

Conversion of Carbon into CF₄ for SI-Traceable Measurements of Absolute Carbon Isotope Amount Ratios: A Feasibility Study

Katrin Russe,* Heinrich Kipphardt,[†] Olivier Bréas, and Philip D. P. Taylor

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

The feasibility of performing SI-traceable carbon isotope amount ratio measurements following conversion of carbon into CF₄ was studied. A procedure for the direct fluorination of carbon with elemental fluorine was developed, and the conversion step was checked for losses, blank contributions, and the absence of systematic isotope effects. Gas chromatography was used to identify and quantify the gaseous fluorination products and to isolate CF₄ from byproducts. After fluorination of graphite carbon, CF₄ and perfluoroalkanes with up to six carbon atoms were observed as reaction products. Within an uncertainty of 10%, the graphite carbon was fully recovered in the gaseous carbon fluorides, with the main product being CF₄ (80–90%) and C₂F₆ as the major byproduct. The fluorination and GC procedures were found to introduce an alteration not bigger than $0.03 \pm 0.04\%$ on the isotopic composition of CF₄. Carbon blank contributions introduced during the fluorination procedure were below 0.5% relative to a typical sample of 4 mg of carbon. For two of the materials investigated, the carbon isotope ratios measured on a differential mass spectrometer were reproducible within a standard deviation of $\sim 0.1\%$ for several individual fluorinations. For these materials, the developed fluorination procedure is a straightforward process, which can be used as a foundation to establish SI-traceable measurements of carbon isotope amount ratios. However, for the third graphite material the formation of byproducts (C₂F₆–C₆F₁₄) was found to induce significant isotopic fractionation.

Isotope ratio measurements of stable isotopes are extremely important in many fields, such as geology, climate research, and food authentication.^{1–3} Usually, stable isotope ratio measurements are performed as differential measurements, i.e., by comparing the isotope ratio of the sample to that of a reference.^{4,5} Relative

variations of carbon isotope ratios are currently expressed versus the internationally recognized primary reference standard “Vienna Pee Dee Belemnite” (VPDB).⁶ VPDB is a virtual material that is supposed to have a carbon isotopic composition identical to that of “Pee Dee Belemnite” (PDB), a material that was used as a standard in the past but is now exhausted. The VPDB scale is currently realized using the material NBS 19. By international agreement, a $\delta^{13}\text{C}$ -value of $+1.95\%$ relative to VPDB is adopted for NBS 19.⁷ Thus, today international comparability of carbon isotope ratio measurements is established via a particular and therefore limited substance (artifact). Traceability to the International System of Units (SI) is given via the absolute carbon isotope amount ratios of NBS 18, NBS 19, and NBS 20 as measured by Chang.⁸ From these values, the absolute carbon isotope amount ratio of PDB has been recalculated.⁶ However, the resulting value is not consistent with the carbon isotope amount ratio of PDB previously reported by Craig.⁹ To clarify this inconsistency and to make carbon isotope ratio measurements independent of artifacts, it is necessary to link measurements of carbon isotope ratios closer to the SI (see Figure 1). Since, furthermore, there is a lack of carbon isotopic reference materials, new materials are required which provide both absolute carbon isotope amount ratios that set up a direct link to the SI and δ -values versus VPDB to maintain a link to the currently used scale. With the aim of establishing such certified carbon isotopic reference materials, a new procedure for SI-traceable measurements of carbon isotope amount ratios is developed at the EC-JRC Institute for Reference Materials and Measurements. This procedure is based on the conversion of carbon into CF₄ by fluorination using elemental fluorine.

For carbon isotope amount ratio measurements, conversion into CF₄ has several advantages compared to the common approach of a conversion into CO₂. CO₂ shows strong adsorption properties, whereas CF₄ is a rather inert gas and therefore shows less memory effects. Furthermore, because oxygen consists of three stable isotopes, in a CO₂ molecule, there are three isotope ratios, namely, $R_{13} = n(^{13}\text{C})/n(^{12}\text{C})$, $R_{17} = n(^{17}\text{O})/n(^{16}\text{O})$, and $R_{18} = n(^{18}\text{O})/n(^{16}\text{O})$, which must be calculated from mass spectro-

* Corresponding author. Phone: +32 14 571 964. Fax: +32 14 571 863. E-mail: katrin.russe@irmm.jrc.be.

[†] Present address: Federal Institute for Materials Research and Testing (BAM), D-12200 Berlin, Germany.

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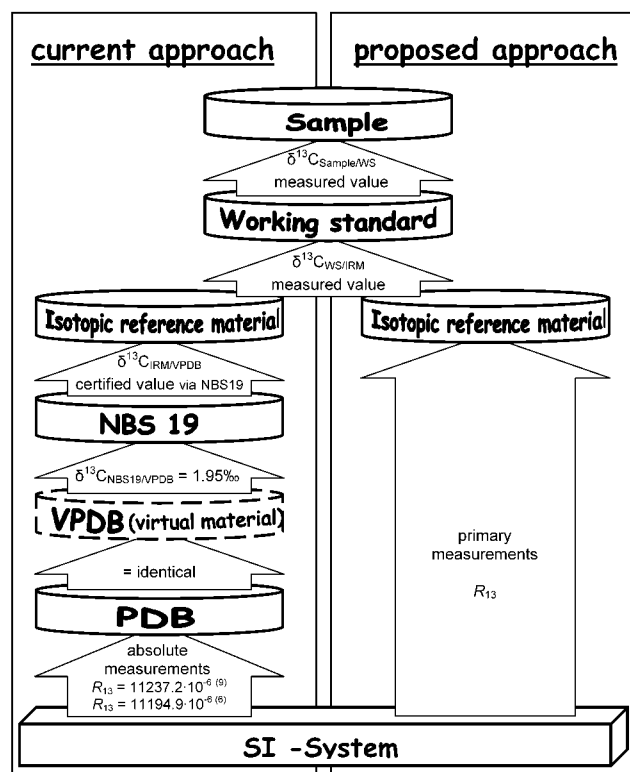


Figure 1. Proposed strategy to link carbon isotope ratio measurements to the SI system compared to the approach currently applied.

metric measurements of only three measurable ion currents from the molecular ions CO_2^+ with the masses 44, 45, and 46.¹⁰ The signal on mass 45 is produced by molecule $^{13}\text{C}^{16}\text{O}_2$ and molecule $^{12}\text{C}^{17}\text{O}^{16}\text{O}$. To calculate the ratio R_{13} , it is therefore necessary to be able to correct for the contribution of the ^{17}O on mass 45, which is usually done by assuming a fixed correlation factor between the ratios R_{17} and R_{18} .^{9,11} In contrast, fluorine is monoisotopic. When CF_4 is used, the carbon isotope amount ratio can be directly determined from the ion currents on masses 69 and 70, originating from the major ion fragments $^{12}\text{CF}_3^+$ and $^{13}\text{CF}_3^+$, respectively.

From a metrological point of view, the use of elemental fluorine in a closed system is a straightforward approach to convert carbon into CF_4 . The direct fluorination of carbon has already been described,^{12,13} but the nonavailability of pure fluorine and the lack of safe handling techniques hampered its widespread use. These problems have largely been overcome by the development of a fluorination apparatus designed for elemental analysis of inorganic materials.¹⁴ The fluorination technique used with this apparatus has been adopted, combined with a method to purify fluorine,¹⁵ and optimized to minimize possible isotope effects. A first feasibility study on the applicability of the fluorination procedure for SI-traceable carbon isotope amount ratio measurements was performed on elemental carbon (graphite). In this study, it is shown that this approach has the potential to deliver absolute

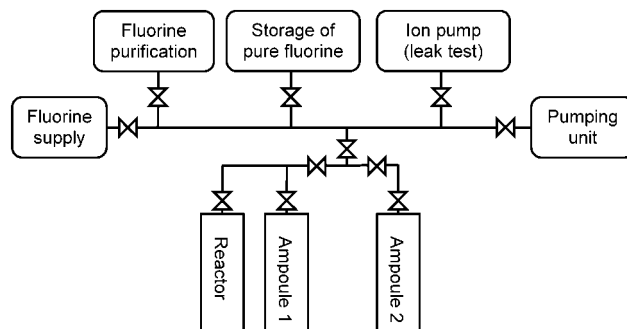


Figure 2. Fluorination line used for the conversion of carbon into CF_4 .

carbon isotope amount ratios with an uncertainty smaller than that reported for absolute carbon isotope amount ratios measured on CO_2 . However, the approach is limited to substances that do not show isotopic effects during the conversion to CF_4 and to higher perfluoroalkanes formed as byproducts.

EXPERIMENTAL SECTION

Reagents. Pure fluorine gas (puriss, pro analysi, not compressed) was supplied by the working group of Prof. Dr. Willner, University of Hanover, Germany. For further purification of the fluorine according to the method of Asprey,^{15,16} a mixture of KF (99+%, Aldrich, Milwaukee, WI) and NiF_2 (99%, Aldrich) was prepared. The calibration of the gas chromatographic procedure was performed using CF_4 , C_2F_6 , and C_3F_8 of ultrahigh purity (Messer Belgium S.A., Machelen, Belgium). Fluorination experiments were performed on graphite samples from three different suppliers, namely, "Merck graphite" (fine powder extra pure, Merck KGaA, Darmstadt, Germany), "Mackay graphite" (99.9995%, -100 mesh, A.D. Mackay Chemicals, Red Hook, NY), and "USGS24" (NIST Reference Material 8541, distributed by IAEA, Vienna, Austria).

Fluorination Line. Figure 2 shows a schematic drawing of the fluorination line used. The fluorination apparatus is constructed from commercially available stainless steel $1/4$ -in. fittings (Cajon, Macedonia, OH) and bellow valves (Nupro, Willoughby, OH). Sealing materials are copper and KEL-F. The reactor ($V \approx 25$ mL) is manufactured from nickel (DIN 17740, Deutsche Nickel AG, Schwerte, Germany). Commercially available small nickel capsules (Lüdi, Flawil, Switzerland) are used as crucibles. The fluorine is stored below atmospheric pressure (e.g., 40–100 kPa) and only in small amounts (maximum, 4.3 mol). The unit for further purification of the fluorine according to the method of Asprey^{15,16} consists of a nickel ampoule filled with K_3NiF_6 prepared from KF and NiF_2 .

The pump line consists of a cryosorption pump (ISA Riber, Rueil-Malmaison, France) filled with TiO_2 (granulate, MAN, Munich, Germany), which efficiently traps the excess fluorine and reactive fluorides when cooled with liquid nitrogen. When allowed to reach room temperature, reactive compounds are converted into more harmless compounds ($\text{TiO}_2 + \text{F}_2 \rightarrow \text{TiOF}_2 + 1/2\text{O}_2$). Additionally, a chemically resistant diaphragm pump equipped with a TiO_2 -filled absorber is used. An ion pump (Varian, Palo Alto, CA) is used as a sensitive leak detector to guarantee leak tightness of the system after assembling and connecting the reactor.

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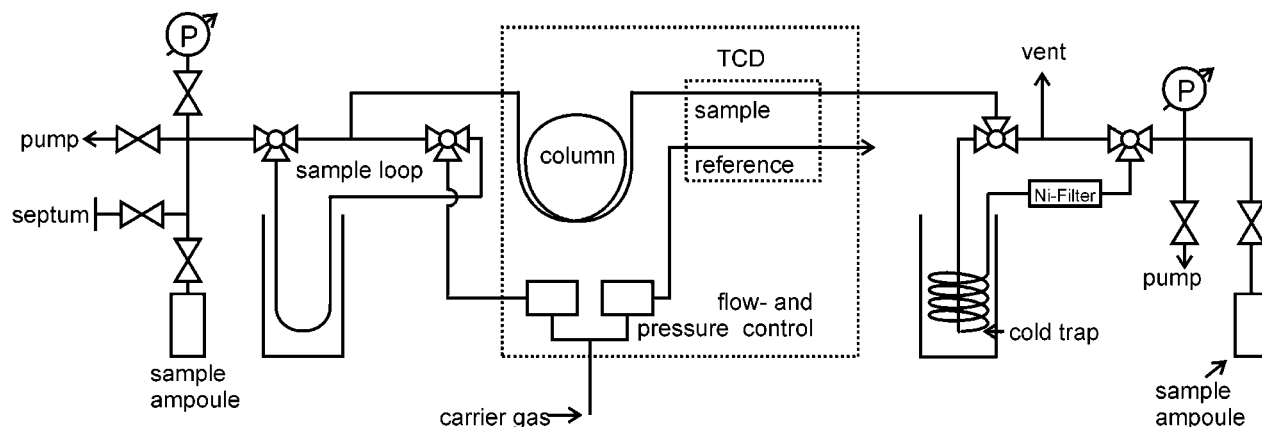


Figure 3. GC line used for the identification, separation, and yield determination of reaction products obtained by the fluorination of graphite powder.

Safety Considerations. Fluorine is a highly toxic and corrosive gas. The fluorination line described above was designed particularly to minimize any risk of contact with fluorine and its often toxic and corrosive reaction products. The apparatus is constructed completely from metals, which, when in initial contact with fluorine, form a fluoride layer. This layer adheres tightly to the metal surface and thereby prevents a further fluorination of the metal. Fluorine and fluorination products can be removed completely by the TiO_2 pump and absorber. Thus, no corrosive gas is released into the environment. Furthermore, the tightness of the apparatus and particularly of the nickel reactor after assembly can be carefully checked with the aid of the ion pump. Except for the fluorination process itself, fluorine is stored and handled only at a reduced pressure, and for each individual fluorination, only small amounts of fluorine (maximum, 4 mmol) are used. Additionally, the whole apparatus is placed in a fume hood. With these precautions in place, the fluorination technique is considered to be safe.

Fluorination Procedure Used for the Fluorination of Graphite. For this feasibility study, elemental carbon in the graphite form was chosen as sample material in order to avoid influences of other elements such as hydrogen and oxygen. At $\sim 700^\circ\text{C}$, graphite can be fluorinated uniformly and safely, whereas at 420°C , graphite forms a solid monofluoride $(\text{CF})_n$ which can explode under certain conditions.¹³ Furthermore, it is known that at high temperatures and high concentrations of fluorine CF_4 is formed as the major reaction product. At lower temperatures and low fluorine concentrations, the formation of other perfluoroalkanes such as C_2F_6 and C_3F_8 becomes more likely.¹³ By means of a high-frequency oven (HTG1500/0.5, Linn, Hirschbach, Germany), the reactor can be heated to $\sim 800^\circ\text{C}$ within 2 min. For safety reasons, a maximum amount of 4 mmol of fluorine was used and the maximum temperature was limited to 750°C . Previous investigations showed that only very short reaction times (< 10 min) are required for materials that form volatile fluorides.¹⁷ Varying decomposition time between 10 min and 1 h indicated no significant influence on the yield and composition of the fluorination products. For a typical conversion, ~ 4 mg of graphite was weighed into a nickel crucible to an accuracy of $5\ \mu\text{g}$ and the

crucible was dropped into the reactor. To remove moisture and adsorbed gases, the reactor was first evacuated at room temperature and then heated at 350 and 750°C for 10 min each. After leak testing using the ion pump, ~ 4 mmol of fluorine was transferred from the storage vessel for purified fluorine into the reactor by cooling the reactor with liquid nitrogen. The amount of fluorine used for an individual conversion was calculated from the pressure difference in the storage vessel (e.g., the pressure in the 4-L storage vessel was lowered by 2.2 kPa for a transfer of 4 mmol of fluorine). All valves were then closed, and the nickel reactor was heated with the high-frequency oven at $\sim 750^\circ\text{C}$ for 15 min. Afterward, the reactor was cooled with liquid nitrogen and most of the excess fluorine was pumped away using the diaphragm pump. Since CF_4 still has a considerable vapor pressure (~ 3 Pa) at a temperature of -196°C , more extensive pumping under these conditions causes losses and isotopic fractionation. To avoid this, the fluorination products and the remaining fluorine were transferred into a 50-mL stainless steel ampoule ("Ampoule 1" in Figure 2), which can be cooled to -210°C using an "improved cooling system". This cooling system consists of a Dewar flask sealed with a lid and filled with liquid nitrogen, the temperature of which can be lowered by continuously pumping off the nitrogen vapor.¹⁸ When the temperature of the ampoule was below -207°C , the residual vapor pressure of CF_4 was estimated to be below 10^{-2} Pa and the remaining fluorine was pumped off using the cryosorption pump. The ampoule was allowed to reach room temperature; then the cooling and pumping step was repeated once. Finally, the fluorination products were transferred into a 2-mL stainless steel tube ("Ampoule 2" in Figure 2), which was also cooled to below -207°C . Ampoule 2 was disconnected from the fluorination line and connected to the GC line to identify and quantify the reaction products.

To reduce the risk of blank contributions and memory effects, before each conversion of graphite, a blank fluorination was performed using the same amount of fluorine and the same temperature settings as described above.

Gas Chromatography. The fluorination products were identified and their amounts were measured using gas chromatography. For this purpose, the gas chromatograph is connected to the line

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Table 1. Settings for Gas Chromatography

gas chromatograph	GC 8000 top, (CE instruments, Milan, Italy)
detector	thermal conductivity detector HW 8000
carrier gas	helium, purity: 99.996%, 40 mL/min
column	silica gel, mesh 50/80, $l = 2.5$ m, diameter $\frac{1}{4}$ in., stainless steel, (Alltech)
reference column	PorapakQ, mesh 80/100, $l = 2$ m, diameter 6 mm, stainless steel, (Alltech)
temperature program	$T_1 = 50$ °C, $t_1 = 4$ min, $R_1 = 15$ °C/min, $T_2 = 200$ °C, $t_2 = 20$ min

as shown in Figure 3, which was originally built for the work described by Ding et al.¹⁹ With this line, gaseous samples can be introduced to the GC either with a syringe via a septum or from an ampule connected to the system. The gases are then separated on a silica gel column and detected by a thermal conductivity detector. Finally, either all the gases or a fraction of them can be trapped in a cold trap, which is cooled to below -207 °C. The technical data of the gas chromatograph and the settings used for all separations described in this paper are given in Table 1.

Mass Spectrometry. Measurements of the isotopic composition of the fluorination products were performed using a MAT 252 differential mass spectrometer (ThermoFinnigan, Bremen, Germany). The mass spectrometer is equipped with a dual-inlet system and a multielement-multicollector (MEMCO) system that is adjusted to simultaneously collect ions with m/z 69 ($^{12}\text{CF}_3^+$) and 70 ($^{13}\text{CF}_3^+$). The settings of the ion source were as follows: The high voltage was 10 kV, the ionizing electron potential was ~ -60 V, the trap was set to 50 V, and the total emission current was 1.5 mA. The pressure in the ion source was $\sim 9 \times 10^{-6}$ Pa. One measurement cycle contained peak centering, pressure adjust, and a sequence of eight measurements of sample and standard, respectively. To reduce the cross contamination between sample and standard gas in the ion source, the idle time prior to an integration time of 8 s was set to 120 s.²⁰ In this work, all measured δ -values are reported together with a standard deviation obtained from 10 replicate measurement cycles.

RESULTS AND DISCUSSION

Fluorination Products. Figure 4 shows a typical chromatogram obtained from the fluorination products of graphite. The eluted compounds were identified by their retention time as well as from mass spectra obtained using a quadrupole gas mass spectrometer with electron impact ionization (QMS 420, Balzers, Liechtenstein). That way, the different peaks in the chromatogram were assigned to CF_4 and to other perfluoroalkanes with up to six carbon atoms. In some earlier tests additionally a small peak eluting between C_2F_6 and C_3F_8 was found. This peak was assigned to CO_2 and indicated the formation of C–O–F compounds due to the presence of moisture in the fluorination process. On the silica gel column, compounds such as CF_2O and CF_3OF are converted to CO_2 . With the perfluoroalkanes, neither reactions with the column material nor memory effects were observed.

GC Calibration. Calibration experiments were performed to determine the yield of conversion. To obtain calibration curves

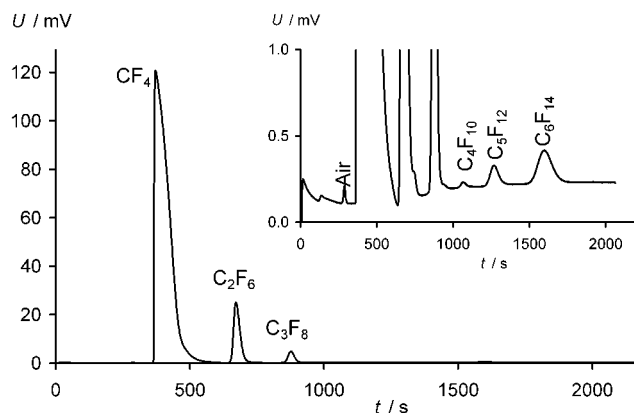


Figure 4. Typical chromatogram obtained from the gas chromatographic separation of graphite fluorination products.

for the fluorination products, different amounts of high-purity gases (CF_4 , C_2F_6 , and C_3F_8 , respectively) were introduced into the GC line through the septum using gastight syringes, and the peak areas of the resulting detector signals were measured. Calibration curves were linear for small sample amounts ($n < 2 \times 10^{-5}$ mol). However, from a conversion of 4 mg of graphite, a maximum amount of 0.33 mmol of CF_4 is expected. In the range of such a sample amount, calibration curves fit to a second-order polynomial regression. The yield of the main product CF_4 was therefore determined by applying a polynomial calibration function, whereas the linear calibration curves were used for the determination of the byproducts C_2F_6 and C_3F_8 . Since pure carbon fluorides with four or more carbon atoms were not available, slopes for calibration curves for these fluorides were extrapolated from the slopes of the linear range of the calibration curves for CF_4 , C_2F_6 , and C_3F_8 .

To take variations of the detector sensitivity into account, calibrations for CF_4 were performed regularly. The relationship between detector sensitivities for different carbon fluorides was assumed to be constant. Since the injection of the gas via the syringe is rather imprecise and some extrapolations and assumptions were made for the determination of the amount of the byproducts ($\text{C}_n\text{F}_{2n+2}$, $n > 1$), the uncertainty of the yield determinations is estimated to be not better than 10%.

Graphite Fluorination Yields. Graphite from three different suppliers (Merck, Mackay, and the isotope reference material USGS24) was investigated. The materials differed in particle size and purity. The Merck graphite was described as “extra pure” with a particle size less than $50 \mu\text{m}$, the Mackay graphite is of 99.9995% purity with a particle size less than $250 \mu\text{m}$, and the USGS24 is of technical grade purity (96%) with a particle size less than $44 \mu\text{m}$.²¹ From each material, several samples of ~ 4 mg were

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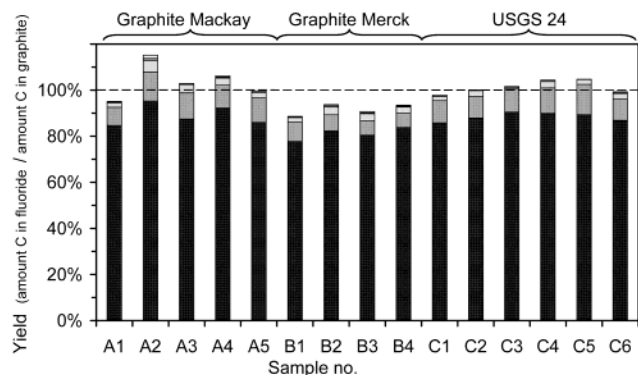


Figure 5. Yields of CF_4 (black), C_2F_6 (medium gray), C_3F_8 (light gray), and $\text{C}_n\text{F}_{2n+2, n \geq 4}$ (no fill) obtained from the fluorination of different graphite samples. The total yield was determined by comparing the amount of carbon used for fluorination and the amount of carbon in fluorides as measured by gas chromatography. The uncertainty on the total yields (containing uncertainties on weighing and on the calibration of the GC) is estimated to be 10%.

fluorinated. The amount of carbon found in the form of different carbon fluorides as determined by GC was compared to the amount of carbon originally weighed into the crucible. Figure 5 shows that similar amounts of the different carbon fluorides were obtained for all three materials, independent of particle size and purity. About 80–90% of the carbon was directly converted to CF_4 , whereas $\sim 10\%$ of the carbon formed C_2F_6 and 3% formed C_3F_8 . Less than 1% of the carbon was recovered in the form of perfluoroalkanes containing more than three C-atoms.

With the exception of one sample, the weighed amounts of graphite and the amounts of carbon recovered in the form of carbon fluorides agree within the assumed uncertainty of 10%. Complete fluorination of the sample was also indicated by the fact that after fluorination no residue was found in the reactor. The isotopic measurements performed on the fluorination products as described later showed that the low precision of the gas chromatographic yield determination is not a limiting factor for accuracy of carbon isotope ratio measurements at this stage. In fact, it is more important to carefully check whether systematic isotopic fractionation occurs due to the fact that $\sim 15\%$ of the carbon is not converted to CF_4 but to other perfluoroalkanes.

Blank Contributions. Carbon blanks might be introduced during sample preparation or released from the nickel reactor, crucible, and copper gaskets during the fluorination procedure. To estimate the amount of carbon blanks, the products from a blank fluorination were analyzed using GC. Figure 6 shows the chromatogram obtained from the fluorination products of a blank fluorination in comparison with a chromatogram obtained from a fluorination of 4 mg of graphite. The blank contribution was found to be less than 0.5%. For estimating the contribution of the blank to the total uncertainty of carbon isotope amount ratio measurements on CF_4 , it was assumed that blank and sample are of natural carbon isotopic composition with a maximum difference of 20%. Further investigation on amount and carbon isotope ratio of the blank are expected to considerably reduce this uncertainty.

Check for Absence of Isotope Effects Introduced during the Fluorination and GC Procedure. The approach of converting carbon into CF_4 for isotopic measurements is based on the assumption that the various condensations and pumping steps

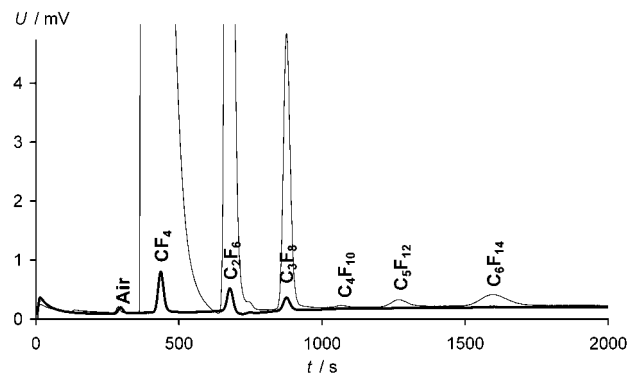


Figure 6. Chromatogram obtained from the products of a blank fluorination (—) compared to a chromatogram obtained from the products of a fluorination of 4 mg of graphite (---).

during the fluorination procedure as well as the gas chromatographic procedure do not induce any systematic alteration of the carbon isotopic composition. In particular, it had to be verified that CF_4 is quantitatively retained and quantitatively transferred using the “improved cooling system” at temperatures below -207°C . This was realized by comparing the isotopic composition of a sample of pure CF_4 before and after passing through the entire fluorination and GC procedures. A CF_4 sample was divided into two subsamples. One subsample was directly filled into one of the bellows of the dual inlet of the MAT 252 mass spectrometer. The second subsample first was introduced into the GC to measure the sample amount and then condensed into the nickel reactor and treated in the same way as a graphite sample during fluorination. Afterward, the sample amount was again checked using GC. Finally, this second part of the CF_4 sample was introduced to the other bellow of the dual-inlet system. Comparing the isotopic composition of the two parts of the CF_4 sample (before and after having passed the fluorination and GC procedures) in the differential mass spectrometer resulted in a δ -value of $0.03 \pm 0.04\text{‰}$; i.e., the procedure described here does not induce any significant change in the isotopic composition of the CF_4 . Additionally, the whole fluorination and GC procedures were checked for losses by comparing the areas of the detector signals for CF_4 obtained by GC before and after the fluorination step. Here, losses during the fluorination procedure were found to be less than 1%.

Reproducibility of Differential Carbon Isotope Ratio Measurements on Graphite Fluorination Products and Check for Absence of Isotope Effects due to the Formation of Byproducts. From each graphite material, several individual fluorinations were performed in order to check the reproducibility of carbon isotope ratio measurements on the fluorination products obtained.

Although the graphite carbon can be quantitatively recovered in the form of gaseous perfluoroalkanes, the fact that several different reaction products are formed may give rise to isotope effects. Such isotope effects are rather implausible, since fluorination is a very fast reaction. Nevertheless, it was checked whether the carbon isotopic composition of the CF_4 was different from that of the fluorination byproducts. Mass spectrometric carbon isotope ratio measurements on CF_4 are performed on the major fragment CF_3^+ resulting from electron impact ionization. The fragment CF_3^+ is formed from CF_4 as well as from the other perfluoroalkanes, but the fragmentation pattern is different for the various fluorides and very dependent on the composition of the gas and the

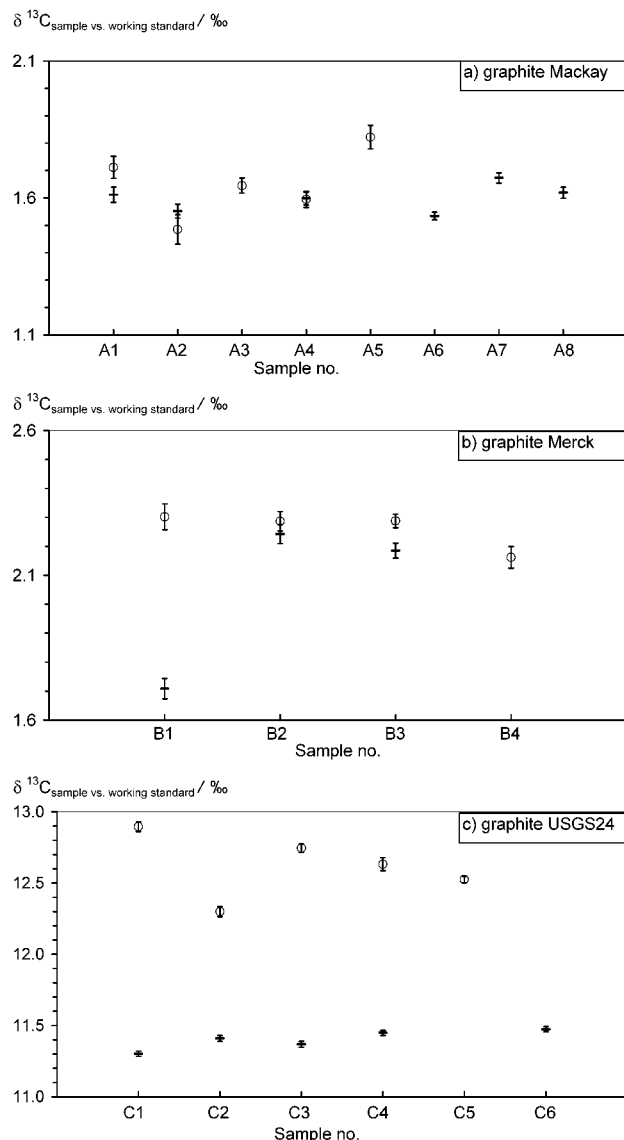


Figure 7. Differential carbon isotope ratio measurements of graphite fluorination products versus a CF_4 working standard. For three different materials, graphite supplied by A.D. Mackay (a), by Merck (b), and the reference material USGS24 (c), measurements were performed on the mixture of fluorination products (○) and on the CF_4 fraction only (●). Error bars indicate the standard deviation obtained from 10 replicate measurement cycles, each containing eight comparisons of standard and sample.

conditions in the ion source. Hence, any difference between the carbon isotopic compositions of CF_4 and the other perfluoroalkanes that are formed as byproducts results in errors in the carbon isotope ratio measurements.

To determine whether isotopic fractionation had occurred, carbon isotope ratios were measured in three or more samples of each graphite material using all fluorination products as well as using the CF_4 fraction only. For the latter measurements, the components of the mixture of fluorides were separated using GC and only the CF_4 fraction was trapped in the cold trap (see Figure 3).

The results obtained for the graphite from Mackay, Merck, and the USGS24 are shown in Figure 7a–c, respectively. δ -Values measured versus a pure CF_4 working standard are displayed. For

the Mackay graphite, no evidence for isotopic fractionation was found since the values obtained using the isolated CF_4 do not differ significantly from those obtained using the whole mixture of fluorides. Similar results were obtained for the Merck graphite, except in one case, where the value obtained for the pure CF_4 is significantly lower. In contrast, the results obtained for the USGS24 (Figure 7c) clearly show a difference of more than 1 ‰ between results obtained for the mixture and those obtained for the CF_4 fraction only. As a consequence, when the method presented here is applied, accurate measurements of the carbon isotope ratio of USGS24 are not possible. At present, the reason for the different behavior of the USGS24 graphite as compared to graphite from Merck or Mackay is not fully understood. One possible reason might be the difference in purity of the materials. The graphite samples from Merck and Mackay are of high-purity grade (see the section Reagents), whereas the USGS24 is of technical grade (96%) only.²¹

A comparison of the results obtained from the mixture of fluorination products and from the chromatographically separated CF_4 fraction shows that the precision of measurements is better if only the CF_4 fraction is used. The δ -values obtained from several individual conversions as measured using all fluorination products are reproducible within a standard deviation of $\sim 0.15\text{‰}$ for the Mackay graphite and $\sim 0.25\text{‰}$ for the USGS24 graphite, respectively. Regarding only those results obtained using the isolated CF_4 , a better reproducibility is obtained. Measurements on the CF_4 fraction from six individual fluorinations of Mackay graphite were reproducible within a standard deviation of 0.05‰ , corresponding to a standard uncertainty of 0.03‰ . The difference in precision can probably be explained by the different behavior of the gases in the differential mass spectrometer resulting in different measurement conditions for a sample that is a mixture of perfluoroalkanes and the pure CF_4 working standard.

Uncertainty Estimation for Carbon Isotope Amount Ratio Measurements on CF_4 . Absolute carbon isotope amount ratios can directly be deduced from measurements of the ion current ratio on m/z 70 and 69 corresponding to the fragments $^{13}\text{CF}_3^+$ and $^{12}\text{CF}_3^+$. At the IRMM, a fully transparent procedure for isotope amount ratio measurements has been developed in the framework of the redetermination of the Avogadro constant.²² With this procedure, ion current ratios measured on the “Avogadro Amount Comparator II”, a specially modified Finnigan MAT 271 mass spectrometer, can be directly converted into absolute isotope ratios following the equation $R = KJ$, with R being the isotope ratio, J the corresponding measured ratio of ion currents, and K a conversion factor accounting for residual systematic effects. The conversion factor can be determined by measuring the ion current ratio of gravimetrically prepared synthetic mixtures of isotopically enriched materials. Mixtures of CF_4 have not yet been prepared, but from measurements of other gases (Kr, Xe, SF_6), the conversion factor has proven to be unity within an uncertainty of 5×10^{-4} .²³ Having measured the ion current ratio $J_{70/69}$ for the CF_4 working standard and assuming a conversion factor of $1 \pm 5 \times 10^{-4}$, one can estimate the combined uncertainty on absolute carbon amount ratios performed using the procedure described here. For the example of the Mackay graphite, the different

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Table 2. Parameters and Values Used for the Calculation of the Uncertainty Budget for Absolute Carbon Amount Ratio Measurements on CF₄ Obtained by the Fluorination of Graphite (Supplied by A.D. Mackay)

parameter	value (± standard uncertainty)
$\delta^{13}\text{C}_{\text{sample vs working standard}}$ (measurements on CF ₄ from six independent conversions)	$1.60 \pm 0.03\text{‰}$
systematic error introduced during the fluorination and GC procedures	$0.03 \pm 0.04\text{‰}$
blank contribution	$0.2\text{--}0.5\text{‰}$
$\delta^{13}\text{C}_{\text{blank vs sample}}$	$-20 \text{ to } +20\text{‰}$
ratio of ion currents of the working standard $J_{70/69}$ measured on the Avogadro Amount Comparator II	$0.01096416 \pm 15 \times 10^{-8}$
conversion factor K	$1.0000 \pm 5 \times 10^{-4}$

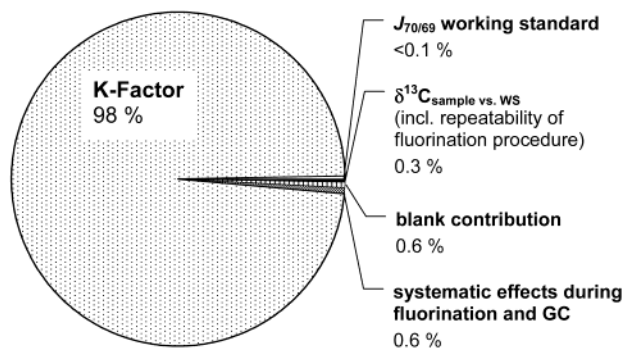


Figure 8. Uncertainty contributions to absolute carbon isotope amount ratios measured on CF₄ obtained by the fluorination of graphite.

uncertainty contributions are listed in Table 2. Using the method of propagation of error according to the GUM²⁴ and EURACHEM²⁵ guidelines, a total uncertainty of 11×10^{-6} (expanded uncertainty, $k = 2$) on the carbon isotope amount ratio is obtained. Absolute carbon isotope amount ratio measurements on CO₂ are reported with uncertainties of 28×10^{-6} ⁸ and 30×10^{-6} ,⁶ with the absolute carbon isotope ratios differing by 5‰.⁸ The method presented here has thus the potential to provide absolute carbon isotope ratios with an uncertainty lower than the one reported for carbon isotope ratio measurements performed on CO₂. Figure 8 shows that at this stage the uncertainty in carbon isotope amount ratio measurements on CF₄ is predominantly determined by the uncertainty of the conversion factor. Accordingly, the total uncertainty can be further reduced by calibrating the mass spectrometer with gravimetric mixtures of CF₄ prepared from starting materials enriched in ¹³C and ¹²C, respectively.

CONCLUSIONS

The conversion of graphite into CF₄ using direct fluorination with elemental fluorine has been shown to be applicable for carbon isotope ratio measurements. Compared to the conventional procedure of combusting carbon with oxygen, the procedure

presented here allows a direct measurement of absolute carbon isotope ratios without the need for corrections for contributions of ¹⁷O and ¹⁸O. The procedure of converting carbon into CF₄ was proven not to introduce any systematic alteration of the carbon isotopic composition. Procedural blanks were shown to be low. It was possible to reproduce differential measurements of carbon isotope ratios on CF₄ within a standard deviation of 0.05‰ for different individual fluorinations of graphite. However, the fact that ~15% of the carbon was converted to perfluoroalkanes other than CF₄ required an additional step to check whether isotopic fractionation had occurred due to the formation of these byproducts.

With the method being straightforward and transparent, it serves as a first step toward SI-traceable measurements of carbon isotope amount ratios. Because transforming carbon into CF₄ instead of CO₂ provides a completely new and independent opportunity to measure absolute carbon isotope amount ratios, the method can contribute to solving the problem of the discrepancy between absolute carbon isotope amount ratios measured on CO₂ so far. The methodology presented here could be used to establish a graphite standard with an SI-traceable absolute ¹³C/¹²C ratio. After a careful study of the influence of other elements such as hydrogen and oxygen, the method could also serve to set up a link to the SI for materials currently used to realize the δ-scale relative to VPDB (e.g., polyethylene, paraffin oil, and sucrose). This way international comparability for carbon isotope ratios obtained using the common method of a conversion to CO₂ and a measurement relative to a standard could be assured over a long time and independent of particular and thus limited substances.

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