



ELSEVIER



Separation and analysis of lanthanides by isotachopheresis coupled with inductively coupled plasma mass spectrometry

Laurent Vio^{a,c,*}, Gérard Crétier^c, Frédéric Chartier^b, Valérie Geertsen^d, Alkiviadis Gourgiotis^a, H  l  ne Isnard^a, Jean-Louis Rocca^c

^a Commissariat    l'Energie Atomique, Saclay, DEN/DPC/SEARS/LANIE, 91191 Gif sur Yvette Cedex, France

^b Commissariat    l'Energie Atomique, Saclay, DEN/DPC, 91191 Gif sur Yvette Cedex, France

^c Universit   de Lyon, Institut des Sciences Analytiques (UMR CNRS 5280), Villeurbanne, France

^d Commissariat    l'Energie Atomique, Saclay, DSM/IRAMIS/SIS2M/LIONS, 91191 Gif sur Yvette Cedex, France

ARTICLE INFO

Article history:

Received 6 February 2012

Received in revised form

7 June 2012

Accepted 15 June 2012

Available online 20 June 2012

Keywords:

Isotachopheresis

Inductively coupled plasma mass spectrometry

Coupled techniques

Lanthanides

Fission products

Nuclear industry

ABSTRACT

This study is a large project initiated by the French Nuclear Agency, and concerns the development of a new electrolyte system for the separation of lanthanides by isotachopheresis. This new system is based on a leading electrolyte that incorporates 2-hydroxy-2-methylbutyric acid as complexing agent. The optimization of separation conditions (complexing agent concentration, pH, capillary dimensions, injection conditions, and current intensity) performed by experiments on a commercial capillary instrument with contactless conductivity detection, which allows to improve the separation of 13 lanthanides (La to Lu, except Pm and Ho). We have also directly coupled the isotachopheresis to an inductively coupled plasma mass spectrometer to visualize the mono-elementary elution bands and demonstrate the potentiality of the method for isotope ratio measurements. The application to a simulated solution representative of a fraction of fission products present in a MOX spent fuel is presented in this paper to demonstrate the possible application in future on nuclear fuel samples.

   2012 Elsevier B.V. All rights reserved.

1. Introduction

In the nuclear industry, the knowledge of isotope composition and elemental concentration of actinides (U, Pu, Am, and Cm) and fission products (lanthanides, Cs, etc) is crucial for qualification of neutronic calculation codes [1], burn-up determination [2] and management of nuclear waste. Fission product solutions, particularly lanthanides are characterized by mass spectrometry techniques i.e. thermal ionization mass spectrometry (TIMS) [3] (TIMS) or multiple-collector inductively coupled plasma mass spectrometry (MC ICP–MS) [4], in order to obtain precision and accuracy on isotope ratio of a few ‰. The direct determination of lanthanide isotope composition by mass spectrometry is hampered by isobaric interferences as well as oxide formation. High resolution mass spectrometers cannot resolve these interferences and so previous chemical separations are then required before mass spectrometric analysis.

This work initiated by the CEA Saclay is a part of a large project concerning the development of a new analytical system for the

isotopic characterization of lanthanides in nuclear fuel samples. This system must be in accordance with the As Low As Reasonably Achievable principle (ALARA [5]), and the goal is to decrease the total effective dose equivalent and the radioactive liquid waste volume during the chemical separation steps.

For the determination of lanthanide isotope composition in nuclear fuel samples two strategies are applied. In the first one, the elements of interest are individually collected by performing successive chemical separations and analyzed by TIMS or MC ICP–MS (ICP–QMS). In this off-line procedure, lanthanides (fission products) are separated by ion exchange chromatography (IEC) [3,4,6]. In the second strategy, IEC is directly coupled to quadrupole ICP–MS [7–11] (ICP–QMS) or MC ICP–MS [12]. This on-line method simplifies the sample preparation procedure and then decreases the handling time of radioactive materials. However, hyphenation of IEC with ICP–MS is not in response to the need of decreasing radioactive liquid waste volume. Capillary electropheresis (CE) is very attractive in the nuclear field because it offers minimal waste generation, high separation efficiency, low cost and fast analysis. So, in order to reduce both the sample amount and the effluent volume, hyphenation of capillary electropheresis (CE) with ICP–MS was developed [13–15]. In this case, the sample injection volume decreases by a factor three without loss of resolution. Nevertheless, due to the insufficient sensitivity,

* Corresponding author at: Commissariat    l'Energie Atomique, Saclay, DEN/DPC/SEARS/LANIE, 91191 Gif sur Yvette Cedex, France.
E-mail address: laurent.vio@gmail.com (L. Vio).

preconcentration processes are usually required [16]. Unlike other CE techniques, isotachopheresis (ITP) separation itself leads to a self-sharpening effect at the zone boundaries and preconcentration capability all along the analysis [17]. The use of ITP as both preconcentration and the separation method provides high stacking effect and separation if the electrolyte system is properly adjusted. ITP is a basic mode of CE using discontinuous electrolyte systems, i.e. leading electrolyte (LE) and terminating electrolyte (TE). The first one governs the migration speed, separation capability and sample preconcentration whereas the second one which has the lowest electrophoretic mobilities in the system closes the electric circuit. After separation of the zones of analytes according to their effective mobility, a pseudo-stationary state is reached where all the adjacent bands of analytes are migrating with a constant speed. In ITP, each element is eluted as a quasi-rectangular band and at a concentration fixed by separate conditions, independent from the element concentration in the sample.

The work presented here deals with the development of the isotachopheretic separation of lanthanides for applications in nuclear fuel samples. The separation of lanthanides is a very old and difficult task due to their similarities in their physical and chemical properties [18]. Whatever the separation techniques used, a significant enhancement of the selectivity between lanthanides can be achieved by the addition of complex-forming agents. The most effective agent is 2-hydroxyisobutyric acid (HIBA) which is frequently reported for the separation of lanthanides by IEC [3,12,19–23], CE [24–27] and ITP [28–29]. Among the other complexing agents tested, 2-hydroxy-2-methylbutyric acid (HMBA) was shown to exhibit higher efficiency for the IEC separation of lighter elements of the lanthanide series [30].

In the first part of this paper, the best composition of leading electrolyte (nature, concentration and pH) and the optimal separation conditions (dimensions of the separation capillary, current intensity, injected amount) are defined from experiments carried out with a commercial capillary equipment using a contactless conductivity detector (ITP-CD). Then, in the second part the separation system interfaced to an inductively coupled plasma quadrupole mass spectrometer (ITP-CD-ICP-QMS) is evaluated for the lanthanides of interest from a simulated spent MOX fuel solution.

2. Materials and methods

2.1. Chemicals and samples

All solutions were prepared with purified water provided by a Purelab UHQ II system (Elga, Le Plessis Robinson, France). For the preparation of electrolyte solutions and the coating of capillaries, chemicals (HIBA (99%), HMBA (98%), sodium acetate (99.99%), ammonia solution (25%), acetic acid (100%), sodium chloride (99.5%), sodium hydroxide (30%), hydrochloric acid (37%) and polyvinyl alcohol (PVA, 89,000–98,000 Da, 99+% hydrolyzed) were obtained from Sigma Aldrich (Isle d'Abeau, France).

Standard solutions of elements obtained from Spex Certiprep Group (Longjumeau, France) were at the concentration of 1000 or 10,000 mg L⁻¹ in 5% nitric acid. In order to prepare stock solutions of each lanthanide at a concentration of 1000 mg L⁻¹ without nitrates, aliquots of stock solutions were evaporated to dryness at 90 °C and dry extracts were dissolved in adequate volumes of pure water. These individual stock solutions were used to prepare four different sample solutions containing 13 lanthanides (La to Lu, except Pm and Ho), 7 lanthanides (La, Pr, Sm, Gd, Dy, Tm and Lu), 6 lanthanides (Ce, Nd, Eu, Tb, Er and Yb) and a mixture of the 4 lanthanides of great interest in nuclear

Table 1
Chemical composition of the fission product fraction of a simulated spent MOX fuel after U and Pu extraction.

Element	Concentration (ng/μL)
Se	0.45
Rb	2.73
Sr	6.33
Y	3.54
Zr	29.55
Mo	29.16
Ru	21.51
Rh	3.21
Pd	15.75
Ag	0.69
Cd	1.23
Sn	0.72
Sb	0.18
Cs	21.03
Ba	15.30
La	10.26
Ce	20.46
Pr	9.45
Nd	34.80
Sm	6.42
Eu	1.53
Gd	2.04
Tb	0.03
Dy	0.03

industry (Nd, Sm, Eu and Gd). Thiourea was added to the mixture of 7 and 6 lanthanides. The simulated sample of spent MOX fuel solution containing 24 elements is prepared from natural standard using the same protocol as lanthanide samples. Its chemical composition is given in Table 1. For all experiments, the free nitrate standards are diluted to a leading electrolyte according to the conditions of the study.

2.2. Preparation of coated capillaries

In some experiments, the separation capillary was coated with PVA prior to use in order to reduce electro-osmotic flow (EOF) and consequent dispersion phenomena. An acidic solution of 5% PVA (pH 1 with HCl) in water is prepared and degassed using sonication. After connection to a pressure vessel (Nanobäume capillary packing unit, Western Fluids Engineering, Wildomar, CA, USA), the capillary is successively rinsed with NaOH 1 mol/L and HCl 1 mol/L by applying 2 bar for 30 min in each rinsing step. Then, the capillary is emptied with N₂ at 2 bar for 10 min. The capillary coating is performed flowing the PVA solution through the capillary for 90 min at 5 bar. Finally, the capillary is placed in a gas chromatography oven (GC 17, Shimadzu, Kyoto, Japan) and heated at 145 °C for 8 h under 2 bar continuous N₂ flow.

2.3. Isotachopheretic separations

Isotachopheretic separations were performed using a HP3D electrophoresis system (Agilent Technologies, Waldbronn, Germany) and a Tracedec contactless conductivity detector (Innovative Sensor Technologies, Vienna, Austria). The silica capillaries (360 μm o.d.) are provided by Cluzeau Info Labo (Sainte Foy La Grande, France).

Different capillary configurations were used. In mono-capillary configuration, the capillary has an inner diameter of 30 or 75 μm and the separation length L_s is defined as the capillary length that is not filled by sample after injection. In coupled capillary configuration, a 150 μm i.d. × 8 cm length injection capillary (corresponding to a volume of 1.4 μL) is connected to a separation capillary (30 μm i.d.) without dead volume by means of a 350 μm

Download English Version:

<https://daneshyari.com/en/article/7686231>

Download Persian Version:

<https://daneshyari.com/article/7686231>

[Daneshyari.com](https://daneshyari.com)