

BIPM Capacity Building & Knowledge Transfer Programme
2021 BIPM - TÜBİTAK UME Project Placement
REPORT

Project Name	Measurement of Isotopic Abundance Ratios of Lead Using ICP-MS.
Description	The project focused on the knowledge transfer on the use of inductively coupled plasma mass spectrometry (ICP-MS) for the measurement of lead isotopic abundance ratios, to determine its isotopic composition, its atomic weight and to quantify it at trace levels using isotope dilution calibration strategies.
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Motivation & Introduction

Lead is a highly toxic element with the potential to affect the central nervous system of humans, causing severe cognitive disorders. The adverse effects of lead exposure are present even when the concentration of lead is low and the consequences are, by far, more dramatic if exposure occurs during childhood [1]. Poisoning for lead is a public health concern, thus lead accurate monitoring in aquatic systems is of uttermost importance. Routine analysis of lead in water matrices relies on calibrating certified reference materials (CRMs) to provide metrological traceability to the measurement results and matrix CRMs to assess the performance of the analytical methods, respectively [2].

For the Instituto Nacional de Metrología de Colombia (INM), as a CRM producer, it is important to build capabilities in the measurement of isotopic abundance ratios of lead for at least two reasons:

1. Calibrating CRMs of lead can be characterized by complexometric titration. Titration has the potential of being a primary method and has shown excellent metrological performance in the related CCQM key comparisons. In this strategy, the standard atomic weight of lead contributes significantly to the uncertainty of the final result. Measuring the lead isotopic composition that applies to the CRM is necessary to calculate a narrower confidence interval for its atomic weight and reduce this uncertainty source [3].
2. Matrix CRM containing lead at low levels can be characterized by isotope dilution mass spectrometry (IDMS). IDMS offers several advantages and can outperform other calibration approaches such as external standard and standard addition for trace-level analysis [4].

The knowledge transfer from a more experienced partner, ideally a leading national metrology institute such as TÜBİTAK UME, is a booster, if not a requirement, to build the measurement capabilities mentioned above. Hence, knowledge transfer was the main objective of the project placement. TÜBİTAK UME has upstanding measurement capabilities of lead isotopic abundance ratios [5] and has successfully applied isotope dilution quantification strategies for the value assignment of properties in matrix CRMs [6].

The most relevant topics to the knowledge transfer on isotopic abundance ratios measurement were sample preparation, corrections of blank signal and contamination control, routines of instrumental performance check and acceptance criteria for the check results, use of CRM of isotope abundance ratios for the correction of mass discrimination effects, data treatment for the generation of results, calculations of measurement uncertainties, use of isotopically enriched materials for IDMS and the design of IDMS experiments. Additional topics that made part of the knowledge transfer were purity determination of pure metallic elements using the impurity assessment approach, strategies of metrological weighing for the value assignment of elemental mass fraction in calibrating CRM solutions by gravimetric preparation, and measurements of relative differences in carbon isotopic composition (δ values), in hazelnut oil and honey samples, by isotope ratio mass spectrometry (IRMS).

Research

Isotope abundance ratio measurements were made using a high-resolution ICP-MS (HR-ICP-MS) (Element 2, Thermo Scientific) and a triple quadrupole ICP-MS (QQQ-ICP-MS) (8900, Agilent Technologies). The sample preparation for isotope ratio measurements consisted of proper gravimetric dilution of all solutions to a final mass fraction of lead of ca. 2 mg kg^{-1} , according to the instruments analytical sensitivity determined before the analysis. Data treatment was made using spreadsheets designed by TÜBİTAK UME Inorganic Chemistry Laboratory. Uncertainty calculations were made

using the software *GUM Workbench*[®] v.2.4 [7]. Alternatively, for comparative purposes, the data treatment was also performed using *R* scripts [8] with the library *metRology* [9] for uncertainty calculations.

Isotopic composition of samples

The lead relative isotopic abundances and the lead atomic masses that apply to the samples NIST SRM 3128b [10], UME CRM 1201 [11] and UME EnvCRM 02 [12] are shown in Table 1. Isotopic fractionation (mass discrimination) effects were corrected using a bracketing approach with the lead isotopic CRM NIST SRM 981 [13], applying a linear model.

Sample	ICP-MS	²⁰⁴ Pb		²⁰⁶ Pb		²⁰⁷ Pb		²⁰⁸ Pb		M_{Pb} (g mol ⁻¹) $U_{k=2}$
		Mean	<i>RSD</i> · %	Mean	<i>RSD</i> · %	Mean	<i>RSD</i> · %	Mean	<i>RSD</i> · %	
NIST SRM 3128b	QQQ~	0.01434	0.43	0.2475	0.11	0.2190	0.03	0.5192	0.05	207.2046 ± 0.0018
	HR~	0.01373	0.12	0.2492	0.03	0.2137	0.02	0.5234	0.02	207.2090 ± 0.0009
UME CRM 1201	QQQ~	0.01418	0.23	0.2534	0.06	0.2166	0.05	0.5154	0.03	207.1948 ± 0.0016
	HR~	0.01351	0.22	0.2554	0.04	0.2125	0.03	0.5196	0.03	207.1996 ± 0.0010
UME EnvCRM 02	QQQ~	0.01438	0.43	0.2469	0.13	0.2192	0.22	0.5196	0.08	207.2055 ± 0.0020
	HR~	0.01368	0.09	0.2480	0.17	0.2143	0.15	0.5241	0.07	207.2110 ± 0.0016

Table 1: Isotopic composition and atomic masses of lead in samples by QQQ-ICP-MS and HR-ICP-MS. Uncertainties in atomic weights are expanded with a coverage factor $k = 2$. The data colored in blue was obtained by Betül Ari in the past.

The atomic weights of lead in the samples are close to the standard atomic weight for this element [14]. The confidence interval around the calculated values is up to two orders of magnitude smaller than the corresponding to its standard atomic weight [14].

Lead quantification at trace levels by different IDMS calibration strategies

The lead mass fraction in UME CRM 1201 and UME EnvCRM 02 was measured using double IDMS (ID2MS), Triple IDMS (ID3MS), and IDMS based on a graphical approach using a linear model. Employing different calibration strategies for IDMS allowed comparing their performance in terms of the expanded uncertainty of their results. The spike solution was a stock solution prepared in the past from an enriched ²⁰⁶Pb CRM (NIST SRM 991 [15]). The Figure 1 summarizes the results obtained for both CRMs.

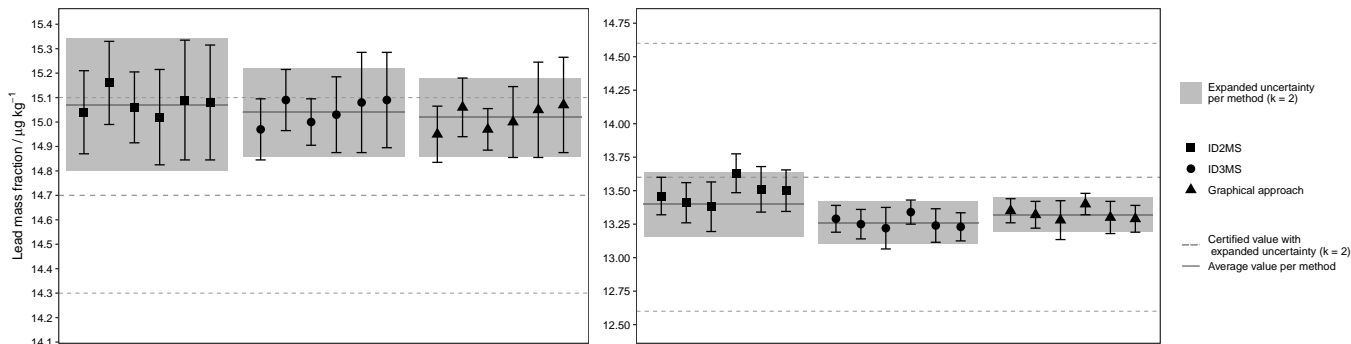


Figure 1: Mass fraction of lead measured in UME CRM 1201 (left) and UME EnvCRM 02 (right) using IDMS.

The results of the three different calibration strategies are metrologically compatible among them and with the certified values of the respective CRM [11, 12]. The ID3MS strategy provides results with lower uncertainty than ID2MS, as previously demonstrated at the TUBITAK UME Inorganic Chemistry Group [16]. Furthermore, the graphical approach results present slightly smaller uncertainties than those obtained by the ID3MS calibration strategy.

Standard-free measurement of isotopic abundances ratios

A new approach, termed triple-isotope calibration, for obtaining absolute isotope ratios of multi-isotopic elements without using any standard has been reported recently by Vogl [17]. The name of the approach comes from the use of three-isotope diagrams that represent the ratio of two different pairs of isotopes with a common denominator (in logarithmic scale), obtained under variable ionization conditions in the ion source of a mass spectrometer. Combining the three-isotope diagrams produced by two different mass spectrometers yields the real (logarithmized) isotopic abundance ratios of interest [17].

The apparent isotopic abundance ratios ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb of the NIST SRM 981 were measured using both the HR-ICP-MS and QQQ-ICP-MS instruments to correct the isotopic abundance ratios of other samples, as described above. The instruments' natural drift provides a small variability in the ionization conditions at the ion source. This small variability could be enough to fulfill the requirements of the triple-isotope calibration approach. The three-isotope diagrams for the ratios ²⁰⁷Pb/²⁰⁶Pb and ²⁰⁸Pb/²⁰⁶Pb constructed from the data of NIST SRM 981 are shown in Figure 2.

The results are 0.9089 and 2.1761 for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$, respectively. The uncertainty of the results is required for assessing if the measurement results are metrologically compatible with the certified values of 0.91464 ± 0.00033 and 2.1681 ± 0.0008 ($k = 2$).

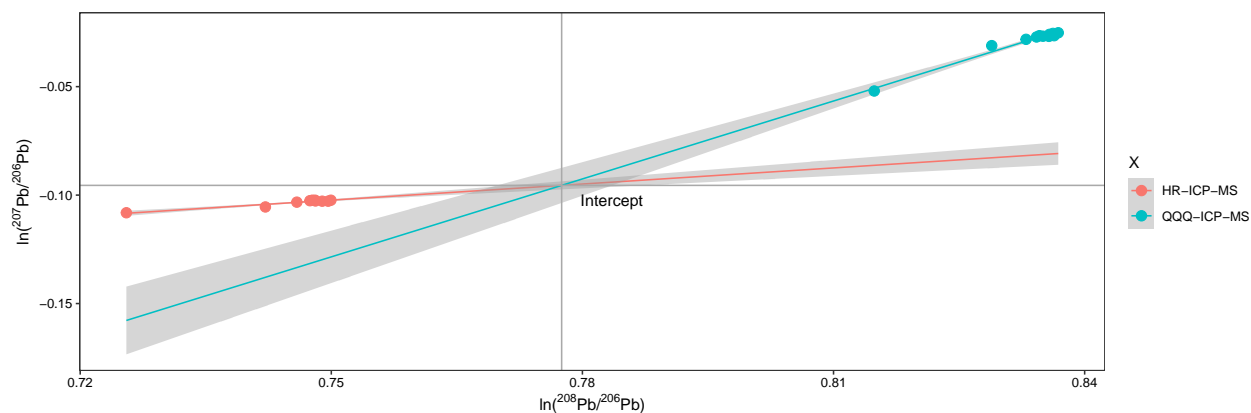


Figure 2: Three-isotope diagram for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ in NIST SRM 981. Calculated values from the intercept of the lines are 0.9089 and 2.1761 for $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$, respectively. The gray shadows represent the confidence interval of the regression models.

Conclusions and Future Work

The lead isotopic composition was measured for several CRMs applying a linear model for the correction of mass discrimination effects. It was possible to establish a small confidence interval for the atomic weight of lead that applies to the materials tested.

Three IDMS calibration strategies were used to successfully quantify the mass fraction of lead, present at trace levels, in two matrix CRMs. The results are metrologically compatible with reference values. The strategy chosen affects the final combined uncertainty of the result. The graphical approach results gave the lower uncertainties from the strategies studied, while requiring the same or fewer measurements than the ID3MS approach.

Regarding the triple-isotope calibration approach for determining isotopic abundance ratios without reference to an standard, it is necessary to assess the uncertainty of our results, to establish if they are metrologically compatible with the reference values. The results for the ratios $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ show a bias of -0.62 % and 0.36 %, respectively, which are comparable to the bias reported for the results in the original study.

Hopefully, the value assignment of lead mass fraction in matrix and calibrating CRM at the INM will benefit from the knowledge obtained during the Project Placement.

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