



وزارة التعليم العالي والبحث العلمي
جامعة القادسية – كلية العلوم
قسم الكيمياء

Determination of lan thanides and Actinides by inductively coupled plasma mass

بحث تقدم به الطالبة (نور عصام جاسم العوادي) الى مجلس
كلية العلوم / قسم الكيمياء وهو جزء من متطلبات شهادة
البكالوريوس علوم الكيمياء .

بأشراف التدريسي

م.د. حسن محمد اللعبي

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صدق الله العلي العظيم

سورة القصص (الاية ٧٧)

الاهداء

الى كل من صحبني في رحلتي هذا البحث داعما ومشجعا وناصحا ومرشدا صابرا

ومضحيا...

الى والدي ... الذي مرعاني وانا رلي دريبي .

الى امي . التي احاطتني بعطفها وحنانها

الى زوجي وحيبي الغالي

الى كل شهيد وجريح دافع من اجل تحرير العراق

الى كل المدافعين عن حقوق الانسان

اهدي هذا الجهد المنواضع

الباحث

نور عصام جاسم

شكر وتقدير

لا يسعني بعد ان اتم الله بنعمته عليّ في انجاز كتابة البحث الا

ان اتقدم بالشكر والامتنان الى استاذي المشرف على

البحث (م. د حسين محمد لعبي) الذي واكب انجاز هذا
البحث و تفضل علي بتوجيهاته السخية وملاحظاته السديدة لتقويم هذا
الجهد واخراجه على ما هو عليه فجزاه الله عني خيرا الجزاء كما اتقدم
بالشكر والعرفان الى اساتذتي الكرام حبا واحتراما واعتزازا و
عرفانا بالجميل كذلك اتقدم بوافر شكري لزملائي في كلية العلوم
قسم الكيمياء .

1.Introduction

1.1Inductively:

Coupled Plasma Mass Spectrometry or ICP-MS is an analytical technique used for elemental determinations. The technique was commercially introduced in 1983 and has gained general acceptance in many types of laboratories. Geochemical analysis labs were early adopters of ICP-MS technology because of its superior detection capabilities, particularly for the rare-earth elements (REEs). ICP-MS has many advantages over other elemental analysis techniques such as atomic absorption and optical emission spectrometry, including ICP Atomic Emission Spectroscopy (ICP-AES), including:

- Detection limits for most elements equal to or better than those obtained by Graphite Furnace Atomic Absorption Spectroscopy (GFAAS).
- Higher throughput than GFAAS
- The ability to handle both simple and complex matrices with a minimum of matrix interferences due to the high-temperature of the ICP source
- Superior detection capability to ICP-AES with the same sample throughput
- The ability to obtain isotopic information .

An ICP-MS combines a high-temperature ICP (Inductively Coupled Plasma) source with a mass spectrometer. The ICP source converts the atoms of the elements in the sample to ions. These ions are then separated and detected by the mass spectrometer^[1].



Figure 1 shows a schematic representation of an ICP source in an ICP

MS. Argon gas flows inside the concentric channels of the ICP torch. The RF load coil is connected to a radio-frequency (RF) generator.

As power is supplied to the load coil from the generator, oscillating electric and magnetic fields are established at the end of the torch. When a spark is applied to the argon flowing through the ICP torch, electrons are stripped off of the argon atoms, forming argon ions. These ions are caught in the oscillating fields and collide with other argon atoms, forming an argon discharge or plasma^[2].

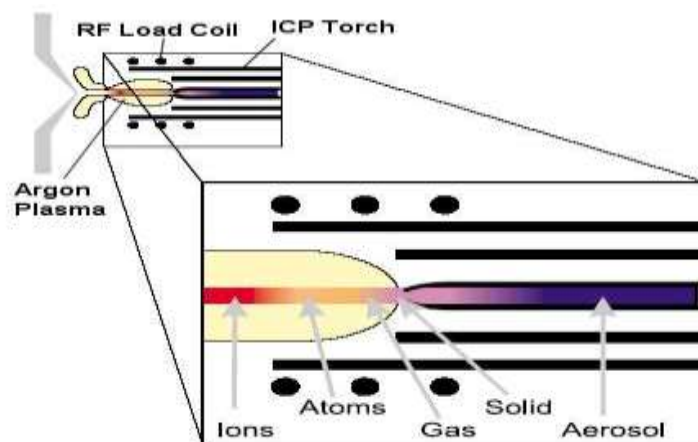


Figure 1. The ICP Torch showing fate of the sample. (Figure reproduced with permission from PerkinElmer, Inc.)

Figure 1 shows a schematic representation of an ICP source in an ICP-MS. Argon gas flows inside the concentric channels of the ICP torch. The RF load coil is connected to a radio-frequency (RF) generator. As power is supplied to the load coil from the generator, oscillating electric and magnetic fields are established at the end of the torch. When a spark is applied to the argon flowing through the ICP torch, electro

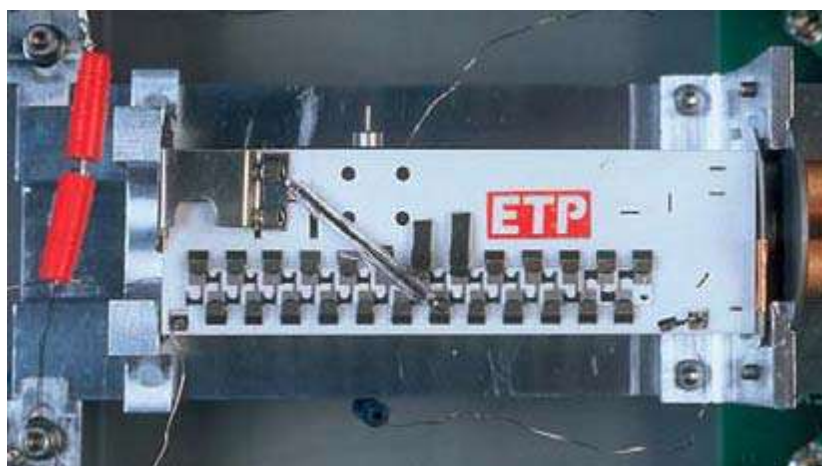


Figure2. Discrete dynode detector used on the ELAN ICP-MS systems. courtesy of PerkinElmer, Inc.

1-2. LANTHANIDES & ACTINIDES NOTE.

Lanthanide	Chemistry	Presents	NO	Problems	Since	Thorough	Yearly	Lectures	Everyone
La	Ce	Pr	Nd	pr	Sm	Tu	ye	Lu	Eu

Although	Theorists	Unusual	Careful	Experiments	New	More	Believe
AC	Th	U	Cf	ES	NO	md	Bk

1-2-1.Objectives

Upon finishing this course the student can successfully:

- Recognize the characteristics of the 4f, 5f elements.
- Distinguish between characteristics of the 4f, 5f elements and 3d elements.
- Understand the different types of radioactive derogations and the extent of its ionization and penetration ability.
- Recognize how to treat and prevent dangerous radioactive elements.
- Recognize the peaceful uses of radioactive isotopes, especially in the medical field and farm.
- Recognize how to make chemical reactions of these elements and their compounds.
- Recognize the electronic and magnetic qualities of these compounds and their colors

1-2-2.Characteristics of the Rare Earth Elements

1. Occur together in nature, in mineralst, e.g. monazite (a mixed rare earth phosphate).
2. Very similar chemical properties. Found combined with non-metals largely in the $+3$ oxidation state, with little tendency to variable valence.
3. Small difference in solubility / complex formation etc. of M^{+3} are due to size effects.

Traversing the series $r(M^{+3})$ steadily decreases – the lanthanide contraction.

Difficult to separate and differentiate, e.g. in 1911 James performed 15000recrystallizations to get pure $Tm(BrO_3)$

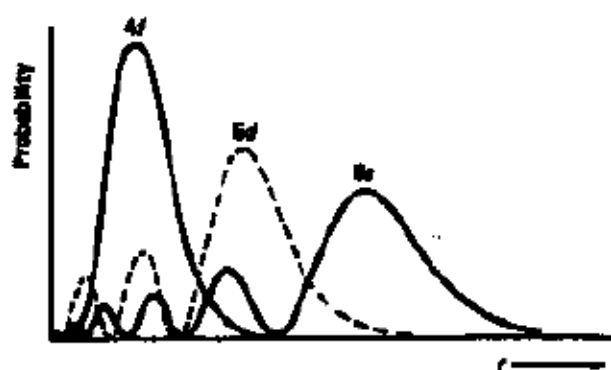
$$V_{eff} = -\frac{Z_{eff}}{r} + \frac{l(l+1)}{2r^2} \quad (a.u.)$$

Coulombic & Centrifugal potentials

1-2-3.The Effective Electron Potential:

- Large angular momentum for an f-orbital ($l = 3$).
- Large centrifugal potential tends to keep the electron away from the nucleus.
 - ☒ Aufbau order.
- Increased Z increases Coulombic attraction to a larger extent for smaller n due to a proportionately greater change in Z_{eff} .
 - ☒ Reasserts Hydrogenic order.

This can be viewed empirically as due to differing penetration effect



Radial Wavefunctions $P_{n,l}$ for 4f, 5d, 6s in Ce

Though only for the next atom, Ce ($Z = 58$) is the 4f electron of sufficiently high binding energy to appear in the ground state configuration.

Which Elements are d-block or f-block?

Most current Periodic tables have:-

- La as first 5d transition element
- Ac as first 6d transition element

Reasons?

Possibly erroneous (early) interpretation of atomic spectra – misleading electronic configurations?

Some ground state electronic configurations:

Calcium [Ar]4s²

Scandium [Ar]4s³d¹

Strontium [Kr]5s²

Yttrium [Kr]5s²4d¹

Barium [Xe]6s²

Lanthanum [Xe]6s²5d¹

Ytterbium [Xe]6s²4f¹⁴

Lutetium [Xe]6s²4f¹⁴5d¹

Radium [Rn]7s²

Actinium [Rn]7s²6d¹

Nobelium [Rn]7s²5f¹⁴

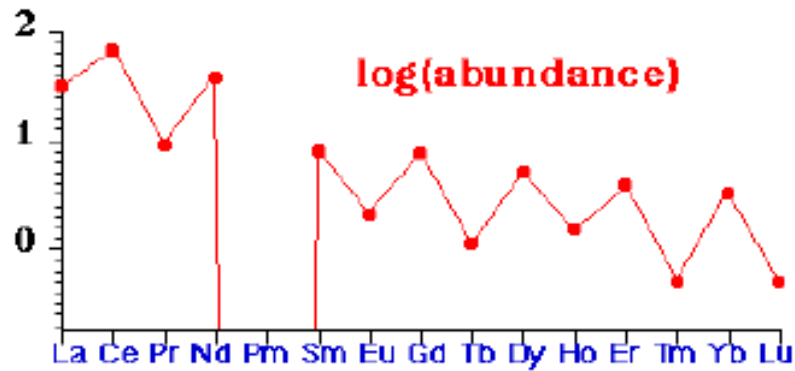
Lawrencium [Rn]7s²5f¹⁴6d¹

In each case: differentiation by (n-1)d¹ - as expected for the start of a transition series.

Lutetium and Lawrencium are just as good candidates to be the first elements of the 3rd and 4th transition series as Lanthanum and Actinium.

Some suggestions why Lu might best be regarded as the first 5d transition element.

- Periodic Trends in Various Properties.
- Structures of Metal, Metal Sesquioxide (M₂O₃) and Metal Chloride (MCl₃).
- Similarities for Sc, Y, Lu



THE ACTINIDES

1. Only Actinium, Thorium, Protactinium & Uranium occur naturally (i.e. $Z \leq 92$).
2. Actinium & Protactinium occur only in trace amounts.
3. Neptunium & Plutonium occur in uranium minerals in minute amounts - not appreciated
4. until after they had been synthesized that the synthesis route might occur naturally!
5. All isotopes of all the actinides are radioactive.
6. Most of the longer-lived isotopes decay by α -emission. Both Thorium and Uranium are.

1)Thorium

- ❖ Widely dispersed, accounts for > 3 ppm of the earth's crust.
- ❖ Natural Thorium is essentially 100% ^{232}Th .
- ❖ Occurs in monazite [with the rare earths] and in uranothorite [a mixed Th, U silicate].
- ❖ Obtained as ThO_2 , thoria, from mineral extraction process.
- ❖ Used as 99% ThO_2 / 1% CeO_2 in thoria gas mantles.

2)Uranium

- ❖ Widely distributed - found scattered in the faults of old igneous rocks.
- ❖ Natural Uranium is 99.27% ^{238}U & 0.72% ^{235}U .
- ❖ Obtained usually as UO_2 .
- ❖ Used for nuclear fuel, and on a smaller scale for colouring glass/ceramics.

Basic Features of Nuclear Structure & Chemistry and Radiochemistry

All Radon isotopes are short half-life α -emitters (but give rise to short-lived β -emitters). Radongas is derived from Thorium content in granite minerals - hazard in igneous areas.

Actinium and Protactinium occur in uranium ores in trace amounts, because of their participation in Actinium Decay series (from ^{235}U).

Synthesis of Trans-Uranium Elements – **bombardment** techniques.

Are there any **uses** for trans-Uranium elements? ⁽⁷⁾

Plutonium:

- ^{239}Pu - produced from ^{238}U by neutron capture in all nuclear reactors.
- Acts as nuclear fuel in fast-breeder reactors.
- Processed for nuclear weapon applications.
- Used as a compact energy source due to the heat from α -decay.
- N.B. α -emission is harmless, unless the emitter is ingested.
- Deep-sea diving suits are heated by ca. 750g of ^{238}Pu
- Combined with PbTe thermoelectric - totally reliable electricity.
- Used in Apollo space missions.

- Human heart pacemakers. (8)

Americium:

- ^{241}Am is used as the α -emission source in smoke alarms

Actinide Metals

Preparation

General method for all Actinides:

Reduction of AnF_3 or AnF_4 with vapours of Li, Mg, Ca or Ba at 1100 - 1400°C

Highly Electropositive.

Typically react with:

- air tarnishing
- boiling water or dilute acid releasing Hydrogen
- most non-metals in direct combination

Structures :

Very dense metals (e.g. $\text{U} = 19 \text{ g cm}^{-3}$) with distinctive structures, e.g. Plutonium has at least 6

General Observations (comparisons with Lanthanides)^[3]

Electronic Configurations of Actinides are not always easy to confirm.

- Atomic spectra of heavy elements are very difficult to interpret in terms of configuration. Competition between $5f^n 7s^2$ and $5f^{n-1} 6d^1 7s^2$ configurations is of interest.

- For early actinides promotion 5f 6d occurs to provide more bonding electrons. Much easier than corresponding 4f 5d promotion in lanthanides.
- Second half of actinide series resemble lanthanides more closely.

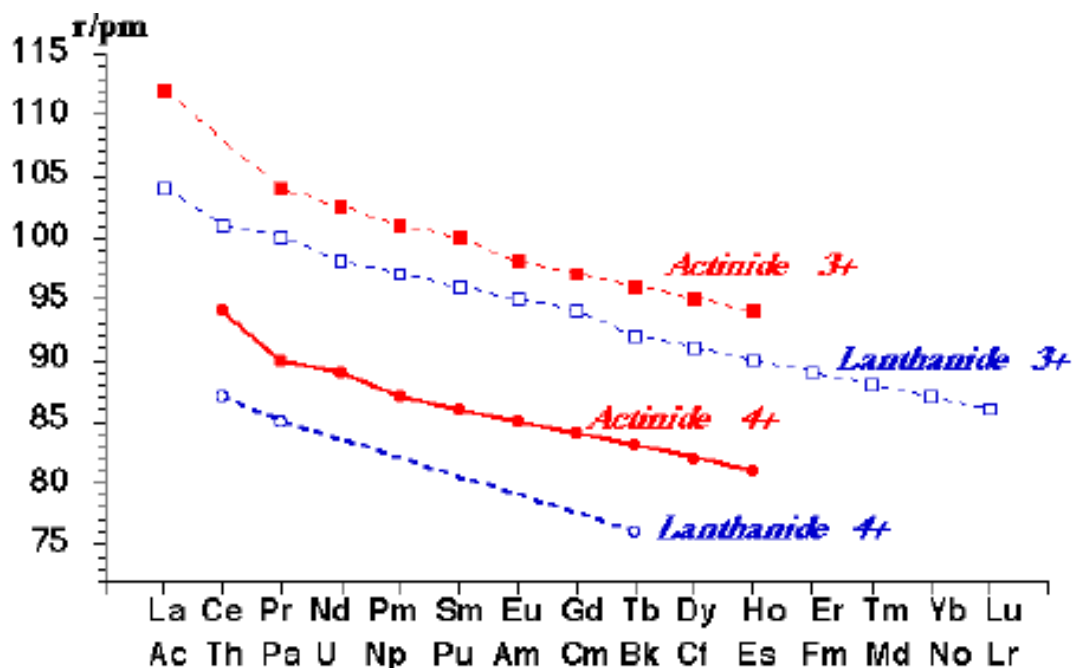
5f orbitals have greater extension wrt 7s and 7p than do 4f relative to 6s and 6p orbitals, e.g. ESR evidence for covalent bonding contribution in UF_3 , but not in NdF_3 .

5f / 6d / 7s / 7p orbitals are of comparable energies over a range of atomic numbers, especially U–Am

- Tendency towards variable valency.
- Greater tendency towards (covalent) complex formation than for lanthanides, including complexation with π -bonding ligands.
- Electronic structure of an element in a given oxidation state may vary between compounds and in solution.
- Often impossible to say which orbitals are being utilized in bonding.

Ionic Radii of ions show a clear "Actinide Contraction"

- Actinide $3+$ or $4+$ ions with similar radii to their Lanthanide counterparts show similarities in properties that depend upon ionic radius (9)



2. Experimental and Reagent .

2.1. Apparatus

A SCIEX ELAN 6000 ICP-MS (Perkin–Elmer, USA), as described elsewhere (10), was used for all data acquisition. It was run in sequential mode, peak hopping to masses of interest. A cross flownebulizer served as a sprayer for sample introduction. In an effort to avoid conductive coupling between the load coil and the plasma, both ends of the load coil were biased with high voltage of equal amplitude but opposite phase. No modification was made to the load coil configuration. The sampling depth between the sampler tip and top coil was fixed at 9 mm for all data acquisition. The coolant gas flow rate and the auxiliary gas flow rate were fixed at 15.0 and 1.0 l/min, respectively, throughout the experiment. The radio frequency (R.F.) power (1150 W) and the aerosol gas flow rate (1.0 l/min) were optimized using 10 ppb Ce solution for maximum Ce^+ signal and the minimum possible CeO^+/Ce^+ ratio . (11)

2.2. Reagent

De-ionized water (Millipore, USA) was used for the preparation of solutions. Indium (1000ppm) and Thorium as thorium nitrate were procured from Merck and Indian Rare Earth Ltd., respectively. All the lanthanides 10 ppm each and Ba (1000 ppm) standard solution were purchased from High-Purity Standards, USA and diluted to desired concentrations by 1% HNO₃. Certified rock samples AGV-1 and G-2 used for the determination of lanthanides and Ba were obtained from United State Geological Survey. Trace Pure grade HNO₃ and Supra grade HF from Merck were used for digestion and dissolution of rock samples. Finally, all the solutions and samples were prepared in 1% HNO₃ for ICP-MS analysis

3. Results and discussion.

It is always advisable that the isotope of an element in a sample used for ICP-MS analysis should have preferably no isobaric interference from atomic isotopes or polyatomic ions. If all the isotopes of an element show isobaric overlaps, then the isotope chosen for analysis should be the one with least overlaps. Lanthanides are the elements that form strongest oxides in the plasma^[6]. The oxide yield is higher for lighter lanthanides than that of heavier lanthanides. As the *m/z* of these high yielding oxides of lighter lanthanides is same as that of heavier lanthanides, they cause serious spectroscopic overlaps over the mass number of heavier lanthanides. Ba shows less oxide or hydroxide yield than lanthanides, but it is normally found at higher concentration in natural samples compared to the lanthanides. This leads to significant interference from the barium oxide and hydroxide overlap with some middle and heavier lanthanides. Keeping these points in mind, asterisk isotopes of lanthanides in Table 1 were accordingly chosen for the ICP-MS analysis in this work. In and Th were added in the samples as internal standard and oxide / hydroxide correction standard, respectively. The use of Th as an oxide and hydroxide correction standard has been reported earlier where both oxide and hydroxide species were normalized by ThO. Our

study shows that the ratio of $\text{ThO}^+/\text{ThOH}^+$ does not remain constant when the optimized parameters like aerosol gas flow rate and RF power were changed (Fig. 1a,b). (12) (13) (14) (15)

Table 1 : Spectroscopic interferences on selected lanthanides isotopes in their ICP-MS analysis

Lanthanide	Mass	% Abundance	Interferences
La	139*	99.91	–
Ce	140*	88.48	–
Pr	141*	100.0	–
Nd	143*	12.18	–
	150	5.64	$^{134}\text{Ba}^{16}\text{O}$, ^{150}Sm
Sm	147*	15.00	$^{130}\text{Ba}^{16}\text{OH}$
	152	26.7	$^{136}\text{Ba}^{16}\text{O}$, $^{136}\text{Ce}^{16}\text{O}$, $^{135}\text{Ba}^{16}\text{OH}$, ^{152}Gd
	154	22.7	$^{138}\text{Ba}^{16}\text{O}$, $^{138}\text{La}^{16}\text{O}$, $^{138}\text{Ce}^{16}\text{O}$, $^{137}\text{Ba}^{16}\text{OH}$, ^{154}Gd
Eu	151*	47.8	$^{135}\text{Ba}^{16}\text{O}$, $^{134}\text{Ba}^{16}\text{OH}$
	153	52.2	$^{137}\text{Ba}^{16}\text{O}$, $^{136}\text{Ba}^{16}\text{OH}$
Gd	156	20.47	$^{140}\text{Ce}^{16}\text{O}$, $^{139}\text{La}^{16}\text{OH}$, ^{156}Dy
	157*	15.65	$^{141}\text{Pr}^{16}\text{O}$, $^{140}\text{Ce}^{16}\text{OH}$
Tb	159*	100.0	$^{143}\text{Nd}^{16}\text{O}$, $^{142}\text{Ce}^{16}\text{OH}$, $^{142}\text{Nd}^{16}\text{OH}$
Dy	161	18.9	$^{145}\text{Nd}^{16}\text{O}$, $^{144}\text{Nd}^{16}\text{OH}$, $^{144}\text{Sm}^{16}\text{OH}$
	162	25.5	$^{146}\text{Nd}^{16}\text{O}$, $^{145}\text{Nd}^{16}\text{OH}$
	163*	24.9	$^{147}\text{Sm}^{16}\text{O}$, $^{146}\text{Nd}^{16}\text{OH}$
Ho	165*	100.0	$^{149}\text{Sm}^{16}\text{O}$, $^{148}\text{Nd}^{16}\text{OH}$, $^{148}\text{Sm}^{16}\text{OH}$
Er	166	33.6	$^{150}\text{Nd}^{16}\text{O}$, $^{150}\text{Sm}^{16}\text{O}$, $^{149}\text{Sm}^{16}\text{OH}$
	167*	22.95	$^{151}\text{Eu}^{16}\text{O}$, $^{150}\text{Nd}^{16}\text{OH}$, $^{150}\text{Sm}^{16}\text{OH}$
	168	26.80	$^{152}\text{Sm}^{16}\text{O}$, $^{152}\text{Gd}^{16}\text{O}$, $^{151}\text{Eu}^{16}\text{OH}$
Tm	169*	100.0	$^{153}\text{Eu}^{16}\text{O}$, $^{152}\text{Sm}^{16}\text{OH}$, $^{152}\text{Gd}^{16}\text{OH}$
Yb	171*	14.3	$^{155}\text{Gd}^{16}\text{O}$, $^{154}\text{Sm}^{16}\text{OH}$, $^{154}\text{Gd}^{16}\text{OH}$
	174	31.8	$^{158}\text{Gd}^{16}\text{O}$, $^{158}\text{Dy}^{16}\text{O}$, $^{157}\text{Gd}^{16}\text{OH}$, ^{174}Hf
Lu	175*	97.41	$^{159}\text{Tb}^{16}\text{O}$, $^{158}\text{Gd}^{16}\text{OH}$

* Isotopes having no or minor interferences selected for qualitative analysis. The remaining isotopes having severe interferences were used for isotope ratio measurement.

Element	Line(nm)	Interfering	Instrumetal	DoL inppb
La	333.749	?	10	ppb
Ce	394.275	?	70	Ppb

Pr	390.844	?	40	ppb
Nd	406.109	?	100	Ppb

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Sm	359.260	?	40	Ppb
Cd	214.438	Fe	3	ppb

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CONTENTS

Abstract

Determination of lanthanides by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using modified mathematical correction method has been studied. Normally, the ICP-MS analysis of middle and heavier lanthanides becomes difficult by severe spectroscopic overlap of M^* , MO^+ or MOH^+ ions from lighter lanthanides and Ba. A correction method based on a single element oxide yield measurement, is a simple approach to correct for the above spectroscopic overlaps. But the uncertainty in the oxide and hydroxide yields measurement of lanthanides and barium over a long period of time can lead to inaccurate results even under fixed plasma conditions. To correct this, thorium was adopted as an oxide and hydroxide correction standard. Using a ratio of lanthanide oxide yield to thorium oxide yield, the lanthanide correction factors (LCF) were established and incorporated in the mathematical correction scheme. The same factors were also established for hydroxide correction. The proposed modified correction scheme was applied to the determination of lanthanides by ICP-MS from the USGS Standard Rock samples AGV-1 and G2. The results are in good agreement with the reported values are

La = 139 ,Ce =140, Pr = 141 , Nd = 143/150 , Sm = 147 , Eu = 151 , Gd =156 /157 , Tb =159 , Dy =161/ 162 /163, Er =166 /167 ,Tm =169 , Yb = 171/ 174 , Lu = 175 , the mass and the %Abundance respectively , 99.91 , 88.84 , 100.0 , 12.18 , 5.64 , 22.7 , 47.8 , 52.2 , 20.47 , 15.65 , 100.0 , 18.9 , 25.5 , 24.9 , 33.6 , 22.95 , 26.80 , 100.0 , 14.3 , 31.8 , 97.41 While element of La = 333.749 , Ce = 394.275 , Pr = 390.844 , Nd = 406.109 , Sm = 359.260 , Cd = 214.438 (nm) and the Instrumental respectively 10 , 70 , 40 , 100 , 40 , 3

References

1. [Author: Ruth E. Wolf, Ph.D., Research Chemist, USGS/CR/CICT, March 2005]
2. www.mri.psu.edu/mcl Henry Gong 312 HoslerBldg 865-1981 hxg3@psu.edu
3. www.alchemyst.f2o.org
4. S.H. Ke, L.S. Huang, J.S. Huang, K.C. Lin, Flowinjection inductively coupled plasma mass spectrometer incorporated with an ultrasonic nebulizer membrane dryer: application to trace lead detection in aqueous solution and sea water, *Appl. Spectrosc.* 55 (2001) 604–610.
5. Lobinski R, Schaumlöffel D, Szpunar J. Mass spectrometry in bioinorganic analytical chemistry. *Mass Spectrom. Rev.* 2006; **25**: 255, DOI: 10.1002/mas.20069.
6. Rosen AL, Hieftje GM. Inductively coupled plasma mass spectrometry and electrospray mass spectrometry for speciation analysis: applications and instrumentation. *Spectrochim. Acta, Part B-Atomic Spectrosc.* 2004; **59**: 135, DOI: 10.1016/j.sab.2003.09.004.
7. Ray SJ, Andrade F, Gamez G, McClenathan D, Rogers D, Schilling G, Wetzel W, Hieftje GM. Plasma-source mass spectrometry for speciation analysis: state-of-the-art. *J. Chromatogr., A* 2004; **1050**: 3, DOI: 10.1016/j.sab.2003.09.004.
8. Jarvis KE, Gray AL, Houk RS. *Handbook of Inductively Coupled Plasma Mass Spectrometry*. Blackie: Glasgow, London, 1992.
9. Montaser A. *Inductively Coupled Plasma Mass Spectrometry*. Wiley-VCH: New York, 1998.
10. Lobinski R, Schaumlöffel D, Szpunar J. Mass spectrometry in bioinorganic analytical chemistry. *Mass Spectrom. Rev.* 2006; **25**:
11. Rosen AL, Hieftje GM. Inductively coupled plasma mass spectrometry and electrospray mass spectrometry for speciation analysis: applications and instrumentation. *Spectrochim. Acta, Part B-Atomic Spectrosc.* 2004; **59**: 135, DOI:

- 10.1016/j.sab.2003.09.004.
12. N.M. Raut et al. / *Spectrochimica Acta Part B* 58 (2003) 809–822 .
 13. F.E. Lichte, A.L. Meier, J.G. Crock, Determination of rare earth element in geological material by inductively coupled plasma mass spectrometry, *Anal. Chem.* 59 (1987) 1150–1157s.
 14. D.J. Douglas, J.B. French, An improved interface for inductively coupled plasma mass spectrometry, *Spectrochim. Acta Part B* 41 (1986) 197–204.
 15. G. Horlick, S.H. Tan, M.A. Vaughan, C.A. Rose, The effect of plasma operating parameters on analyte signals in inductively coupled plasma mass spectrometry, *Spectrochim. Acta Part B* 40 (1985) 1555–1572.
 16. M.A. Vaughan, G. Horlick, S.H. Tan, Effect of operating parameters on analyte signals in inductively coupled plasma mass spectrometry, *J. Anal. At. Spectrom.* 2 (1987) 765–772.
 17. Stewart II, Olesik JW. The effect of nitric acid concentration and nebulizer gas flowrates on aerosol properties and transport rates in inductively coupled plasma sample introduction. *J. Anal. At. Spectrom.* 1998; **13**: 1249, DOI: 10.1039/a804966a.
 18. J.K. Aggarwal, M.B. Shabani, M.R. Palmer, K. Vala Ragnarsdottir, Determination of the rare earth elements in aqueous samples at sub ppt levels by inductively coupled plasma mass spectrometry and flow injection inductively coupled plasma mass spectrometry, *Anal. Chem.* 68 (1996) 4418–4423.
 19. A.J. Walder, I.T. Platzner, P.A. Freedman, Isotope ratio measurement of lead, neodymium and neodymium–samarium mixtures, hafnium and hafnium–lutetium mixtures with a double focussing multiple collector inductively coupled plasma mass spectrometer, *J. Anal. At. Spectrom.* 8 (1993) 19–23.

- 20 . I.T. Platzner, Isotope ratio mass spectrometry—state of the art, Proceedings of the Eighth ISMAS Symposium on Mass Spectrometry, Hyderabad, India, December, 1999, pp. 307–319.
21. J. Anal. At. Spectrom., 2000, 15, 1343±1348
22. P. Jandik and G. Bonn, Capillary Electrophoresis of Small Molecules and Ions, VCH Publishers, Inc., New York, 1993.