spectrometric measurement of ion current ratios, the conversion factor K, which is intended to be determined via the synthetic mixture, already needs to be known. The carbon isotope amount ratios of the mixtures were therefore calculated in an iterative way. For the initial measurements of the staring materials the conversion factor was assumed to be unity. By comparing the measured isotope ratio of a mixture to the one calculated from the volumetric or gravimetric mixing procedure, a first estimate for the conversion factor was obtained. This was used for recalculating the isotope ratios of the starting materials and to subsequently obtain a closer estimate. The iteration was continued until no change of the value for K was observed anymore. The iteration converged rapidly and already after three iterative steps the conversion factor was constant within a range of 1×10^{-4} relative to the value.

Values for K obtained from the different mixtures are given in Table 1.

The average conversion factor for all volumetrically prepared mixtures is 0.98747 (70), with the stated uncertainty in this case being the standard deviation of the mean. This experimental uncertainty is larger than the uncertainties on the single mixtures as calculated from the mixing process, indicating that not all uncertainty components were correctly taken into account. The values for K obtained from mixtures A1 and A2 (with $R_{13} \approx 1$) are lower than the ones from the mixtures with natural carbon isotopic composition. The reason for this discrepancy might be a small systematic error in the preparation of the mixtures with natural isotopic composition, e.g. a slight non-linearity of the pressure sensor. For the gravimetric approach (mixture A1), the resulting conversion factor is 0.9865 (11), which is in good agreement with the values from the volumetric approach.

In contrast to conversion factors for different other gases obtained via the "Avogadro measurement procedure" so far [15], the conversion factor for CF_4 obtained from the mixtures is significantly lower than unity. Obviously, the measurement process for CF_4 contains parts, which are not fully understood and are therefore not included in the mathematical model. Presumably, isotope effects occur in the ion source during the ionisation and fragmentation of CF_4 into CF_3^+. Further investigation will be carried out in order to better understand and describe the processes going on during electron impact ionisation in gas mass spectrometry.

4.2. Calculation of R_{13}(VPDB) via calibrated measurements of the absolute carbon isotope amount ratio of PEF1, NBS22 and USGS24

Knowing the conversion factor, ion current ratios measured on CF_4 from the fluorination of carbon containing materials can be converted into absolute carbon isotope amount ratios. The results are listed in Table 2. The uncertainty

Table 1
Prepared isotope ratios R_{13}, measured ion current ratios $J_{70/69}$ and resulting conversion factors K for nine synthetic mixtures prepared volumetrically from isotopically enriched CF_4 and isotopically depleted CF_4

Mixture	Prepared isotope ratio R_{13}	Measured ion current ratio $J_{70/69}$	Conversion factor $K = R_{13}/J_{70/69}$
A1 ($R_{13} \approx 1$)	0.998 21 (20).	1.012 620 (41)	0.985 77 (20)
A2 ($R_{13} \approx 1$)	0.963 71 (19)	0.977 455 0 (80)	0.985 94 (20)
B1 ($\delta^{13}C_{VPDB} \approx -68‰$)	0.010 470 7 (39)	0.010 589 28 (47)	0.988 78 (37)
B2 ($\delta^{13}C_{VPDB} \approx -45‰$)	0.010 730 9 (39)	0.010 871 28 (28)	0.987 09 (36)
B3 ($\delta^{13}C_{VPDB} \approx -22‰$)	0.010 990 8 (40)	0.011 126 42 (31)	0.987 82 (36)
B4 ($\delta^{13}C_{VPDB} \approx -2‰$)	0.011 211 8 (40)	0.011 348 52 (33)	0.987 96 (35)
B5 ($\delta^{13}C_{VPDB} \approx +20‰$)	0.011 462 0 (40)	0.011 603 42 (28)	0.987 81 (35)
C1 ($R_{13} \approx 0.1$)	0.103 261 (29)	0.104 575 2 (64)	0.987 43 (29)
C2 (C1 diluted)	0.011 042 7 (37)	0.011 169 94 (48)	0.988 62 (34)

Table 2
Ion current ratios measured on CF_4 obtained by direct fluorination of NBS22, PEF1 and USGS24, and calculated SI-traceable absolute carbon isotope amount ratios for these intercomparison materials

Sample	Measured ion current ratio $J_{70/69}$	Absolute carbon isotope amount ratio $R_{13} = KJ_{70/69}$
PEF1 polyethylene	0.010 883 87 (27)	0.010 747 5 (77)
NBS22 paraffin oil	0.010 906 62 (35)	0.010 770 0 (77)
USGS24 graphite	0.011 066 26 (38)	0.010 927 6 (78)

Table 3
Absolute carbon isotope ratios R_{13} for VPDB, the hypothetical material on which the “delta”-scale for carbon isotope ratio measurements is based

Sample	Assigned carbon isotope ratio $\delta^{13}C_{VPDB}$ (‰) [16]	Calculated carbon isotope amount ratio for VPDB R_{13}(VPDB)
PEF1 polyethylene	-31.77 ± 0.08	0.011 100 1 (79)
NBS22 paraffin oil	-29.73 ± 0.09	0.011 100 0 (79)
USGS24 graphite	-15.9 ± 0.25	0.011 104 2 (81)

The ratios are calculated from the $\delta^{13}C_{VPDB}$-values assigned to the intercomparison materials NBS22, PEF1 and USGS24 (first column) and their respective absolute carbon isotope amount ratios R_{13}(sample) (see Table 2), following the equation $R_{13}(\mathrm{VPDB}) = R_{13}(\mathrm{sample})/[\delta^{13}C_{VPDB}/1000 + 1]$.

on the carbon isotope amount ratios mainly stems from the uncertainty of the conversion factor. Measurement precision and repeatability (including repeatability of the fluorination procedure and mass spectrometer stability) contribute only less than one percent to the total combined uncertainty. A further optimisation of the mixing procedure thus could most probably help to decrease the total uncertainty.

NIST and IAEA provide NBS22 oil, PEF1 polyethylene foil and USGS24 graphite as intercomparison materials. Knowing the assigned carbon isotopic compositions relative to VPDB, $\delta^{13}C_{VPDB}$ [16] and the absolute carbon isotope amount ratios R_{13}(sample) it is possible to calculate the absolute carbon isotope amount ratio of VPDB, R_{13}(VPDB), via the equation $\delta^{13}C_{VPDB}$ (in ‰) $= [R_{13}(\mathrm{sample})/R_{13}(\mathrm{VPDB}) - 1] \times 1000$ (see Table 3). For the three different materials, the obtained value for R_{13}(VPDB) is consistent within the stated uncertainty. VPDB is defined to be the common reference and zero-point of the carbon “delta”-scale, which is set up by relative measurements performed on CO_2. Therefore, this result indicates a good consistency—within the stated uncertainty—between the relative and the absolute carbon isotope ratio measurements as well as between the approaches of fluorination to CF_4 and combustion to CO_2.

The resulting average absolute carbon isotope amount ratio of VPDB is $R_{13}(\mathrm{VPDB}) = (11\,101 \pm 16) \times 10^{-6}$. The value obtained is significantly lower than the values reported in literature, $(11\,237 \pm 60) \times 10^{-6}$ [2,17] and $(11\,180 \pm 28) \times 10^{-6}$ [1,17].

With the approach described in this report the uncertainty on absolute carbon amount ratios is two and four times smaller than the uncertainty reported for measurements by Chang [1] and Craig [2], respectively. However, it is still more than one order of magnitude larger than typical uncertainties claimed for “delta”-measurements.

5. Conclusions

Several mixtures were prepared from isotopically enriched CF_4 and isotopically depleted CF_4 to calibrate carbon isotope amount ratio measurements using the “Avogadro measurement procedure”. In combination with a fluorination procedure to convert carbon-containing materials into CF_4, absolute carbon isotope amount ratios were assigned to commonly available carbon isotopic intercomparison materials. This approach allows for the first time to report SI-traceable carbon isotope amount ratios, which do not depend on any assumptions to be able to correct for the oxygen contribution, such as all previously reported carbon isotope amount ratios based on measurements on CO_2. Furthermore, a link was established between the current “delta” measurement scale, which is based on comparisons to an artefact, and the SI. This link makes carbon isotope ratios independent from particular materials as carrier of the scale, such as is currently the case with the limestone NBS19. However, even though the obtained uncertainties are the smallest obtained so far for absolute carbon isotope ratio measurements, they still need to be improved to meet the requirements for “delta”-measurements.

Acknowledgements

The authors acknowledge the technical support and the set-up of the pressure measurement equipment for the mixing line by D. Vendelbo. We thank Y. Aregbe for sharing her experience in the preparation of gas mixtures and P. De Bièvre for his constructive review of this manuscript.

References

[1] T.L. Chang, W.J. Li, Chin. Sci. Bull. 35 (1990) 290.
[2] H. Craig, Geochim. Cosmochim. Acta 12 (1957) 133.

[3] G. Hut, Consultants' group meeting on stable isotope reference samples for geochemical and hydrologiccal investigations, Report to the Director General, IAEA, Vienna, 1987.
[4] T. Ding, S. Valkiers, H. Kipphardt, C. Quétel, P. De Bièvre, P.D.P. Taylor, R. Gonfiantini, Int. J. Mass Spectrom. 197 (2000) 131.
[5] T.B. Coplen et al., US Geological Survey Water-Resources Investigations Report 01-4222, Reston, Virginia, 2002.
[6] C.E. Allison, R.J. Francey, H.A.J. Meijer, IAEA TECDOC 825, IAEA, Vienna, 1995, p. 155.
[7] J. Santrock, S.A. Studley, J.M. Hayes, Anal. Chem. 57 (1985) 1444.
[8] R.M. Verkouteren, G.A. Klouda, L.A. Currie, IAEA TECDOC 825, IAEA, Vienna, 1995, p. 111.
[9] K. Russe, H. Kipphardt, O. Bréas, P.D.P. Taylor, Anal. Chem. 74 (2002) 3199.
[10] P. De Bièvre, S. Valkiers, F. Schaefer, H.S. Peiser, P. Seyfried, PTB Mitteil. 104 (1994) 225.
[11] P. De Bièvre, S. Valkiers, H.S. Peiser, P. Hansen, P.D.P. Taylor, Metrologia 33 (1996) 447.
[12] http://properties.nist.gov/Semiprop/Gases/CF4.html#6, "Selected Values of Properties of Chemical Compounds" Data Project Thermodynamics Research Center, Texas A&M University, College Station, TX, 1980.
[13] S. Valkiers, Y. Aregbe, G. Van Baelen, K. Russe, European Patent Application EP no. 02257766.2 of 08/11/2002.
[14] International Organization for Standardization, Guide to the Expression of Uncertainty in Measurement, ISO, Switzerland, 1995.
[15] H. Kipphardt, S. Valkiers, P.D.P. Taylor, Int. J. Mass Spectrom. 198 (2000) 71.
[16] NIST Report of Investigation, Reference Materials 8538–8542 (1992).
[17] R. Gonfiantini, W. Stichler, K. Rozanski, IAEA TECDOC 825, IAEA, Vienna, 1995, p. 13.