

Research Article

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Trace-level impurity quantification in lead-cooled fast reactors using ICP-MS: Methodology and challenges

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Abstract: Lead-cooled fast reactors (LFR), such as the ALFRED Demonstrator, are pivotal in advancing nuclear technology. This study presents a method for quantifying trace-level impurities generated through various nuclear reactions in lead coolant. It combines inductively coupled plasma mass spectrometry with Sr-resin-based matrix separation to analyze trace impurities in lead matrices. The Sr-resin effectively removes lead, a highly interfering matrix, enhancing the precision and reliability of detecting trace elements. The study evaluates the effectiveness of lead matrix removal and assesses the method's reliability for monitoring trace impurities in LFR systems. The results indicate the method's suitability for tracking small changes in lead composition during the operation of lead-cooled facilities.

Keywords: ALFRED, LFR, trace-level analysis, activation and fission products, ICP-MS

1 Introduction

Lead-cooled fast reactors (LFRs) are at the forefront of Gen IV nuclear technology, representing a promising route for advancing the field [1]. Thanks to the intrinsic features

of using lead as a coolant, LFRs can claim unparalleled safety performances [2]. The ALFRED (Advanced Lead Fast Reactor European Demonstrator) project aims to build a 125MWe nuclear reactor demonstrator as a critical milestone toward the commercial deployment of LFR technology [3]. The project addresses the current gaps in infrastructure across Europe that are necessary to support the design of an LFR [4]. In this way, the expanded ALFRED Research Infrastructure (ALFRED-RI) will cover all aspects of technology advancement through a systemic and integrated approach involving universities, research institutions, industry, utilities, and safety authorities [5].

One aspect of LFR technology that requires further investigation is the production of hazardous radioactive elements generated by nuclear fission or neutron activation of the coolant and their volatilization from the liquid metal. These processes are essential role in evaluating the radioactivity released under both normal and accidental conditions [6].

The main phenomena that determine or influence the transport of impurities in the reactor vessel, such as lead activation products (APs) or fission products (FPs) (in the event of fuel cladding failure), include phase transformation, deposition, adsorption/desorption, dissolution/precipitation, and vaporization/condensation leading to the formation of new species in both liquid lead and cover gas [7].

The non-volatile APs or FPs will be retained in lead, while the volatile ones with no or low affinity for lead and a half-life longer than the time needed to cross the lead pool will migrate to the cover gas. The fission and APs that are volatile or show non-negligible volatility in an LFR system are tritium, noble gases (Xe, Kr), some APs (Po, Hg, Cd), and some FPs such as Cd, Cs, I, and Te.

The volatile products are either transported to the cover gas or deposited on the structural materials. While there are studies on their behavior [8], there is still insufficient data on their retention in lead or the chemical species they form with dissolved oxygen or among each other.

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An experimental effort is planned for supporting the safety analysis of ALFRED, and a suitable infrastructure to support the R&D efforts, also addressing the challenges related to severe accidents in an LFR system, a dedicated infrastructure will be established in Romania, at the RATEN-ICN platform site. The experimental facility, named Meltin'Pot, is designed to investigate the behavior of impurities in liquid lead and study phenomena associated with severe accidents. It will include four experimental modules, each focused on a specific area of study: fuel-coolant interaction; fuel dispersion and relocation after a severe accident scenario; FPs retention in lead and/or migration in cover gas; investigation on retention in lead of polonium isotopes; and gas/steam – FPs/Po stripping from lead to cover gas [9].

For studying the retention in lead of different impurities, a precise methodology for quantifying trace-level impurities in both lead and the cover gas is essential. This study presents a methodology for measuring trace-level impurities in lead based on a matrix separation procedure followed by inductively coupled plasma mass spectrometry (ICP-MS) analysis.

2 Radionuclide inventory in ALFRED

To gain a comprehensive understanding, it is essential to have a clear picture of all the impurities formed under specific operating conditions, whether normal or abnormal, in a lead-cooled reactor.

To identify volatile hazardous radionuclides transported in the cover gas above the lead coolant-free level of the ALFRED, and to estimate their quantities during normal operation, the inventory of the ALFRED reactor at the End-of-Cycle (EOC) and End-of-Life (EOL) was considered. This evaluation, conducted for all 171 fuel subassemblies [10] and the entire lead coolant [11] after 5 years (EOC) and 40 years of irradiation (EOL), was performed using the Monte Carlo radiation transport computer code (MCNPX 2.7.0) and FISPACT activation code in the framework of EU FP7 – LEADER project [12].

The ALFRED reactor radionuclide inventory is derived from the following dataset:

- The total amount of lead coolant is 3,400 tons, equivalent to 1.64×10^7 mol of lead;
- FP inventory at EOC, representing the maximum residence time of the fuel in the reactor, was averaged over 171 subassemblies;
- The lead AP inventory was calculated for both 5 years (corresponding to EOC) and 40 years (corresponding to EOL) of irradiation;
- The inventory includes the isotopes with a half-life greater than 6.5 h.

Figure 1 illustrates the inventory of the APs formed in lead through neutron activation after 5 and 40 years of irradiation, respectively. The elements denoted in the figure in black represent the intrinsic impurities of lead, while the red ones are generated through lead activation. The lead coolant activation analysis was performed for

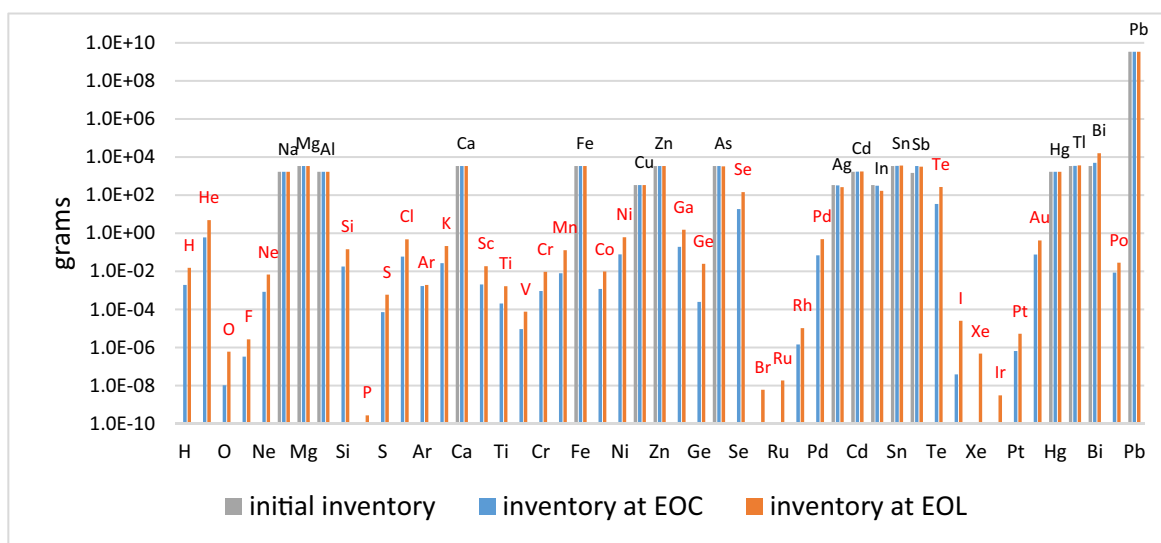


Figure 1: The amount of impurities from lead activation: grey columns – Pb initial composition; blue columns – APs formed in lead after 5 years of irradiation; orange columns – APs formed in lead after 40 years of irradiation.

weight compositions similar to the C00 lead brand (purity level of 99.9985%) [11].

Figure 2 presents the inventory of the FPs at EOC averaged over 171 subassemblies. The inventory of lead impurities may increase only in the case of fuel cladding failure. Even in this case, most of the elements released from the fuel element will be retained by lead, and only a few will end up in the cover gas of the reactor [6]. These are elements that are volatile or exhibit non-negligible volatility in normal operating conditions of a lead-cooled reactor.

The critical impurities, either the APs or FPs, are those exhibiting significant volatility or non-negligible volatility under normal operating conditions of the ALFRED reactor and are mainly represented by tritium, noble gases (Xe, Kr), lead APs (Po, Hg, Cd, Te), and FPs (Cs, I, Cd, Te). To study the behavior of these impurities both in gaseous and liquid phases, a dedicated infrastructure is foreseen to be developed at RATEN-ICN Pitesti [13].

The methodology selected for the quantification of impurities, whether volatilized or retained in lead, relies on mass spectrometry. Thus, the volatilized fraction in the cover gas above the molten lead will be measured using a Quadrupole Mass Spectrometer. Additionally, the fraction retained in the liquid lead will be assessed using an ICP-MS.

Measuring the impurities retained in lead represents a methodological challenge due to the trace levels of impurities formed by activation, ranging from parts per trillion (ppt) to parts per billion (ppb). The amount of impurities can increase in case of a fuel cladding failure that leads to the spread of FPs into the molten lead.

Table 1 outlines the maximum concentration of APs that can be found in the ALFRED reactor at EOC and

EOL, respectively, without any fuel failure. Also, this estimation takes into account two accident scenarios by considering an increase in concentration resulting from the release of FPs due to either a single subassembly failure (0.6% FPs release) or the worst-case scenario of seven subassemblies failing (5% FPs release).

Accurate quantification of trace impurities that may be released from the molten lead contributes to better control of the coolant's chemical composition, essential in maintaining safety in operation and preventing accidental releases into the environment. Additionally, these insights support the reactor design and licensing by providing valuable data on impurity behavior, ensuring compliance with safety standards, and facilitating the development of LFR technology.

This study is focused on two elements, cadmium and tellurium, both generated through lead activation and fission. Cadmium, in particular, holds significance due to its high volatility in normal operating conditions. This high volatility is due to the weak interaction of cadmium with lead, which prevents its retention in the molten metal matrix [7]. It has a melting point of 321°C and a boiling point of 767°C, being completely miscible with lead at temperatures higher than 327°C, but no intermetallic compounds with lead are known indicating no retention of Cd in liquid lead. Although there are studies of pure Cd vapor pressure, investigations of the Cd-Pb system have shown deviations from ideal behavior [8]. As a consequence, a comprehensive study of Cd behavior in molten lead is needed all the more as it is considered as one of the most volatile elements after Mercury.

Tellurium emerges as a noteworthy impurity with a substantial impact on the radioactivity release. It is

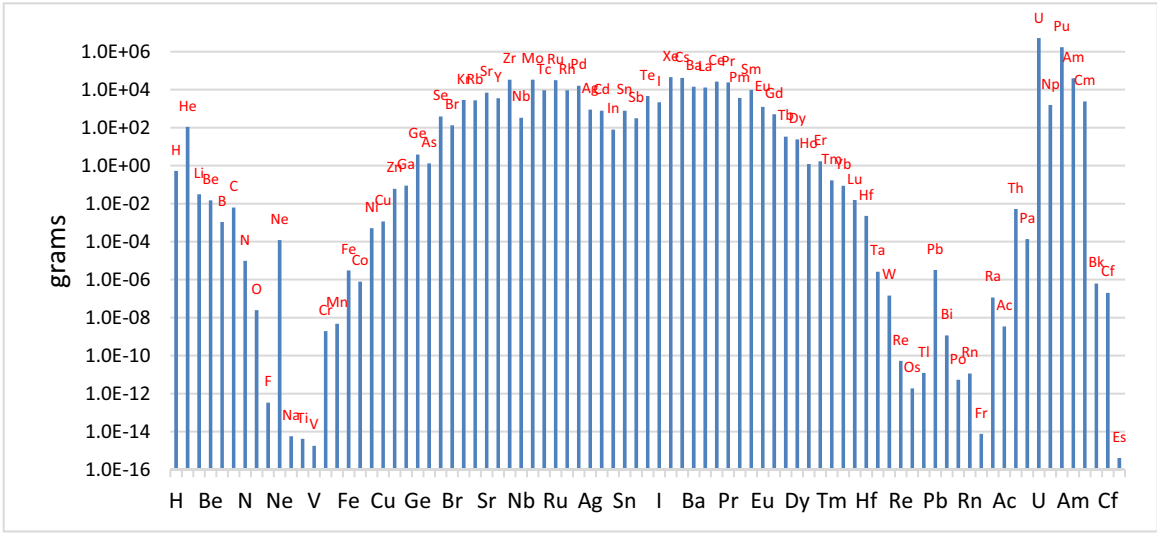


Figure 2: The total amount of FPs at EOC.

Table 1: Maximum impurities concentration within lead in different scenarios for ALFRED

Volatile impurities	APs concentration (ppb)		APs + FP concentration at EOC (ppb)	
	EOC	EOL	1 subassembly	7 subassemblies
Polonium	2.53×10^{-3}	8.33×10^{-3}	—	—
Mercury	5.00×10^{02}	5.00×10^{02}	—	—
Cadmium	5.03×10^{02}	5.21×10^{02}	5.05×10^{02}	5.13×10^{02}
Tellurium	1.01×10^{01}	7.93×10^{01}	1.01×10^{01}	1.05×10^{01}
Iodine	1.13×10^{-8}	7.42×10^{-6}	3.71×10^{00}	2.60×10^{01}
Cesium	—	—	7.11×10^{01}	4.98×10^{02}
Rubidium	—	—	4.75×10^{00}	3.33×10^{01}

produced both by lead neutron activation and fission processes. Notably volatile, Te primarily evaporates as a compound with lead [14]. However, recent investigations at the European level suggest the intriguing possibility that Te could also evaporate as a diatomic molecule [15]. This dual behavior emphasizes the complexity of Te's interactions in the lead cooled reactor environment.

Of particular interest is the tellurium's homology with the radiotoxic polonium, a by-product formed through lead activation in a lead-cooled reactor [16]. Understanding the behavior of Te in lead becomes essential, not only due to its volatility but also for the insights it provides into the chemistry of Po, which is a radiotoxic element with potential impact on reactor safety and the environment. This knowledge becomes essential for our understanding of the complex processes occurring within a lead-cooled reactor.

To gain a comprehensive understanding of the behavior of impurities in molten lead, it is compulsory to make use of a reliable method for the quantification of trace-level impurities. In this regard, the ICP-MS method was considered in this study due to its versatility as one of the most robust trace elemental analysis techniques available today.

2.1 Trace-level analysis methodology

In trace elemental analysis, X-ray fluorescence (XRF), atomic absorption spectrometry (AAS), and ICP-MS are commonly used techniques. XRF is fast and non-destructive but lacks the sensitivity needed for ultra-trace detection, especially in heavy matrices like lead [17–19]. AAS offers comparable sensitivity to ICP-MS but is limited to single-element analysis [20]. ICP-MS, with its ppt-level sensitivity and multi-element capability, is the most suitable for complex matrices [21]. This study applies a methodology that combines ICP-MS with Sr-resin-based matrix separation to analyze trace impurities in lead matrices. The Sr-resin effectively removes lead – a highly interfering

matrix – thereby improving the precision and reliability of detecting trace elements such as cadmium (Cd) and tellurium (Te) [22].

The application of ICP-MS combined with matrix separation on crown ether resin has been demonstrated in experiments using lead-bismuth eutectic (LBE), as reported by Tindemans *et al.* [23]. An offline analyte/matrix separation process was used to diminish matrix effects, using AG 1-X4 anion-exchange resin (100–200 mesh) and extraction chromatographic Pb-Spec resin (100–150 mm). This underscores the versatility of this methodology for similar matrices. The Pb-resin's high selectivity for lead ensures accurate impurity quantification, even in complex systems where matrix effects are prevalent [24].

While ICP-MS stands out as a powerful analytical technique, it is important to acknowledge the intricate processes that unfold throughout sample introduction, transport to the ICP, within the ICP itself, and during the extraction of ions from the ICP [25]. Furthermore, the subsequent transport of ions through the ion optics to the detector can give rise to both spectroscopic and non-spectroscopic interferences. Spectroscopic interferences occur when another ion is detected at the same mass-to-charge ratio (m/z) as the analyte. On the other hand, non-spectroscopic interferences, often termed matrix effects, encompass variations in analyte signal intensity, involving either suppression or enhancement. These variations are in contrast to the expected signal derived from the same analyte concentration in a matrix-free solution [26].

The influence of the lead matrix on the analyte is substantial, with observed variations of up to 40% suppression in the determined intensity for different constituents [27] in samples with 80% lead matrix content. Given the elevated lead concentration in our samples ($\geq 99.999\%$ Pb), a meticulous approach is imperative to accurately determine trace-level impurities retained by lead. Therefore, the mitigation or elimination of matrix effects becomes a critical prerequisite.

To reduce or eliminate the matrix effect, various techniques have been evaluated, such as diluting the sample, precipitating the lead matrix and solid-phase extraction. Even though dilution will reduce the matrix effect it will also diminish the concentration of the analytes already present at trace level. On the other hand, precipitating the lead matrix carries the risk of co-precipitating analytes, thereby introducing complexities in the separation process.

This study focuses on the solid-phase extraction method, an effective technique for removing the interfering lead matrix while preserving the analyte concentrations. The methodology uses Sr-spec, a crown ether resin derived from the same crown ether as Pb-spec, specifically 4,4'(5')-di-*t*-butylcyclohexano 18-crown-6, dispersed in *n*-octanol and immobilized on an inert polymeric support. In contrast to the Pb-spec resin, Sr-spec contains a higher concentration of the crown ether facilitating stronger lead retention, with a capacity of 29 mg Pb·g⁻¹ dry resin. The maximum lead affinity is observed at 1M nitric acid concentration [22].

The Sr-Spec resin-based solid-phase extraction method was applied to remove the lead matrix from samples similar to those from a lead-cooled facility. Following the removal of the lead matrix, the concentrations of Cd and Te were subsequently determined using ICP-MS and the quantitative recovery from separation was assessed.

3 Materials and methods

3.1 Reagents and instrumentation

Quantitative measurements were conducted using the ICP-MS ELAN DRC II (Perkin Elmer SCIEX). The instrument settings and the data acquisition parameters are summarized in Table 2. Before usage, the instrument was optimized using a standard solution (Elan Smart Tune) containing 10 µg·L⁻¹ of the following elements: Ba, Be, Ce, Co, In, Mg, Pb, Rh, and U in 1% HNO₃. The instrument was tuned before starting the measurements for the count rates of ²³Mg, ¹¹⁴In, and ²³⁸U to the values of $\geq 5 \times 10^5$, 2.5×10^5 , and 2×10^5 counts/ppb, respectively.

The quantitative analysis of Cd and Te was achieved through an external calibration method. This method assesses the analyte concentration via a calibration curve established by the analysis of separately measured standards in the range of expected concentration [21]. The intensities of the calibration standards were plotted vs their concentrations, and a linear regression line was calculated. Applying the corresponding linear equation of the form $y = ax + b$,

Table 2: ELAN DRC II Instrument settings for quantitative analysis

Setting/parameter	Value/description
Nebulizes gas flow	0.99 L·min ⁻¹
Auxiliary gas flow	1.2
Plasma gas flow	15
ICP RF power	1,400 W
Detector mode	Dual
Runs	3
Number of replicates	3
Signal profile processing mode	Average
Dead time	45 ns
Total analysis time per run	~9 s
Nuclides monitored	¹¹¹ Cd, ¹³⁰ Te

where a is the calibration slope and b is the y -axis intercept, the analyte concentration in the sample (x) can be calculated from the analyte intensity (y). The calibration curves were plotted linearly through zero. Data from the ICP-MS was collected and visualized using the ELAN 3.4 Instrument Control Software and Microsoft Excel 2016.

The samples and standards were prepared by mass concentration. In this process, reagents and solutions were weighed with high precision using the analytical scale, Mettler Toledo Model XP504, with 0.1 mg readability.

The reagents used in the analytical preparation of both samples and standard solutions were of analytical grade or certified reference material. For lead sample preparation, a Pb powder with a purity exceeding 99% from Thermo Scientific (Cat. No. 198110010, Lot A0451253) was used and further dissolved in a solution of 2M nitric acid prepared from HNO₃ 67–68 wt% (EcoMold Invest Lot NL20415802). Standard calibration solutions were prepared using ICP multi-element standard solution VI 30 components in 5% HNO₃ from CPAchem (ref. 110580.L1) [28]. This standard solution holds certified values for Te and Cd of 9.934 ± 0.051 mg·L⁻¹ and 9.999 ± 0.030 mg·L⁻¹, respectively. Throughout the matrix-removal procedure, all samples, solutions, and dilutions were prepared with ultra-pure water (UP) from Milli-Q SimPak[®] 2 that had a resistivity of ≥ 18.2 MΩ.

For the retention of lead, 2 mL prefilled columns containing Sr-resin (SR-C20-A Lot FSRA230821) with a particle size of 100–150 µm and a density of 0.33 g·mL⁻¹ were procured from Triskem International.

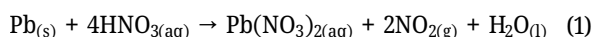
3.2 Experimental method

The objective of this study was to assess the effectiveness of lead matrix removal for trace-level elements present in

samples extracted from lead-cooled facilities. The study aimed to determine the recovery percentage of these elements after their separation from the matrix.

The lead sample, designed to contain a known lead concentration alongside trace-level impurities, aimed to be representative of an actual sample extracted from the experimental facility or the lead-cooled reactor. The composition of the real sample involves 50 mg of lead, dissolved in 25 mL of nitric acid, resulting in a final sample with a lead concentration of 20 mg·mL⁻¹.

In the dissolution of lead samples, it is important to consider that the solubility of Pb in nitric acid is approximately 0.2 g·mL⁻¹ at a concentration of 2 M, reaching a maximum (~0.23 g·mL⁻¹) at 2.5 M [29]. Nitric acid is a strong oxidizing agent, reducing metallic lead to Pb(II) according to reaction (1). At a concentration higher than 2.5 M of HNO₃, Pb(II) changes to Pb(IV), leading to the formation of a PbO₂ layer on the metallic surface, which is very difficult to dissolve.



The Pb samples, approximately 1 g each, were dissolved in quartz vessels in 20 mL of 2M nitric acid on a hot plate set to 80°C and were left overnight to cool. The resulting solution was clear, with no visible impurities. The solution was further diluted with UP water up to a final volume of 50 mL, resulting in a final concentration of approximately 20 mg·mL⁻¹.

The lead stock solution was subsequently spiked with a known quantity of elements that are under investigation, yielding concentrations ranging from 5 to 125 ppb using the ICP-MS standard solution. The amount of trace-level impurities is significant in the context of the element estimation conducted for the ALFRED reactor, as detailed in Table 1.

A volume of 1 mL from the prepared stock solution, spiked with trace-level impurities, was passed through a 2 mL column filled with Sr-resin that had been preconditioned with 10 mL of 0.2 M nitric acid. The crown ether selectively binds Pb(II) ions, preventing their passage through the column. The column was rinsed with 20 mL of 1M HNO₃. The elution process occurred gravitationally, with a solution flow rate of approximately 0.3 mL·min⁻¹. Eluate 1 (E1) was collected, and the elements separated from the lead matrix were measured using ICP-MS. The column was washed again, this time with 20 mL of 0.2 M HNO₃, and eluate 2 (E2) was collected and measured accordingly. The schematic representation of the lead matrix separation procedure is presented in Figure 3.

In selecting this method, a key consideration was its environmental impact and alignment with the principles of green analytical chemistry [30,31]. This includes

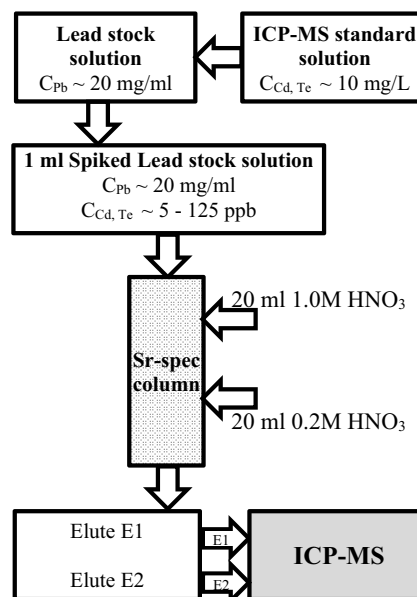


Figure 3: Schematic representation of the lead matrix separation procedure.

reducing the use of hazardous materials, minimizing waste, and ensuring robust, transparent analytical processes [32]. In the context of impurity quantification in LFRs, these factors are particularly relevant due to the environmental risks posed by lead and the hazardous radioactive elements generated during operation. The proposed method for trace-level impurity analysis in lead-cooled reactors supports sustainability by promoting cleaner nuclear energy through safer reactor designs and better impurity control, ultimately contributing to a low-carbon future. Additionally, the use of ICP-MS – an ultra-sensitive analytical technique – further enhances the method's green profile by conserving resources and reducing the need for repeated experiments.

The procedure described aligns with the integrated management system requirements at RATEN-ICN, complying with quality standards (SR EN ISO 9001:2015 [33]), environmental standards (SR EN ISO 14001:2015 [34]), occupational health and safety standards (SR ISO 45001:2018 [35]), and relevant legal and regulatory requirements.

4 Results and discussion

Several lead samples, each spiked with various amounts of Cd and Te, were meticulously prepared, subjected to separation on Sr-resin and subsequently analyzed. This process aimed to evaluate the effectiveness of matrix removal for lead compositional analysis.

In the lead solution with a concentration of $\sim 20 \text{ mg}\cdot\text{mL}^{-1}$ Pb, the Cd and Te impurities were spiked using an ICP multi-standard solution. The resulting solutions contained trace-level impurities ranging from 5 to 120 ppb, a spectrum reflective of concentrations observed in different scenarios within the ALFRED reactor. The concentrations obtained in the solutions used in these experiments are presented in Table 3.

The Sr-resin column (2 mL prefilled) was first conditioned with 10 mL of 0.2 M nitric acid to activate the resin before sample loading. A 1 mL aliquot of the lead solution, spiked with Cd and Te, was then passed through the column, allowing lead to be retained while the impurities flowed through. To elute the spiked elements, the resin was first rinsed with 20 mL of 1 M HNO_3 , and the eluent was collected as E1. The separation was conducted under gravitational flow at an approximate rate of $0.3 \text{ mL}\cdot\text{min}^{-1}$. A subsequent wash with 20 mL of 0.2 M HNO_3 was performed, with the eluent collected as E2, maintaining the same flow rate of $0.3 \text{ mL}\cdot\text{min}^{-1}$ throughout the process.

The solutions E1 and E2 were subjected to analysis to determine the recovery of each spiked element that underwent separation from the lead matrix. The recovery of each spiked element was calculated as the percentage of the theoretical concentration expected in case of full separation of the impurity from the lead matrix, relative to the measured concentration, as follows:

$$\text{Recovery (\%)} = \frac{\text{measured concentration}}{\text{theoretical initial concentration}} \times 100 \quad (2)$$

To quantify the amounts of the elements of interest in the eluted solutions using ICP-MS, the external standardization method was employed. This methodology involves measuring a blank solution, followed by a series of standard solutions with known concentrations. These standards were used to construct a calibration curve within the desired concentration range.

Four distinct calibration curves were constructed using standard solutions of Cd and Te. These standards

were prepared from ICP-MS multi-element standard solution, dissolved in 1% (v/v) nitric acid. The certified value for Cd is $9.999 \pm 0.030 \text{ }\mu\text{g}\cdot\text{mL}^{-1}$, and for Te, it is $9.923 \pm 0.051 \text{ }\mu\text{g}\cdot\text{mL}^{-1}$. Using this solution, two calibration curves were developed for each investigated element: one spanning the concentration range from 1 to 7 ppb and another from 0.1 to 1 ppb.

The calibration curves for Cd and Te are visually depicted in Figure 4, showing good linearity (correlation coefficient >0.995) and the calibration equation for each curve. The Limit of Detection was calculated as the analyte concentration giving a signal equal to the blank signal, y_B , plus three standard deviations of the blank, s_B [36].

The calibration curves serve as a foundation for accurate quantification of Cd and Te in eluate solutions and samples containing the lead matrix. Each sample was analyzed three times to ensure reliable measurements.

Table 4 provides the measurements of Cd and Te concentrations in the eluate solutions from each experiment. For the first elution (E1 – 20 mL 1M HNO_3), the relative standard deviation (RSD) of the measured concentrations was below 2% for most cases, ensuring the precision of the measurements. In the second elution (E2 – 20 mL 0.2 HNO_3), Cd and Te concentrations were not measured or were very close to the detection limit, indicating efficient separation.

The recoveries of the target elements are expressed as percentages of their initial theoretical concentrations, as expected in E1 ($\sim 20 \text{ g}$ of solution), assuming complete separation from the lead matrix.

The results show strong enrichment of the investigated elements in E1 solutions, while no or very small concentrations were found in the second elution. This enrichment phenomenon raises questions about its source, and a plausible explanation could be traced back to the lead powder used in the sample preparation process. According to the Certificate of Analysis [37], the lead powder has a tested purity of 99.5% Pb, but there is no mention of the impurity contained in the powder.

To assess the Cd and Te content in the Pb powder and to adjust the recovery of each element measured in the eluted solutions, 1 mL aliquot of the lead stock solution ($\text{Pb-}18.68 \text{ mg}\cdot\text{mL}^{-1}$), without any spiked elements, was passed through a 2 mL Sr-spec column. The column was further eluted with 20 mL of 1M HNO_3 . The eluate was collected, weighed, and analyzed to determine the concentrations of Cd and Te impurities present in the powder. The measurements were repeated three times, yielding the following results: the concentration of Cd in the elute was $3.01 \pm 0.07 \text{ ppb}$ (RSD 2.2%), and the concentration for Te 0.54 ± 0.02 (RSD 3.1%). These values correspond

Table 3: Initial data of the samples prepared for the matrix separation procedure

Experiment	Pb concentration ($\text{mg}\cdot\text{g}^{-1}$)	Cd concentration (ppb)	Te concentration (ppb)
Exp. 1	18.68	78.88	78.28
Exp. 2	18.68	125.75	124.73
Exp. 3	18.68	4.24	4.21
Exp. 4	18.68	7.47	7.53

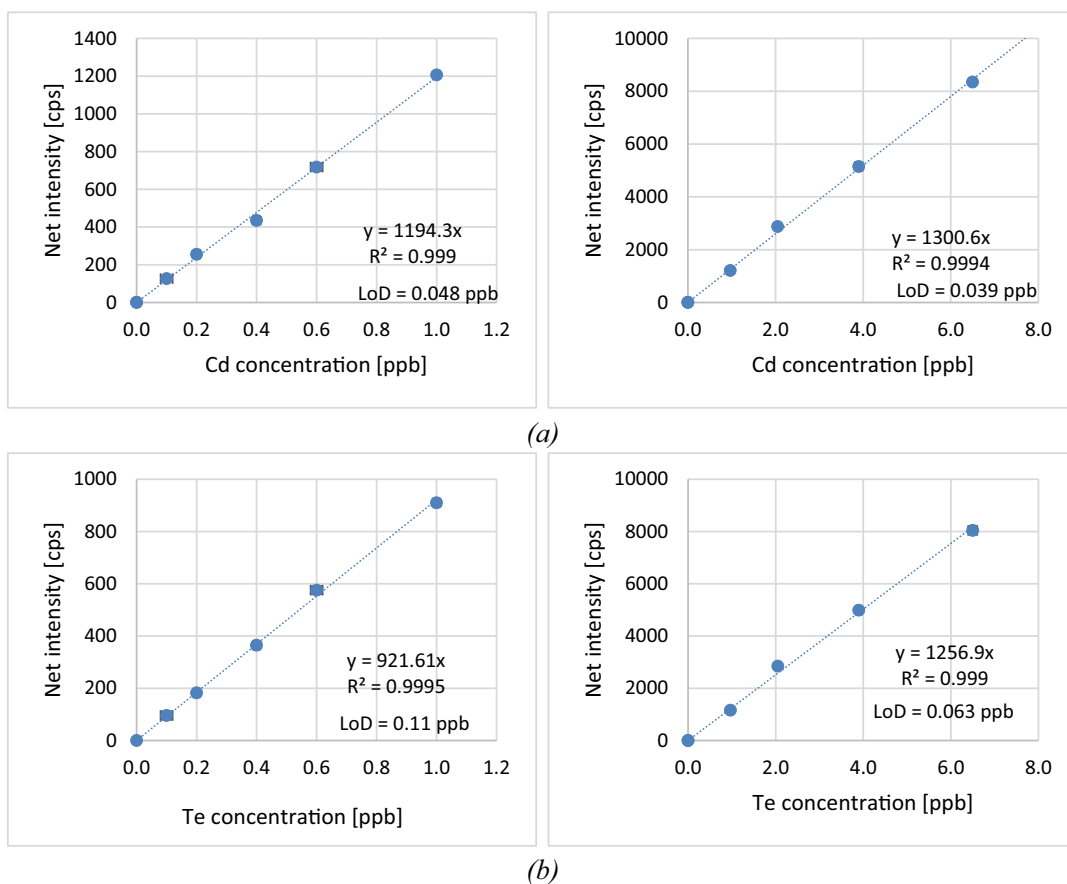


Figure 4: The calibration curves for quantitative analysis of Cd (a) and Te (b).

Table 4: Obtained recoveries by applying the separation procedure to lead samples $\sim 20 \text{ mg} \cdot \text{mL}^{-1}$ Pb and 5–125 ppb of target elements

Element	Experiment/elution	Initial concentration (ppb)	Measured concentration (ppb)	Concentration RSD (%)	Recovery (%)
Cd	Exp. 1/E1	3.50	6.39 ± 0.05	0.8	182.3
	Exp. 1/E2	—	0.05 ± 0.01	9.2	
	Exp. 2/E1	5.53	7.86 ± 0.05	0.6	142.2
	Exp. 2/E2	—	0.04 ± 0.00	6.8	
	Exp. 3/E1	0.20	3.67 ± 0.04	1.2	1,785.6
	Exp. 3/E2	—	BDL*		
	Exp. 4/E1	0.37	3.94 ± 0.04	1.0	1,075.5
	Exp. 4/E2	—	0.22 ± 0.04	16.2	
Te	Exp. 1/E1	3.48	3.62 ± 0.03	0.9	103.9
	Exp. 1/E2	—	BDL*		
	Exp. 2/E1	5.48	5.19 ± 0.05	0.2	94.7
	Exp. 2/E2	—	0.04 ± 0.00		
	Exp. 3/E1	0.20	0.93 ± 0.05	5.8	455.8
	Exp. 3/E2	—	BDL*		
	Exp. 4/E1	0.36	1.11 ± 0.03	2.7	304.9
	Exp. 4/E2	—	BDL*		

*BDL = below detection limit.

to the impurity content of $3.34\text{ }\mu\text{g}\cdot\text{g}^{-1}$ of Cd and $0.60\text{ }\mu\text{g}\cdot\text{g}^{-1}$ of Te in the lead powder.

The intrinsic impurity content of the lead powder is notably high, leading to challenges in measuring the very low concentrations separated from the lead matrix. A discrepancy of three orders of magnitude for Cd and Te highlights the difficulty of precisely measuring extremely small amounts in the presence of such significant inherent contaminants.

The recovery percentages of elements separated from the lead matrix were adjusted based on the measured impurity content in the lead powder. The impurity content that enriched the sample’s concentrations of Cd and Te was assessed for each experiment, considering the lead mass passed through the column, corresponding to the 1 mL aliquot (~19 mg Pb). The amount of Cd and Te originating from the lead powder (~0.066 μg Cd and ~0.012 μg Te) was added to the amount of spiked element for each experiment, corresponding to the 1 mL aliquot passed through Sr-column, and, knowing the mass of elute, the initial theoretical concentration was corrected. Using the relation (2) for recovery, the corrected recovery of each element was determined, where the initial theoretical concentration includes the contribution from the lead powder impurities. The corrected recovery values, along with corresponding data, are presented in Table 5.

The recovery values for Cd and Te were largely within the acceptable range for ICP-MS analysis (85–115%) [38], although some values slightly exceeded the upper limit, likely due to intrinsic matrix effects. These deviations were considered acceptable, given the experimental challenges and the corrections applied. Therefore, this method is considered suitable for monitoring small changes in the chemical composition of lead in experimental facilities or a fast reactor.

The average recovery of each element was compared with the results reported by T. Tindemans, who conducted analogous analytical determinations of trace-level

impurities in LBE samples using Pb-spec resin for lead retention. The findings of this work are in good agreement with those reported by Tindemans et al. [23].

Using the described method, two samples of approximately 1 g each from commercially available lead ingots (Pb-99.95%) were provided by SC ROM PLUMB Group SRL. Each sample was dissolved in 20 mL of 2M of HNO_3 , and further diluted to a final volume of 50 mL using UP water. An aliquot of 1 mL was analyzed for their cadmium, tellurium, and bismuth content. Bismuth is one of the most significant intrinsic impurities found in lead, as it can result in the formation of the hazardous volatile impurity polonium-210 (Po-210) through neutron activation in an LFR [39]. The results, presented in Table 6, show that volatile impurities such as Cd and Te are present at parts per million level, while the Bi content is much higher. This higher Bi concentration is expected to impact the production of Po-210 in a lead cooled reactor.

Distinct analyses were conducted to evaluate the impact of the lead matrix on trace-level impurities. In these experiments, an aliquot of 1 mL from the lead stock solution, spiked with Cd and Te at concentrations ranging from 0.005 to 0.01 $\mu\text{g}\cdot\text{mL}^{-1}$, was added to 20 mL of 1 M HNO_3 to replicate the matrix of elution E1. Subsequently, the mixture was analyzed using ICP-MS. The results presented in Figure 5 reveal a significant signal suppression, exceeding 86% for Cd and 92% for Te, respectively.

5 Study limitation and future prospect

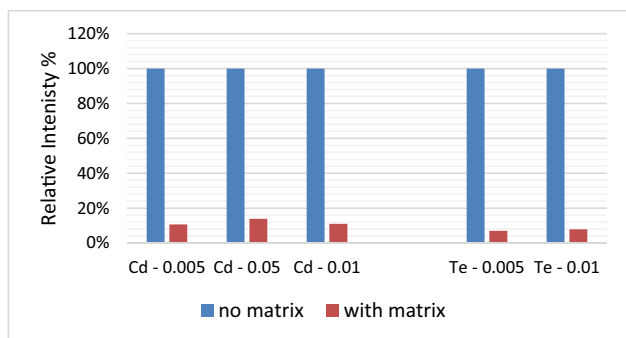
Though the described method is highly sensitive and reliable for trace impurity measurement in lead, it does present several challenges. The procedure is labor-intensive,

Table 5: Recoveries corrected for the contribution of the lead powder

Element	Experiment/ elution	Mass from spike (μg)	Mass of elution (g)	Corrected initial concentration (ppb)	Corrected recovery (%)	Average recovery from LBE samples [23] (%)
Cd	Exp. 1/E1	0.083	23.769	6.28	101.8	
	Exp. 2/E1	0.132	23.819	8.27	95.0	
	Exp. 3/E1	0.004	21.798	3.23	113.6	
	Exp. 4/E1	0.008	21.782	3.40	115.9	
				The average recovery of Cd	106.6 ± 8.6	107.5 ± 5.2
Te	Exp. 1/E1	0.083	23.769	3.98	90.8	
	Exp. 2/E1	0.131	23.819	5.98	86.8	
	Exp. 3/E1	0.004	21.798	0.75	123.7	
	Exp. 4/E1	0.008	21.782	0.91	121.4	
				The average recovery of Te	105.7 ± 17.0	96.0 ± 4.8

Table 6: Average measured impurities in lead ingots

Element	Concentration measured by ICP-MS ($\mu\text{g}\cdot\text{g}^{-1}$)
Cd	2.64 ± 0.02
Te	0.09 ± 0.01
Bi	$3,530.57 \pm 68.96$

**Figure 5:** Effect of the lead matrix on the signal intensity of the trace level impurities.

requiring careful handling during sample preparation, lead dissolution, and matrix separation.

Another major challenge arises from inherent impurities in the lead matrix. These must be well-characterized to discriminate them from impurities generated through nuclear reactions. Addressing these issues requires the use of higher-purity lead in nuclear facilities to prevent an increase in highly volatile products caused by intrinsic impurities.

This approach can be readily applied to the experimental facilities planned for development at the RATEN-ICN site [13], dedicated to study the behavior of impurities in molten lead. These facilities will use stable isotopes to simulate activation and FPs, and the volume of lead samples will be small enough to avoid the challenge of processing large quantities of samples simultaneously.

The implementation of this method for the ALFRED reactor requires automating the sample collection process and setting a frequency that allows for continuous monitoring of impurities generated by lead activation. These impurities gradually accumulate in the reactor's coolant during operation. Continuous monitoring of the coolant's chemical composition can facilitate early detection of any abnormal enrichment, which might indicate a failure in the fuel element cladding and the subsequent release of FPs into the molten lead.

Further investigation will include additional elements, such as Fe, Ni, and Cr, components of the structural

materials used in lead-cooled facilities. Additionally, actinides such as U, Am, and Pu, originating from nuclear fuel, will also be examined using ICP-MS technology. The detection of these elements in lead may indicate a potential breach in the fuel cladding and provides insight into the mechanisms of fuel-coolant interaction.

6 Conclusion

The aim of the study was to evaluate the effectiveness of lead matrix removal for detecting trace-level elements in samples from lead-cooled facilities and to assess the method's reliability for monitoring trace impurities in LFR systems. A solid-phase extraction method using the Sr-spec crown ether resin was applied to remove the lead matrix from mock samples ($\sim 20 \text{ mg}\cdot\text{mL}^{-1}$ of lead spiked with 5–125 ppb of Cd and Te) to simulate conditions similar to those found in a lead-cooled facility. After matrix removal, the concentrations of Cd and Te were determined using ICP-MS, and the quantitative recovery from separation was evaluated.

While the method is highly sensitive and reliable for detecting trace impurities in lead, it does present challenges, such as being labor-intensive and time-consuming. Furthermore, inherent impurities in the lead matrix need to be well-characterized to differentiate them from impurities generated during the operation of lead-cooled facilities. To mitigate these challenges, the use of higher-purity lead in nuclear facilities is recommended, as it would reduce the production of volatile by-products caused by intrinsic impurities.

The findings suggest that this approach is effective for monitoring small variations in the chemical composition of lead in experimental facilities.

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