



A novel combined countercurrent chromatography – inductively coupled plasma mass spectrometry method for the determination of ultra trace uranium and thorium in Roman lead

Petr S. Fedotov^{a,b}, Natalia N. Fedyunina^{a,*}, Dmitry V. Filosofov^c, Evgeny A. Yakushev^c, Guillaume Warot^d

^a National University of Science and Technology “MISIS”, 4 Leninsky Prospect, Moscow 119049, Russia

^b Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 19 Kosygin Street, Moscow 119991, Russia

^c Laboratory of Nuclear Problems, JINR, 6 Joliot-Curie, Dubna, 141980, Moscow region, Russia

^d Laboratoire Souterrain de Modane, CNRS, Modane 73500, France

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ABSTRACT

The concentration of uranium and thorium in lead shields, which are used in underground particle physics research, should be monitored at sub-ppt levels. A combination of extraction chromatography and inductively coupled plasma mass spectrometry can resolve this analytical task. However, a multi-step complicated separation procedure and clean room are required. Besides, the recovery yields for U and Th do not exceed 80% and 60%, correspondingly. We propose an alternative approach. U and Th were pre-concentrated and separated from Pb by countercurrent chromatography, which is a support-free liquid-liquid chromatography. A series of two-phase extraction systems were tested. Under the optimized conditions, U and Th were extracted using a system 1 M HNO₃/0.01 M tetraphenylmethylenediphosphine dioxide in chloroform and then eluted by 0.01 M aqueous solution of etidronic acid and determined by inductively coupled plasma mass spectrometry. The separation is performed in one chromatographic run, takes less than 1 h, and provides the quantitative recovery of U and Th. The limits of detection are 3 and 1 ppt for U and Th, correspondingly. The concentrations of U and Th in Roman lead, which was raised from the sea bottom, were lower than the limits of detection. It sounds unbelievable, nevertheless, the antique lead manufactured by Romans can indeed serve as a high-purity low-background material for the construction of Pb shields. Apart from the analysis of antique lead, the proposed approach can be easily extended to the determination of ultra trace impurities in different materials due to a very wide variety of two-phase extraction systems, which can be used in countercurrent chromatography.

1. Introduction

It sounds unbelievable that materials manufactured by Romans can be now in demand for the most advanced scientific research. Nevertheless, it happens. The antique lead, which was manufactured more than 1500 years ago at the Roman mines in Spain and England and found nowadays on the seabed of a shipwreck site, can be considered as one of the promising source of lead needed in underground particle physics research and low background research. It should be noted that neutrino physics and direct dark matter search are an important field in modern particle physics. The information regarding the properties of neutrinos, such as their mass and how they interconvert, can provide a better understanding of how subatomic particles have affected the evolution of the Universe [1]. The dark matter is a still

theoretical particle that could account for 26% of the total universe mass and might explain the observed rotation speed of galaxies. Its direct detection would confirm these theories [2]. The detectors for this research must be placed deep underground to protect them from natural cosmic rays, which interfere with the detection. Moreover, all materials selected for use in the detector should be of high purity. The detector used for selecting these material also benefits from the underground location and from shielding with Roman lead. One particular concern is the concentration of U and Th in the Pb shield as these elements increase the background because their decay chain generates emission of γ ray simulating the signal of underground experiments. U and Th can be tolerated in high-purity Pb only at the level of 1–3 ppt [3]. Besides, recently manufactured lead has a contamination from radioactive ²¹⁰Pb (T_{1/2} 22.2 years) as well as its daughter isotopes ²¹⁰Bi

* Corresponding author.

E-mail address: nataliafedyunina@mail.ru (N.N. Fedyunina).

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and ^{210}Po ($T_{1/2}$ 5 and 138 days, respectively), which are part of the natural radioactive series ^{238}U . All Pb ores have a contamination in ^{238}U leading to this contamination in ^{210}Pb of modern lead. To reduce the radioactive background from ^{210}Pb by 1000 times, it is necessary to withstand lead for more than 10 half-lives, i.e. more than 222 years. Hence “aged” Roman lead is a good candidate for the material of Pb shield for underground physics research.

Despite the rapid development of instrumental methods of analysis, the analytical control of high-purity materials and the determination of impurities at ultra trace levels remains a complicated task. Although U and Th have been traditionally measured by radiometric techniques, such as γ spectroscopy and neutron activation analysis, these methods are not ideally suited to rapid or accurate determinations [4]. Inductively coupled plasma mass spectrometry (ICP-MS) is of the most powerful analytical methods for trace and ultratrace analysis offering detection limits at the level down to 1 ppt. However, the method has a significant limitation. The content of matrix elements in the solution being analyzed should not exceed 0.1–0.5% depending on the atomic number and the ionization potential [5]. In connection with this limitation, as well as the need to transfer the analyzed sample into a solution, the actual limits of determination in the analysis of various materials are usually not lower than 100 ppt. The cardinal way of overcoming this drawback is the pre-separation of the analytes from the matrix. Several methods such as ion exchange, co-precipitation, solvent extraction, flotation, distillation, sorption etc. have been used for this purpose [6]. However, these techniques often leads to additional analytical problems, including contamination during sample pretreatment, increased blank levels (consequently, a deterioration of the detection limits), and an increase in the time of analysis. So far, a combination of extraction chromatography with ICP-MS has been regarded as the most suitable method for the determination of U and Th at ppt levels in high-purity Pb samples. Following acid digestion, uranium and thorium were separated from the lead matrix using UTEVA resin. U was eluted with 0.025 M HCl and Th then recovered using 0.5% oxalic acid. The back-extraction was not quantitative. Recovery yields for U exceeded 80% whereas those for Th were typically 60%. Procedural detection limits of 0.5 and 1.5 ppt were obtained for U and Th, respectively [4].

Countercurrent chromatography (CCC), a support-free liquid-liquid partition chromatography can be an attractive alternative to the extraction chromatography. CCC is based on the retention of either phase (stationary) of a two-phase liquid system in a rotating column under the action of centrifugal forces while the other liquid phase (mobile) is being continuously pumped through [7]. The coiled column rotates around its own axis and at the same time revolves around the central axis of the planetary centrifuge. Solutes are subjected to a partition process between two phases and eluted in order of their partition coefficients. A main distinguishing feature of CCC as chromatographic method is the absence of porous or adsorptive matrix for retaining the stationary phase. This feature defines the main advantages of the method, such as: the absence of losses of the substances being separated due to interaction with the sorbent matrix; variety of two-phase liquid system which may be used; easy change from one partition system to another; possibility to change a volume of the sample solution from 0.1 to 1000 ml or more; high preparation capacity provided by a high ratio (up to 0.9) of the liquid stationary phase volume and the total column volume (this ratio is much higher than that for the stationary phase used in HPLC or extraction chromatography). The separation efficiency is dependent on the composition of a two-phase liquid system. For the separation of elements, extracting reagents in organic solvents are used as the stationary phase whereas aqueous solutions of complexing reagents, mineral salts and acids are used as the mobile phase [8]. Varying the sample volume up to one liter or more provides high concentration factors. The application of CCC in the analysis of high-purity substances looks promising since the entire separation process occurs in a close system, namely, coiled column made of Teflon. The use of this pure inert material practically excludes additional

contaminations. The applicability of CCC to the analysis of high-purity materials has been preliminary proved taking calcium chloride as an example [9,10].

The aim of this work is to demonstrate the advantageous of the combination of CCC and ICP-MS for the determination of ultra trace U and Th in high-purity materials, in particular, in a unique sample of Roman lead found at the sea bottom on the shipwreck site.

2. Materials and methods

2.1. Samples and reagents

The sample of antique lead was manufactured more than 1500 years ago at the Roman mines in England. 271 ingots of lead were found in 1983 on the seabed of a shipwreck site near the archipelago Les Sept Îles on the northwest coast of France [11]. A part of this lead now belongs to the LSM underground laboratory (www.lsm.fr) and is used as one of the cleanest available γ -ray shield in modern physics research. As an example, the Roman lead presents the internal part of the shield for the EDELWEISS experiment [12] aimed at the search of Dark Matter particles. The sample of lead ingot N 184 (Fig. 1) was taken by vertical drilling; the distance from the surface was 9.15 cm. For the analysis, the sample (1 g) was dissolved in a closed system using 5 ml of 3 M HNO_3 .

Di-2-ethylhexylphosphoric acid (D2EHPA) was purchased from Merck (Germany). Tetraphenylmethylenediphosphine dioxide (DPO) was synthesized in the Institute of Physiologically Active Substances of the Russian Academy of Sciences. Chloroform and *n*-hexane (“pure” grade) were used for the preparation of the stationary liquid phase. Etidronic acid monohydrate ((1-Hydroxyethylidene)bisphosphonic acid monohydrate) as well as nitric (65%) and hydrochloric (32%) acids of “suprapur” grade were purchased from Merck (Germany). Multielement standards ICM-MS-68A-A and B (High Purity Standards, USA) were employed for the preparation of model and calibration solutions. De-ionized water (18.2 M Ω /cm, Millipore Simplicity, France) was used throughout.

Prior to the analysis of Roman lead the method was developed and optimized using a standard solution containing 10 g/l of lead in 4% nitric acid (High Purity Standards, USA). The solution is prepared on the basis of metallic high purity lead.

2.2. Pre-concentration and separation of U and Th by countercurrent chromatography

The separations were performed on a planetary centrifuge equipped with a one-layer coiled PTFE column (tubing bore 1.6 mm) with an inner capacity of 20 ml. The ratio of rotation and revolution radii (β value) is 0.28, the number of loops is 30. The scheme of the planetary centrifuge is given in Fig. 2. The device was fabricated in the Institute of Analytical Instrumentation (Saint-Petersburg, Russia). It should be noted that similar planetary centrifuges manufactured by Dynamic Extraction (UK) are commercially available. The rotation and



Fig. 1. Sample of Roman lead, which was raised from the seabed of a shipwreck site.

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