International Journal of Mass Spectrometry 189 (1999) 27–37

Measurement of the isotopic composition of germanium using GeF_4 produced by direct fluorination and wet chemical procedures

H. Kipphardt[a], S. Valkiers[a], F. Henriksen[a], P. De Bièvre[a], P.D.P. Taylor[a,]*, G. Tölg[b]

[a]*Institute for Reference Materials and Measurements, European Commission—JRC, B-2440 Geel, Belgium*
[b]*Institut für Spektrochemie und angewandte Spektroskopie (ISAS), Bunsen-Kirchhoffstrasse 11, D-44137 Dortmund, Germany*

Received 15 December 1998; accepted 15 March 1999

Abstract

Two methods are described for the preparation of GeF_4 from Ge and GeO_2 for isotopic measurements: a direct reaction with elemental fluorine and a wet chemical procedure. Germanium isotope amount ratios were obtained using the same measurement procedures and instruments as developed in the framework of the redetermination of the Avogadro constant and taking all significant sources of uncertainty into account. The repeatability of measurements on an individual sample was 5×10^{-5} relative. The results on the abundance ratios for different sample materials and preparation techniques agree to within 7×10^{-5} relative. All uncertainty statements were made following the ISO/BIPM Guide to the Expression of Uncertainty in Measurements (Geneve, 1993). The calibrated isotope abundance ratios are calculated to be $n(^{70}\mathrm{Ge})/n(^{74}\mathrm{Ge}) = 0.5635$ (29); $n(^{72}\mathrm{Ge})/n(^{74}\mathrm{Ge}) = 0.7519$ (38); $n(^{73}\mathrm{Ge})/n(^{74}\mathrm{Ge}) = 0.2123$ (11); $n(^{76}\mathrm{Ge})/n(^{74}\mathrm{Ge}) = 0.2118$ (11) resulting in an atomic weight $A_r(\mathrm{Ge}) = 72.6276$ (32). These results are compared to values previously published for the isotopic composition and atomic weight of Ge. (Int J Mass Spectrom 189 (1999) 27–37) © 1999 Elsevier Science B.V.

Keywords: Germanium; Fluorination; Isotopic composition; Atomic weight; Isotopes

---

1. Introduction

The uncertainty regarding the atomic weight of Ge is one of the largest of all the atomic weights [1], although all four isotope abundance ratios, normalised to the most abundant isotope ^{74}Ge, are larger than 0.2, which is advantageous for the isotopic measurement. Measurements of the isotopic composition of Ge using thermal ionisation mass spectrometry (TIMS) and gas isotope mass spectrometry (GIMS) have been published [2–9]. However, there is a discrepancy between the published values of Green and coworkers [2], Shima [3], and Reynolds [4]. Moreover, Ge is recognised to be a potential starting material for the redetermination of the Avogadro constant with a smaller uncertainty [10], because the technology to grow large single crystals of high perfection and purity is highly developed.

Fluorides are very suitable compounds for GIMS, because fluorine is monoisotopic and stable fluorides exist for all elements— except for the lighter noble gases—and many of them are sufficiently volatile for GIMS (Fig. 1). From a methodological point of view,

---

* Corresponding author.

PII S1387-3806(99)00047-0

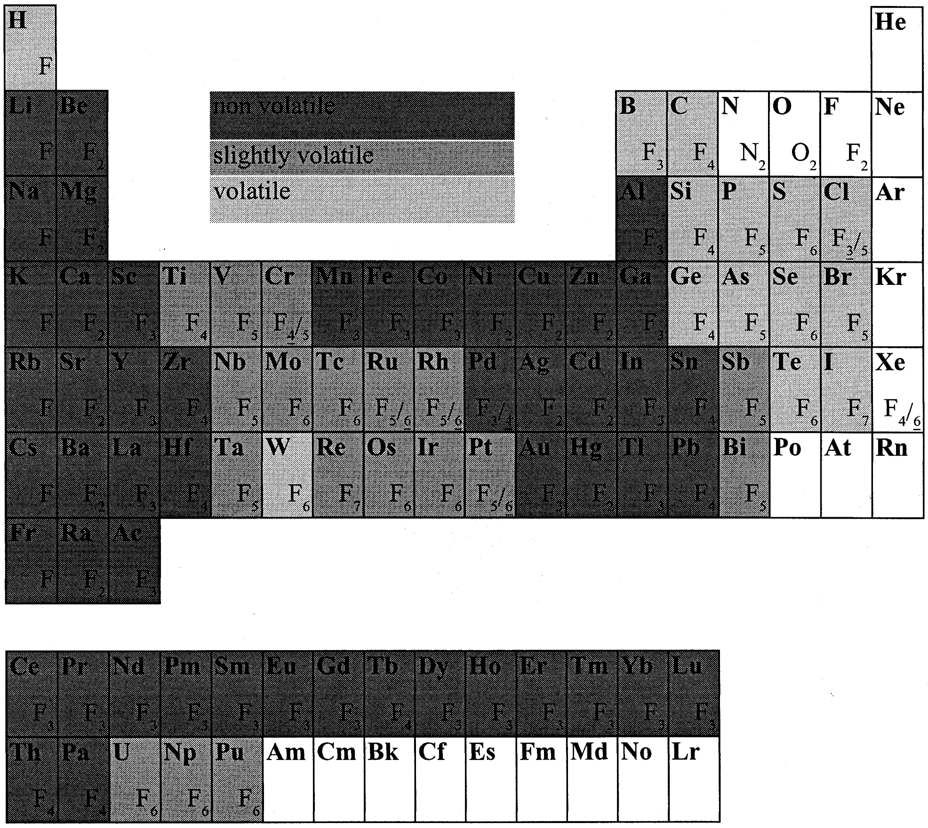

Fig. 1. Reaction products by fluorination of the elements (typical conditions $p(F_2)$ = 1–20 bar, T = 300–600 °C).

the use of elemental fluorine (following ${}^{i}E + nF_2 \rightarrow {}^{i}EF_{2n}$) in a closed system, is direct and straightforward, but the widespread use of fluorine was hampered by the nonavailability of pure fluorine, the lack of safe fluorine handling techniques and experience. Jacob solved many of these problems, when pioneering a broader use of fluorine for the decomposition of refractory materials, even for routine analysis [11], through establishing acceptable ways to handle F_2. Recent demands from the laser industries have accelerated the development of fluorine technology.

Since GeF_4 is volatile and easy to measure in GIMS, the applicability of the direct fluorination of Ge and GeO_2 samples for isotopic measurements with small combined uncertainty was studied and compared to wet chemical conversions.

An important aspect to clarify in this article is the method of calibration that was used. By means of a calibration process (see IUPAC document of Analytical Chemistry Division [12]) an observed quantity (e.g. a ratio of electrical currents) is converted into what is intended to be measured (e.g. the isotope amount ratio), i.e. the function between both is established experimentally including its uncertainty. Various tools can be used to achieve this.

Often, depending on the purpose of the measurements, various degrees of “care” can go into establishing this function. *These differences in metrological quality should be reflected in the uncertainty statement*. However, isotopic measurements are rarely accompanied by reliable uncertainty statements, that is statements as defined by the ISO Guide on the Expression of Uncertainty in Measurements [13]. Such a statement seems to be a prerequisite for “calibrated measurements,” and has been applied throughout this work.

In the specific field of isotopic measurements, calibration is often synonymous to the use of synthetic isotope mixtures and is defined as such in the Technical Document of the Commission of Atomic Weights and Isotope Abundances [14]. The authors have used such mixtures (for other elements than Ge) to obtain calibrated measurements for Si, Xe, Kr, and S. These experiments have shown however that the methods and instrumentation used (also applied in the framework of the redetermination of the Avogadro constant) are, to a high degree, only dependent on the physical processes occurring in the spectrometer (bias is mainly caused by effusion of the gas from the molecular inlet system). Moreover, procedures have been developed to assess whether other gases introduced behave (during the experiment!) in the predicted manner (i.e. an effusion fractionation factor equal to $(M_i/M_j)^{0.5}$, where M is the molar mass of the effusing molecules and the indices refer to the different isotopes). Proper calibration can be achieved in this way if correct uncertainties are assessed for each step in the measurement process. This is exactly the subject of this paper.

2. Experimental

2.1. Material description/chemicals

Ge single crystalline material (Wackertronic, Burghausen Germany) and GeO_2, suprapur (Merck, Darmstadt, Germany) were used. Reagents were employed in pro analysis or suprapur (Merck, Darmstadt, Germany) quality. F_2 was made and purified by E. Jacob (MAN, München, Germany) using a low temperature distillation column [15].

Safety warning: Fluorine is a highly corrosive and toxic gas reacting with many substances—especially organic materials—violently even at room temperature. Special care has to be taken to avoid contact as well as liberation of fluorine in the environment [16].

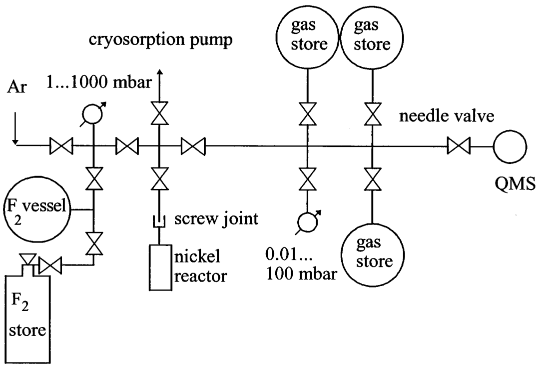

Fig. 2. Fluorination line.

2.2. Sample preparation

2.2.1. Direct fluorination

For safety reasons, fluorine is handled in an all-metal apparatus and stored below atmospheric pressure (i.e. 40–100 kPa) and only in small amounts (i.e. <4.3 mol). The fluorination apparatus (Fig. 2) was built of commercially available stainless steel $\frac{1}{4}$ in. fittings (CAJON, USA) and bellows valves (NUPRO, USA). The reactor ($V \approx 25$ mL) and the crucible are manufactured of nickel (DIN 17740, Deutsche Nickel AG, Schwerte). The pumping line consists of a TiO_2 filled and liquid nitrogen cooled cryosorption pump (Riber, France), which traps the excess of fluorine and reactive fluorides. Rather than to improve the vacuum, an ion getter pump (Varian, USA) is used as a sensitive leak detector to guarantee leak tightness of the systems after assembling. The amount of fluorine needed for the individual conversion is transferred from the storage vessel by cooling the reactor with liquid nitrogen. The reactor can be heated up to 800 °C by means of a high frequency oven (LINN, Hirschbach, Germany) in a few minutes. After the conversion, the reactor is cooled with liquid nitrogen and the excess of fluorine and the oxygen formed is pumped off. The argon line allows to flush the apparatus until fluorine free.

Prior to the conversion, the reactor is filled three times at $p(F_2) \approx 18$ kPa at 70 °C and twice at $p(F_2) \approx 200$ kPa at 550 °C for 15 min for passivation. The specific conditions for each conversion ($GeO_2 + 2F_2$

Table 1
Specific conditions for direct fluorinations (GeO_2, Ge → GeF_4); numbers in parentheses are combined standard uncertainties u_c, they apply to the last digit of the value

Sample	Material	m (mg)	$n(F_2)$ (mmol)	T (°C)	t (min)	Yield (%)
6	GeO_2	30.00 (3)	2.8 (1)	550 (10)	10	100 (1)
7	GeO_2	66.23 (3)	2.8 (1)	550 (10)	10	100 (1)
11	Ge	99.85 (3)	3.0 (1)	600 (10)	10	100 (1)

$\rightarrow GeF_4 + O_2$ and $Ge + 2F_2 \rightarrow GeF_4$) are summarised in Table 1.

2.2.2. Wet chemical conversion of Ge and GeO_2 [17]

About 100 mg of GeO_2 were dissolved in 8 mL 40% HF at 60 °C in a Teflon beaker and diluted with 60 mL Milli-Q water ($GeO_2 + 6HF \rightarrow H_2GeF_6 + 2H_2O$). Approximately 70 mg Ge single crystals were dissolved in a mixture of 4 mL 40% HF and 4 mL 65% HNO_3 at 55 °C in about 4 h in a Teflon beaker and diluted with 60 mL Milli-Q water ($Ge + 6HF \rightarrow H_2GeF_6 + 4H^+$). After adding dropwise a 1% excess of $BaCl_2$ solution [$\omega(BaCl_2) \approx 0.1$ g/g] to the H_2GeF_6 solutions, $BaGeF_6$ precipitates ($H_2GeF_6 + BaCl_2 \rightarrow BaGeF_6 + 2HCl$). The precipitate and the solution were heated to dryness on a hot plate at 125 °C for 14 h.

The $BaGeF_6$ was transferred to a monel container ($V \approx 50$ mL) and, after leak testing, baked at 330 °C for 30 min. Finally the product was decomposed at $T_{dec} = 650$ °C in vacuum for 30 min ($BaGeF_6 \rightarrow GeF_4 + BaF_2$), and the GeF_4 was collected in a monel spiral cooled by means of liquid nitrogen. After replacing the cooling bath by acetone/dry ice, the sample was collected in a liquid nitrogen cooled ampoule. The specific conditions for each conversion are summarised in Table 2.

2.3. Measurement procedure

Prior to the isotope abundance ratio measurements, the gas samples were checked for impurities, particularly for interferences in the mass region m/z: 127–133, where the most abundant ions (${}^iGeF_3^+$) are measured, using a BALZERS QMS 420 quadrupole gas mass spectrometer directly attached to the fluorination line. For sample 6, ions in the mass range m/z: 143–151 and 162–170 were found, which can be interpreted as traces of GeF_2Cl^+ and GeF_3Cl^+. The influence of interfering ions in the mass region m/z: 125–135 is estimated to be less than 2×10^{-4} relative. In all samples, traces of SiF_4 and BF_3 were detected.

The ion current ratios were measured on the “Avogadro II amount comparator” using the procedure developed in the framework of the redetermination of the Avogadro constant (described in [19]). For Ge, the ion current ratios were measured on the most abundant ion ${}^iGeF_3^+$ at mass positions m/z: 127, 129, 130, 131, and 133. Each sample was measured in four

Table 2
Specific conditions for wet chemical conversion (GeO_2, Ge → $BaGeF_6$ → GeF_4); numbers in parentheses are combined standard uncertainties u_c, they apply to the last digit of the value

Sample	Material	$m(BaGeF_6)$ (mg)	T_{dec} (°C)	Yield (%)
9	GeO_2	147.6 (1)	650 (5)	100.5
10	GeO_2	157.7 (1)	700 (5)	96.1
12	Ge	137.0 (1)	650 (5)	97.4

Table 3
Observed current ratios $J_{i/74} = I(\text{at } m/z = i + 57)/I(\text{at } m/z = 74 + 57)$ ($1s$, $n = 4$); numbers in parentheses are combined standard uncertainties u_c, they apply to the last two digits of the value

Sample	$J_{70/74}$	$J_{72/74}$	$J_{73/74}$	$J_{76/74}$
6	0.564 151 (32)	0.752 279 (50)	0.212 336 (09)	0.211 620 (07)
7	0.563 542 (15)	0.752 020 (47)	0.212 255 (08)	0.211 774 (09)
9	0.563 520 (18)	0.751 914 (22)	0.212 279 (09)	0.211 746 (24)
10	0.563 543 (24)	0.751 897 (42)	0.212 283 (13)	0.211 753 (05)
11	0.563 570 (48)	0.751 911 (38)	0.212 278 (14)	0.211 780 (07)
12	0.563 562 (07)	0.751 895 (25)	0.212 262 (15)	0.211 750 (22)

individual runs. The mass fractionation coefficients were determined for sample 12 only.

3. Results and discussion

The observed current ratios $J_{i/j} = I(\text{at } m/z = i + 57)/I(\text{at } m/z = j + 57) \approx I(^{i}\text{GeF}_3^+)/I(^{j}\text{GeF}_3^+)$ with $j = 74$, a first approximation for the isotope amount ratios $R_{i/j} = n(^{i}\text{Ge})/n(^{j}\text{Ge})$, are summarised in Table 3. The uncertainties indicated in brackets (typically 5×10^{-5} relative) are based on the repeated measurements of an individual sample. Because sample 6 was contaminated with chlorine compounds their measurement values, show significant differences compared to the other samples. Moreover, lack of conditioning of the mass spectrometer and apparatus walls could in this case not be fully excluded. On the basis of this doubt, data from sample 6 were excluded when pooling the data from different samples.

The observed ion current ratios $J_{i/j}$ for the different chemical preparation routes for GeF_4 are identical within the expanded uncertainty $U = 3u_c$, indicating that no—or identical—isotope fractionation during the chemical preparation occurs. Furthermore, the current ratios $J_{i/j}$ for the different starting materials are identical within 1 part in 10^4, confirming the observation of Green and co-workers [2] on the absence of variations in the isotopic composition of Ge estimated conservatively within 1 part in 10^3—probably even better. Green investigated more than ten different materials of which three were mineral samples.

The ratios of the experimentally determined values for the mass fractionation factors for sample 12 as compared to the values predicted by kinetic gas theory (as explained in [25]) in Table 4 seem to confirm the absence of isobaric interferences. However, the uncertainty on the observed mass fractionation coefficients of 6×10^{-4} relative is quite large. For smaller uncertainties, longer measurement times would have been required. To convert the ion current ratios $J_{i/j}$ to isotope amount ratios $R_{i/j} = n(^{i}\text{Ge})/n(^{j}\text{Ge})$ (which are given in Table 6) a conversion factor K_c has to be applied [Eq. (1)], because both quantities are of a different nature. This conversion factor must include all significant influencing quantities and parameters with their associated uncertainties, otherwise the results reported would not be isotope amount ratios $R_{i/j}$.

Table 4
Mass ratios for GeF_4 (sample 12); numbers in parentheses are combined standard uncertainties u_c, they apply to the last digit of the value

	Kinetic gas theory ($\Phi = \frac{1}{2}$)	Observed value	Relative difference ($\times 10^{-4}$)
$[M(^{70}\text{GeF}_4)/M(^{74}\text{GeF}_4)]^{\Phi}$	0.986 6	0.987 1 (6)	5.3
$[M(^{72}\text{GeF}_4)/M(^{74}\text{GeF}_4)]^{\Phi}$	0.993 3	0.992 9 (6)	−4.0
$[M(^{73}\text{GeF}_4)/M(^{74}\text{GeF}_4)]^{\Phi}$	0.996 7	0.995 6 (6)	−11.0
$[M(^{76}\text{GeF}_4)/M(^{74}\text{GeF}_4)]^{\Phi}$	1.006 6	1.007 2 (6)	6.0

In literature such a conversion is often expressed as a calibration [12]:

$$R_{i/j}(\mathrm{Ge}) = \frac{n(^{i}\mathrm{Ge})}{n(^{j}\mathrm{Ge})} = K_{\mathrm{c}} \frac{I(\mathrm{at}\ m/z = i + 57)}{I(\mathrm{at}\ m/z = j + 57)} = K_{\mathrm{c}} J_{i/j} \qquad (1)$$

In mass spectrometry the conversion factor is often dominated by isotope fractionation during generation, transport, and ion formation. Usually mixtures of pure and highly enriched isotopes with known isotopic composition are required to determine an "overall" conversion factor with small uncertainty. Treating the isotope mixtures chemically in exactly the same way as the sample, even enables to cancel isotopic effects originating from the chemical sample preparation. However, highly enriched isotopes in sufficient amounts as needed to prepare synthetic mixtures with sufficiently small uncertainties, are very expensive.

A different approach is to investigate a measurement process until all steps are well understood, including sample preparation, instrumentation, measurement procedures, and data algorithms. More insight into the measurement process enables one to split up the conversion factor K_{c} in its components and establish the uncertainty of each component. [In a formal approach this can be described by Eq. (2).] However, this approach can not be used for every mass spectrometric technique with small uncertainty, but only for those which are very transparent. Gas isotope mass spectrometry, where the gases effuse from a batch volume via a molecular leak into an electron impact ion source, is such a measurement process, which has been studied to extreme detail at IRMM until all steps were well understood within the stated uncertainty. Monitoring the difference between prediction from the theory (i.e. kinetic gas theory) and the experimental values can not only serve as an internal and external consistency check for the measurement [25], but, in fact, can serve to measure the "degree of imperfection" of the measurement. When applied to the measurement of synthetic isotope mixtures, the degree of understanding of the measurement process can also be quantified against the known values of the mixtures (based on gravimetric preparation), eventually reaching a much reduced uncertainty. The latter was not done for Ge in this work.

A work mode as described above was "uncovered" as having a potential for high "accuracy" isotopic measurements of Si in SiF_4 in the framework of the redetermination of the Avogadro constant [18,19]. Needless to say that this required modifications and rather drastic refinements of the mass spectrometer as well as development of appropriate measurement procedures. The potential for "high accuracy" was realised in measurements of inert gases such as Xe [20], SF_6 [21] and Kr [22] leading to uncertainties on K_{c} of 10^{-4} relative.

$$K_{\mathrm{c}} = K_{\mathrm{chem}} K_{\mathrm{ads}} K_{\mathrm{mad}} K_{\mathrm{ion}} K_{\mathrm{res}} \qquad (2)$$

where the following conversion factors are identified: K_{chem} for chemical sample preparation, K_{ads} for adsorption, K_{mad} for mass discrimination in the inlet system (here: effusion), K_{ion} for ionisation efficiencies, K_{res} for small residual systematic effects.

We now return to Eq. (2). The conversion factor for the chemical preparation in this work is estimated (type B uncertainty [13]) to be $K_{\mathrm{chem}} = 1.000\,0$ with an uncertainty of 3×10^{-4} relative since both chemical routes are independent and involve only pure chemicals and reactions with experimentally determined quantitative yields (see Tables 1 and 2). When similar preparation chemistry is used for the wet chemical fluorination as done in the case of silicon in the framework of the redetermination of the Avogadro constant, the absence of isotope fractionation in the chemical preparation process was concluded by carrying out repeated cycles from the solid starting material to the sample gas and back to the solid material [23].

The influence of adsorption effects is estimated from experience with SiF_4 [24] to be $K_{\mathrm{ads}} = 1.000\,0$ with an uncertainty of 1×10^{-4} relative since the individual samples were not different in isotopic composition.

The behaviour of the sample including the transition from viscous to molecular flow K_{mad} as well as the formation of the ions K_{ion}, are now well understood on theoretical grounds [25,26]. In fact the

Table 5
Conversion factors for small residual systematic effects K_{res}; numbers in parentheses are combined standard uncertainties u_c, they apply to the last two digits of the value

Element	Ion current ratio	K_{res}
Si [18]	$I(^{29}\mathrm{SiF}_3^+)/I(^{28}\mathrm{SiF}_3^+)$	1.001 711 (40)
	$I(^{30}\mathrm{SiF}_3^+)/I(^{28}\mathrm{SiF}_3^+)$	0.997 892 (69)
Kr [22]	$I(^{80}\mathrm{Kr}^+)/I(^{84}\mathrm{Kr}^+)$	1.000 39 (19)
	$I(^{82}\mathrm{Kr}^+)/I(^{84}\mathrm{Kr}^+)$	1.000 07 (29)
	$I(^{83}\mathrm{Kr}^+)/I(^{84}\mathrm{Kr}^+)$	1.000 01 (27)
	$I(^{86}\mathrm{Kr}^+)/I(^{84}\mathrm{Kr}^+)$	0.999 961 (81)
Xe [20]	$I(^{128}\mathrm{Xe}^+)/I(^{132}\mathrm{Xe}^+)$	1.000 22 (13)
	$I(^{129}\mathrm{Xe}^+)/I(^{132}\mathrm{Xe}^+)$	1.000 35 (14)
	$I(^{130}\mathrm{Xe}^+)/I(^{132}\mathrm{Xe}^+)$	1.000 422 (85)
	$I(^{131}\mathrm{Xe}^+)/I(^{132}\mathrm{Xe}^+)$	1.000 345 (20)
	$I(^{134}\mathrm{Xe}^+)/I(^{132}\mathrm{Xe}^+)$	0.999 588 (43)
	$I(^{136}\mathrm{Xe}^+)/I(^{132}\mathrm{Xe}^+)$	0.999 46 (16)
S [21]	$I(^{33}\mathrm{SF}_5^+)/I(^{32}\mathrm{SF}_5^+)$	1.000 05 (24)
	$I(^{34}\mathrm{SF}_5^+)/I(^{32}\mathrm{SF}_5^+)$	0.999 786 (46)

values of $J_{i/j}$ and their uncertainties reported in Table 3 include already the conversion using K_{mad} and K_{ion} with their uncertainties.

Measurements of synthetic isotope mixtures for different elements confirm that the conversion factor K_{res} for residual systematic effects of unknown nature approaches unity to within 3×10^{-3} (often even a factor of 8 better) with a typical uncertainty of 4×10^{-4} (see Table 5). Since in GIMS this conversion factor was found to be less dependent on the chemical nature of the compound under investigation, the conversion factor for small residual systematic effects in this work was estimated to be $K_{\mathrm{res}} = 1.000\,0$ with an uncertainty (type B evaluation) of 5×10^{-3} relative.

From the isotope amount ratios and the tabulated [27] atomic masses $M(^i\mathrm{E})$ (known within an uncertainty of 10^{-8} relative) the molar mass $M(\mathrm{E})$, numerically equal to the atomic weight $A_r(\mathrm{E}) = \Sigma(R_{i/j}M(^i\mathrm{E}))/\Sigma R_{i/j}$ can be calculated. The results for $A_r(\mathrm{Ge})$ are summarised in the last column of Table 6.

The approach of calibration—not using synthetic isotope mixtures of the same element, but based on understanding and splitting up the measurement process as described above and reflected in a critical and complete uncertainty budgeting—chosen by the authors leads to the statement, that the values for the isotopic composition and atomic weight (molar mass) of Ge reported in Table 6 can considered to be calibrated. The authors do not claim having performed a calibration by measuring synthetic isotope mixtures of the same element, and the authors are aware of the fact that synthetic isotope mixtures could probably result in smaller combined uncertainties.

Published data (A—M) according to IUPAC recognised references [28] for the isotopic composition and the atomic weight of Ge [2–4,6–9,29] are summarised in Table 7 and displayed in Figs. 3–7.

The isotopic composition of an element can be described in different ways. Thus the originally published isotope abundances ratios normalised to various "normalising" isotopes have been converted to isotope abundance ratios using the ^{74}Ge abundance as

Table 6
Calibrated isotope amount ratios $R_{i/74}(\mathrm{Ge}) = n(^i\mathrm{Ge})/n(^{74}\mathrm{Ge})$ and atomic weight $A_r(\mathrm{Ge})$—numerically equal to molar mass; all uncertainties indicated are expanded uncertainties $U = ku_c$, where u_c is the combined standard uncertainty estimated following the ISO/BIPM Guide to the Expression of Uncertainty in Measurement [13], they are given in parentheses and include a coverage factor $k = 1$; they apply to the last two digits

No.	$R_{70/74}$	$R_{72/74}$	$R_{73/74}$	$R_{76/74}$	$A_r(\mathrm{Ge})$
6	0.564 2 (29)	0.752 3 (38)	0.212 3 (11)	0.211 6 (11)	72.626 7 (32)
7	0.563 5 (29)	0.752 0 (38)	0.212 3 (11)	0.211 8 (11)	72.627 6 (32)
9	0.563 5 (29)	0.751 9 (38)	0.212 3 (11)	0.211 7 (11)	72.627 6 (32)
10	0.563 5 (29)	0.751 9 (38)	0.212 3 (11)	0.211 8 (11)	72.627 6 (32)
11	0.563 6 (29)	0.751 9 (38)	0.212 3 (11)	0.211 8 (11)	72.627 6 (32)
12	0.563 6 (29)	0.751 9 (38)	0.212 3 (11)	0.211 8 (11)	72.627 6 (32)
Mean 7–12	0.563 5 (29)	0.751 9 (38)	0.212 3 (11)	0.211 8 (11)	72.627 6 (32)

Table 7
Published isotope amount ratios and atomic weight of Ge as calculated from $R_{i/74}$; numbers in parentheses are uncertainties based on the original publications—often not including all significant sources of uncertainty—they apply to the last two digits of the value

	$R_{70/74}$	$R_{72/74}$	$R_{73/74}$	$R_{76/74}$	A_r(Ge)
A	0.571 4 (31)	0.735 8 (32)	0.212 9 (29)	0.175 2 (29)	72.579 3 (48)
B	0.559 34 (31)	0.744 96 (32)	0.208 76 (29)	0.208 76 (29)	72.629 55 (48)
C	0.568 2 (13)	0.754 82 (32)	0.216 3 (12)	0.212 44 (26)	72.623 5 (14)
D	0.565 9 (19)	0.752 2 (28)	0.215 1 (18)	0.213 7 (15)	72.627 8 (26)
E	0.548 7 (19)	0.740 4 (21)	0.208 84 (85)	0.214 27 (85)	72.648 0 (23)
F	0.556 07 (65)	0.746 79 (69)	0.212 28 (28)	0.213 37 (28)	72.638 25 (76)
G	0.566 6 (62)	0.755 (11)	0.211 9 (21)	0.211 6 (21)	72.623 7 (72)
H	0.561 6 (55)	0.750 7 (76)	0.212 4 (22)	0.212 4 (22)	72.630 6 (63)
I	0.584 80 (65)	0.766 7 (21)	0.212 87 (42)	0.206 43 (37)	72.596 81 (78)
J	0.590 77 (43)	0.769 60 (41)	0.214 684 (51)	0.207 11 (16)	72.591 38 (45)
K	0.590 8 (11)	0.769 6 (11)	0.214 70 (15)	0.207 10 (42)	72.591 4 (12)
L	0.575 (32)	0.759 (34)	0.213 1 (44)	0.210 0 (13)	72.613 (34)
M	. . .	. . .	. . .	. . .	72.61 (2)
N	0.563 5 (29)	0.751 9 (38)	0.212 3 (11)	0.211 8 (11)	72.627 6 (32)

A: Aston [9]; $Ge(CH_3)_4$; gas-MS; abundances reported; no uncertainty statement.

B: Ingraham et al. [8] as reported in [4]; Ge^+; TIMS; abundances reported; no uncertainty statement.

C: Hibbs et al. [6]; GeI^+ from GeF_4; gas-MS; abundances reported; uncertainties based on statistics (different instruments, ion sources and samples).

D: Idem; GeF_3^+ from GeF_4.

E: Graham et al. [5]; $GeCl^+$ from $GeCl_4$; gas-MS; abundances from ratios with different reference isotopes reported; no uncertainty statement for the abundances; "...the isotope abundances calculated from GeF_3^+; analyses are considered the more reliable;" therefore, uncertainty of 3 times the uncertainty of F was assumed.

F: Idem; GeF_3^+ from GeF_4; gas-MS; abundances from ratios with different reference isotopes reported; uncertainty statement based on statistics only; even if "although absolute mass spectrometric abundance ratios cannot consistently be determined with a reproducibility better than 0.5%, relative abundance measurements can be made with a reproducibility of 0.1%."

G: Dibeler [7]; $Ge(CH_3)_4$; gas-MS; abundances reported; "uncertainties . . . are estimated errors probably present in the recording system only; for principal isotopes, the reproducibility was at least factor 10 better than the estimated error."

H: Reynolds [4]; GeF_3^+ from GeF_4; gas-MS; abundances calculated from $R(^{i}Ge/^{74}Ge)$; uncertainties include mass discrimination.

I: Shima [3]; Ge^+; electron multiplier, TIMS; data set III; ratios $R(^{i}Ge/^{70}Ge)$ reported; uncertainty statement: standard deviations; "data . . . are not corrected for mass discrimination and instrumental drift, because of the purpose of this work is only to compare the isotopic abundances of Ge . . . ."

J: Green et al. [2]; Ge^+; electron multiplier; TIMS; abundances calculated from $R(^{i}Ge/^{73}Ge)$; uncertainty statement: two standard errors of the mean; self-suspected correction of 7% per mass unit for electron multiplier not included.

K: IUPAC: Isotopic Composition of the Elements 1997 [29]; best measurement abundances reported, values based on *J*; original standard errors of the mean converted to single standard deviations.

L: Idem; representative isotopic composition; abundances reported, values based on *J* corrected for mass discrimination at electron multiplier; the uncertainties based on *J* were enlarged by factors of 10–28; the uncertainty statement on the abundances is inconsistent (due to the CAWIA calculation method [14]); to obtain a consistent uncertainty statement for comparison a factor of 30 was applied here.

M: Standard atomic weight (IUPAC Table 1995) [1].

N: This work; GeF_3^+ from GeF_4; single Faraday cup; GIMS; ratios $R(^{i}Ge/^{74}Ge)$ reported; total combined uncertainty u_c coverage factor $k = 1$.

reference by means of the IRMM computer programme SPIRIT [30]. Very often, however, the uncertainty statements are missing in the original literature or are at least incomplete, which means that not all parameters explicit in Eq. (2) have been taken into account. This makes a comparison of the published values difficult. If no uncertainty statement was given, a (most likely too optimistic) uncertainty of unity was assumed on the last published digit.

The data set I from Shima was not considered here because the data was not corrected for mass discrimination (see Table 7). Knowing that the measurements of B, C, D, E, F, G, and H have incomplete uncertainty statements (i.e. are not combined uncertainties)

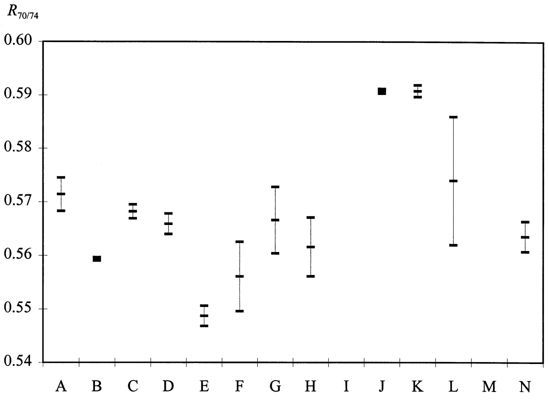

Fig. 3. Values for isotope amount ratio $R(^{70}Ge/^{74}Ge)$ from published data.

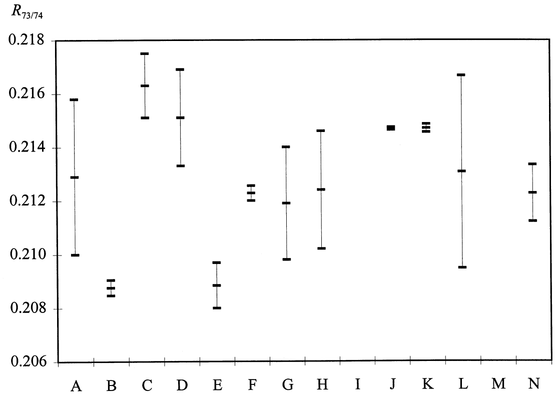

Fig. 5. Values for isotope amount ratio $R(^{73}Ge/^{74}Ge)$ from published data.

the agreement with this work (N) is quite favourable. The discrepancy between Green et al. (J) and this work (N) is not as severe as it might be considered on first glance, because making a comparison between L—the values obtained for the representative isotopic composition by IUPAC from the data of Green et al. by applying corrections for the electron multiplier and including a conservative uncertainty evaluation according to [14]—and N is more applicable. However, comparing N to L shows a general trend of higher isotope amount ratios $R(^{70}Ge/^{74}Ge)$, $R(^{72}Ge/^{74}Ge)$, and $R(^{73}Ge/^{74}Ge)$ and of a lower $R(^{76}Ge/^{74}Ge)$. This may indicate the influence of an unrecognised mass dependent fractionation in this or the work of Green et al., since they did not find any significant variations in the isotopic composition of Ge of different origin. The work of Green et al. (J) was selected in 1985 by the subcommittee on Atomic and Isotopic composition (SIAC) of the IUPAC as "best measurement," which then led to a change in the atomic weight of Ge [31,32,33]. The enlarged uncertainty statements on the isotope abundances for L (see also remark Table 7) originate from the IUPAC CAWIA technical guidelines to calculate the representative isotopic composition [14]. This conservative evaluation is performed to avoid frequent changes in the tabulated values for the isotopic composition.

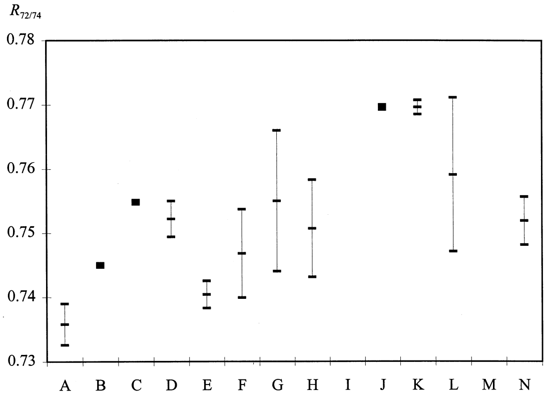

Fig. 4. Values for isotope amount ratio $R(^{72}Ge/^{74}Ge)$ from published data.

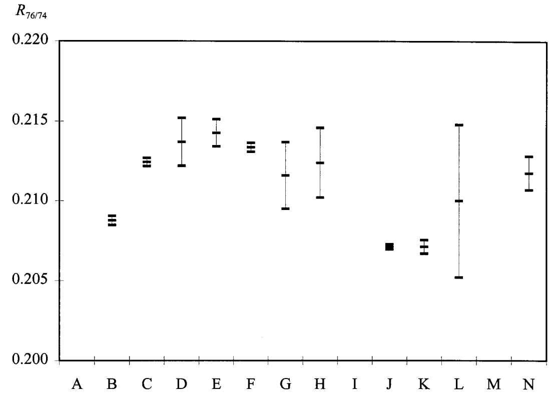

Fig. 6. Values for isotope amount ratio $R(^{76}Ge/^{74}Ge)$ from published data.

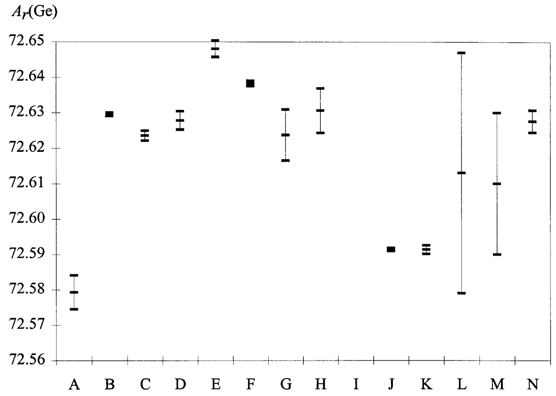

Fig. 7. Values for the atomic weight of Ge from published data.

4. Conclusion

The results obtained from gas isotope measurements on GeF_4 produced by direct and wet chemical fluorinated Ge and GeO_2 are identical within 1 part in 10^4 relative uncertainty. No indication for different isotope fractionation during chemical processing could be detected for the two preparation methods.

The direct fluorination has demonstrated its potential for use in the preparation of gaseous GeF_4 samples for isotopic measurements with small combined uncertainties. Advantages are the short reaction times needed, the closed system and the applicability for many elements. Disadvantages are the relatively high costs and a more complex apparatus. The technique for fluorine handling is developed and—from our experience (more than 600 fluorinations)—considered to be safe. Between two different starting materials, no significant difference in the isotopic composition of Ge was found.

Compared to other published data on Ge the reproducibility of the measurements of the isotope abundance ratios on individual gas samples, is very good (7×10^{-5} relative). Using the Avogadro II amount comparator and measurement procedure and strictly applying the ISO/BIPM Guide to the Expression of Uncertainties in Measurements [13], this leads to calibrated isotope abundance ratios for Ge with relative combined uncertainties of 5×10^{-3}, and an atomic weight (molar mass) with a relative combined uncertainty of 5×10^{-5}. However, the use of synthetic isotope mixtures of Ge could further reduce the uncertainty on the conversion factor for small residual systematic effects.

As redundancy is a good metrological concept in general, the authors look forward to the confrontation with data from future measurements obtained by other authors using synthetic isotope mixtures of Ge.

Acknowledgements

A special tribute is due to E. Jacob, MAN, Munich for making the fluorination line and know-how available. The authors would like to thank H.S. Peiser and J.R. de Laeter for helping to track the history of the isotopic composition of Ge. DAAD (Deutscher Akademischer Austauschdienst) and BALZERS, Liechtenstein (J. Herrmann) are acknowledged for grant no. D/94/01138 and instrumental support.

References

[1] IUPAC: Atomic Weights of the Elements 1995, Pure Appl. Chem. 68 (1996) 2339.
[2] M.D. Green, K.J.R. Rosman, J.R. de Laeter, Int. J. Mass Spectrom. Ion Processes 68 (1986) 15.
[3] M. Shima, J. Geophys. Res. 68 (1963) 4289.
[4] J.H. Reynolds, Phys. Rev. 90 (1953) 1047.
[5] R.P. Graham, J. Macnamara, I.H. Crocker, R.B. MacFarlane, Can. J. Chem. 29 (1951) 89.
[6] R.F. Hibbs, J.W. Redmond, H.R. Gwinn, W.D. Harman, Phys. Rev. 75 (1949) 533.
[7] H. Dibeler, J. Res. Natl. Bur. Stand. 49 (1952) 235.
[8] M.G. Ingraham, R.J. Hayden, D.C. Hess, Argonne National Laboratory, Plutonium Project Report No. ANL-4082, 1947, p. 6.
[9] F.W. Aston, Mass Spectra and Isotopes, Arnold, London, 1933, p. 154.
[10] P. Becker, PTB, private communication, 1998.
[11] E. Jacob, Fres. Z. Anal. Chem. 333 (1989) 761.
[12] IUPAC: Guidelines for Calibration in Analytical Chemistry, Pure Appl. Chem. 70 (1998) 993.
[13] Guide to the Expression of Uncertainty in Measurements, ISO, Geneve, 1993.
[14] IUPAC: CAWIA Technical Booklet, 4th ed., 1996.
[15] E. Jacob, Z. Anorg. Allgem. Chem. 377 (1970) 267.
[16] Gefährliche Arbeitsstoffe, R. Kühn, K. Birett (Eds.), Ecomed Verlag, München, 1994.

[17] IRMM Internal Report No. GE/R/MS/31/94.
[18] P. De Bièvre, S. Valkiers, Metrologia 31 (1994) 245.
[19] P. De Bièvre, S. Valkiers, F. Schaefer, H.S. Peiser, PTB Mitteilungen 104 (1994) 225.
[20] S. Valkiers, Y. Aregbe, P.D.P. Taylor, P. De Bièvre, Int. J. Mass Spectrom. Ion Processes 173 (1998) 55.
[21] T. Ding, S. Valkiers, H. Kipphardt, R. Damen, P. De Bièvre, P.D.P. Taylor, unpublished.
[22] Y. Aregbe, S. Valkiers, P.D.P. Taylor, P. De Bièvre, unpublished.
[23] S. Valkiers, unpublished.
[24] R. Gonfiantini, S. Valkiers, P.D.P. Taylor, P. De Bièvre, Int. J. Mass Spectrom. Ion Processes 171 (1997) 231.
[25] P. De Bièvre, S. Valkiers, H.S. Peiser, P.D.P. Taylor, P. Hansen, Metrologia 33 (1996) 447.
[26] R. Gonfiantini, S. Valkiers, P.D.P. Taylor, P. De Bièvre, Int. J. Mass Spectrom., submitted.
[27] G. Audi, A.H. Wapstra, Nucl. Phys. A 565 (1993) 1.
[28] IUPAC: Isotopic Abundances and Atomic Weights of the Elements, J. Phys. Chem. Ref. Data 13 (1984) 809.
[29] IUPAC: Isotopic Compositions of the Elements, Pure Appl. Chem. 70 (1998) 217.
[30] F. Schaefer, P.D.P. Taylor, S. Valkiers, P. De Bièvre, Int. J. Mass Spectrom. Ion Processes 133 (1994) 65.
[31] IUPAC: Atomic Weights of the Elements 1985, Pure Appl. Chem. 58 (1986) 1678.
[32] IUPAC: History of the Recommended Atomic Weight Values from 1882 to 1997, Pure Appl. Chem. 70 (1998) 257.
[33] IUPAC: Element by Element Review of their Atomic Weights, Pure Appl. Chem. 56 (1984) 695.