

Letter to the Editor

*Silicon Reference Materials Certified
for Isotope Abundances*

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In a series of gas mass-spectrometric measurements performed near the highest attainable accuracy, samples from two highly homogeneous batches of silicon crystals and silica powder were compared directly with a synthetic mixture of the three stable isotopes of silicon. Thereby, this work not only established the “absolute” atomic weight of these batches, but also makes portions of these batches available as an Isotopic Reference Material for accurate isotopic abundance measurements in geochemical and other isotope-abundance studies of silicon.

Key words: absolute abundances; atomic weights; isotope abundances; isotopic mass spectrometry; isotope reference materials; silicon; silicon tetrafluoride.

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A precise determination of differences of a property between similar specimens is more easily achieved than absolute accuracy in the measurement. In mass-spectrometric determinations of isotope abundances, variations are often small—but significant relative to achievable precision—between specimens from differing chemical, physical, geological, or biological processes. It is just these variations that open new fields of study in geochemistry, chemical technology, solid-state physics, archeology, analysis of trace elements, etc. Thus, as in other fields, credible isotope reference materials

(IRMs) are needed which must fulfill the following criteria:

- i) near perfect homogeneity within and between samples of the IRM;
- ii) wide and open availability of IRM samples in adequate amounts so that different laboratories can refer to the “same” material;
- iii) full chemical and physical characterization of the IRM; and
- iv) direct absolute measurement of the isotopic composition of the IRM near the highest contemporary accuracy.

The fourth criterion demands a direct atomic-weight and isotopic composition determination recognized to have been carried out near the highest accuracy so far achieved. That in turn implies the preparation of synthetic mixtures from highly enriched isotope constituents. During the past 25 years such measurements have been rarely made and only on a total of about 15 elements. The introduction therefore of two new silicon IRMs is an event of note.

A smaller batch of small silicon single crystals (total mass ~ 10 g) and a larger batch of SiO₂ grains (10 kg Optipur Merck¹) have been characterized for their isotopic homogeneity, isotopic composition and relative atomic weight, $A_r(\text{Si})$. This has resulted in two IRMs: IRM-017 (Si) and IRM-018 (SiO₂), portions of which are now available from the Central Bureau for Nuclear Measurements (CBNM).

The isotopic measurements on the three stable isotopes of silicon were performed by gas isotope mass spectrometry [1] on samples which were converted to SiF₄ gas by the following chemical steps carried out on a large number of portions. In step 1 samples of the silicon candidate reference material were dissolved in warm dilute sodium hydroxide, and the solution of sodium silicate was converted to aqueous silicic acid in an acidic ion exchanger. Water from that solution was evaporated and the residue heated to 950 °C to form silica (SiO₂). Steps 2 and 3 were applied to samples of both candidate reference materials. In step 2 the silica was dissolved in hydrofluoric acid from which barium hexafluorosilicate was precipitated. In step 3 the barium salt was heated to 540 °C in an evacuated vessel, and the silicon tetrafluoride was frozen out.

The isotope-abundance ratio measurements on SiF₄ (²⁹SiF₃⁺/²⁸SiF₃⁺, ³⁰SiF₃⁺/²⁸SiF₃⁺) were calibrated by means of a gravimetric mixture of the three enriched isotopes [2]. The amounts of the enriched isotopes used to prepare the mixture were chosen such that the prepared ratios were close to those for natural silicon. With this synthetic isotope mixture the mass-spectrometric correction factors K ($K = \text{ratio as prepared}/\text{ratio as observed}$) for the observed ratios were determined. The IRMs were measured in the same series of tightly controlled

measurements from which the effect of any inevitable instrumental drift could be minimized. In this way the above correction factors could be applied to these IRM measurements, resulting in "absolute" isotope abundances and atomic weights for both materials (Table 1). The measurement technique for gas isotopic measurements as it was developed by the authors for this work will be described in more detail in other future publications.

Table 1. Isotopic Composition and $A_r(\text{Si})$ for both IRMs. Uncertainties are indicated under the digits to which they relate and are computed on a two-standard deviation basis. (The mass spectrometric measurements on isotopic reference materials 017 and 018 were carried out during a period just before a filament change became necessary. An increasing instability of the old filament was mainly responsible for the larger uncertainties when compared with those for an entirely different silicon crystal that happens to have a virtually identical relative atomic weight.)

	CBNM-IRM-017 Si	CBNM-IRM-018 SiO ₂
Molar isotope abundance ratios		
²⁹ Si/ ²⁸ Si	0.050 69 12	0.050 83 12
³⁰ Si/ ²⁸ Si	0.033 52 10	0.033 60 10
Molar abundances (fractional)		
²⁸ Si	0.922 33 14	0.922 14 14
²⁹ Si	0.046 75 11	0.046 88 11
³⁰ Si	0.030 92 8	0.030 98 8
Mass percentages		
²⁸ Si	91.877 14	91.857 14
²⁹ Si	4.823 11	4.836 11
³⁰ Si	3.300 8	3.307 8
Relative atomic mass (atomic weight)		
$A_r(\text{Si})$	28.085 40 19	28.085 65 19

¹ Certain commercial equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Similarly, the required chemical preparation techniques of the samples deserve fuller description and critical analysis elsewhere. The atomic-weight measurements here described are in experimental agreement with the previously recognized best silicon measurements by Barnes et al. [4]. It was possible to include a sample from those earlier measurements in the self-same series described above. The consistency of all these measurements was thereby further established.

References

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About the authors: S. Valkiers received a degree in chemical engineering in 1976 from Hk University, Geel, Belgium. P. De Bièvre is a PhD from Gent University and also Professor in Isotope Mass Spectrometry at Antwerpen University in addition to his position at CBNM. G. Lenaers received his PhD from Antwerpen University in 1990 with a dissertation on the chemical procedures summarized in this paper. H. S. Peiser, now retired, was at one time Chief of the Crystal Chemistry Section at the National Bureau of Standards (now the National Institute of Standards and Technology).