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Inductively coupled plasma mass spectrometry in comparison with neutron activation and ion chromatography with UV/VIS detection for the determination of lanthanides in plant materials

Ewa Bulska [a,*], Bożena Danko [b], Rajmund S. Dybczyński [b], Agnieszka Krata [a], Krzysztof Kulisa [b], Zbigniew Samczyński [b], Marcin Wojciechowski [a]

[a] Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
[b] Laboratory of Nuclear Analytical Methods, Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland

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ABSTRACT

Analytical performance of inductively coupled plasma mass spectrometry (ICP-MS) for determination of lanthanides in plant materials was investigated and compared with neutron activation analysis (NAA) as well as ion chromatography (IC) with UV–VIS detection. Two sample preparation protocols were tested: (i) microwave assisted digestion by concentrated nitric acid; (ii) microwave digestion involving silica and fluoride removal, followed by the selective and quantitative lanthanides group separation from the plant matrix. Several Certified Reference Materials (CRM) of plant origin were used for the evaluation of the accuracy of the applied analytical procedures. The consistency of results, obtained by various methods, enabled to establish the tentative recommended values (TRV) for several missing elements in one of CRMs. The ICP-MS, due to its very high sensitivity, has the potential to contribute to this aim. The discrepancy of the results obtained by various methods was discussed in a view of possible matrix effects related to the composition of investigated materials.

1. Introduction

The importance of lanthanides has been growing over the last years, especially considering the usefulness of their compounds in modern technology, agriculture and medicine [1–4]. It has been also reported that the lanthanides may play an important role in the life system. Entering plants and human cells, they may interfere with biological functions and in particular cellular processes, by replacement of essential bio-metals (e.g. calcium), chelation of organic molecules, etc [3,5–7]. It is known that lanthanides can replace calcium in bone and encourage bone formation by activating the cells responsible for bone production [8]. Furthermore, they also may promote plant growth and yield increase but the reasons for that are yet not sufficiently understood [9]. There is also evidence indicating that the lanthanides could act as scavengers of free radicals and therefore, protect cells and tissues from oxidative stress-induced injury [6]. It has been known that the lanthanides selectively accumulate in tumor tissue. The use of them has been suggested for the treatment against selected diseases [10].

A number of medically relevant therapeutic applications of lanthanides as well as their role for diagnostics as contrast enhancing agents for magnetic resonance imaging [11–13] are rapidly growing. Therefore, widely and frequently used lanthanides may enter the ecosystem and consequently the determination of the lanthanides in the environmental samples, including plants, is becoming a highly important issue.

It is worth emphasizing, that the determination of the lanthanides in plant materials is a difficult task, owing to their low abundance, chemical similarity and matrix effects occurring in different measurement methods [14,15]. Therefore, despite the rapid progress in the field of modern analytical techniques, still only a few methods can assure reliable determination of the individual lanthanides at trace and ultra-trace levels (10^{-6} g g^{-1}–10^{-9} g g^{-1}). Due to this fact, the biological reference materials certified for the lanthanide content are scarce and for most of them, certified or information values for the content of individual elements are available only for a few members of the group [16]. A complete set of certified values is available for only one reference material of biological origin: the BCR 670 Aquatic Plant, issued in 2001 by the BCR—European Commission Joint Research Center, Institute for Reference Materials and Measurements (Geel, Belgium) [17].

Among the analytical techniques used for lanthanides quantification, Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

* Corresponding author. Tel.: +48228220211; fax: +48228225996.
E-mail address: ebulska@chem.uw.edu.pl (E. Bulska).

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is nowadays widely employed due to its large dynamic range, low detection limits ($\leq$ ng g^{-1} range), and the ability to monitor a number of elements and their isotopes simultaneously [18,19]. However, it should be stressed that ICP-MS is also not free from interferences, mostly caused by the isobaric and/or polyatomic ions. The detection of middle and heavier lanthanides is complicated by the possible overlap of M^+, MO^+ or MOH^+ ions of lighter lanthanides and Ba isotopes and oxide ions [18]. It should be nevertheless emphasized that the most essential advantage of ICP-MS over Ion Chromatography (IC) with UV/VIS detection or Neutron Activation Analysis (NAA) is its very good limits of detection (LOD) for all lanthanides.

In order to examine the accuracy of results obtained by a given analytical method the use of appropriate standards is required as part of the validation processes [20,21]. Following the definition, certified reference materials (CRMs) are considered as transfer standards assuring the traceability of the measurements of particular analyte in a given matrix [22,23]. The characterization of CRMs towards establishing the certified values is a complex and expensive process. A lot of effort is therefore focused on the development of the validated analytical procedures enabling the support of these activities [24].

The aim of this study was the critical evaluation of analytical performance of ICP-MS for the determination of lanthanides in plant CRM's. For these purposes two sample preparation protocols were used:

(1) Microwave assisted digestion of plants in nitric acid medium followed by direct ICP-MS measurements.
(2) Microwave-assisted digestion of plants in mixture of nitric acid and hydrofluoric acid medium, enabling complete digestion of silica, followed by selective and quantitative separation of the lanthanides group and yttrium by ion exchange chromatography [25–27]. The final fraction containing lanthanides and yttrium was used for the ICP-MS measurements.

The accuracy of the lanthanides determination by ICP-MS was evaluated by several CRMs of botanic origin [16,17,28–30] followed by the comparison with results obtained by NAA and IC-UV/VIS. In the case of NAA and IC-UV/VIS, the second protocol for the sample preparation was employed.

In the case of Tea Leaves (INCT-TL-1) CRM, it was possible to establish tentative recommended values (TRVs) for a number of elements (Pr, Nd, Gd, Dy, Ho, Er and Tm), which originally were not certified in this material.

2. Experimental

2.1. Materials and reagents

BCR 670 Aquatic Plant [17], Chinese DC73349 Bush Branches and Leaves [16] and three CRMs of Polish production: CTA-OTL-1 Oriental Tobacco leaves [28], INCT-TL-1-Tea Leaves [29] and INCT-MPH-2 Mixed Polish Herbs [30] were used for this study. The contents of major and some minor elements in those materials, e.g. Al, Ca, K, Mg, P, S, Si and Ba, Pb, respectively, are presented in Table 1.

Hydrochloric and nitric acid (analytical reagent grade, POCh, Poland) were purified by sub-boiling distillation using quartz sub-boiling still (Kuerner Analysentechnik, Rosenheim, Germany). Hydrofluoric acid, 40%, commercial suprapure grade (Merck, Germany) was used. All other reagents used in the procedure: H_2O_2, H_3BO_3 (POCh, Poland) were of analytical reagent grade.

Lanthanide oxides (Koch Light, 5 N) were used for preparation of stock standard for NAA and IC-UV/VIS measurements. Multi-element stock standard solution of lanthanides (Merck, Germany) was used for ICP-MS measurements and rhodium chloride (Merck, Germany) was used as internal standard. Multi-element standard solution (Merck, Germany) containing In, Mg, Pb, Ce and Ba was used for daily performance check of ICP-MS spectrometer.

Ultrapure water (18 MΩ cm resistivity) from Milli-Q RG Ultra Pure Water System (Millipore) was used throughout. All the vessels used for solutions and samples were soaked in 7 mol L^{-1} nitric acid, followed by rinsing with ultrapure water.

Table 1
Concentration of major and minor elements in CRM's used in this work [16,28–30].

Element, concentration	DC 73349 Bush Branches and Leaves	CTA-OTL-1 Oriental Tobacco Leaves	INCT-TL-1 Tea Leaves	INCT-MPH-2 Mixed Polish Herbs	BCR 670 Aquatic Plant
Al, %	0.20 ± 0.03	0.17 ± 0.03	0.23 ± 0.03	0.07 ± 0.01	–
Ca, %	1.68 ± 0.11	3.17 ± 0.12	0.58 ± 0.05	1.08 ± 0.07	–
K, %	0.92 ± 0.10	1.56 ± 0.05	1.70 ± 0.12	1.91 ± 0.12	–
Mg,%	0.48 ± 0.04	0.45 ± 0.21	0.22 ± 0.02	0.29 ± 0.02	–
P, %	0.10 ± 0.04	0. 29 ± 0.01	(0.18)	(0.25)	–
S, %	0.73 ± 0.06	0.73 ± 0.08	0.25 ± 0.03	0.24 ± 0.01	–
Si, %	0.60 ± 0.07	~0.8	~0.06	~0,4	–
Ba, mg kg^{-1}	18 ± 2	84.2 ± 11.5	43.2 ± 3.9	32.5 ± 2.5	–
Pb, mg kg^{-1}	47 ± 3	4.91 ± 0.80	1.78 ± 0.24	2.16 ± 0.23	2.06

2.2. Sample preparation

2.2.1. Protocol 1

Approximately 0.5 g sample was weighted in a Teflon vessel. The digestion was performed in presence of (i) 4 mL of concentrated HNO_3, (ii) 0.5 mL of 30% hydrogen peroxide under the following conditions: (i) 500 W/10 min; (ii) 1000 W/15 min; (iii) cooling/5 min. A microwave-assisted unit (Anton Paar Mutliwave Sample Preparation System, Austria) with Teflon vessels was used. Digested samples were filtered through sterile syringe-driven 0.45 μm nylon membrane filters (Millex, France).

2.2.2. Protocol 2 (including preliminary group separation of the lanthanides and yttrium)

Approximately 0.5 g sample was weighed in a Teflon vessel. The digestion was performed in presence of 6 mL of concentrated HNO_3, 1 mL of concentrated HF and 1 mL of 30% hydrogen peroxide under the following conditions: 5 min—60%, 5 min—80% and 10 min 100% of the maximum power 650 W. UniClever TM II, a focused microwave high pressure single vessel digestion system, which is controlled using a microprocessor console, was used.

The digested samples were evaporated to dryness and treated with a mixture of concentrated HCl (2 mL) and 5% (w/v) H_3BO_3 (1 mL) to remove the fluorides, then evaporated again, dissolved in 3 mL of 8 mol L^{-1} HCl and subjected to column chromatographic separation. Details of the separation/preconcentration procedure are described in refs. [25–27]. In order to minimize the analytical blank signal, the evaporations of the sample solutions, during the preparation of the sample prior to measurements, were carried in a laminar flow hood. The blank values checked by NAA, for most of the lanthanides were below the detection limits. In the case of Ce, La and Eu, blank values were above the detection limit (typically e.g. 0.06 μg g^{-1}, 0.02 μg g^{-1}; and 0.001 μg g^{-1}, respectively). Thus, blanks were monitored in the course of every run and appropriate corrections introduced whenever necessary.