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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

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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)

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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.

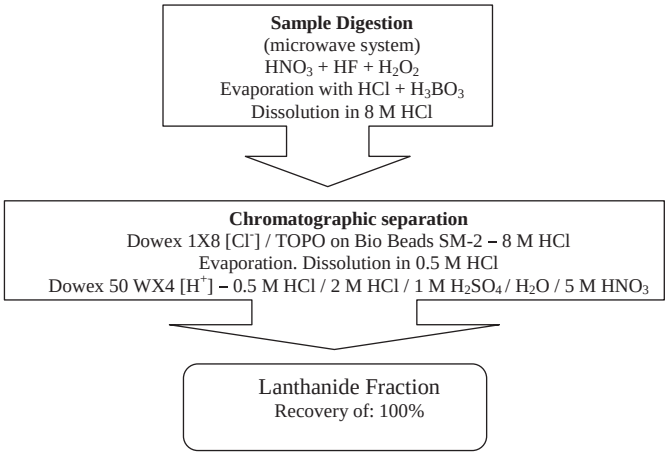

Fig. 1. Flow chart of the selective and quantitative isolation of lanthanide group (and yttrium) from biological materials.

The anion-exchange resins Dowex 1×8 [Cl^-] 100–200 mesh (Serva) and cation-exchange resin Dowex 50WX4 [H^+] 200–400 mesh (Serva) as well as extraction chromatographic column with tri-*n*- octylphosphine oxide (TOPO) supported on Bio Beads SM-2 were conditioned as described earlier [25]. When the entire procedure was completed, the lanthanide fraction containing all lanthanides and Y in 5 mol L^{-1} HNO_3 was used for measurement of the analytes. In the case of ICP-MS, all solutions were filtered according to protocol 1.

The sample preparation procedure (protocol 2) used in this work consists of the following steps (see also block scheme in Fig. 1):

- microwave assisted digestion of the plant material including the removal of silica and the excess of fluorides by volatilization of SiF_4 and BF_3, respectively;
- chromatographic separation, which employs: (i) tandem of strongly basic anion exchanger and extraction chromatographic columns (TOPO on Bio Beads SM-2); (ii) stepwise elution from strongly acidic cation exchanger column.

In the case of protocol 2, the recovery of the lanthanide separation was checked with the use of radioactive tracers: ^{141}Ce, ^{140}La, ^{153}Sm, ^{160}Tb, ^{175}Yb and ^{177}Lu in the presence of non-activated isotopes in plant sample. The yield of the examined lanthanides was invariably quantitative: $99.4\pm0.7\%$. It was additionally confirmed in the experiments with a model radioactive sample of high lanthanide content [27].

2.3. Instrumental and measurements

2.3.1. ICP- MS measurements

An inductively coupled plasma quadruple mass spectrometer equipped with dynamic reaction cell (DRC) ELAN 6100 DRC (Perkin-Elmer/Sciex) was used. Prior to analyte quantification, the ICP-MS spectrometer performance was optimized for maximal intensity of In^+, Mg^+ and Pb^+. The oxide formation by means of the ratio CeO^+/Ce^+, and the formation of double-charged ions by means of the Ba^{2+}/Ba^+ ratio couple were considered. The levels of CeO^+/Ce^+ and of Ba^{2+}/Ba^+ were monitored and measurements were executed only when both ratios were less than 3%, according to daily performance check recommended by the ICP-MS instrument manufacturer. Rhodium was used as internal standard with the concentration of 10 μg L^{-1}, it was introduced by additional channel on peristaltic pump and mixed with sample by Y tube before entering the nebulizer and spray chamber.

The experimental conditions for ICP-MS measurements were optimized towards the best signal to noise ratios for all the lanthanides. The isotopes selected for measurement were as follow: ^{139}La, ^{140}Ce, ^{141}Pr, $^{143,145}Nd$, $^{147,149,152}Sm$, $^{151,152,153}Eu$, $^{155,157}Gd$, ^{159}Tb, $^{161,163}Dy$, ^{165}Ho, $^{166,167}Er$, ^{169}Tm, $^{172,173,174}Yb$ and ^{175}Lu.

The plasma was operated at 1050 W: coolant, auxiliary and nebulizer argon flow were 15 L min^{-1} 1.2 L min^{-1} and 0.86 L min^{-1}, respectively. A Meinhard type nebulizer in combination with a cyclonic spray chamber was used; sample uptake rate was 1 mL min^{-1}.

2.3.2. NAA measurements

The solution containing all elements of interest was concentrated to a small volume and quantitatively transferred to high density polyethylene capsules (HDPE, Faculty of Biology, University of Vrije, Amsterdam). After evaporation, encapsulated samples were ready for neutron irradiation. Samples (including blank) standards and flux monitors (Eu - 0.5 μg) in HDPE capsules, wrapped in Al foil were irradiated in the nuclear reactor MARIA (Świerk, Poland) in the thermal neutron flux of approximately 10^{14} n cm^{-2} s^{-1} for 30 min. Cooling time as well as counting time was optimized, depending on the half-life of the element of interest in order to achieve low uncertainty due to counting statistics.

Measurements were carried out using a gamma-ray spectrometer with HPGe detector (Canberra), active volume 255 cm^3, well type, resolution 2.4 keV for the 1332.4 keV peak of ^{60}Co, relative efficiency 24% with the GENIE-2000 Canberra Gamma Spectrometry System.

The irradiated sample, after the measurement of short-lived radionuclides (^{142}Pr, ^{152m}Eu, ^{165}Dy ^{171}Er) as well as medium-lived radionuclides (^{140}La, ^{153}Sm, ^{166}Ho, ^{175}Yb, ^{177}Lu) was washed quantitatively from a PE capsule with 6 mol L^{-1} HCl. After addition La and Lu carriers (50 μg each) the solution was evaporated to dryness. The residue was dissolved in 2 mL of 0.0025 mol L^{-1} Na_2H_2Y, (ethylenediaminetetraacetic acid disodium salt) and introduced onto the top of Dowex 1×4 [H_2Y^{2-}] column (13.5 cm × 0.126 cm^2; 200–400 mesh). Then 40 mL of 0.0025 mol L^{-1} Na_2H_2Y solution was passed (the first sub-fraction was collected), followed by the elution with 20 mL of 0.1 mol L^{-1} Na_2H_2Y (the second sub-fraction). The cooling time employed for measurement of the individual radionuclides in these fractions ranged from days to weeks. Measurements were performed in two series, with respect to the half life of particular radionuclides: ^{140}La, ^{153}Sm ^{166}Ho, ^{175}Yb, ^{177}Lu (from 2 to 7 day of cooling) and ^{141}Ce, ^{147}Nd, ^{152}Eu, ^{160}Tb, ^{170}Tm, ^{169}Yb (4 weeks cooling).

2.3.3. IC UV/VIS measurements

Separation of lanthanides and yttrium was performed as shown in Fig. 1. Dionex 2000 i/SP ion chromatograph (Dionex Corporation, 1228 Titanway, Sunnyvale, Ca., USA) equipped with a VDM-II Dionex UV/VIS detector and a gradient pump (Dionex, AGP). Ion Pac CS3 analytical column (with guard column Ion Pac CG3) was used for the separation of lanthanide cations, with α-hydroxyisobutyric acid (α-HIBA) as a complexing eluent and Arsenazo III as a post column reagent. A combined linear gradient and isocratic elution mode was essentially the same as that described elsewhere [26].

The solution of 5 mol L^{-1} HNO_3 containing all lanthanides was evaporated to dryness, dissolved in 1 mL of 0.125 mol L^{-1} HNO_3 and injected into the chromatographic column using 530 μL sample loop. All chromatograms were recorded at 25 °C or 70 °C (the run at 70 °C was necessary to enable resolution of Dy and Y).

Before each run at a given temperature, the whole system was stabilized for ca. 45 min. For lanthanides quantification, standard solution containing all measured elements was run at the same conditions, and peak area of standards was measured.

3. Results and discussions

The usefulness of ICP-MS for the determination of lanthanides in plant materials was evaluated by the use of various CRM's of botanic origin. The evaluation of the accuracy of the ICP-MS method was aimed as a main goal of this project and the obtained results were compared to the certified values as well as to those obtained by NAA and IC. Moreover, the attempt was made towards possible enhancement of the list of certified elements in the investigated CRMs.

The determination of lanthanides by ICP-MS was performed either directly after microwave assisted wet digestion of the sample (protocol 1) or after applying the separation procedure (recovery of 99.4% ± 0.7) according to protocol 2. The protocol 2 was applied according to the analytical scheme, originally developed for NAA, which has been carefully investigated with the use of radiotracers, as well as model radioactive sample [27].

In order to evaluate the results obtained by three analytical methods applied in this work (ICP-MS, NAA and IC-UV/VIS), BCR 670 (Aquatic Plant) and four other CRMs were used. The obtained results were compared with the certified values for all lanthanides [16,17,28–30].

3.1. Characterization of various measurement techniques used for the determination of lanthanides

The aim of this work was to perform cross-evaluation of the analytical performance ICP-MS method versus NAA and IC-UV/VIS as well as to validate the proposed analytical method for ICP-MS measurements, as it is recommended by ISO/IEC 17025:2005 standard [20]. In the case of acceptable agreement between the results obtained by various analytical scenarios, it would be possible to establish a tentative recommended value for particular element in a CRM, in which this element is not certified.

3.1.1. Inductively coupled plasma mass spectrometry

For a number of lanthanides the measurements were based on the analysis of a single isotope only, i.e. ^{139}La, ^{140}Ce, ^{141}Pr, ^{159}Tb, ^{165}Ho, ^{169}Tm and ^{175}Lu, due to either their occurrence as single isotope elements (Pr, Tb, Ho and Tm.), or clear dominance of one of the isotopes (^{139}La, ^{140}Ce and ^{175}Lu, with abundances of 99.9%, 88.5% and 97.4%, respectively). The concentration of the remaining seven lanthanides was measured by monitoring all listed isotopes: ^{143,145}Nd, ^{147,149,152}Sm, ^{151,153,152}Eu, ^{155,157}Gd, ^{161,163}Dy, ^{166,167}Er and ^{172,173,174}Yb. In the last case it was considered as an in-situ quality check of the results, since under ideal conditions, i.e. without interferences, measurement performed for various isotopes of the element of interest should result in the same concentrations. It was found that the results evaluated from the measurements of ^{152}Sm and ^{155}Gd always gave higher values compared to other isotopes of both elements. This could be explained by polyatomic ions interferences, most likely due to the formation of oxide ions of ^{136}Ba, ^{136}Ce and ^{139}La in the plasma. Consequently, ^{152}Sm and ^{155}Gd were excluded from further measurements. For the remaining isotopes of Sm and Gd as well as other lanthanides, the intensities of the signals were practically identical, and therefore the isotopes for which the lowest value of standard deviation was observed were selected for further measurements.

3.1.2. Neutron activation analysis (NAA)

NAA offers favorable detection limits for most of rare earth elements and is recognized as a recommended technique for the lanthanides determination owing to its generally good accuracy. However, due to typically low abundance of lanthanides in biological materials, suppressive effect of highly radioactive biological matrix on gamma-ray spectrum as well as numerous nuclear and spectral interferences, usually only La, Ce, Nd, Sm and Eu can be easily determined in biological samples by purely instrumental version of nuclear activation analysis (INAA) [14,15,32].

In the present work procedures with selective pre-irradiation isolation of the lanthanides from accompanying elements, as well as with the post irradiation division of lanthanides into two subgroups were employed. The removal of practically all other elements, at the pre-irradiation stage, eliminates some sources of errors normally encountered in INAA, such as high activity of matrix constituents, formation of some of the analyte radionuclides from uranium fission reaction [33], as well as spectral interferences from ^{239}Np and ^{233}Pa (uranium and thorium daughters) and other radionuclides. Additionally, the pre-irradiation separation allows employment of larger masses of the samples than in classical radiochemical version of neutron activation analysis (RNAA) and consequently increases the number of determined elements. On the other hand, as the sample was subjected to the chemical operation prior to irradiation, this operation deprives NAA of its unique advantages, such as absence of blank signal. Therefore, blank was controlled in the course of every run and appropriate correction was introduced whenever necessary.

Post-irradiation division of the lanthanides into two groups enables to minimize spectral interferences originating from the rare earth elements themselves [27]. It is based on the differences in ion-exchange affinity of the individual lanthanide—EDTA (EDTA=H_4Y) complexes (LnY^-) towards strongly basic anion exchange resins [34,35]. In the course of ion-exchange chromatographic separation, lanthanides are divided into two sub-fractions by means of a stepwise elution with Na_2H_2Y solutions (Fig. 2). The first sub-fraction comprises Lu, Yb, Tm, Ho, Er, Dy and most of La. In the second fraction: Ce, Pr, Nd, Sm, Eu, Gd, Tb and the rest of La are present (Fig. 2). This post irradiation analytical stage is indispensable to determine Tm accurately, which otherwise is hidden in the Compton background [27].

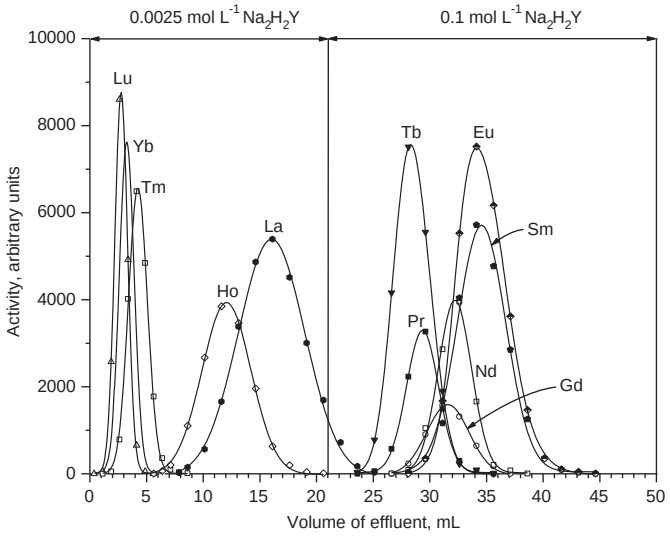

Fig. 2. Separation of lanthanides into two groups by stepwise elution of their complexes with disodium EDTA (EDTA=H_4Y), pH ≈ 4.8. Column: 13.5 cm × 0.126 cm^2 Dowex 1 × 4[H_2Y^{2-}] (200–400 mesh); flow rate 1.5 cm min^{-1}, temp. 25 °C (after B. Danko et al. [25], by permission of the copyright holders).

3.1.3. Ion chromatography with UV/VIS detection

Ion chromatography with UV/VIS detection was selected due to its multi-elemental capability, despite its lower sensitivity for lanthanides as compared with ICP-MS and NAA and appearance of interferences in case of non-effective removal of accompanying elements from the lanthanide fraction. Successful separation of lanthanides and yttrium by IC was described by Dybczyński and Kulisa [31]. The procedure was later modified by involving the post column reaction with the use of Arsenazo III [26] and was also employed in this work. Thus, the combination of selective and quantitative procedure for separation of lanthanides with ion chromatography employing Dionex Ion Pac CS3+CG3 column, α-HIBA as an isocratic-gradient eluent and Arsenazo III resulted in method able to determine all the lanthanides and yttrium at ng g^{-1} levels.

3.2. Analytical performance of the employed techniques

3.2.1. Detection limits

The limits of detection (LOD) of the analytical procedures were compared by using the same plant materials which were digested and underwent the same chromatographic separation. All LODs refer to 500 mg sample and the respective data calculated according to each method [36,37] (Table 2). As it was expected, the lowest LODs, between 0.1 ng g^{-1} and 0.3 ng g^{-1} were obtained by ICP-MS, while the LODs obtained by IC-UV/VIS and NAA were between 5–10 ng g^{-1} and from 0.1 ng g^{-1} (for Eu and Yb) up to 50 ng g^{-1} for Pr, respectively.

Recently [38] it was postulated that "LODs of the lanthanides should follow a zigzag pattern with the odd atomic number elements having systematically lower LODs than the even atomic number neighbors elements". This claim was made on the basis of ICP-MS literature data on "representative results for quadruple inductively coupled plasma mass spectrometry applications" in various matrices and the authors' own results from reversed phase high performance chromatography (RP-HPLC) experiments [39]. It was suggested to be a universal rule. Our results do not support this claim, because the experimentally obtained LODs depend on many factors, e.g. in NAA, LODs depend on irradiation, cooling and counting regime as well as the entire composition of the sample, because low energy peaks lie on Compton background of the higher energy peaks. Even considering "interference free LODs", zigzag pattern is not followed, e.g. LOD for Dy ($Z=66$) is lower than LOD of Tb and Ho; LOD of Yb ($Z=70$) is lower than LOD of Tm, etc. [40]. It should be stressed that the same applies to activation cross sections, $\sigma_{act.}$ (the greater $\sigma_{act.}$, the lower potential LOD) for the most useful nuclear reactions for particular lanthanides do not follow the described expectations [38] because: ($\sigma_{act.(Dy)} > \sigma_{act.(Ho)} > \sigma_{act.(Tb)}$; $\sigma_{act.(Gd)} > \sigma_{act.(Tb)}$) [41].

3.2.2. Accuracy and precision

In order to validate the ICP-MS method for determination of lanthanides, BCR 670 Aquatic Plant, where the concentration of lanthanides is certified and other reference materials were used. Certified values for all reference materials together with all results obtained in this work are given in Table 3. Focusing firstly on the results obtained for BCR 670, it could be concluded that for NAA very good agreement with certified values was obtained, except Gd, which was not determined by NAA because of relatively unfavorable detection limit and spectral interference from Sm. In the case of ICP-MS, when the digestion was performed in the absence of HF, lower results than certified values were obtained for six lanthanides. When the chromatographic separation was applied, good agreement with the certified values (the uncertainty ranges of both values overlap) was obtained for La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Er and Lu, measured using ICP-MS.

Table 2
Limits of detection of analytical procedures.

Element	Limit of detection, ng g^{-1}		
	ICP-MS[a]	**NAA**[b]	**IC**[c]
La	0.1	1.5	4.8
Ce	0.1	1.4	4.8
Pr	0.1	50	4.8
Nd	0.3	15	4.8
Sm	0.1	0.2	4.8
Eu	0.1	0.1	4.8
Gd	0.1	9.2	4.8
Tb	0.1	0.4	4.8
Dy	0.1	1.4	4.8
Ho	0.1	1.8	4.8
Er	0.1	22	4.8
Tm	0.1	0.2	8.2
Yb	0.1	0.1	9.2
Lu	0.3	0.2	9.2

The detection limits calculated:

[a] As 3 standard deviation of a blank sample.
[b] After Currie [36] for 0.5 g of plant sample.
[c] According to convention suggested by Small [37].

Considering the four analytical procedures used, sample preparation according to protocol 1 followed by direct lanthanides determination using ICP-MS (I); sample preparation according to protocol 2, involving lanthanides separation prior determination using ICP-MS (II), IC-UV/VIS (III) and NAA (IV), three different situations can be distinguished:

(a) All results obtained using different methods are in satisfactory agreement (within the associated uncertainties) and are also in agreement with the certified values.
(b) The results obtained involving the matrix separation, are in satisfactory agreements with certified values, unlike those obtained without matrix separation.
(c) The results obtained by both procedures involving ICP-MS (with and without matrix separation) differ from certified value and the results obtained by NAA and IC.

The graph shown in Fig. 3 illustrates these three situations.

In the case of BCR-670 (Aquatic Plant) results for Pr, Ho, Tm and Yb obtained by ICP-MS vary significantly from the certified values (concentrations of Pr, Ho and Yb are too low and that of Tm too high) although none of the known spectral interferences could be identified so far. Unfortunately Pr, Ho and Tm were not certified in the rest of available CRMs, thus it was not possible to ascertain whether the observed deviations are typical for the method or are associated with a given matrix. Dressler et al. [18] used water desolvation-nebulizer system for the reduction of interferences. In this type of nebulizer the amount of water molecules entering the plasma could be reduced, thus reducing oxide and hydroxide formation. Unfortunately, in our work this system did not influence the obtained results, which means that other source of interference influence the results.

Interestingly, Yb concentration found in INCT MPH-2 (Mixed Polish Herbs) by ICP-MS after chromatographic separation is in agreement with the certified value, while the results obtained by direct determination using ICP-MS are significantly lower (see Table 3). In the case of INCT TL-1, both results found by ICP-MS agreed with the certified value for Yb.

As can be seen in Table 3, the precision of ICP-MS measurements, especially in its direct mode, is generally better than the precision of other methods applied during the certification.

3.2.3. General observations and the search for the origin of systematic errors

The thorough scrutiny of analytical results presented in Table 3 reveals that NAA provided accurate results practically for all investigated CRM's and for all elements whose concentrations are certified. Similarly, results obtained by IC-UV/VIS in CTA-OTL-1, INCT-TL-1 and INCT-MPH-2 in all cases are within the uncertainty of the certified values. Thus, occurrence of negative systematic errors by using ICP-MS and chromatographic separation of the lanthanides may not be due to non-quantitative recovery of individual elements.

It is worth noting that in the most of cases, ICP-MS results after chromatographic separation are higher than those obtained by direct analysis. Examples of negative systematic errors observed in direct determination by ICP-MS are: La, Tb and Lu in BCR 670; Ce, Nd and Yb in NCS DC73349; La and Ce in CTA-OTL-1.

Table 3
Concentration of lanthanides measured in CRMs.

Element	Certified value ± Uncertainty[a]	ICP-MS		NAA	IC
		Direct analysis	*After separation*		
BCR 670, Aquatic Plant, ng g^{-1}					
La	**487 ± 47**	404 ± 22	477 ± 25	532 ± 60	–
Ce	**987 ± 62**	933 ± 31	954 ± 54	943 ± 65	–
Pr	**121 ± 15**	65.0 ± 8	78 ± 14	126 ± 23	–
Nd	**473 ± 30**	455 ± 17	467 ± 25	485 ± 32	439
Sm	**94.2 ± 10.0**	85.0 ± 6.0	87.0 ± 8	98.6 ± 7.3	–
Eu	**23.2 ± 2.4**	22.3 ± 3.4	21.5 ± 5.5	23.1 ± 1.4	18.7
Gd	**97.8 ± 13.4**	85.0 ± 6.5	94.0 ± 6.5	–	98.2
Tb	**14.0 ± 1.6**	10.0 ± 0.5	12.1 ± 0.5	14.3 ± 0.8	16.5
Dy	**78.9 ± 8.8**	77.2 ± 4.9	79.3 ± 5.4	80.3 ± 6.2	76.4
Ho	**15.8 ± 2.6**	6.1 ± 0.5	7.9 ± 1.5	14.2 ± 1.1	14.2
Er	**44 ± 4.5**	42.0 ± 1.5	42.5 ± 2.6	41.3 ± 1.2	47.5
Tm	**5.70 ± 0.93**	10.1 ± 0.5	9.2 ± 1.4	5.7 ± 0.4	5.71
Yb	**39.9 ± 4.4**	23.5 ± 3.2	20.7 ± 5.7	40.7 ± 2.1	36
Lu	**6.33 ± 0.69**	4.6 ± 0.4	4.9 ± 0.8	7.2 ± 0.4	7.4
NCS DC73349, Bush Branches and Leaves, ng g^{-1}					
La	**1250 ± 60**	950 ± 23	1030 ± 138	1171 ± 148	920
Ce	**2200 ± 100**	1890 ± 70	2130 ± 236	2400 ± 280	2120
Pr	**240**	210 ± 10	177 ± 13	290 ± 24	180
Nd	**1000 ± 100**	830 ± 60	877 ± 68	1095 ± 11	850
Sm	**190 ± 20**	160 ± 20	150 ± 20	195 ± 12	150
Eu	**39 ± 3**	26 ± 1	27 ± 2	39 ± 3	25
Gd	**190**	160 ± 20	167 ± 24	–	200
Tb	**25 ± 3**	18 ± 1	17 ± 1	29 ± 3	24
Dy	**130**	110 ± 10	120 ± 11	134 ± 10	120
Ho	**33**	13 ± 2	14 ± 2	36 ± 3	20
Er	**–**	41 ± 3	63 ± 3	56 ± 26	58
Tm	**–**	2 ± 0.7	7 ± 1	9 ± 1	7
Yb	**63 ± 9**	34 ± 2	45 ± 5	69 ± 8	47
Lu	**11**	0.5 ± 0.1	8 ± 1	10 ± 2	9
CTA-OTL-1, Oriental Tobacco Leaves, ng g^{-1}					
La	**1440 ± 160**	1083 ± 30	1397 ± 113	1370 ± 100	1360 ± 200
Ce	**2690 ± 300**	1600 ± 70	2490 ± 570	2690 ± 70	2400 ± 300
Pr	**–**	182 ± 11	180 ± 15	261 ± 26	–
Nd	**–**	704 ± 12	827 ± 61	825 ± 83	830 ± 26
Sm	**229 ± 52**	131 ± 13	146 ± 8	201 ± 12	200 ± 44
Eu	**38 ± 9**	38 ± 6	35 ± 3	40 ± 4	41 ± 9
Gd	**–**	153 ± 10	158 ± 14	127 ± 8	122 ± 5
Tb	**32 ± 6**	15 ± 1	18 ± 2	33 ± 9	26 ± 4
Dy	**–**	101 ± 5	134 ± 9	157 ± 8	87 ± 19
Ho	**–**	17 ± 6	17 ± 2	16 ± 4	–
Er	**–**	46 ± 1	68 ± 1	63 ± 12	23 ± 15
Tm	**–**	1.4 ± 0.4	7.8 ± 1.2	7.7 ± 1.5	–
Yb	**130**	50 ± 5	117 ± 23	60. ± 1	–
Lu	**–**	1.9 ± 0.3	8.2 ± 1.0	8.7 ± 1.4	–
INCT TL-1, Tea Leaves, ng g^{-1}					
La	**1000 ± 70**	895 ± 26	936 ± 47	1018 ± 58	999 ± 116
Ce	**790 ± 76**	703 ± 11	741 ± 23	816 ± 11	826 ± 181
Pr	–	192 ± 6	184 ± 12	220 ± 47	186 ± 42
Nd	**810**	783 ± 12	765 ± 34	826 ± 127	743 ± 75
Sm	**177 ± 22**	152 ± 16	164 ± 19	179 ± 14	169 ± 23
Eu	**49.9 ± 9.4**	51 ± 4	47.4 ± 6.5	48 ± 3	40 ± 7
Gd	–	185 ± 14	173 ± 21	–	188 ± 41
Tb	**26.5 ± 2.4**	24.7 ± 0.9	23.1 ± 1.5	27.3 ± 1.2	27.3 ± 12
Dy	–	156 ± 5	159 ± 10	151 ± 14	71.3 ± 30
Ho	–	29 ± 2	25.6 ± 5.6	22 ± 1.6	14.8 ± 4
Er	–	91 ± 3	88.5 ± 8.5	70 ± 4	69 ± 17
Tm	**17**	11.5 ± 1.8	12.6 ± 2.4	18.0 ± 5.1	17 ± 11
Yb	**118 ± 19**	100 ± 8	106 ± 9	96 ± 5	95 ± 40
Lu	**16.8 ± 2.4**	14.6 ± 1.4	15.6 ± 1.9	17.3 ± 1.4	15.3 ± 3

Table 3 (*continued*)

Element	Certified value ± Uncertainty[a]	ICP-MS		NAA	IC
		Direct analysis	*After separation*		
INCT MPH-2, Mixed Polish Herbs, ng g^{-1}					
La	**571 ± 46**	523 ± 85	460 ± 71	613 ± 45	489 ± 76
Ce	**1120 ± 100**	966 ± 202	917 ± 34	1065 ± 162	996 ± 120
Pr	**–**	86 ± 14	75 ± 7	141 ± 12	97
Nd	**457 ± 91**	420 ± 43	381 ± 9	511 ± 36	448 ± 26
Sm	**94.4 ± 8.2**	69.6 ± 13.9	76.5 ± 1.9	93.7 ± 14	83 ± 10
Eu	**15.7 ± 1.8**	18.0 ± 3	15.3 ± 1.97	16 ± 1	15.6 ± 1.0
Gd	**–**	88 ± 11	77 ± 8	–	61.6 ± 13.6
Tb	**13.5 ± 1.1**	4.8 ± 1.3	6.3 ± 1.6	13.7 ± 0.7	14.9 ± 1.9
Dy	**–**	47 ± 11	55 ± 3	66 ± 1	45.1 ± 11.2
Ho	**–**	7 ± 2	36 ± 7	18 ± 4	21.0 ± 7.4
Er	**–**	19 ± 2	34 ± 2	29 ± 3	32.1 ± 3.0
Tm	**–**	–	4 ± 0.2	7 ± 0.1	10.4 ± 1.4
Yb	**52.7 ± 6.6**	19.9 ± 2.0	47.8 ± 5.9	51.0 ± 12	49.6 ± 19.3
Lu	**9 ± 1.5**	–	5.1 ± 0.7	7.9 ± 0.9	9.0 ± 0.6

[a] U express as expanded uncertainty (coverage factor $k=2$) [17].

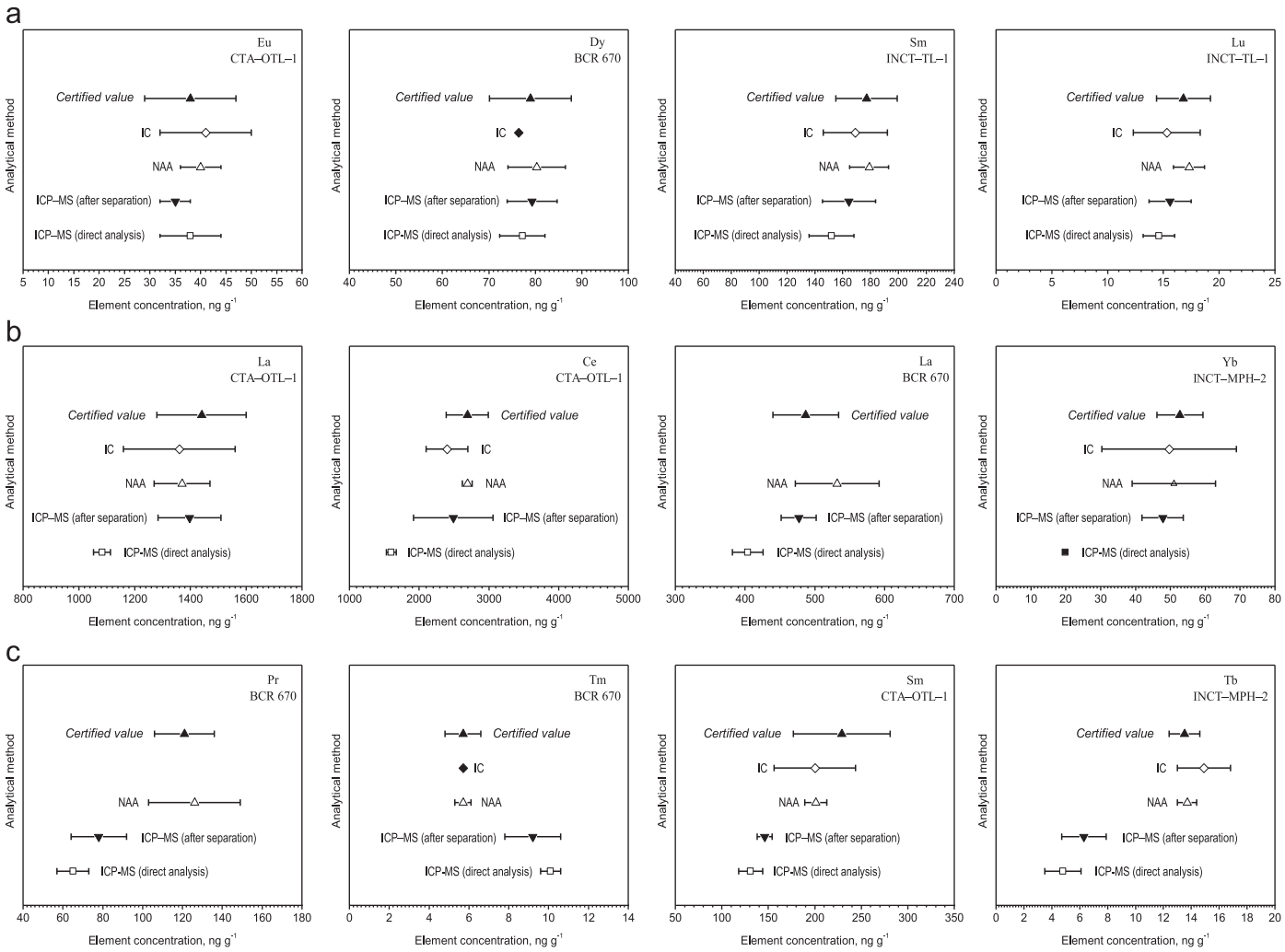

Fig. 3. Selected examples of various situations concerning the results: (a) ICP-MS results, by using both sample preparation protocols, agreed with the certified value as well as with the results obtained by NAA and IC-UV/VIS. (b) All results obtained for the solutions obtained accordingly to protocol 2 (group separation involved) are in agreement with the certified value (Note: direct ICP-MS do not provided agreeable results). (c) Results obtained by ICP-MS, for the solutions obtained accordingly to both protocols, did not agree with certified value.

Matrix effects are a potential source of systematic errors. According to Table 1 the content of major and some minor elements in the analyzed CRMs vary broadly. Unfortunately, the analogous data for BCR 670 are not available. One should note that the INCT-TL-1 is the only material for which direct ICP-MS results (with single slight deviation in the case of La) agree well

with the certified values. It is worth noting that INCT-TL-1 has silicon content in an order of magnitude lower than other CRMs listed in Table 1.

To check whether the formation of tiny particles of silica and perhaps also other insoluble compounds could be the reason for some systematic errors in ICP-MS measurements, the following experiments were carried out: 0.55 g samples of CTA-OTL-1 were digested under the conditions described in protocol 1. The solution was evaporated, taken up in 8 mol L^{-1} or 0.5 mol L^{-1} HNO_3, and filtered through quartz filter (Whatman QM). The filter, together with standards of La, Ce, Eu, Co, K, Rb, Th, and Zn was irradiated in a nuclear reactor at a thermal neutron flux of approximately 10^{14} n cm^{-2} s^{-1} for 30 min and measured by γ-ray spectrometry. According to Table 4 quite considerable and variable amounts of various elements are adsorbed on particulate matter under those conditions. The variations are considerable within the lanthanide series, i.e., individual lanthanide behaves in an individual manner. This phenomenon can be the origin of some negative systematic errors observed. There is the possibility of adsorption on tubing walls etc. and, perhaps, different ability of lanthanides to be ionized in the plasma in comparison with ions present in solution.

3.3. Evaluation of tentative recommended values

Good agreement of analytical results obtained for INCT-TL-1 (Fig. 3) by all methods applied in this study justifies an attempt to propose tentative recommended value (TRV) for lanthanide elements not certified in this material. In the case of seven elements (Pr, Nd, Gd, Dy Ho, Er, and Tm) TRVs were calculated as arithmetic mean of the results listed in Table 3, which were obtained by using different techniques. The proposed TRVs ($\pm$U), where U is expanded uncertainty ($k=2$) are as follows:

Pr : $\overline{X} = (196 \pm 64)$ ng g^{-1}
Nd : $\overline{X} = (779 \pm 152)$ ng g^{-1}
Gd : $\overline{X} = (182 \pm 48)$ ng g^{-1}
Dy : $\overline{X} = (155.3 \pm 17.9)$ ng g^{-1}
Ho : $\overline{X} = (25.6 \pm 6.2)$ ng g^{-1}
Er : $\overline{X} = (79.6 \pm 19.6)$ ng g^{-1}
Tm : $\overline{X} = (14.0 \pm 5.9)$ ng g^{-1}

Data for Dy and Ho obtained by IC UV/VIS were not included because the ratio of Y content to neighboring elements in the sample was more than 4. In this case the Ho-Y-Dy peaks cannot be completely separated and inaccurate values are expected. Data for Tm obtained by IC UV/VIS were also not included because of very poor precision.

Under the above described conditions, chondrite normalized plot for lanthanides in INCT-TL-1 (in which certified values are presented together with TRV's) is shown in Fig. 4 for the naturally occurring lanthanides. The values used for normalization were taken from Anders and Grevesse [42]. As can be seen, except the negative anomalies of Ce and Eu that are common for such plots because of natural existence of the additional stable valencies +4 and +2 of Ce and Eu, respectively (in addition to +3 valency), the plot profile has rather regular shape, which indirectly supports the validity of TRV's. In comparison with similar plots for most of the rocks and shales [43,44], fly-ash [45] etc., the depletion of lanthanides content in INCT-TL-1 in the region of Tb-Tm is worth noting.

Table 4
Amount of elements retained on filter, after passing the digest solutions of the Oriental Tobacco Leaves (CTA-OTL-1).

Element	Range of the mass retained*, %
La	5.9÷13.9
Ce	7.8÷17.6
Eu	18.2÷36.4
Co	6.1÷7.3
K	1.5÷2.5
Rb	8.9÷9.4
Th	19.2÷27.3
Zn	1.3÷1.9

* The range indicate the lower and higher values obtained for 3 parallels sample digestion and filtration.

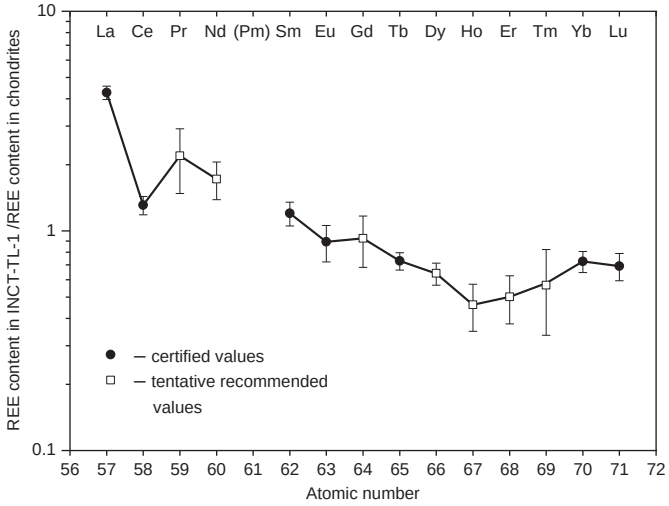

Fig. 4. Chondrite normalized pattern for lanthanides in Tea Leaves (INCT-TL-1). Full symbols—certified values, open symbols—tentative recommended values, with associated uncertainties.

4. Conclusions

Several certified reference materials were analyzed in order to evaluate the accuracy of applied analytical procedures. Selected instrumental techniques, NAA, IC and ICP-MS were applied after quantitative and selective isolation of lanthanide group by ion exchange chromatography, and their potential for the determination of trace amounts of all lanthanides in plant materials was proved. Moreover, the possible simplification of sample preparation (digestion with $HNO_3+H_2O_2$ mixture) followed by ICP-MS measurements was evaluated. In the last case, several problems with respect to accuracy of results were encountered. The formation of tiny particular matter (most probably silica) in the solution of digested sample and its ability to act as a sorbent for lanthanides was experimentally justified. Thus, the sample preparation protocol involving lanthanides separation is required in order to achieve good accuracy in ICP-MS determinations.

In the case of INCT-TL-1 (CRM with the lowest silicon content), good agreement of results by all employed analytical procedures was obtained. Thus, it was possible to propose tentative recommended values (TRV's) for lanthanides not certified in this CRM.

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