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“Calibration” in isotopic measurements

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Abstract

The meaning of calibration in general and in the field of isotopic measurements in particular is described, stressing the fundamental difference between calibration as an aim and tools to achieve calibration. The role of proper uncertainty budgeting as a prerequisite for establishing a “calibrated” measurement is explained. It leads to the recommendation that the quality of the uncertainty statement should be heavily weighed when ranking or judging “calibrated” isotopic measurement results evaluated by the Commission on Atomic Weight and Isotopic Abundances. (Int J Mass Spectrom 198 (2000) 71–76) © 2000 Elsevier Science B.V.

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1. Introduction

In the specific field of measurements of isotope amount ratios, “calibration” is often synonymous with the use of synthetic isotope mixtures. It is claimed in the technical documents of the Commission on Atomic Weight and Isotopic Abundances (CAWIA) that this results in “absolute” isotope amount ratios: ‘C’ is appended when calibrated mixtures have been used to correct the mass spectrometer for bias, giving an ‘absolute’ result within the errors stated in the original publication” [1]; “C is fully calibrated through either (1) the NBS/CBNM approach: (linearity + fractionation) is determined by measuring synthetic mixtures of isotopes whose abundance ratios approximate all the ratios in the mass spectrum of the natural element or (2) the double spike approach: nonlinearity is adequately determined and then fractionation is corrected by adding a synthetic mixture of isotopes to the sample prior to sample processing and isotopic analysis” [2].

That is somewhat different from the general interpretation as given in the technical document of the IUPAC Analytical Chemistry Division [3] in that the CAWIA document stresses certain *tools* to achieve a calibrated measurement rather than what the IUPAC document describes as the *aim* of calibration. To understand the conclusions presented here it is important to remember that all measurements—including isotopic measurements—require a measurement model, formulated in a measurement equation, and that all measurement results are associated with measurement uncertainty. Please note that “differential” isotopic measurements (δ measurements) are left out of the scope of this article.

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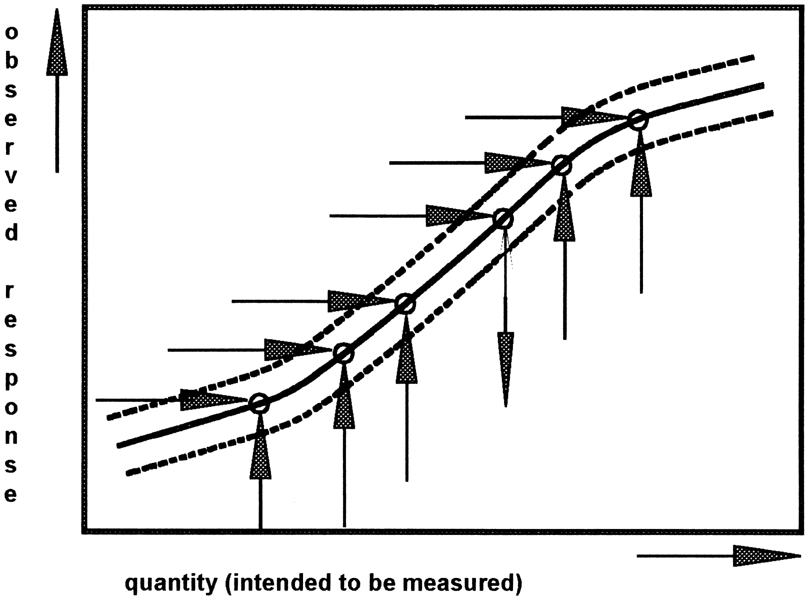

Fig. 1. Graphical representation of the calibration process as adapted from [4].

2. What is a calibration?

The technical document of the IUPAC Analytical Chemistry Division [3] states, "In general, calibration is an operation that relates an output quantity to an input quantity for a measuring system under given conditions." In other words, by means of a calibration process, an observed quantity q_{obs} (e.g. a ratio J of electrical currents) can be converted into what is intended to be measured q_{int} (e.g. a ratio R of isotope amounts). This is illustrated for the general case in Fig. 1 as adapted from [4]. When isotopic measurements are described, the observed quantity and quantity intended to be measured, are often taken as identical (presumably because both quantities are ratios), which is wrong, of course. One ratio needs to be converted into another ratio. The calibration function represented by a calibration curve establishes the relation between two quantities, and one should be aware of all the boundary conditions for the validity of a calibration. Note that the main problem in a calibration process is often to define correctly the quantity observed and the quantity claimed to have been measured (or at least intended to have been measured).

Here we focus on a case when the calibration is only done in a narrow range close to the value of the measurand and we assume the calibration curve is linear. When applying this in practice, note that the uncertainty of this assumption needs to be taken into account (see Fig. 1). In mathematical terms this can be expressed as $q_{\mathrm{int}} = K_c \times q_{\mathrm{obs}}$, where K_c is the so-called calibration factor. Note that it would be more appropriate to define K_c as the conversion factor because it is used to convert a value of a directly observed quantity into a value of another quantity of a completely different nature. Occasionally, K_c is also called the correction factor, a name that is not appropriate here (a conversion is done) and should therefore not be used. Finally it is useful to point out that various *tools* can be used to achieve a calibration, i.e. to establish K_c.

The term "uncalibrated" or "not fully calibrated" measurement is used in CAWIA when the value of an actually observed quantity (an ion current ratio J) is directly attributed to the quantity which is intended to be measured (an isotope amount ratio R), thus disregarding significant influencing quantities (e.g. mass fractionation, linearity, etc.) and their uncertainties. From a metrological point of view, this formulation of the statement of a measurement result is simply wrong. (It is possible that the numerical value of the observed quantity is close to the numerical value of the quantity intended to be measured, but this is certainly not the case for the associated uncertainties.)

Note that the above applies to many of the measurements selected by CAWIA as ("best measurements" [1]. Using the technical document [2], CAWIA is accounting for the incomplete uncertainty statement by considerably increasing the originally reported uncertainty, an approach that is perfectly acceptable and fully in line with the recent Guide on the Expression of Uncertainty in Measurements (GUM) [5]. CAWIA has, in fact, been applying this practice for many years and, hence, has rarely if ever been proven wrong [6].

3. Uncertainty in calibration

The novel concept of the evaluation of uncertainties in measurements (where error is not synonymous with uncertainty), is described in detail in the ISO [5]. The uncertainty of a measurement is of key importance: "In general, the result of a measurement . . . is only an approximation or estimate . . . of the value of the measurand and thus is complete only when accompanied by a statement of the uncertainty . . . of that estimate."

This concept also applies to chemical and isotopic measurements. The quality of the calibration process (i.e. the uncertainty of the calibration) should be reflected in the (combined) uncertainty of the measurement result. It is observed that isotopic measurement results are rarely accompanied by complete uncertainty statements, evaluated according to the ISO Guide rules.

A reliable uncertainty statement must be accompanied by information on the sources of the uncertainty and this picture must be transparent to (1) enable the reader to identify which influencing quantitities have (not) been taken into account, and (2) to enable judgment on whether the combined uncertainty of the measurement result from the estimation of the individual uncertainty contributions is realistic.

4. How to achieve a calibration in isotopic measurement

The traditional method used to achieve calibration of isotopic measurements is the use of synthetic isotope mixtures of the same element (in the same chemical form and of the same isotopic composition as the sample material) in order to determine an overall calibration factor (better: "conversion factor" from a current ratio to an isotope amount ratio). This approach is taken to enable the cancellation of many influencing effects such as those occurring from the chemical sample preparation, the mass fractionation, and any deviation from linearity of the spectrometer and of the detector. It should be noted that this approach has been used only by a couple of highly experienced laboratories that had the means to purchase the expensive, highly enriched isotopes in sufficient amounts to achieve sufficiently small uncertainty on the synthetically prepared isotope amount ratio.

The question arises of whether accounting for a mixture of many influencing quantities in an overall calibration factor results in the smallest possible (but still complete) combined uncertainty. The triviality that a calibration result is only strictly valid for the calibration process itself is often not recognised and not accounted for, especially when "single point calibrations" are performed: unknown samples and calibration samples are measured at different times (there is never exact reproducibility of the measurement conditions) and/or the sample material is of a different (chemical) origin than the calibrating material (matrices are different).

Example: When calibrating the measurement of the isotopic composition of iron oxide extracted from a rock by means of measurements of synthetic isotope mixtures prepared from high purity enriched iron isotopes, the different chemical processings of the materials and the different chemical nature of the sample and the calibration material must be taken into account. All uncertainties coming from these different origins must therefore be taken into account in order to get a calibrated measurement result, and that will increase the uncertainty associated with the measurement result. When disregarding significant uncertainty contributions as these, the measurement can, regretfully, not be called calibrated, even if synthetic isotope mixtures of the same element were involved in the calibration process.

Thus the use of synthetic isotope mixtures in itself does not unconditionally guarantee a valid calibration. Rather, it is the degree of care, as reflected in the uncertainty budget and its statement, that determines the metrological quality of the measurement result. Is it possible to eliminate the use of synthetic isotope mixtures of the same element, in the same chemical form, and of the same isotopic composition? And when would it qualify as a "calibration" for isotopic measurements? This is discussed in the next section.

5. An alternative "calibration" approach in isotopic measurements

It was explained above that all quantities with significant uncertainty contributions must be taken into account in order to result in a calibrated measurement. Thus, instead of determining an overall calibration factor, one *can* split up this factor into its individual components. This evidently requires *full insight into the measurement process*. At the Institute for Reference (IRMM) this approach is followed in measurements leading to the redetermination of the Avogadro constant, which requires the measurement of the molar mass (mean relative atomic weight) of silicon with very small uncertainty ($<5 \times 10^{-7}$ relative, requiring total combined uncertainties on the isotope amount ratios of $<2 \times 10^{-5}$ relative). Needless to say, this demands a careful measurement strategy (apart from the numerous improvements of the measurement equipment). The resulting measurement procedure and instrument, based on a gas source mass spectrometer with molecular gas inlet and a single Faraday detector, was applied so far for isotopic measurements of several gases: Xe, Kr, and SF_6. The accuracy was *verified* at a very small uncertainty level by means of measurements of synthetic isotope mixtures [7–10]. From the measurement of these synthetic isotope mixtures the conversion factor was proven to be unity within 5×10^{-4} (see Table 1).

Table 1
Conversion factors for small residual systematic effects K_{res} for isotopic measurements of different elements

Element	Ion current ratio	$K_{\text{res}} = R/J$
Kr [8]	$I(^{80}Kr^+)/I(^{84}Kr^+)$	1.00039 (19)
	$I(^{82}Kr^+)/I(^{84}Kr^+)$	1.00007 (29)
	$I(^{83}Kr^+)/I(^{84}Kr^+)$	1.00001 (27)
	$I(^{86}Xe^+)/I(^{84}Kr^+)$	0.999961 (81)
Xe [7]	$I(^{128}Xe^+)/I(^{132}Xe^+)$	1.00022 (13)
	$I(^{129}Xe^+)/I(^{132}Xe^+)$	1.00035 (14)
	$I(^{130}Xe^+)/I(^{132}Xe^+)$	1.000422 (85)
	$I(^{131}Xe^+)/I(^{132}Xe^+)$	1.000345 (20)
	$I(^{134}Xe^+)/I(^{132}Xe^+)$	0.999588 (43)
	$I(^{136}Xe^+)/I(^{132}Xe^+)$	0.99946 (16)
S [10]	$I(^{33}SF_5^+)/I(^{32}SF_5^+)$	1.00005 (24)
	$I(^{33}SF_5^+)/I(^{32}SF_5^+)$	0.999786 (46)

Moreover, the conformity of the physical–chemical processes occurring in the spectrometer can be monitored during the isotope amount ratio measurement by measuring the effusion fractionation factor at the inlet system against the well known values of $(M_j/M_i)^{\Phi}$ as predicted by kinetic gas theory, a theory that is sufficiently accepted to be valid as "stated reference." Experimental values for the exponent were proved to coincide with the theoretical value $\Phi = \frac{1}{2}$ within (small) measurement uncertainty. Thus, monitoring the difference between experimentally obtained values and those predicted by kinetic gas theory enabled us to measure the degree of imperfection of the measurement process against a reliable reference *during* the measurement. The measurements show that the results are independent of the chemical nature of the atoms or molecules in the gas (see Fig. 2). They are only dependent on the mass of the atoms/molecules and complete accountancy for the mass dependent effect (within measurement uncertainty) is possible by calculation. The effect is concordant with the theoretical value (again, within the measurement uncertainty). It cannot be stressed

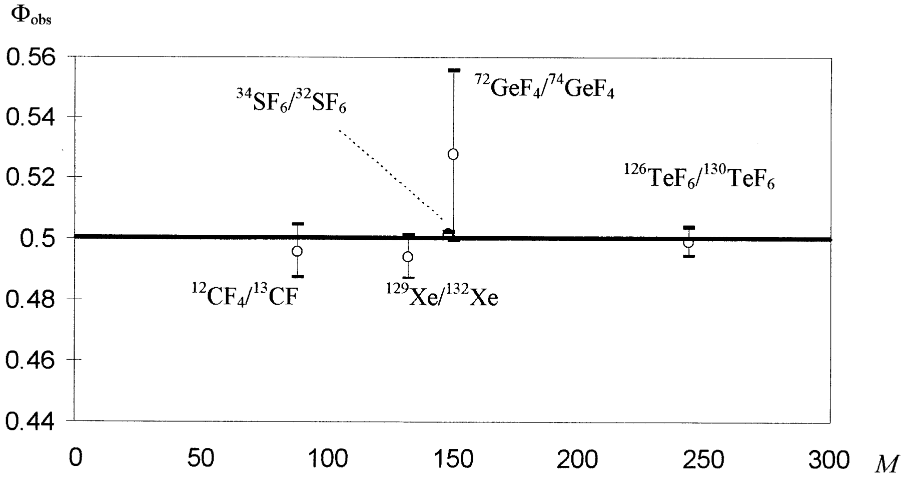

Fig. 2. Mass fractionation exponent Φ_{obs} as derived from measurement of mass fractionation $(M_j/M_i)^{\Phi}$ at the inlet system (effusion) vs. molecule mass M. Kinetic gas theory (KTG) predicts $\Phi = \frac{1}{2}$. M is the molar mass of the effusing species and the indices refer to the different isotopes. Data for CF_4, TeF_6, SF_6, Xe, Kr, and GeF_4 are taken from [12,12,9,7,8,13], respectively.

enough that considerable effort must be spent to realise near-ideal conditions in the inlet and ion source of the mass spectrometer.

Hence, the measurement procedure developed by the authors [11] seems to be applicable without using synthetic isotope mixtures. The uncertainty of the measurement result following this approach must, of course, be correctly evaluated and this has been done. In addition, conservative coverage factors ($k = 3$, see GUM) were applied, and even then the remaining uncertainty can still be comparable to or smaller than the one resulting from many other techniques—sometimes even smaller than when these techniques include calibration by means of synthetic isotope mixtures. Thus, this described measurement procedure (DMP) seems to be in order and can be used in such measurements.

6. Conclusion

In general, proper calibration can be achieved when all significant influencing quantities and all significant uncertainty contributions are taken into account in the uncertainty budget. Ranking or judging isotopic measurement results evaluated by CAWIA should be done according to the quality of the uncertainty statement, which is reflected by the visibility of a complete and transparent uncertainty budget. For understanding and credibility, this in turn requires a description of how the calibration has been performed. In isotopic measurements, the use of synthetic isotope mixtures of the same element, in the same chemical form, and of the same isotopic composition possibly results in the smallest combined uncertainty achievable; this has the potential to give the measurement result a "primary" character (an uncritical use of synthetic mixtures does not guarantee that). However, proper calibration does not necessarily require the use of synthetic isotope mixtures of the same element in the same chemical form, provided the uncertainty introduced by not using synthetic isotope mixtures of the same element, form, and isotopic composition is conservatively taken into account within the uncertainty budget of a measurement procedure that is understood within the stated uncertainty. For measurement procedures that are understood in detail this approach can result in measurement results with valid (combined) uncertainties. Moreover, the possibility of measuring against other reliable references (such as values derived from kinetic gas theory *during* the isotope amount ratio measurement) can serve as an independent calibration tool.

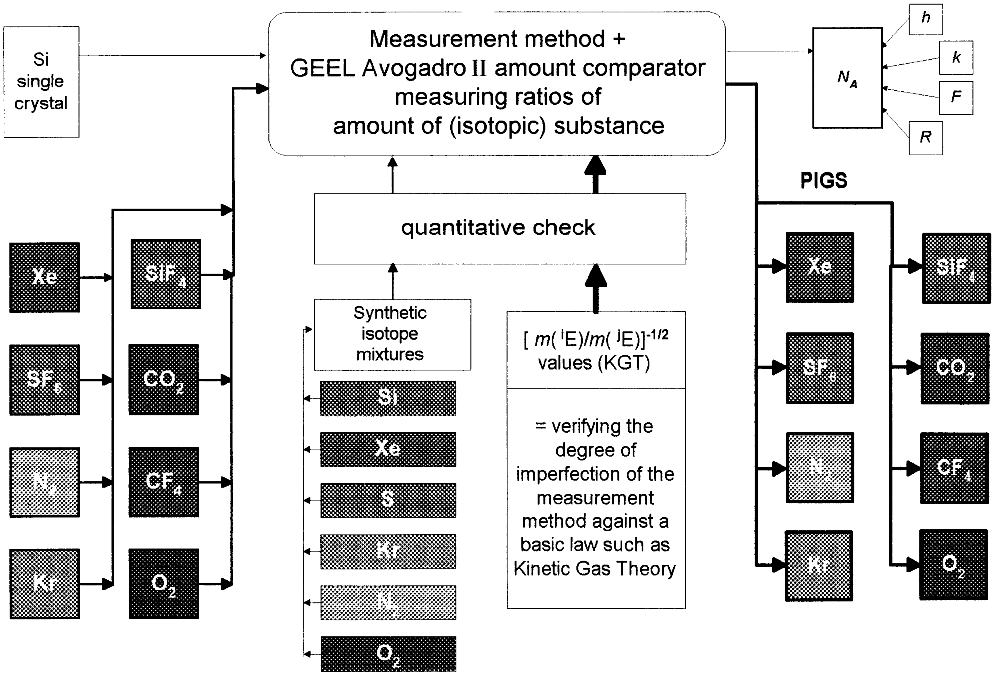

Fig. 3. Calibration strategy for measurements of the isotopic composition (by means of the Avogadro II amount comparator) leading to primary isotopic gas standards.

Of course, the combination of both calibration approaches (using isotope mixtures of the same element, in the same chemical form, and of the same isotopic composition as well as a measurement procedure understood in high detail) as illustrated in Fig. 3 is considerably better. It is used at IRMM to certify primary isotopic gas standards. Both procedures convert the isotopic measurement into a comparison of an unknown value to a known value, the definition of measurement.

Acknowledgement

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