

Solution to lead quantitation challenge

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The winner of the Lead quantitation challenge (published in volume 411 issue 9) is: Sami T. Tuomivaara, University of California, San Francisco, CA 94107, USA.

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Our Congratulations!*

Mass spectrometry has reached a broad diffusion as a diagnostic tool in many branches of life sciences and analytical chemistry. In the field of elemental analysis, inductively coupled plasma mass spectrometry (ICPMS) has become the standard technique for performing quantitation of elements at the ultratrace level. In a typical analysis, the ICPMS response of standard solutions is first acquired and plotted against concentration. Then, the calibration curve is obtained by linear fitting and is used to calculate analyte concentration in the samples. In mass spectrometric analysis, one must bear in mind that the detector responds to the isotopes of an element and not to the element itself. For example, in the case of lead, the analyst can choose to acquire m/z of 204 (^{204}Pb), 206 (^{206}Pb), 207 (^{207}Pb), or 208 (^{208}Pb). Usually, quantitation is obtained on m/z 208, which corresponds to the most abundant isotope in the mass spectrum of lead (Fig. 1).

In the *Lead quantitation challenge* [2], we consider a situation where quantitation of lead is performed by two laboratories on a water sample. In both cases, signals corresponding to ^{206}Pb , ^{207}Pb , and ^{208}Pb were calculated and used for quantitation. Surprisingly, large discrepancies were obtained between and within laboratory

when quantitation was performed on the basis of different isotopes.

For the interpretation of this result, we must consider that the abundance of lead isotopes can vary in nature by more than 20%. For a quantitation model that does not take this effect into account, large biases are therefore expected. In this case, a single isotope is not sufficient to represent the element and a comparison between sample and standard cannot be made relying uniquely on a single isotope without information on its abundance in the material.

In this challenge, the data provided [2] were simulated starting from the isotopic compositions listed in Table 1. For the water sample, the lead isotopic composition was consistent with the average values reported by Millot and Négrel in French groundwater [3]. The two laboratories used primary standard solutions modeled after the isotopic composition of two international standards: the ERM-EB400 [4] and the HIPB-1 CRM [5]. As shown in Table 1, the lead isotopic composition for these materials is quite different and such discrepancies must be considered for data analysis.

Laboratory 1 normalized results:

$$\begin{aligned}^{206}\text{Pb}: w(\text{Pb})_{\text{A}} &= 4.7 \cdot 0.249/0.237 = 4.9 \mu\text{g/l} \\^{207}\text{Pb}: w(\text{Pb})_{\text{A}} &= 5.1 \cdot 0.214/0.223 = 4.9 \mu\text{g/l} \\^{208}\text{Pb}: w(\text{Pb})_{\text{A}} &= 4.9 \cdot 0.524/0.525 = 4.9 \mu\text{g/l}\end{aligned}\quad (1)$$

Laboratory 2 normalized results:

$$\begin{aligned}^{206}\text{Pb}: w(\text{Pb})_{\text{A}} &= 4.3 \cdot 0.271/0.237 = 4.9 \mu\text{g/l} \\^{207}\text{Pb}: w(\text{Pb})_{\text{A}} &= 5.4 \cdot 0.204/0.223 = 4.9 \mu\text{g/l} \\^{208}\text{Pb}: w(\text{Pb})_{\text{A}} &= 5.0 \cdot 0.513/0.525 = 4.9 \mu\text{g/l}\end{aligned}\quad (2)$$

When the results are normalized by taking into account the isotopic composition of lead, the biases disappear and a general agreement within and between laboratory is observed.

In mass spectrometry analysis, this correction is mostly overlooked because, for the majority of elements, the differences between isotopic composition of samples and standards are too small to be noticed. However, for metrological

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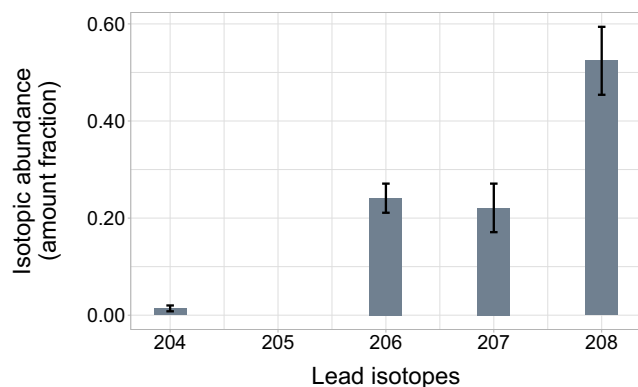


Fig. 1 Isotopic composition of lead: amount fraction of its isotopes and their natural variations in common lead [1]

Table 1 Isotopic abundance (amount fraction) of lead in the sample and in the primary standards employed to model the data for the *Lead quantitation challenge* [2]

Isotope	Sample ^a	Lab. 1 ^b	Lab. 2 ^c
²⁰⁴ Pb	0.014	0.014	0.013
²⁰⁶ Pb	0.237	0.249	0.271
²⁰⁷ Pb	0.223	0.214	0.204
²⁰⁸ Pb	0.525	0.524	0.513

^a Similar to a groundwater sampled in France [3]

^b Primary standard Lab. 1: from dilution of ERM-EB400 [4]

^c Primary standard Lab. 2: from dilution of HIPB-1 CRM [5]

applications, this assumption should be verified in each case.

The exercise proposed for this challenge constitutes a simple scenario where the samples are compared to the primary standards with a linear external calibration curve. Further investigations are needed to evaluate the effects of variable isotopic composition when more complex

quantitation models, such as standard addition [6] or isotope dilution [7], are employed.

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