



**An evaluation of chromatographic modes for the
determination of rare earth elements in geological
materials by HPLC-ICP-MS**

by

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ABSTRACT

Scandium, Y and 15 lanthanides, commonly classified as rare earth elements (REE) are indispensable to modern technology and constitute integral components for the manufacture of advanced technological materials. Their determination in geological materials by ICP-MS are susceptible to numerous spectroscopic and matrix interferences that inhibit accurate quantification. The chromatographic separation of individual REE from interferences prior to detection by ICP-MS has been established as an effective approach for overcoming these interferences. However, application of this approach in literature does not address both mutual REE and matrix induced spectroscopic interferences. Furthermore it requires extensive sample pre-treatment, introducing errors in analysis.

This study investigates established chromatographic modes of REE separation (ion pair and ion exchange chromatography) on their capability to separate individual REE and sample matrix components without sample pre-treatment. It further aims to evaluate the potential of these chromatographic methods to be integrated to a hyphenated HPLC-ICP-MS technique for elimination of interferences which affect ICP-MS REE quantification. Ion pair and ion exchange methods were optimised using HPLC with post-column derivatisation and UV-Vis detection (as a preliminary detection method). These methods were compared on the basis of their REE separation efficiency and capability to address ICP-MS spectroscopic interferences that affect REE determination. The potential integration of the preferred chromatographic method (ion pair chromatography) prior to ICP-MS detection was evaluated by analysis of CRMs before and after separation. The influence of mobile phase composition on analytical performance of ICP-MS for REE determination was assessed.

This study has shown that ion pair chromatography has the potential to achieve complete separation of individual REE without interference from sample matrix components and avoiding sample pre-treatment procedures. However, the surfactant properties of the ion pair reagent and organic and sodium content of its mobile phase composition can impair ICP-MS sensitivity. This study also provides insight to challenges that will be encountered during application of ion pair chromatography with ICP-MS detection (HPLC-ICP-MS) and presents appropriate suggestions and improvements. These will enhance the potential application of ion pair chromatography with HPLC-ICP-MS such that a more effective means for accurate and precise determination of REE in geological materials can be achieved.

PREFACE

The experimental work described in this dissertation was carried out in the School of Chemistry and Physics, University of KwaZulu-Natal, Westville campus, from March 2014 to March 2016 under the supervision of Dr. Letitia Pillay. ICP-MS analysis was carried out at the analytical services division at Mintek, Johannesburg.

These studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where use has been made of the work of others it is duly acknowledged in the text.

DECLARATION - PLAGIARISM

I, Risa Bagwandin declare that

1. The research reported in this thesis, except where otherwise indicated, is my original research.
2. This thesis has not been submitted for any degree or examination at any other university.
3. This thesis does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.
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Signed: _____

Risa Bagwandin

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DEDICATION

This dissertation is dedicated to the following individuals:

- To my parents (Monica and Sanjay Bagwandin), whom have instilled in me a strong work ethic, a great will to succeed and most of all the motivation set high goals along with the determination achieve them
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ABBREVIATIONS

AAS	Atomic absorption spectrometry
CRM	Certified reference material
EDTA	Ethylenediaminetetraacetic acid
FAAS	Flame atomic absorption spectrometry
GFAAS	Graphite furnace atomic absorption spectrometry
HIBA	α -hydroxyisobutyric acid
HPLC	High performance liquid chromatography
HPLC-ICP-MS	High performance liquid chromatography- inductively coupled plasma mass spectrometry
HR-ICP-MS	High resolution inductively coupled plasma mass spectrometry
HREE	Heavy rare earth elements (Tb – Lu and Y)
ICP	Inductively coupled plasma
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ID-TIMS	Isotope dilution – thermal ionisation mass spectrometry
IEC	Ion exchange chromatography
IPC	Ion pair chromatography
IUPAC	International union of pure and applied chemistry

LOD	Limit of detection
LOQ	Limit of quantification
LREE	Light rare earth elements (La – Gd)
MREE	Middle rare earth elements
NAA	Neutron activation analysis
PAR	4-(2-pyridylazo)resorcinol
PDCA	2,6-pyridinedicarboxylic acid
PTFE	Polytetrafluoroethylene
REE	Rare earth elements
RF	Radio frequency
RSD	Relative standard deviation
TDS	Total dissolved solids
USGS	United States geological survey
UV	Ultraviolet
XRF	X-ray fluorescence

CHAPTER 1 – INTRODUCTION

Rare earth elements (REE) are integral components of modern, high technological materials and constitute vital inputs for the manufacture of mass produced consumer electronic devices and equipment¹. With implementation of REE in recent advances of green and renewable energy technologies, the existing great demand of these high commercial value elements is expected to rise considerably^{2, 3}.

China, who produce more than 90% of the world's REE⁴, enforced export and production restrictions of these elements from 2009 until early 2015⁵. These restrictions were initiated in an effort to constrain illegal mining, over-exploitation and environmental deterioration within the country^{3, 6-8}. As a direct consequence of these past regulations, much attention and emphasis have been placed on re-establishing REE supply chains outside of China due to the increased concern of diminishing access of REE and projected supply risks².

South Africa is one of the few countries outside China with a history in REE mining and production. Due to the apprehension and current affairs of the rare earth industry, South Africa is presently involved in two projects in an attempt to reinstate its REE supply^{7, 8}. These include: the refurbishment of the previously abandoned Steenkampskraal thorium and REE mine in the Western Cape⁹ and development of a new REE mine in the Northern Cape, entitled Zandkopsdrift Rare Earths Project, which is currently undergoing a feasibility study^{10, 11}.

This renewed interest and initiation of REE mining in the country will require development of sophisticated, accurate and sensitive methods of analysis to determine the composition of mined REE ores. Furthermore, these methods of analysis can be extended to aid in prospective exploration of national REE mineral resources.

1.1 Rare Earth Elements (REE)

Rare earth elements (REE), also collectively termed as rare earths, makes reference to a combination of 17 elements situated in Mendeleev's periodic table. These elements include: scandium, yttrium and the 15 lanthanides (atomic numbers 21, 39 and 57-71 respectively) as defined by the International Union of Pure and Applied Chemistry (IUPAC)^{12, 13}. In spite of the established IUPAC REE definition, which is adhered to in this research study, inconsistencies are observed in geochemical literature in which geochemists and geologists associate REE with members of the lanthanide series only^{14, 15}.

The inclusion of the term "rare" in REE is a misrepresentation of the group itself. Most of these elements are relatively abundant in the earth's crust in comparison to other trace elements such as the platinum group metals^{13, 14}. The term originated from chemists in the late 18th and early 19th centuries, on account of early metallurgical processes that were inefficient in separating REE into pure metals and their equivalent oxides¹³. Resultantly, these elements were difficult to obtain and commonly perceived as rare¹⁶. The only true REE, befitting of the title, is promethium (atomic number 61)¹⁷. Promethium possesses isotopes, all of which are radioactive with exceptionally short half-lives, and consequently is present in infinitesimal amounts in nature¹⁶.

1.1.1 Classification of REE

REE are conventionally assigned into two sub groups, light rare earth elements (LREE) and heavy rare earth elements (HREE) although, some authors infrequently include a third subgroup, the middle rare earth elements (MREE)^{8, 15, 18, 19}. The exact assignment of REE in each of these subgroups are ambiguous, as variations exist between a number of authors, however the United States Geological Survey (USGS) has provided a rationalisation for their classification of REE and is accordingly adopted in this study^{3, 8, 15, 16, 19-21}.

The USGS designates REE into LREE and HREE subgroups only (Fig 1.1). The LREE is associated with lanthanides of lower atomic numbers and concerns elements lanthanum to gadolinium (atomic numbers 57-64). Conversely, HREE are associated with lanthanides of higher atomic numbers and involves the remaining lanthanides terbium to lutetium (atomic numbers 65-71). The basis for distinction between the two subgroups arises from the arrangement of 4*f* electrons. The LREE have unpaired electrons in the 4*f* orbital, whereas HREE have paired electrons in the 4*f* orbital. Yttrium (atomic number 39) is also included in the HREE subgroup due to its strikingly comparable chemistry with HREE lanthanides, whilst scandium (atomic number 21), despite being included in the REE definition, is not included in either of the HREE or LREE subgroups⁸.

																				□	LREE		
																				□	HREE		
1A																		8A					
1 H																		2 He					
2A																		3A	4A	5A	6A	7A	
3 Li	4 Be																	5 B	6 C	7 N	8 O	9 F	10 Ne
3B		4B		5B		6B		7B		8B		1B		2B		13 Al	14 Si	15 P	16 S	17 Cl	18 Ar		
11 Na	12 Mg	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr						
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe						
55 Cs	56 Ba	57-71	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn						
87 Fr	88 Ra	89-103	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo						
Lanthanide Series		57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu							
Actinide Series		89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr							

Figure 1.1 Designation of REE and respective REE sub groups on the periodic table²²

1.1.2 General Chemical Properties of REE

REE are strongly electropositive with their chemistry comprised predominantly of ionic bonding¹⁵. The prevalent and most stable oxidation state exhibited by this group of elements is +3 in both their chemistry and geochemistry¹⁵. REE have occasionally exemplified a +2 or +4 oxidation states in their chemistry, however only cerium and europium display these oxidation states in their geochemistry or in geological systems (Table 1.1)^{15, 23}. REE cations are hard Lewis acids, due to their preference for fluoride and oxygen containing ligands, and form highly labile complexes²⁴.

Table 1.1 REE electron configuration, oxidation states and trivalent ionic radii²³

Atomic Number	Chemical Symbol	Element	Electron Configuration*	Oxidation States	M ³⁺ Radius/ Å
21	Sc	Scandium	[Ar]3d ¹ 4s ²	+3	0.68
39	Y	Yttrium	[Kr]4d ¹ 5s ²	+3	0.88
57	La	Lanthanum	[Xe]5d ¹ 6s ²	+3	1.06
58	Ce	Cerium	[Xe]4f ¹ 5d ¹ 6s ²	+3, +4	1.03
59	Pr	Praseodymium	[Xe]4f ³ 6s ²	+3, +4	1.01
60	Nd	Neodymium	[Xe]4f ⁴ 6s ²	+3	0.99
61	Pm	Promethium	[Xe]4f ⁵ 6s ²	+3	0.98
62	Sm	Samarium	[Xe]4f ⁶ 6s ²	+2, +3	0.96
63	Eu	Europium	[Xe]4f ⁷ 6s ²	+2, +3	0.95
64	Gd	Gadolinium	[Xe]4f ⁷ 5d ¹ 6s ²	+3	0.94
65	Tb	Terbium	[Xe]4f ⁹ 6s ²	+3, +4	0.92
66	Dy	Dysprosium	[Xe]4f ¹⁰ 6s ²	+3	0.91
67	Ho	Holmium	[Xe]4f ¹¹ 6s ²	+3	0.89
68	Er	Erbium	[Xe]4f ¹² 6s ²	+3	0.88
69	Tm	Thulium	[Xe]4f ¹³ 6s ²	+3	0.87
70	Yb	Ytterbium	[Xe]4f ¹⁴ 6s ²	+2, +3	0.86
71	Lu	Lutetium	[Xe]4f ¹⁴ 5d ¹ 6s ²	+3	0.85

*Ground state electron configuration

1.1.2.1 *Chemical similarity of REE*

REE are well acknowledged for their chemical resemblance amongst individual members of the group and is one of their most distinguishing features¹³⁻¹⁵. They are unique in relation to other metals of the periodic table, in which two neighbouring elements in a period frequently exhibit a substantial difference in chemical properties²⁵. It is this pronounced chemical similarity of REE which contributes to the complexity of separation and quantification of these elements, as reported by a number of authors^{17, 26-29}.

The uniformity of chemical properties displayed by REE are attributed to their distinct electron configuration and is further reinforced by the phenomenon termed as lanthanide contraction³⁰. These aspects and the manner in which they confer REE their characteristic chemical similarity is described in further detail.

- *Electronic arrangement of REE*

The distinct electron configuration of REE is observed specifically with elements comprising the lanthanide series of the periodic table. It involves the distribution of a single electron which accompanies an increase in atomic number across the periodic table¹³. Conventionally, this electron enters the outermost orbital of the atomic structure, contributing to the number of valence electrons of the element concerned¹³. With lanthanides, however, this electron enters an inner $4f$ orbital, leaving the number of valence electrons undisturbed¹³. Since $4f$ electrons are adequately shielded by completed outer $5s^2$ and $5p^6$ orbitals, they do not actively influence chemical bonding and chemical interactions, thus rationalising the similar chemical behaviour of REE¹⁵.

- *Lanthanide contraction*

The unusual electron configuration of REE also effectuates another characteristic feature, termed as lanthanide contraction. Lanthanide contraction pertains to the gradual decrease in the ionic radii of REE with an increase in atomic number (Fig 1.2, Table 1.1)^{13, 15, 23, 25}. The origin of this occurrence is due to the inadequate shielding of one $4f$ electron by another as the nuclear charge increases with atomic number¹⁵. Resultantly, each $4f$ electron is pulled closer towards the nucleus leading to the reduction in the size of the $4f$ orbital and overall size of the ion itself²³.

One of the major consequences of lanthanide contraction is the resemblant ionic radii of trivalent (M^{3+}) REE ions²¹. The ionic radii is of considerable importance taking into account that the chemistry of REE are predominantly ionic, which is primarily influenced by the size of the element ion concerned¹⁵. Consequently, REE ions of the same charge exhibit uniformity in their chemical behaviour due to the similar sizes of their ions²¹.

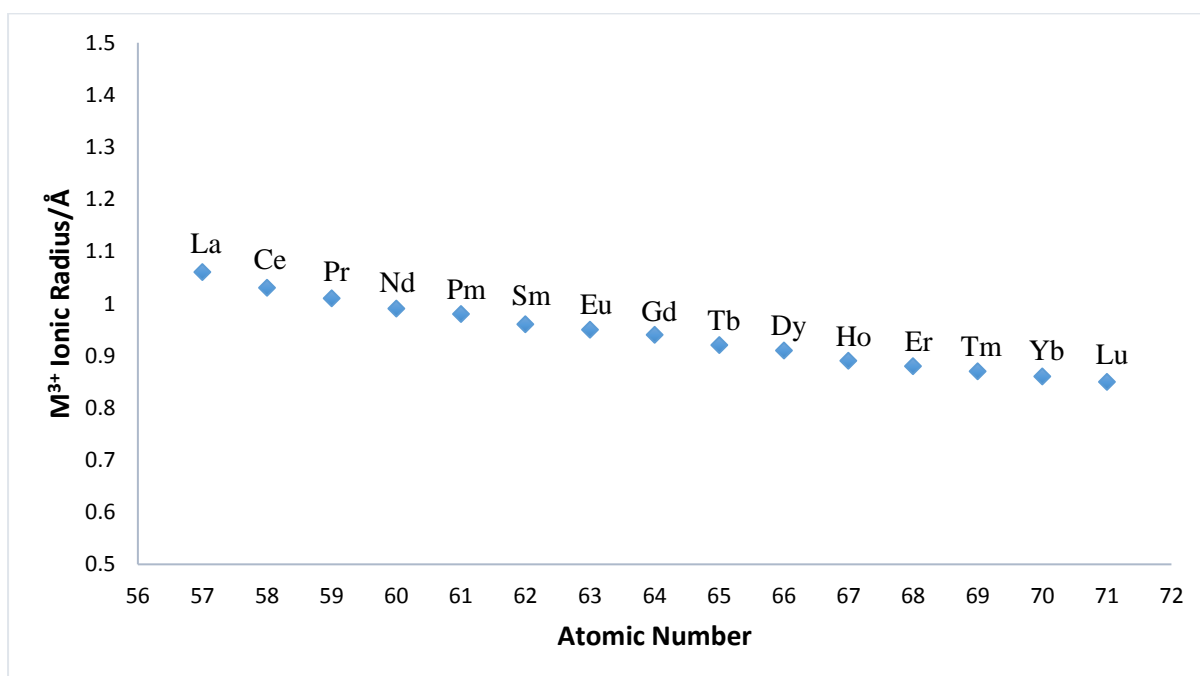


Figure 1.2 Lanthanide contraction: decrease in ionic radii with an increase in atomic number²³

1.2 Occurrence of REE

REE are geochemically classified as lithophile elements since they predominantly exist in oxygen containing minerals such as silicates, phosphates and carbonates^{15, 16, 23, 30}. Naturally, these elements occur together as a group in mineral assemblages as opposed to individually or as pure metals^{15, 16, 30, 31}. This is owing to the similarity of the ionic radii exhibited by trivalent REE ions which permits their mutual substitution in host minerals^{16, 21}. The abundance of REE in the Earth's crust clearly exhibit the odd-even effect (Oddo-Harkins rule), whereby even atomic number elements are present in higher concentrations than odd atomic number elements^{14, 15, 17, 25}. As a consequence, neighbouring REE on the periodic table are observed to possess unequal concentrations in geological materials^{14, 25}. In addition to this observation, LREE are frequently more abundant in geological materials than their HREE counterparts^{15, 17}.

To date, approximately 200 minerals are known to contain REE as constituents³². Despite their occurrence in numerous minerals, REE seldom occur in concentrations that are economically feasible to mine and, as a result, are challenging to procure^{3, 15, 21, 31}. The main sources of REE that are of economic interest include: bastnäsite, monazite, xenotime and ion adsorption clays.

1.2.1 Bastnäsite

Bastnäsite, $(\text{REE})(\text{CO}_3)\text{F}$; is a fluorocarbonate mineral. It is the main source of REE and is responsible for more than 80% of the world's REE production^{15, 33}. It is made up of mostly LREE with a 70-75 wt.% REE content that comprises mainly of Ce, La, Pr and Nd^{15, 30, 34}. Countries involved in bastnäsite mining include China (Bayan Obo)³³ and USA (Mountain Pass)³³ with deposits found in Burundi and Madagascar^{34, 35}.

1.2.2 Monazite

Monazite, $(\text{REE,Th})\text{PO}_4$; is a phosphate mineral. It is composed mainly of LREE with a 55-60 wt.% REE content¹⁵. Despite its significant REE content, mining of monazite has been widely discontinued due to its high thorium content and the associated challenges with handling and disposal of radioactive waste^{15, 16, 33}. Countries with monazite deposits include South Africa, Brazil, Australia, India, China and USA^{16, 34}.

1.2.3 Xenotime

Xenotime, $(Y,REE)PO_4$; is a yttrium phosphate mineral which contains 25-60 wt.% REE³³. Its REE constitution is different to that of monazite and bastnäsite as it contains a higher amount of HREE than LREE and is a major source of HREE^{15, 30, 31}. Xenotime deposits are located mainly in Asian countries including China, Malaysia, Indonesia and Thailand^{33, 35}.

1.2.4 Ion adsorption clays

Ion adsorption clays are formed by the weathering of rocks that are abundant in REE resulting in the generation of aluminosilicate clay minerals^{17, 33, 36}. These clay deposits consists of fine particles that are capable of adsorbing REE ions and are currently only exploited in China for their REE content^{17, 33}. Although ion adsorption clays possess a significantly low REE content (below 0.3 wt.%), their small particle sizes eliminates the need for beneficiation making it easier to obtain REE in comparison to other minerals^{31, 33, 36}.

Global distribution of REE deposits, reserves and mines are illustrated (Fig 1.3).

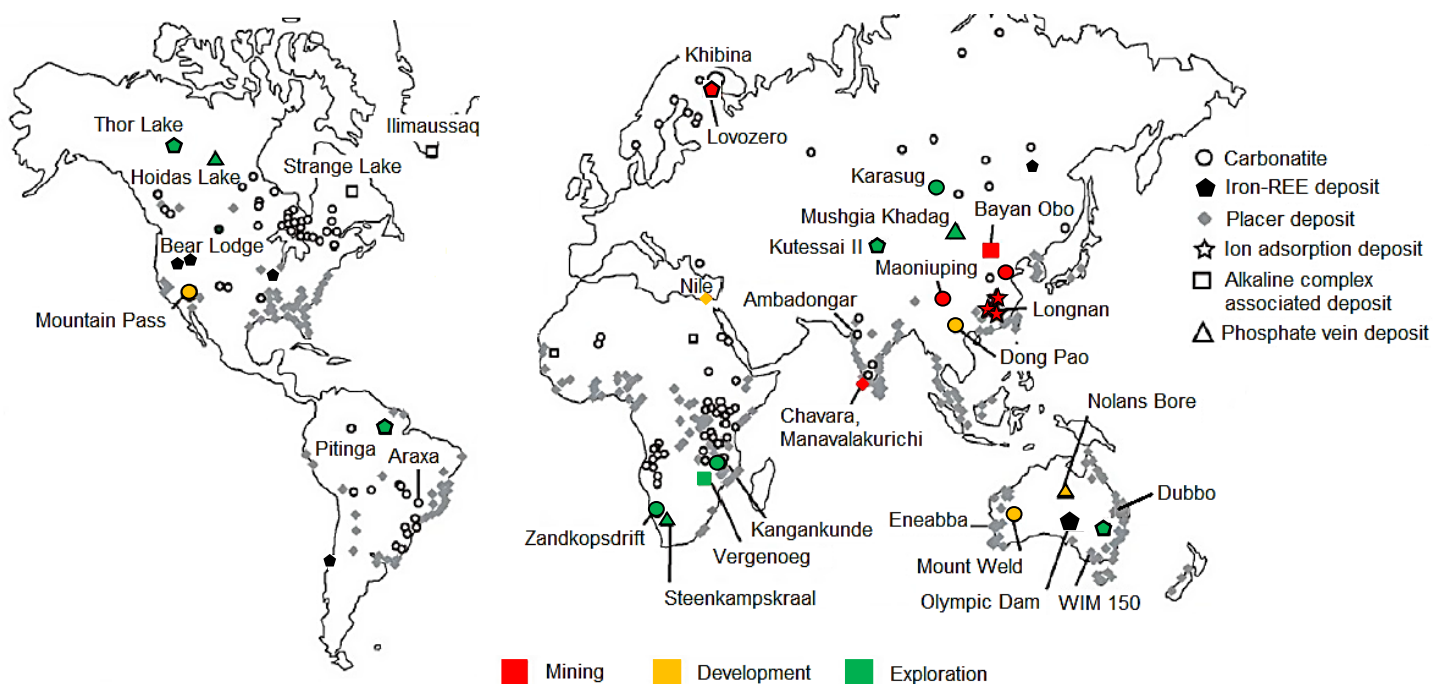


Figure 1.3 Location of world REE reserves, deposits and mines³⁷

1.3 Significance of REE

REE are of considerable technological significance. They constitute vital inputs for manufacture of advanced technological materials and are indispensable to modern technology^{14,38}. REE constitute one of the most extensive array of consumer products than any other elemental groupings¹⁶. These products include consumer electronics such as mobile phones, televisions, laptops and computers which are frequently used on a daily basis^{7,25}. The multitude of REE applications (Table 1.2) are owing to their unique magnetic, optical, luminescent, electronic and catalytic properties^{25,39}. In addition to these applications, REE are at the forefront of green technological innovations which have increased the awareness of their commercial value¹⁶. Recent advances in green technology implement REE as phosphors in energy efficient lighting; light weight permanent magnets in wind turbine generators; and high capacity rechargeable batteries used in electric/hybrid motor vehicles^{40,41}.

REE have also gained appreciable economic significance due to an increase in environmental awareness and resultant global progression into a green economy⁴². In fact, recent applications of REE in green technologies are expected to generate a surge in REE demand which may induce supply shortages in the future^{40,41}. Resultantly, both the European Commission and United States Department of Energy have classified REE as “critical” due to their importance in technological developments and the substantial economic impact that eminent supply disruptions may impose^{40,41}.

Furthermore, REE are of substantial scientific significance, especially in the disciplines of geology and geochemical sciences. In these fields of study, the abundance of REE provides valuable information on geochemical processes involved in the origin and formation of rocks and mineralogical deposits^{25,28}. This inference is achieved by exploiting differences in oxidation states exhibited by cerium (Ce^{4+}) and europium (Eu^{2+}) relative to the conventional trivalent oxidation state displayed by remainder of the group²⁸. The varied oxidation states results in a concentration difference of cerium and europium in relation to other REE that are fractionated during mineralogical processes²⁸. The type and extent of fractionation provides an indication of processes involved in the origin of a specific rock formation including environmental conditions at which these processes have occurred²⁸.

Table 1.2 Applications of REE^{7, 16, 43, 44}

Element	Applications
Scandium	High strength Al-Sc alloys in aerospace industry
Yttrium	Red phosphors in liquid crystal displays (LCDs); microwave filters in satellite communications; lasers; oxygen sensors; capacitors
Lanthanum	Fluid catalytic cracking catalysts; rechargeable batteries in electric/hybrid motor vehicles and laptops; catalytic convertors; fuel cells
Cerium	Polished silicon microprocessors and disk drives in computers; UV filters; solar panels; catalytic convertors; phosphors in fluorescent lighting
Praseodymium	Super magnets; fibre optics; photographic lenses; ceramics; pigments
Neodymium	High powered, permanent NdFeB magnets in computer hard drives, smartphones, wind turbine generators and electric/hybrid motor vehicles
Promethium	Beta radiation source; miniature nuclear batteries in guided missiles
Samarium	High temperature permanent magnets in military applications; nuclear reactor control rods; microwave filters
Europium	Red phosphors in LCDs; fluorescent lighting; nuclear reactor control rods
Gadolinium	Magnetic resonance imaging (MRI) contrasting agents; optical and magnetic detection; ceramics
Terbium	Green phosphors for lighting and displays; lasers; fuel cells
Dysprosium	Permanent magnets in wind turbine generators and electric/hybrid motor vehicles; white phosphors; nuclear reactor control rods
Holmium	Alloys in magnets; lasers; nuclear reactor control rods
Erbium	Optical fibres; lasers; ceramics
Thulium	Radiation source in X-ray machines; lasers
Ytterbium	Solar cells; optical fibres; lasers
Lutetium	X-ray radiation source; catalysts in petroleum refining

CHAPTER 2 - ANALYTICAL CHEMISTRY OF REE

This study involves the determination of REE in geological materials, particularly those which possess a significant proportion of REE bearing minerals (REE ores). The determination of REE in these materials are imperative in ascertaining the feasibility of exploiting their mineral compositions for REE.

The analytical chemistry of REE is reviewed in this chapter, with particular focus on the quantification of these elements in geological matrices.

2.1 Determination of REE in Geological Matrices: Analytical Considerations

The determination of REE in geological materials presents a number of significant analytical challenges^{1, 27-29, 45-48}. These are mainly attributed to complex matrices associated with geological samples in which REE are frequently present at trace concentrations²⁸ (ranging from $\mu\text{g g}^{-1}$ for LREE to ng g^{-1} for HREE⁴⁵). Geological materials are also characterised by major elemental constituents including Si, Fe, Al, Ca and Mg, which are present at considerably higher concentrations relative to REE. The presence of these major constituents, together with additional matrix components present in minor concentrations, gives rise to high levels of spectral and chemical interferences^{1, 28, 49}. The occurrence of such interferences compromises the accuracy of REE determinations and are not consistent amid various geological materials due to their diverse elemental compositions⁴⁵. Other analytical concerns involve the inherent chemical similarity of REE^{27, 29, 46, 48}. This results in mutual interferences amongst individual REE and contributes to the complexity of quantifying select REE in the presence of other REE^{29, 46}. It is due to these outlined challenges that necessitates careful selection of analytical techniques applied for the determination of these elements.

2.2 Previous Analytical techniques

A number of critical reviews on the determination of REE in geological matrices are present in literature^{27-29, 45-48}. These reviews have focused mainly on spectrometric determinations of REE, owing to the predominance of these techniques in research. Analytical techniques applied for the determination of REE and their associated limitations are outlined. Only techniques prior to development of ICP-MS are discussed in order to provide an appreciation past REE quantification restraints and how these were alleviated by the development of more recent, sophisticated instrumentation. These include classical analytical methods (volumetry, gravimetry and colourimetry) and instrumental analytical techniques such as: AAS, XRF, ID-TIMS, NAA, ICP-OES and HPLC.

2.2.1 Classical analytical methods

Quantification by classical analytical methods rely on chemical reactions involving the analyte. These methods include gravimetry, volumetry and colourimetry, in which the amount of products formed or reagents consumed are measured and related to the analyte concentration⁵⁰. The use of such methods for REE determination in geological materials are limited owing to their poor sensitivities which are inadequate for quantification of REE present at trace concentrations^{27, 28, 46}. In addition, chemical reagents used in these methods are not specific to REE which increases potential of interferences that compromise the analysis²⁷. These interferences are a result of sample matrix components that render the desired chemical reaction unstable, or possess a higher selectivity towards the chemical reagent relative to the analyte²⁷. Separation of matrix components have been proposed to overcome these interferences, however, mutual interferences arising from REE as a group itself emerges⁴⁸. The chemical similarity of REE makes it exceptionally difficult to distinguish between individual REE by these methods, since each REE reacts with chemical reagents in the same manner²⁹. This results in the employment of classical analytical methods for quantification of REE as a group instead of individual REE⁴⁸. The poor selectivity of these methods together with its inability to quantify trace concentrations, necessitates the application of instrumental analytical techniques for determination of REE in geological samples²⁸.

2.2.2 Instrumental analytical techniques

2.2.2.1 Atomic absorption spectrometry (AAS)

Atomic absorption spectrometry (AAS) is one of early instrumental analytical techniques applied for REE quantification^{27, 47, 48}. It involves quantitative measurement of electromagnetic radiation absorbed by free analyte atoms, which is directly proportional to the analyte concentration⁵¹. AAS techniques, which include flame atomic absorption spectrometry (FAAS) and graphite furnace atomic absorption spectrometry (GFAAS), are capable of element specific detection⁴⁷. This allows for quantification of individual REE in geological materials that could not be previously accomplished by classical analytical methods. Nevertheless, AAS techniques possess their own set of limitations with regard to REE analysis. The high ionizability of these elements together with their propensity to form thermally stable, non-volatile REE oxides results in chemical interferences which reduces sensitivity of the analysis^{47, 52, 53}. Additionally, AAS techniques possess a single element detection capacity. As a result, only one analyte can be detected within a single analytical run, which substantially increases the time required to analyse all REE²⁸.

2.2.2.2 X-ray fluorescence spectrometry (XRF)

X-ray fluorescence spectrometry (XRF), concerns the irradiation of samples with primary x-rays that induces emissions of secondary/fluorescent x-rays from the sample. These emitted fluorescent x-rays possess energies characteristic to each sample elemental constituent, of which its measurement allows for quantification⁴⁷.

XRF possesses many attractive analytical features which include direct sample analysis and multi-element detection capability. The combination of these aspects permits rapid determination of REE since little to no sample preparation is required, as well as the quantification of all REE within a single analysis²⁹. However, despite these features, severe spectral interferences restrict application of this technique. These spectral interferences are a result of emissions from matrix elements which overlap x-ray energies or 'lines' that are used for REE detection⁴⁷.

The limitation of XRF for REE quantification is further exemplified by its poor detection limits²⁸. These are confined to the $\mu\text{g g}^{-1}$ (ppm) range which are unsatisfactory for REE concentrations in geological samples, particularly those of HREE which occur in ng g^{-1} (ppb) concentrations⁵⁴.

2.2.2.3 *Isotope dilution – thermal ionisation mass spectrometry (ID-TIMS)*

Early mass spectrometers integrated electrothermally heated filaments to convert sample element constituents into ions (thermal ionisation)²⁷. These element ions are separated according to their mass to charge ratios (m/z) and subsequently detected by the mass spectrometer. The number of ions detected is converted to a measurable electronic signal that is related to the concentration of the corresponding element⁴⁷. The combination of this technique with isotope dilution methods, permit quantification of trace REE concentrations at ng g^{-1} levels with high accuracy and precision⁵⁵. However, the shortcoming of this technique concerns the pre-requisite of performing isotope dilution for quantification. Isotope dilution exploits the principle that the natural abundance of most elements consist of a number of isotopes that are present in a fixed ratio. By spiking a sample with one of the isotopes of an analyte, the natural isotopic composition of that analyte is altered. Measurement of the altered isotopic ratio and taking into account the amount of isotope spiked, allows quantification of the analyte originally present in the sample^{47, 56}. In light of the above, in order for quantification, elements require at least two stable isotopes. As a consequence, REE that possess only one stable isotope such as Sc, Y, Pr, Tb, Ho and Tm cannot be quantified using ID-TIMS⁵⁵.

2.2.2.4 *Neutron activation analysis (NAA)*

Neutron activation analysis (NAA) has been extensively applied for determination of these elements in a variety of geological matrices⁴⁸. The principles of this technique involves the irradiation of a sample with neutrons, which generates radionuclides of sample element constituents. The generated radioactive isotopes subsequently undergo nuclear decay resulting in emission of gamma radiation characteristic to each element. Quantification of these sample elements takes place by measuring the intensity of emitted gamma radiation⁴⁷. The success of this technique is mainly attributed to its high sensitivity for REE with detection limits in the order of ng g⁻¹ levels. This, in conjunction with its high accuracy and precision, results in the acknowledgment of NAA as a principal reference technique for REE determinations in geological materials²⁹. Despite its prevalence, the main limitation of NAA is the long period of time required before detection of emitted gamma radiation commences^{27, 29, 55}. This time (also referred to as cooling time) is dependent on the half-lives of radioactive isotopes that are generated upon sample irradiation with neutrons⁴⁷. Generally, sample irradiation times are within the range of 6 – 16 hours for REE, with measurement of gamma radiation carried out after 20 minutes to a month for long lived REE radionuclides²⁹. As a consequence of these exceptionally long cooling times, NAA is commonly used for analysis of only seven REE (La, Ce, Nd, Sm, Tb, Yb and Lu) on a routine basis^{28, 47}. The incomplete coverage of the REE group and time consuming analysis methods no longer makes NAA attractive for routine determination of these elements in geological materials²⁹.

2.2.2.5 *Inductively coupled plasma optical emission spectrometry (ICP- OES)*

Inductively coupled plasma optical emission spectrometry (ICP-OES) involves quantitative measurement of electromagnetic radiation emitted by ions and atoms generated from a sample solution⁵¹. This measurement is used to quantify the concentration of sample elemental constituents⁵¹. ICP-OES provides notable analytical advantages including a wide linear dynamic range, high specificity as well as good accuracy and precision^{28, 29, 47, 57}.

It surpasses NAA with respect to analytical speed and element coverage as it is capable of performing simultaneous multi-element determination of the entire REE group within 1-2 minutes^{55, 56, 58}. However, the sensitivity of NAA for REE quantification is superior in comparison to ICP-OES⁵⁹. The poor sensitivity of ICP-OES for REE determination in geological materials is due to spectral interferences arising from complex sample matrices and REE as a group itself^{1, 28, 47, 55, 57}. The presence of sample matrix constituents such as Fe, Al, Ba and Na results in a high background signal in addition to spectral overlap with REE spectral lines^{60, 61}. As a result, ICP-OES methods for REE determination are frequently accompanied by REE group separation and preconcentration procedures to minimise matrix interferences and increase sensitivity^{28, 47, 55, 60}. A number of group separation procedures have been described in literature involving ion exchange techniques, however none of these separation procedures address mutual REE interferences^{1, 55, 58, 61-67}. These mutual interferences are owing to the complex emission spectra of REE whereby a number of REE emission lines overlap each other^{47, 61}. As a consequence, REE that do not possess sensitive spectral lines such as Pr, Tb and Tm, are measured with difficulty^{47, 58}.

2.2.2.6 *High performance liquid chromatography (HPLC)*

High performance liquid chromatography (HPLC) is a technique used to separate sample components prior to detection. The principles of chromatography and how it achieves separation of REE are discussed in further detail (Section 2.4). Many HPLC methods have been proposed as an inexpensive alternative to ICP and NAA for REE determination^{68, 69}. However, conventional HPLC methods rely on UV-Vis absorbance detection. This detection method is the main limitation of HPLC as its sensitivity is inadequate for trace REE concentrations in addition to its non-specific nature. As a consequence, detection of matrix ions that absorb light at the wavelength set for REE detection can occur, complicating chromatograms used for quantification^{70, 71}. Resultantly, HPLC methods with UV-Vis detection are not as popular as spectrometric methods for REE determination in geological matrices.

Analytical techniques applied for REE determination in geological materials, prior to the development of ICP-MS, exemplified a number of considerable drawbacks which hindered the routine quantification of REE^{55, 57}. Despite the number of techniques that were available, selection of any of the reviewed techniques often resulted in a compromise between: duration of analysis; detection specificity and sensitivity; freedom of interferences; complete REE coverage; and suitable detection limits for quantification of REE at trace concentrations^{29, 55, 56}.

2.3 REE Determination by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Since its establishment in 1980, ICP-MS has demonstrated a number of attractive analytical features which revolutionised REE analysis^{56, 72}. These features include: superior sensitivities and detection limits; rapid multi-element detection; and complete REE coverage. The most significant ICP-MS feature for REE analysis is the ability to determine REE in complex matrices with a linear dynamic range of nine orders of magnitude^{28, 29, 73, 74}. This permits analysis of samples in which REE concentrations range from sub ppb to high ppm levels within a single analytical run⁵⁶. As a consequence, ICP-MS is currently the leading analytical technique for REE determination in a number of matrices including geological materials^{29, 75}.

2.3.1 Fundamental principles of ICP-MS

Conventionally, sample solutions are introduced into the instrument by means of a peristaltic pump. The sample solution is pumped to a pneumatic nebuliser where it is converted into an aerosol with the aid of a stream of argon gas⁵⁶. The sample aerosol is then transported to a spray chamber, whereby large sample droplets are separated by gravity and discarded into a drain, allowing only fine sample droplets to enter the ICP torch⁷⁶.

The ICP torch comprises of a series of concentric quartz tubes surrounded by a radio frequency (RF) coil in which argon gas flows through. The intense magnetic field created by the RF coil together with a high voltage spark, results in the ionisation of the argon gas generating a high temperature plasma ($\sim 10\,000\text{ K}$)⁵⁶.

Introduction of the sample aerosol into the heated plasma results in several processes including: desolvation, vaporisation, conversion into free atoms and finally ionisation²⁸. The generated sample ions exit the plasma and are directed to the interface region between the plasma and mass spectrometer⁷⁶.

The interface region permits the transmission of sample ions generated from the plasma at atmospheric pressure (760 torr) to a significantly lower pressure/high vacuum (10^{-6} torr) required for operation of the mass spectrometer. This is achieved by the use of two cones known as the sampler and skimmer cones that are maintained at a low vacuum (10^{-3} torr), allowing for a stepwise reduction in pressure. These interface cones, which are made of nickel or platinum, possess small orifices (0.6 – 1.2 mm) that are used to direct sample ions into the vacuum chamber of the mass spectrometer⁵⁶.

Once in the vacuum chamber, sample ions are electrostatically directed towards the mass analyser by the use of ion focusing lenses. The use of an electrostatic potential with an opposite charge than that of the analyte ions results in attraction of these ions towards the mass analyser. This electrostatic potential also repels oppositely charged ions and prevents photons and neutral species from entering the mass analyser⁷⁶.

The standard configuration of a commercially available ICP-MS is equipped with a quadrupole mass analyser. The quadrupole essentially serves as a mass filter, allowing only ions of a specific mass to charge ratio (m/z) to reach the detector. It consists of four cylindrical parallel rods, whereby varying voltage and radio frequency allow ions of a specific m/z to have a stable trajectory through the rods and reach the detector. The remaining ions that are of a different m/z , will have an unstable trajectory within the quadrupole and are consequently rejected⁷⁶.

Ions that emerge from the quadrupole mass analyser are converted to a measurable signal by means of an electron multiplier detector. Detection occurs by the interaction of ions with a charged surface (known as a dynode) which releases electrons. These released electrons subsequently strike a second dynode, releasing more electrons, hence inducing the electron multiplication process. The cascade of electrons produced generates a measurable electrical signal. This signal is processed by a data handling system and is related to the concentration of an element in the sample by the use of calibration standards⁵⁶.

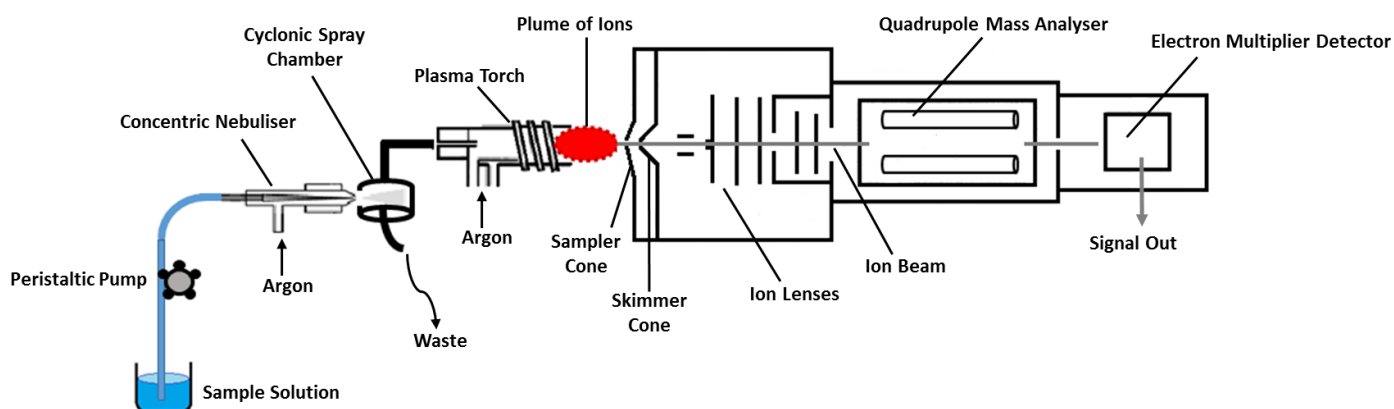


Figure 2.1 Adapted schematic of an ICP-MS instrumentation⁷⁷

2.3.2 Interferences

Despite the several advantageous analytical features which make the ICP-MS suitable for the routine determination of REE, incorporating all of these characteristics into a single analytical method is not always achievable due to interferences⁷³. REE are considered as “problematic elements” as they are inherently predisposed to ICP-MS interferences. These include matrix and spectroscopic interferences that induce suppression or enhancement of the analyte signal as well as variations in analyte signal over time (signal drift)^{56, 78}. Due to the high sensitivity of the ICP-MS, any fluctuations of the analyte signal, magnifies the interference resulting in significant errors. As a result, compensation of interferences must take place to prevent inaccurate quantification. The source of interferences that affect REE determination and approaches used to overcome them are discussed in further detail.

2.3.2.1 *Matrix interferences*

Matrix interferences are a result of the physicochemical behaviour of sample constituents and their impact on processes that occur during analysis⁷⁹. These processes include sample transport, ionisation within the plasma and ion interactions that occur in the interface region and ion optics⁷⁸.

ICP-MS determination of REE in geological materials are highly susceptible to these interferences⁷⁸. This is due to highly complex matrices of geological samples that generate solutions with high total dissolved solids (TDS)⁵⁶. High TDS solutions affect nebulisation efficiency of the sample introduction system, resulting in physical suppression of an analyte signal⁷⁸⁻⁸⁰. Furthermore, it provokes salt deposition on sample and skimmer cones resulting in orifice clogging. This causes signal suppression and changes in analytical signal intensity over time^{56, 78-80}. Another source of matrix interferences is high concentrations of easily ionisable matrix elements in sample solutions. These elements generate a defocusing effect on transmission of analyte ions in the ion beam, resulting in suppression or enhancement of an analyte signal^{78, 81}. The extent of this effect is also affected by the mass of matrix ions, whereby high mass ions tend to suppress signal intensities of lower mass ions (space-charge effect)^{56, 80, 81}.

Matrix induced signal suppression or enhancement effects can be compensated by the use of internal standards⁵⁶. This approach involves the addition of an element in equivalent amounts in blanks, calibration standards and sample solutions prior to analysis. The selected element, known as an internal standard, must have a low natural abundance in samples and be free from spectral interferences. More especially, it should possess a similar mass and ionisation potential as the analyte^{78, 79}. This similarity suggests the instrument response of the analyte and internal standard signals are affected in a similar manner. Consequently any variations in the intensities of the internal standards in the sample, to that of the calibration standards, are used to correct analyte concentrations in samples⁵⁶.

For REE analysis, usually more than one internal standard is used due to the wide mass range of group members. Elements that are applied as internal standards in these analyses include Re, Ru, Rh, In, Bi and Ir^{79, 82-84}. The reduction of matrix interferences associated with analytical solutions of high TDS can be achieved by dilution of these solutions to below 2% TDS^{56, 85}. However, caution should be exercised for analytes that are initially present at sub ppb levels as dilution can result in concentrations in close proximity to the detection limit, affecting quantification.

2.3.2.2 *Spectroscopic interferences*

Spectroscopic interferences are also frequently encountered during REE analyses and present significant challenges in their accurate quantification. These interferences are associated with charged atomic and molecular species, which possess the same nominal m/z as the analyte isotope. This results in the summation of signals generated by both the analyte and interferent species, which bias the signal intensity measured at the m/z of interest^{56, 78, 81}. The two types of spectroscopic interferences that affect REE determination are described.

- *Elemental isobaric interferences*

Elemental isobaric interferences are generated by isotopes of elements that form ions of the same nominal m/z as the analyte^{78, 80}. These interferent isotopes may originate from matrix elements within the sample such as Ba and Hf. However, the main contributors to elemental isobaric interferences encountered in REE determination are caused by isotopes of REE themselves (Table 2.1)^{56, 78, 80}.

Elemental isobaric interferences can be compensated by choosing an alternative isotope of an analyte, which is essentially free of isobaric interferences. Regardless, isotopes of elements are of differing natural abundance. As a result, remaining isotopes available for analysis may not include that which is most abundant, compromising sensitivity of the analysis^{28, 56}. This is evident for $^{142}\text{Nd}^+$, $^{152}\text{Sm}^+$, $^{158}\text{Gd}^+$, $^{164}\text{Dy}^+$ and $^{174}\text{Yb}^+$, which are the most abundant isotopes affected by elemental isobaric overlap by $^{142}\text{Ce}^+$, $^{152}\text{Gd}^+$, $^{158}\text{Dy}^+$, $^{164}\text{Er}^+$ and $^{174}\text{Hf}^+$ respectively^{55, 86, 87}.

- *Polyatomic isobaric interferences*

In addition to singly charged analyte ions, the plasma of the ICP-MS also generates ions associated with the sample matrix and solvent; acids used in sample dissolution; entrained atmospheric gases; and gases used to sustain the plasma itself^{56, 78}. Combination of these ions whilst in the plasma or proceeding through the interface region may result in polyatomic ions of the same nominal m/z as the analyte. This gives rise to polyatomic isobaric interferences^{56, 80, 81}.

The most significant polyatomic isobaric interference associated with REE determination is due to the combination of sample constituent ions with $^{16}\text{O}^+$ or $^{16}\text{O}^1\text{H}^+$ ions, generating oxide and hydroxide molecular species respectively^{56, 88, 89}. This occurrence is particularly notable for LREE ions as they readily form oxide and hydroxide molecular species that overlap HREE isotopes within the group (Table 2.1). The impact of this spectral overlap is apparent in most geological samples as LREE are frequently present at much greater concentrations ($\mu\text{g g}^{-1}$ levels) than HREE (ng g^{-1} levels), affecting accurate quantification of Tb-Lu^{29, 56}.

Polyatomic interferences are also matrix induced. Silicon, which is as a major constituent in geological samples, forms $^{29}\text{SiO}^+$ and $^{28}\text{SiOH}^+$ ions that overlap monoisotopic $^{45}\text{Sc}^+$. Additionally, the presence of Ba can also generate BaO^+ and BaOH^+ ions that interfere with REE elements Nd-Gd (Table 2.1)⁹⁰⁻⁹². Apart from these interferences, careful consideration of acids used for sample dissolution is required as Ba can combine with chloride and fluoride ions. These BaCl^+ and BaF^+ charged polyatomic molecular species generate a number of ions which overlap the mass range of REE^{90, 91}.

Table 2.1 REE isotopes and their potential spectroscopic interferences^{87, 90, 92, 93}

Element	Mass	Abundance/ %	Interferences					
			Elemental	Polyatomic				
Sc	45	100		²⁹ SiO ⁺	²⁸ SiOH ⁺			
La	139	99.1		¹²³ TeO ⁺	¹²³ SbO ⁺			
Ce	140	88.48		¹²⁴ SnO ⁺	¹²⁴ TeO ⁺			
Pr	141	100		¹²⁵ TeO ⁺				
Nd	142	27.13	¹⁴² Ce ⁺	¹²⁶ TeO ⁺	¹²⁵ TeOH ⁺			
	144	23.8	¹⁴⁴ Sm ⁺	¹²⁸ TeO ⁺				
	146	17.19		¹³⁰ BaO ⁺				
Sm	152	26.7	¹⁵² Gd ⁺	¹³⁶ BaO ⁺	¹³⁵ BaOH ⁺			
	154	22.7	¹⁵⁴ Gd ⁺	¹³⁸ BaO ⁺	¹³⁷ BaOH ⁺			
	148	11.3	¹⁴⁸ Nd ⁺	¹³² BaO ⁺				
Eu	153	52.2		¹³⁷ BaO ⁺	¹³⁶ BaOH ⁺	¹³⁴ BaF ⁺		
	151	17.8		¹³⁵ BaO ⁺	¹³⁴ BaOH ⁺	¹³² BaF ⁺		
Gd	158	24.84	¹⁵⁸ Dy ⁺	¹⁴² NdO ⁺	¹⁴² CeO ⁺	¹⁴¹ PrOH ⁺	¹³⁷ BaF ⁺	
	160	21.86	¹⁶⁰ Dy ⁺	¹⁴⁴ NdO ⁺	¹⁴⁴ SmO ⁺	¹⁴³ NdOH		
	156	20.47	¹⁵⁶ Dy ⁺	¹⁴⁰ CeO ⁺	¹³⁹ LaOH ⁺			
	157	15.65		¹⁴¹ PrO ⁺	¹⁴⁰ CeOH ⁺	¹³⁸ BaF ⁺		
Dy	164	28.2	¹⁶⁴ Er ⁺	¹⁴⁸ NdO ⁺	¹⁴⁸ SmO ⁺	¹⁴⁷ SmOH ⁺		
	162	25.5	¹⁶² Er ⁺	¹⁴⁶ NdO ⁺	¹⁴⁵ NdOH ⁺			
Tb	159	100		¹⁴³ NdO ⁺	¹⁴² NdOH ⁺	¹⁴² CeOH ⁺		
Er	166	33.6		¹⁵⁰ NdO ⁺	¹⁵⁰ SmO ⁺	¹⁴⁹ SmOH ⁺		
	168	26.7	¹⁶⁸ Yb ⁺	¹⁵² GdO ⁺	¹⁵² SmO ⁺	¹⁵¹ EuOH ⁺		
Ho	165	100		¹⁴⁹ SmO ⁺	¹⁴⁸ NdOH ⁺	¹⁴⁸ SmOH ⁺	¹³⁰ Ba ³⁵ Cl ⁺	
Tm	169	100		¹⁵³ EuO ⁺	¹⁵² GdOH ⁺	¹⁵² SmOH ⁺	¹³⁴ Ba ³⁵ Cl ⁺	
Yb	174	31.8	¹⁷⁴ Hf ⁺	¹⁵⁸ GdO ⁺	¹⁵⁸ DyO ⁺	¹⁵⁷ GdOH ⁺		
	172	21.9		¹⁵⁶ GdO ⁺	¹⁵⁶ DyO ⁺	¹⁵⁵ GdOH ⁺	¹³⁷ Ba ³⁵ Cl ⁺	
	176	12.7	¹⁷⁶ Lu ⁺	¹⁶⁰ GdO ⁺	¹⁶⁰ DyO ⁺	¹⁵⁹ TbOH ⁺		
Lu	175	97.41	¹⁷⁶ Hf ⁺	¹⁵⁹ TbO ⁺	¹⁵⁸ GdOH ⁺	¹⁵⁸ DyOH ⁺	¹³⁸ Ba ³⁷ Cl ⁺	

The most significant polyatomic isobaric interferences on REE analysis has been identified as: $^{143}\text{NdO}^+$ on monoisotopic ^{159}Tb ; $^{141}\text{PrO}^+$ on $^{157}\text{Gd}^+$ (most abundant elemental isobaric interference free isotope of Gd); BaO^+ and BaOH^+ ions on all isotopes of Eu; and GdO^+ and GdOH^+ which overlap all isotopes of Yb and Lu^{55, 90, 94-96}. These listed polyatomic spectral interferences clearly justifies why the use of alternative isotopes are unsuitable for overcoming these interferences.

As a consequence, significant research has been devoted to the investigation of various approaches to compensate for polyatomic isobaric interferences and is still a current topic of investigation^{29, 97}. One of the methods proposed is optimisation of various instrumental operating conditions to reduce oxide and hydroxide formation^{56, 78}. Parameters investigated include nebuliser gas flow, RF power and ion lens settings. However, optimisation of these parameters results in a compromise between reduction of oxide and hydroxide formation and the overall sensitivity of analysis^{74, 96, 98}. Since this approach does not completely eliminate the formation of polyatomic ions, further action is required⁹⁸.

An alternative approach is application of mathematical correction equations^{56, 78}. This method makes use of constant correction factors to amend the contribution of an interferent species on the m/z of interest. Various types of mathematical corrections have been applied in REE analysis. These typically involve measurement of MO^+/M^+ and MOH^+/M^+ ratios in single element monitor solutions or in solutions that resemble the sample composition⁹⁷. From these measurements, oxide and hydroxide formation rates of the interferent species can be determined and used to correct for its contribution at the analytes m/z ratio^{96, 97, 99}. The use of such correction factors necessitate knowledge of sample elemental composition and further insight of interferences that constituent elements may generate^{78, 97}. Other elaborate correction schemes that have been proposed include: multiple linear regression, principal component analysis and partial least squares regression^{86, 97, 100}. The main disadvantage of applying mathematical corrections involves the assumption that contribution of the interferent on an analytes m/z remains constant throughout the analysis⁹⁷. However, due to poor stability of oxide and hydroxide polyatomic ions, drift in formation of these interferent ions over time have been observed, even under constant plasma conditions^{74, 85, 88}.

The use of alternative ICP-MS instrumental components to overcome polyatomic interferences is the most recent approach present in literature. These include the use of various sample introduction systems such as laser ablation, electrothermal vaporisation and cryogenic desolvation¹⁰¹⁻¹⁰³. The application of these systems reduces or eliminates the introduction of sample solvent ions into the plasma. Consequently, the occurrence of polyatomic interferences that are sourced from sample solvents (particularly water) is minimised^{1, 97}. High resolution ICP-MS (HR-ICP-MS) incorporating double focusing magnetic sector mass analysers has also been investigated. These provide an improved resolution capability in comparison to conventional quadrupole mass analysers^{56, 78, 81}. The improved resolution permits elucidation of species which have similar m/z ratios and thus is capable of differentiating between analyte ions and those which constitute polyatomic interferences. Regardless, the main limitation of HR-ICP-MS is that a high degree of resolution accompanies a sacrifice in sensitivity. This is particularly observed in REE analyses since a high degree of resolution is required to resolve interferences in the mass region of REE⁹¹.

2.3.3 Sample Preparation

The use of pneumatic nebulisation in the sample introduction system of ICP-MS necessitates aqueous samples. As a result, preparation of geological samples which are predominantly solid, accompany the use of sample decomposition techniques¹. These techniques involve application of strong chemical reagents with high temperatures, in order to disintegrate a mineral structure and liberate constituent ions for analysis. In addition, the sample is converted into a form that is soluble in water or dilute mineral acids, allowing for it to be brought into solution⁵¹

Decomposition of geological samples are particularly challenging as they frequently contain varying amounts of refractory minerals. These minerals are highly resistant to chemical attack, even at considerably high temperatures, which makes them difficult to break down. Many refractory minerals are rare earth bearing, such as xenotime, pyrochlore, euxenite and florencite, while others are carriers of REE including zircon and fluorite^{75, 104, 105}. As a result, refractory minerals are commonly encountered during REE analyses, requiring careful selection of decomposition techniques^{1, 28}. The two main techniques applied for geological samples are acid digestion and alkali fusion.

2.3.3.1 Acid digestion

Acid digestion methods involve mixtures of highly corrosive and oxidising acids such as HF, HClO₄, HNO₃ and HCl^{75, 83, 84, 106, 107}. The use of HF is essential for decomposition of silicate minerals, which is the main component of geological matrices. HF is capable of breaking Si-O bonds due to ability of its fluoride ions to complex with Si, resulting in the formation of volatile SiF₄¹⁰⁵. The reaction causes the release of ions contained within the silicate mineral structure, promoting dissolution of the sample^{75, 107}. Since HF is non-oxidising, it is frequently used in combination with strong oxidising acids to decompose remaining sample mineral components, such as sulfides and oxides¹⁰⁵. These acids include: HNO₃, HClO₄ and aqua regia (1 HNO₃ : 3 HCl).

Despite the necessity of HF, its usage results in formation of insoluble REE fluorides, causing errors in analysis⁷⁵. To reduce formation of these precipitates, removal of excess HF in sample solutions are required. This is achieved by addition of HClO₄ and heating sample solutions to temperatures at which HF is removed by fuming¹⁰⁵. The dissolution of any remaining insoluble fluorides is carried out by further addition of HNO₃, HClO₄ or aqua regia. The removal of HF and subsequent reconstitution steps are repeated several times until a visibly clear sample solution is achieved¹. Consequently, acid digestion methods are time consuming with typical open system digestions carried out over three days^{75, 83, 106, 107}. Digestion times can be considerably reduced by the use microwave assisted acid digestion^{20, 53, 107, 108}. This technique involves the decomposition of a sample by acid digestion in chemically inert closed vessels. The vessels are subjected to high temperatures and pressures, increasing the rate of decomposition¹⁰⁹. Regardless, the removal of excess HF and re-digestion steps are still required to dissolve fluoride precipitates, resulting in repeated microwave runs^{1, 20, 75, 110, 111}.

Although acid digestion methods involve strong acids and lengthy digestion times, a significant proportion of refractory minerals remain intact^{75, 106-108}. As a result, complete sample decomposition, which is the pre-requisite of quantification, is not achieved. Repeated steps in these procedures not only increases the opportunity of sample loss but also involves the repeated use of hazardous acids. HClO₄ is highly oxidising and at high temperatures can react explosively with organic materials.

Consequently, safety precautions and specialised laboratory infrastructure must be established¹⁰⁹. The application of HF also necessitates safe handling as it is capable of causing severe skin burns. In addition, sample solutions containing excess HF can corrode glass or quartz components of traditional sample introduction systems¹¹². A significant drawback of using HF, HClO₄, and HCl for sample digestion is that these acids introduce fluoride and chloride ions into the sample solution^{78, 90}. The presence of these ions contribute to serious spectral interferences on REE analyses.

2.3.3.2 *Alkaline fusion*

Alkaline fusion methods involve the combination of a sample with an alkali salt (flux) and heating the resultant mixture at temperatures above the flux melting point. The result is a reaction between the sample and molten flux, producing a melt that is readily soluble in dilute mineral acids such as HNO₃¹⁰⁹. Alkali fusion is highly efficient at decomposing refractory minerals that are resistant to acid attack. This is due to high temperatures utilised (400 – 1000 °C), which cannot be attained by acid digestion because of the low boiling points of acids employed¹⁰⁵. As a result, alkaline fusion is conventionally used for decomposition of geological samples. Alkali salts utilised in these methods include: LiBO₂, Li₂B₄O₇, Na₂O₂ and Na₂CO₃, which are capable of complete dissolution of refractory minerals^{1, 83, 84, 106-108}. The most prevalent are fusions performed with LiBO₂, due to its capability of decomposing most minerals^{51, 84, 105-107, 109}. The choice of crucible material used for fusion is dependent on the flux and its corresponding melting point¹⁰⁹. Platinum crucibles are frequently used as they are resistant to molten alkali salts and are capable of withstanding high temperatures required for fusion^{51, 109}. An alternative to platinum is disposable graphite crucibles. However, these oxidise at temperatures exceeding 430 °C and are unsuitable for lengthy fusions^{83, 84, 109}. The use of graphite crucibles also results in fine carbon particles in sample solutions which need to be filtered prior to analysis¹¹³.

The main shortcoming of alkali fusion is the high flux to sample ratios resulting in solutions with high TDS^{1, 106, 107}. Solutions of high TDS causes poor sample nebulisation and is a significant contributor to matrix interferences⁷⁸. Consequently, samples are excessively diluted to reduce the TDS below 2% to meet the operational requirements of ICP-MS. This dilution presents a challenge as REE present in trace concentrations can be diluted to the extent where they cannot be quantified with certainty^{83, 104, 107, 108}. The high flux to sample ratios also necessitate the use of high purity alkali salts as any impurities can introduce a significant amount of contaminants to the sample solution^{1, 105}.

The selection between alkali fusion and acid digestion is highly dependent on the mineralogical composition of the sample^{1, 28}. Alkali fusion is generally favoured for samples containing a significant proportion of refractory minerals. Regardless, its use is unsuited for ultra-trace analyses due to high sample dilution factors. This can be overcome by use of acid digestion which do not result in excessive sample dilution. However, studies implementing these methods, have indicated difficulties in achieving complete decomposition of samples containing refractory minerals^{20, 75, 107, 110}. As a result, choosing one technique over the other becomes especially difficult in preparing large batches of samples with unknown or varying mineralogical compositions. The development of decomposition methods for geological samples is still an active area of research. Recent studies have investigated use of alternative ICP-MS sample introduction accessories such as electro-thermal vaporisation and laser ablation. These permit analysis of samples with little to no sample preparation, reducing sample preparation time and risk of contamination^{1, 29}.

The compensation of ICP-MS matrix and spectroscopic interferences arising from: sample decomposition methods; complex geological matrices; as well as REE as a group itself, can be eliminated by the separation of analytes from interferent ions prior to detection. This approach has been suggested as an improvement to those previously outlined, as complete separation will eliminate interferences instead of compensating or minimising their effects. The separation of REE from sample matrix ions as well as individual REE from each other can be achieved by ion chromatography. The chromatographic behaviour of REE and methods used to achieve their separation are reviewed in following section.

2.4 Ion Chromatographic Separation of REE

The chromatographic separation of metal ions are typically achieved by differentiating ions on the basis of their oxidation state and respective ionic radii in solution¹⁸. REE ions are unique in relation to other metals, as they cannot be differentiated based on these factors alone. This is attributed to the existence of all REE ions in the trivalent oxidation state and is further effectuated by their resemblant ionic radii due to lanthanide contraction^{13, 15}. As a consequence, REE ions possess similar properties in solution, contributing to the complexity of their separation^{12, 17, 26-29, 114, 115}.

Ion chromatographic methods that are successful in achieving REE separation have been reviewed by many authors^{12, 14, 24, 114, 115}. An overview of the principles ion chromatography is presented, followed by description of specific ion chromatographic modes prevalent in REE separation.

2.4.1 Principles of Ion Chromatography

Ion chromatography achieves separation of ionic sample constituents by exploiting differences in the manner in which they interact and distribute themselves between a stationary and mobile phase¹⁴.

The stationary phase consists of spherical silica or polymer particles, which are tightly packed into a cylindrical column (analytical column). The surface of these spherical particles are functionalised with ionic groups, which possess an opposite charge than that of the ions to be separated. The mobile phase comprises of an eluent (or combination of eluents) which are continuously passed through the stationary phase. Its flow transports sample contents to the analytical column. Here sample ions are electrostatically attracted to the oppositely charged functionalised sites of the stationary phase and are effectively retained on the column¹¹⁶.

The difference in affinities between various sample ions for ionic sites on the column serves as a basis for separation. Sample ions that interact strongly with the column are retained for a longer period of time relative to ions that possess weak interactions with the column. The strength of this interaction is dependent on the identity of the functionalised ionic site and oxidation states of sample ions to be separated. In the event that sample ions possess the same ionic charge, interaction is then dependent on size of their respective hydrated ions in solution^{12, 18}. Differences in retention are also influenced by the eluent strength of the mobile phase. A gradual increase in concentration of the mobile phase facilitates desorption of retained ions based on their relative affinities between the stationary and mobile phases. This affects the rate at which different sample ions exit the column, effectively achieving separation⁵¹.

Ion chromatographic modes that are well established for REE separation include ion exchange (IEC) and ion pair chromatography (IPC). These chromatographic modes can be differentiated by the stationary phases employed to effectuate REE separation. Nevertheless, both these separation modes apply the same principles to achieve separation of ions^{14, 115}.

2.4.1.1 Ion exchange chromatography (IEC)

Ion exchange chromatography (IEC) involves the reversible interchange of ions in solution with exchangeable counter ions of functionalised ionic groups of the analytical column⁵¹. This separation mode is further subdivided into cation and anion exchange chromatography, depending on the charge of the functionalised ionic group of the stationary phase. Cation exchange chromatography involves the partition of positively charged ions on negatively charged ionic sites of the stationary phase, whilst anion exchange chromatography permits separation of negatively charged ions on positive ionic exchange sites of the stationary phase¹¹⁷. Functionalised ionic groups used for cation exchange chromatography (cation exchangers) include sulfonate or carboxylate groups, whereas secondary, tertiary or quaternary ammonium groups are applied as anion exchangers⁵¹.

2.4.1.2 *Ion pair chromatography (IPC)*

Ion pair chromatography (IPC), also referred to as dynamic ion exchange chromatography, permits separation of sample ionic constituents on a reverse phase column using ion pair reagents. These reagents are long chain alkyl cations or anions whose chemical structure possesses both an organic and ionic ends. Typical ion pair reagents include C₅-C₁₀ alkyl sulfonates (for separation of cations) and C₅-C₈ alkyl ammonium salts for the separation of anions¹¹⁷.

The column stationary phases utilised in this chromatographic mode are comprised of long carbon chains (C₈ or C₁₈) that are fixed onto a solid silica support. This stationary phase is preconditioned with an ion pair reagent, which is present in dilute concentrations in the mobile phase⁵⁶. During this process, the organic tail of the ion pair reagent strongly interacts with the long carbon chains of the column (hydrophobic interaction), immobilising the ionic end of the reagent. It is this end of the ion pair reagent, which provides a charged surface that can be used to achieve separation based on ion exchange principles^{18, 116}.

The use of IPC provides a number of advantages in comparison to conventional IEC such as faster ion exchange, improved separation efficiency and enhanced resolution^{118, 119}. In addition, the use of an ion pair reagent provides greater versatility in separation conditions. By varying the concentration of the ion pair reagent in the mobile phase, the ion exchange capacity of the column is modified. This property can be used to an advantage for altering selectivity of the separation^{117, 120}.

2.4.2 Chromatographic separation of REE

The chromatographic separation of REE can be distinguished into two categories, namely separation of REE as a group from matrix elements and the separation of individual REE members from each other. The chromatographic behaviour of REE and methods used to achieve their separation are further outlined.

2.4.2.1 REE group separation

REE group separation is predominantly achieved by the application of cation exchange resins in combination with strong mineral acids as eluents (HCl or HNO₃). These methods frequently accompany REE analyses to pre-concentrate and isolate these elements from sample matrix components^{66, 103, 115, 121-123}.

Group separation of REE is attained due to differences in the affinity of ions with varying oxidation states for cation exchangers¹⁸. In principle, an ions affinity for the resin increases with an increase in oxidation state ($M^{3+} > M^{2+} > M^{+}$). Consequently, trivalent REE ions possess a greater affinity for cation exchangers in comparison to other mono- and di-valent ions present in the sample. It is this property which is exploited to effectuate separation of REE from sample matrix components^{12, 115}.

Methods that accomplish REE group separation have been optimised by various authors^{64, 124}. Conventionally, these methods achieve separation of REE by sequential acid elution in the following manner:

- Dilute HCl or HNO₃ solutions are used to introduce a sample onto a pre-conditioned cation exchange resin (Dowex AG 50W-X8 and Bio-Rad AG 50W-X8). The various sample cations are retained on the column whilst anionic and neutral species are allowed to pass through.
- The concentration of the acid solution (eluent) is ramped up to 2 – 4 M, which facilitates elution of alkali earth and first row transition metal ions, leaving REE ions retained on the column.
- Once these ions have exited the column, the concentration of the acid solution is further increased to 6 – 8 M, resulting in the elution of retained REE ions.

Due to the retention characteristics of REE ions and their similar ionic radii in solutions, these separation methods do not possess adequate selectivity to effectively distinguish and separate individual REE ions from each other^{24, 115}.

2.4.2.2 Separation of individual REE

To accomplish separation of individual REE from one another, aqueous complexing agents are used as eluents^{12, 24}. The application of these complexing agents results in a competition between ionic sites of the stationary phase and the complexant itself for REE ions. This reduces the affinity of REE ions for the column stationary phase, eliminating the requirement of strong mineral acids to effectuate their elution. Furthermore, the introduction of complexing agents promotes differences in the retention behaviour of individual REE based on their respective complex stabilities with the complexant¹¹⁵. The greater the stability of the REE complex, the more easily is the ion transferred from stationary phase to the mobile phase, resulting in elution. As a result, differences in REE complex stabilities essentially promotes the elution of individual REE at different rates, thus achieving separation¹²⁵.

To completely resolve REE ions from one another, complexing agents need to be sensitive to small differences in REE ionic radii. Furthermore, the stability of resultant REE complexes need to exhibit a consistent trend from La-Lu or vice versa¹¹⁵. A number of complexing agents have been investigated for these attributes including: mandelic acid, lactic acid and α -hydroxy- α -methylbutyric acid.^{24, 73, 126, 127}. However, each of these separate REE to varying degrees of success. For example, lactic acid is not capable of separating Gd, Eu and Sm whilst α -hydroxy- α -methylbutyric acid can separate individual HREE but not LREE^{73, 127}.

The most prominent complexing agent used to separate individual REE is α -hydroxyisobutyric acid (HIBA). Its practicality is due to the stability of REE-HIBA complexes which decreases in a linear fashion from Lu-La¹¹⁵. Currently chromatographic methods that employ HIBA, display the greatest separation efficiency for individual REE and are the most prevalent in literature^{12, 14, 24, 115, 116}.

Both IPC and cation exchange chromatographic methods have achieved separation of individual REE using HIBA. Of these two separation modes, IPC has been reviewed as the most efficient for the separation of individual REE^{14, 115}. These methods typically involve the separation of REE on a C₁₈ column using sodium *n*-octanesulfonate as the ion pair reagent.

The separation of individual REE is achieved due to the sorption of REE ions on immobilised sulfonate groups of the ion pair reagent, followed by their separation according to their relative affinity for HIBA^{120, 128}. IPC methods for the separation of REE have been successfully applied for a number of matrices including geological materials, sediments, mine tailings, steels and alloys^{18, 23, 129-132}.

A comparable mechanism of separation takes place using cation exchange methods for the separation of individual REE. However, REE ions are sorbed on sulfonate groups which are functionalised directly onto the column stationary phase. This is followed by the separation of REE ions based on their relative complex stabilities with HIBA. Cation exchange columns predominantly used in these methods concern sulfonate group cation exchangers and include sulfonated divinylbenzene-polystyrene co-polymers and sulfonated bonded phase silicas^{24, 64, 67, 124, 126, 133, 134}.

Anion exchange chromatography also accomplishes the separation of individual REE. Since REE form cations in solution, the transfer into an anionic state is facilitated by the addition of complexing agents¹²⁵. These include: oxalic acid, diglycolic acid, ethylenediaminetetraacetic acid (EDTA) and nitriloacetic acid¹³⁵⁻¹³⁸. Studies using this chromatographic mode involve REE separation using the above listed complexing agents on quaternary ammonium groups (anion exchangers). Separation of individual REE is achieved based on the differences of REE complex stabilities. Regardless, the application of anion exchange methods for REE separation are not as prominent in comparison to other modes of ion chromatography, due to its poor separation efficiency^{12, 24, 115}.

2.4.3 HPLC Instrumentation

Modern chromatographic methods are performed using HPLC instrumentation. Its application permits interaction of analytes with the stationary and mobile phases under high pressures, providing many favourable attributes such as speed of separation, high resolution and improved separation efficiency¹¹⁵.

A typical HPLC instrument consists of five main components: a mobile phase delivery system, sample introduction system, separation system and detection system (Figure 2.2).

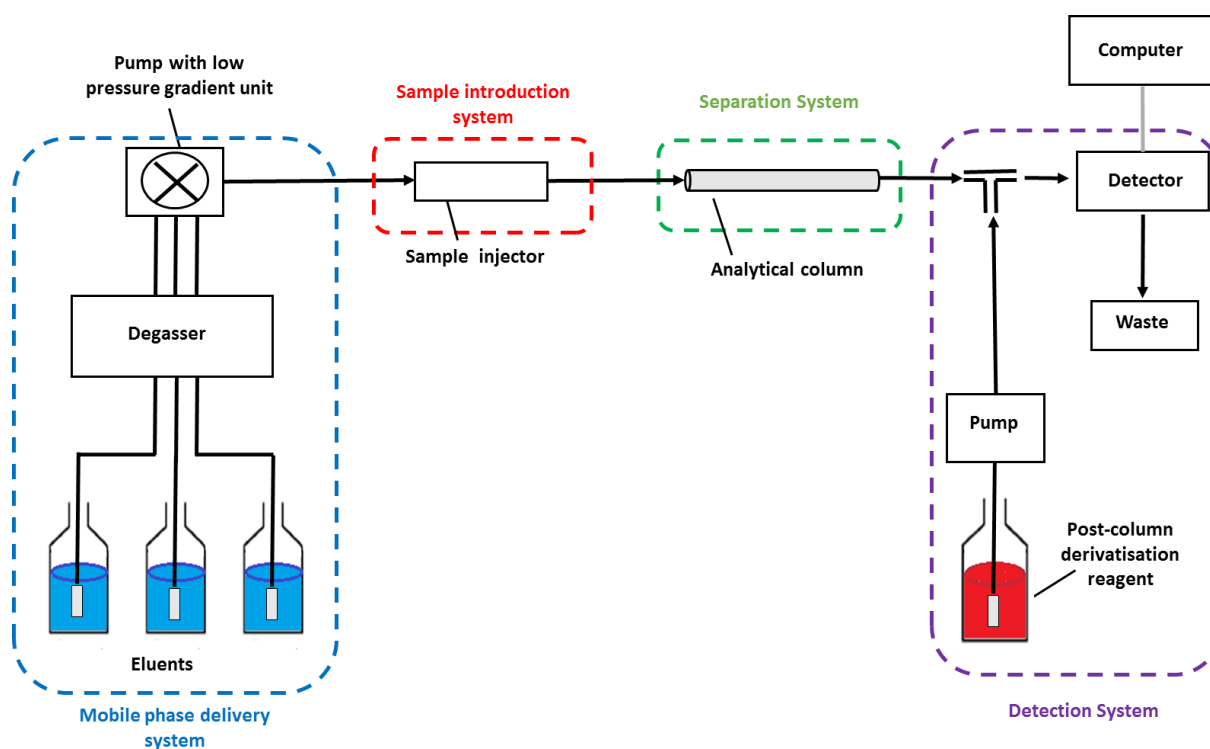


Figure 2.2 Adapted schematic of an HPLC instrumentation^{14, 134}

The mobile phase delivery system comprises of an eluent reservoir (used to store the mobile phase) and a high pressure mechanical pump. The application of a low pressure gradient unit in the delivery system, allows for more than one eluent to be introduced into the system by use of a single pump. Here, respective eluents are withdrawn from their reservoirs by use of micro-proportioning valves according to a pre-determined ratio. These eluents are transported to a low pressure mixing module, where they are combined and subsequently pumped through the system at a specified flow rate¹⁴. The mobile phase delivery system can be operated in both isocratic and gradient modes. In isocratic mode, a fixed mobile phase composition is used throughout the chromatographic process. In gradient mode, the composition of the mobile phase is changed over the duration of the chromatographic process. Gradient elution is preferable for difficult separations whereby the eluent strength needs to be increased to promote the elution of strongly retained analytes^{51, 117}.

The sample is introduced into the HPLC system by means of a sample loop and valve mechanism that can be operated either manually or automatically. The flow of the mobile phase transports the sample to the analytical column whereby separation of sample constituents takes place. The type of column stationary phase employed dictates the chromatographic mode and the separation mechanism¹¹⁶.

Once the separated analyte fractions exit the column, it is carried with the mobile phase flow towards the detector. Conventionally, a standard HPLC is equipped with a UV-Vis detector. Here, separated analyte fractions are measured based on their ability to absorb light at a specific wavelength. Since most metal ions do not possess significant absorption in the UV-Vis region, they cannot be directly measured using this detector.

The sensitivity of the detection method can be considerably improved by reacting separated ions once they exit the column with a suitable colourimetric indicator ligand, prior to reaching the detector. This process, known as post-column derivatisation, is performed by introducing a derivatisation reagent into the flow path of the separated analyte fraction by means of a mixing tee and reaction coil. Here, the analyte is combined with the derivatisation reagent, generating a metal complex that is capable of absorbing light. The reaction coil results in a delay time, providing adequate time for formation of these complexes to take place before entering the detector. These metal-complexes are subsequently measured at a specific wavelength. For REE ions, common post-column derivatisation reagents include 4-(2-pyridylazo)resorcinol (PAR) and 2,2'-(1,8-dihydroxy-3,6-disulfonaphthylene-2,7-bisazo)bisbenzenearsonic acid (arsenazo III). These form strongly coloured complexes with REE enabling detection at 530 and 658 nm respectively^{46, 116, 139}.

The output of an HPLC separation is a plot of the detector response over the duration of the chromatographic process, known as a chromatogram. Sample components, as they elute from the column, are depicted as a series of peaks emerging from the baseline (detector response of the mobile phase). Chromatograms can be used for qualitative analysis in which analytes are identified by their respective retention times as well as quantitative analysis in which the height or area of an analyte peak is related to its concentration^{14, 51, 116}.

The performance of a chromatographic system can be described using the following terms:

Retention time: The elapsed time measured from the injection of a sample until detection of a separated sample component elution peak. Retention times are assigned to each sample component and provides an indication of the length of time the component is retained on the column prior to detection¹⁴⁰.

Resolution: The difference in retention time between two peaks. The resolution provides a measure of the effectiveness of a chromatographic system to adequately separate two adjacent elution peaks¹⁴.

Peak shape: The peak shape of separated sample components provide an indication of the efficiency of the separation conditions. For effective separations, peaks are symmetrical, narrow with adequate height to be sufficiently resolved and distinguished from the baseline allowing for higher sensitivity¹¹⁷.

Band broadening: The process in which a chromatographic peak increases in width as the sample travels through the analytical column. The broadening or spreading of the peak results in decrease in height affecting both its resolution from neighbouring peaks and its detection. Band broadening is inevitable in chromatographic separations, however the rate at which it occurs can be controlled such that the resolution and quantification of separated sample components are not compromised¹⁴⁰.

The key objective of HPLC separations is to achieve optimum resolution of separated sample components within a reasonable time. In addition sample components must be separated into discrete peaks by minimising the factors that influence band broadening. This can be achieved by optimisation of various chromatographic parameters and conditions such as: column stationary phase, eluents used to effect separation, concentration of the eluent, the rate at which concentration of the eluent changes during separation (elution program), flow rate, pH and temperature. The effect of changes to these factors on separation, is dependent on the interaction of the analyte between the stationary and mobile phases¹⁴¹.

2.5 Determination of REE by Ion Chromatographic Separation using ICP-MS Detection

The application of chromatographic separation with ICP-MS detection for REE determination, permits the elimination of interferences that impair their accurate quantification by ICP-MS alone^{56, 78}.

The use of these methods for REE determination in geological materials are frequently performed in consecutive steps, as opposed to an online method in which separation and detection takes place concurrently. In other words, chromatographic separation of REE takes place, followed by retrieval of separated REE fractions and finally, analysis of separated fractions as individual sample solutions by ICP-MS. Studies which have adopted this approach for REE analysis predominantly employ chromatographic methods that achieve group separation of REE^{89, 103, 122, 142-145}. The use of such methods accomplishes pre-concentration of REE as well as separation of these elements from matrix ions, thus improving the sensitivity of ICP-MS detection^{28, 29}. However, the use of REE group separation prior to ICP-MS analysis has the following limitations:

- The separation of REE as a group does not address ICP-MS spectroscopic interferences that individual REE impose on each other⁷⁸. These include: elemental isobaric interferences as well as polyatomic isobaric interferences of LREE oxide and hydroxide molecular species on isotopes of HREE. As a result, the use of REE group separation methods does not eliminate mutual REE interferences that affect their quantification by ICP-MS, requiring additional means for their compensation⁸⁹.

- The efficiency of REE group separation procedures are highly dependent on the sample composition. It is well established that Fe, Al, Ca and Ba are capable of co-eluting with REE, especially for geological samples that possess significant amounts of these elements^{63, 64, 115, 121, 124}. Ba is the most significant of these matrix ions as it can form BaO⁺ and BaOH⁺ ions which interfere with the analysis of Nd-Gd⁷⁸. Furthermore, application of these methods results in the removal of Sc amongst matrix ions. This is attributed to its smaller ionic radii (0.68 Å) in comparison to the remaining REE (0.85-1.06 Å), which allows it to demonstrate a different elution behaviour²¹. Since Sc is absent from the separated REE group fraction, its quantification is precluded.
- Samples of varying compositions exhibit column overloading, which affects the rate at which REE exit the column^{63, 85, 130}. The dependency of REE elution rate on the sample composition introduces uncertainties with respect to their retention time. This can result in inadequate retrieval of separated REE group fractions due to the inconsistent times at which these elements exit the column. As a result, the REE elution behaviour of samples of varying compositions need to be assessed such that fraction collection occurs at the correct time interval and to prevent poor recoveries^{63, 130, 143}. Due to high sensitivity of ICP-MS detection, errors attributed analyte loss are magnified such that the accurate quantification of REE present at trace concentrations are significantly impaired⁵⁶.

To overcome these limitations, a recent approach is the direct coupling of chromatographic separation to an ICP-MS, creating an on-line separation and detection method (HPLC-ICP-MS)⁷¹.

2.5.1 Coupling of HPLC and ICP-MS instrumentation for REE determination

The combination of HPLC and ICP-MS instrumentation to form a hyphenated HPLC-ICP-MS analytical technique is achieved by connecting polymeric or stainless steel tubing from the end of the HPLC analytical column to the sample introduction system of the ICP-MS⁵⁶. The chromatographic methods used in this coupled technique for REE determination concern the separation of individual REE from each other, rather than REE group separation^{73, 138, 146}. This eliminates mutual REE spectroscopic interferences prior to ICP-MS detection.

The applicability HPLC-ICP-MS for REE analysis has been demonstrated for multi-element REE standard solutions in addition to high purity REE oxides^{73, 147}. However, its use for more complex sample matrices necessitates REE group separation by sample pre-treatment prior to analysis^{73, 148}. The REE group separation procedure is performed off-line, followed by injection of the separated REE group fraction into the HPLC-ICP-MS, in which separation and detection of individual REE take place.

The main requirement of REE group separation/ matrix removal prior to analysis by HPLC-ICP-MS is to prevent column overloading (which affects separation efficiency) and to avoid the potential incompatibility of mobile phase constituents with sample matrix components¹³⁰. Nevertheless, the application of matrix removal prior to analysis contributes to the overall error of the analytical method. This is owing to the potential introduction of contaminants from separation reagents, incomplete separation of matrix elements, sample losses due to inefficient fraction collection and poor REE recoveries.

A few HPLC-ICP-MS methods have exemplified the capability of separating matrix elements and individual REE within a single analytical run. This eliminates the requirement of matrix removal prior to analysis as it is essentially carried out as part of the online HPLC-ICP-MS method. Consequently, the direct injection of sample solutions is permitted, conferring the analytical method greater speed and accuracy. These methods are yet to be applied for REE analysis in geological matrices, having already been performed on seawater sample matrices and spent nuclear fuels^{129, 149, 150}. As a result, the efficiency of HPLC-ICP-MS for the direct analysis of REE in geological matrices need to be further evaluated.

The combination of a chromatographic method with ICP-MS detection requires careful forethought before developing an online HPLC-ICP-MS analytical method. This takes into consideration that the mobile phase composition and its accompanying flow rate needs to be compatible with the ICP-MS, such that its sensitivity is not compromised^{56, 70, 71}.

2.5.1.1 Compatibility of mobile phase composition with ICP-MS

Separation reagents that constitute the mobile phase may contain a high content of organic solvents or salts. These reagents can considerably impair sample nebulisation, the plasma ionisation efficiency and overall performance of the ICP-MS itself⁷⁰.

Mobile phases that possess high concentrations of salts can induce clogging of the nebuliser. This affects the conversion of the eluent into an aerosol, inhibiting its transport to the plasma and its subsequent analysis. Nebulisation efficiency can also be affected by changes in eluent composition during separation (gradient elution). This causes variations in the viscosity of the column effluent resulting in differences in the rate at which it is introduced into the spray chamber^{70, 71}.

The use of volatile organic solvents as the main components of the mobile phase, such as methanol and acetonitrile, can extinguish the plasma due to an increase in solvent vapour pressure^{56, 71}. Furthermore, the combustion of organic compounds in the mobile phase results in carbon formation. This carbon is capable of depositing on the sample and skimmer cones of the ICP-MS, resulting in a drift in analyte signal over time^{70, 73}.

In the event that carbon deposition results in the orifice clogging, suppression of the analyte signal is observed with an accompanying deterioration of detection sensitivity. A comparable effect is also caused by mobile phases with high salt content in which deposition of Li, Na and K on the interfacial cones of the ICP-MS has been reported⁵⁶.

Separation reagents can also contribute to the background signal of the detector, resulting in the decreased sensitivity of analysis. This limits the concentration range that can be measured with confidence and can potentially inhibit quantification of elements present at trace concentrations⁸⁵.

2.5.1.2 *Compatibility of mobile phase flow rate with ICP-MS sample introduction system*

The efficiency of the nebuliser to convert a sample solution into an aerosol is dependent on the rate at which the mobile phase is introduced into the nebuliser. To maintain a reproducible sample aerosol during analysis, the flow rate of the mobile phase and the flow rate capacity of the nebuliser must be matched⁷⁰. With respect to flow rates in the order of 1.0 mL min⁻¹, a high flow concentric nebuliser is recommended, however specially designed nebulisers are required for flow rate in the order of 1.0 μ L min⁻¹ or 1.0 nL min⁻¹. These include micro-concentric nebulisers, direct injection nebulisers and high pressure nebulisers. The selection of nebulisers to match the mobile phase flow rate should also accommodate an increase in volume, due to the introduction of internal standards. This is usually performed online, in which an internal standard solution is introduced into the flow path of separated ions prior to nebulisation, at a constant rate. This is accomplished by the use of an additional pump and mixing tee⁵⁶.

The length of the connection leading from the analytical column to the nebuliser, in addition to the connections within the sample introduction system of the ICP-MS must be kept to a minimum. This reduces the extra-column volume that separated analytes travel before reaching the spray chamber, minimising the occurrence of band broadening⁷¹. It is for this reason that application of self-aspirating nebulisers which generate short aerosol paths (such as concentric nebulisers) are favourable⁵⁶.

Once these key aspects have been successfully optimised, HPLC-ICP-MS possesses a combination of advantageous analytical features demonstrated by HPLC and ICP-MS alone. This includes the capability of attaining high separation efficiency with element specific detection capacity, making it a highly effective analytical tool for overcoming interferences and achieving accurate quantification of REE.

2.6 Validation of Analytical Data

To determine whether the application of a newly developed analytical method is suitable for its intended purpose, or if an established method is performed correctly, the accuracy, precision, traceability and reliability of the analytical data obtained needs to be verified. This can be achieved by carrying out the analytical procedure on certified reference materials (CRMs).

A CRM is a reference material whose properties are characterised by at least two or more reference methods of analysis. These methods are performed by a number of accredited laboratories. The results of which, are pooled to generate a mean (certified value) and its corresponding uncertainty at a stated level of confidence. These values are provided in a certificate of analysis which accompanies each CRM¹⁵¹.

CRMs used for method validation must be relevant to the type of sample matrix and analyte concentrations for which the analytical method will be used for on a routine basis. The agreement between the certified values of the CRM with that obtained from the analytical procedure to be validated indicates its applicability. This is established by whether the uncertainty range accompanying certified values and measured values of the CRM overlap¹⁵². The application of CRMs is an integral part of method development and verification as it provides credibility to the results obtained from the implemented analytical methodology. It is accepted that if a particular analytical procedure can generate results which are in agreement with certified values of a CRM, then it is also capable of generating valid results for the analysis of real samples. Furthermore, CRMs can also be used to calibrate an instrument prior to analysis. This is particularly advantageous for the analysis of samples which contain sample matrix components that affect the detector response for a particular analyte. Since CRMs contain a similar matrix to the samples analysed, these effects are taken into account during calibration¹⁵¹.

There are a number of international and local distributors of CRMs that are suitable for REE analysis in geological materials including USGS, Central Geological Laboratory of Mongolia (CGL), Ore Research and Exploration Pty Ltd. and African Mineral Standards (AMIS). The matrix composition of these CRMs varies significantly and is dependent on the mineralogical composition, the area from which it was derived and type of REE bearing minerals it possesses.

CHAPTER 3 - AIMS AND OBJECTIVES

3.1 Research Rationale

REE are of high commercial value owing to their significance in technological advancements^{2, 3}. Due to recent projected supply risks together with an increase in demand of these elements, a number of countries (including South Africa) have gained awareness of the profitability of their REE deposits and reserves^{3, 7}. In order to ascertain the feasibility of mining REE, the distribution and concentration of these elements in mineral deposits must be evaluated. This necessitates the development of sensitive, accurate and precise analytical methods for REE quantification in geological materials.

The determination of REE in these materials presents a number of significant analytical challenges^{26-29, 47, 48}. These are attributed to the inherent chemical similarity amongst individual REE as well as the complex matrices associated with geological materials in which REE are present at trace concentrations^{13-15, 29, 46}.

Several analytical techniques have been applied for REE determination in geological matrices, each possessing a number of considerable drawbacks which hinder the routine quantification of these elements^{29, 55-57}. ICP-MS, the leading analytical technique applied for determination of REE, is prone to a number of serious spectral and matrix interferences associated with: matrix components of geological materials, sample preparation methods and REE as a group itself. Due to the high sensitivity of this technique, errors caused by these interferences are magnified, resulting in inaccurate quantification. As a consequence, compensation of interferences must take place to prevent significant errors of analysis^{56, 78}.

In view of current literature, a number of research studies have been devoted to the investigation of various approaches to compensate for ICP-MS interferences on the determination of REE^{29, 91, 96, 97, 102}.

The most advantageous approach involves the application of chromatography to separate interferent ions from an analyte prior to detection by ICP-MS. This takes into consideration that complete separation eliminates interferences instead of compensating or minimising their effects. Chromatography also provides a compelling solution for overcoming interferences as separation methods can be combined with an ICP-MS⁷⁸.

Numerous studies have performed the determination of REE in geological materials using chromatographic separation prior to ICP-MS detection. However, these studies typically implement chromatographic methods that achieve separation of REE as a group rather than the separation of individual REE from each other^{89, 103, 122, 142-145}. The use of such chromatographic methods may have a number of limitations which include variable separation of matrix interferences in addition to the removal of Sc, precluding its analysis. Most of all, these chromatographic methods fail to address ICP-MS interferences that individual REE impose on each other^{63, 64, 78, 115, 121, 124}. The determination of REE in complex sample matrices by HPLC-ICP-MS also requires extensive sample pre-treatment procedures to prevent column overload and sample incompatibility with mobile phase constituents^{73, 130, 148}. The application of sample pre-treatment methods contributes to the overall error of analysis due to: contaminants present in reagents used to effect matrix removal/pre-concentration, sample losses due to inefficient retrieval of REE fractions and poor REE recoveries.

The development of specific chromatographic methods that are able to accomplish the separation of both individual REE and matrix elements, without performing sample pre-treatment procedures, addresses many of the limitations exemplified in literature. Consequently, the capability of HPLC-ICP-MS to perform the direct analysis of REE in geological materials can be evaluated by investigating the potential integration of these specific chromatographic methods and determining their influence on detection and overall analytical performance of the ICP-MS.

3.2 Aims and Objectives

- ✚ To validate the effectiveness of the sample decomposition method by ICP-MS analysis of CRMs

- ✚ To investigate the efficiency of established REE chromatographic methods (ion pair and ion exchange chromatography) for the separation of individual REE in geological materials without the requirement of matrix removal/sample pre-treatment. The objectives are to:
 - Optimise chromatographic conditions of selected methods for separation of individual REE
 - Demonstrate separation efficiency of optimised chromatographic conditions and establish limitations with respect to the separation of REE
 - Identify the influence of select matrix ions on REE separation under optimised separation conditions
 - Apply optimised chromatographic conditions for the direct separation of REE in geological sample matrices and identify the potential of sample matrix components to impair separation efficiency of REE
 - Ascertain the necessity of sample pre-treatment/ matrix removal for separation of REE in geological matrices

- ✚ To compare selected chromatographic methods and establish which method is most suitable for REE separation prior to ICP-MS analysis. Basis for comparison will include:
 - Proficiency to attain complete separation of individual REE and eliminate mutual REE ICP-MS spectroscopic interferences
 - Capability to separate matrix ions from individual REE and eliminate matrix induced spectroscopic interferences
 - The necessity of sample pre-treatment procedure prior to separation
 - Applicability of separation times for routine analysis

✚ To evaluate potential integration of the preferred chromatographic method to a hyphenated HPLC-ICP-MS analytical technique for direct analysis of REE in geological materials. This will be achieved by:

- Calculation of LOD, LOQ, precision and accuracy using standards and CRMs
- Investigation of the influence of mobile phase composition of the preferred chromatographic method on analytical performance of ICP-MS by:
 - Using validated CRM data to identify sources of error prior to separation
 - ICP-MS analysis of separated REE fractions obtained from the preferred chromatographic method
 - Comparison of REE analytical data before and after separation to establish errors attributed to the separation process

CHAPTER 4 – EXPERIMENTAL

4.1 Analytical Methodology

A flow diagram of the analytical methodology implemented in this study is presented (Fig 4.1).

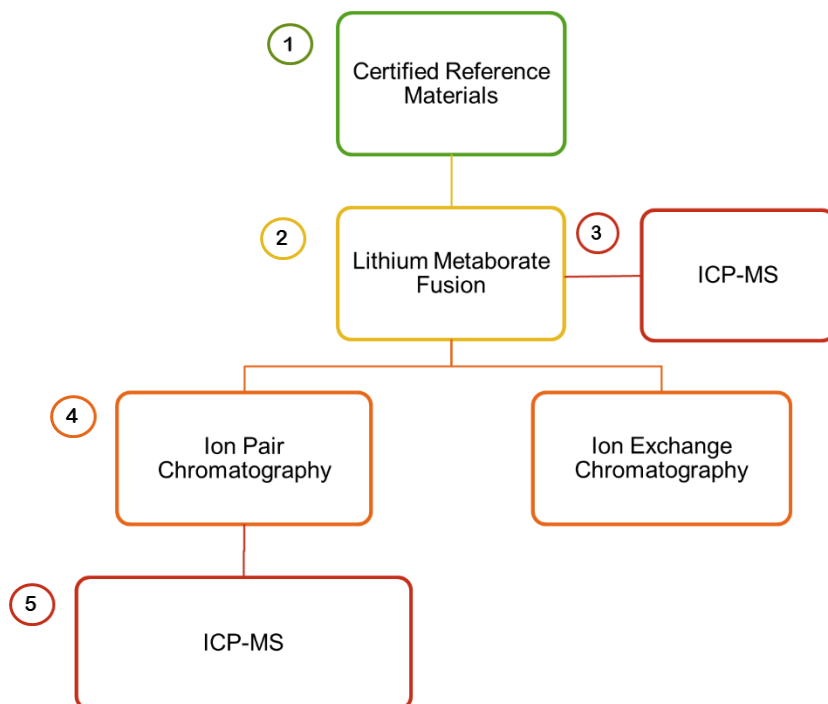


Figure 4.1 Flow diagram of the analytical methodology implemented in this study

The five main steps include:

1. Certified reference materials (CRMs) to validate analytical procedures used at each step of the analysis.
2. Lithium metaborate fusion for the decomposition of CRMs.
3. ICP-MS analysis of CRM solutions to validate the effectiveness of the lithium metaborate fusion procedure. The results of which allow for identification of errors due to fusion. This is imperative to:
 - Establish errors arising from the sample preparation procedure in advance, as these errors are transferred to subsequent steps of the analytical method.
 - Provide a reference point of the analytical performance of ICP-MS prior to separation. This further allows for the influence of mobile phase constituents after separation to be unequivocally identified.
4. HPLC separation with post-column derivatisation system and UV-Vis detector to investigate the efficiency of ion pair and ion exchange chromatographic methods for REE separation. This was performed using both standards and CRM solutions. Comparison of both chromatographic techniques were subsequently performed to establish the most suitable separation method prior to ICP-MS analysis.
5. ICP-MS analysis of REE fractions obtained from separation of CRM solutions by IPC (preferred chromatographic method). The results of which are compared with CRM REE data obtained from Step 3. This was performed in order to:
 - Establish the influence of ion pair chromatographic mobile phase constituents on ICP-MS analysis of REE
 - Evaluate the potential of this separation method to be applied with ICP-MS detection for HPLC-ICP-MS analysis of REE.

4.2 Certified Reference Materials

A total of five certified reference materials (CRMs) were analysed in this study. They exhibit a wide array of analyte concentrations and mineralogical compositions to validate the proposed analytical method. Certificates of analysis accompanying each CRM are provided (Appendix A). Description of these CRMs are presented in Table 4.1

Table 4.1 Selected CRMs studied

Designation	Description	Source
AMIS0185*	From Wigu Carbonatite Complex, near Dar es Salaam, Tanzania. Comprised of mainly bastnäsite with minor amounts of synchisite, parasite, monazite and apatite.	African Mineral Standards (AMIS), South Africa
AMIS0304	From Glenover Carbonatite Complex near Thabazimbi, Limpopo Province, South Africa. Consists of beforosite and sovite	African Mineral Standards (AMIS), South Africa
AMIS0356*	From Wigu Carbonatite Complex, near Dar es Salaam, Tanzania. Comprised of mainly bastnäsite with minor amounts of synchisite, parasite, monazite and apatite.	African Mineral Standards (AMIS), South Africa
CGL-111	REE ore from Mushgia Khudag deposit, Umnogobi Province, Mongolia. Comprised of apatite with minor amounts of secondary phosphate and hydrous ferric oxide.	Central Geological Laboratory (CGL), Mongolia
CGL-124	REE ore from Lugiin Gol deposit, Dornogobi Province, Mongolia. Composed of major amounts of synchisite-bastnäsite, quartz and dolomite, with minor amounts of muscovite and potassium feldspar	Central Geological Laboratory (CGL), Mongolia

*AMIS0185 and AMIS0356 consist of the same mineral constituents, however the wt.% composition of these minerals vary, resulting in different REE and matrix element concentrations.

4.3 Sample Dissolution by Lithium Metaborate Fusion

4.3.1 Materials and Reagents

Platinum crucibles were used to perform sample dissolution. High purity reagents were used to minimize contamination during sample preparation. These include: HNO₃ (70% v/v, platinum grade, Associated Chemical Enterprises), lithium metaborate (99.9% trace metals basis, Sigma-Aldrich) and potassium iodide (> 99.5%, Sigma-Aldrich). Potassium bisulphate (≥ 99%, Sigma-Aldrich) was used to clean crucibles between fusions. Millipore purified water (18 M Ω) was used for dilution of acids and samples as well as cleaning and rinsing of crucibles and glassware.

4.3.2 Analytical Procedure

The finely powdered certified reference materials (< 0.71 μm) were oven dried overnight at 105 °C and stored in a desiccator prior to weighing. A mass of 0.50 g of CRM and 1.50 g of lithium metaborate was carefully weighed in a platinum crucible. Potassium iodide (0.04 g) was added as a non-wetting agent. This reduced adherence of the fused sample material onto the crucible, aiding its removal after fusion. The crucible was placed into a muffle furnace at 1000 °C for 90 minutes. Once the melt was cooled, the resultant glass bead was separated from the crucible and transferred into a 100 mL beaker containing 25 mL of 2% v/v HNO₃. Dissolution of the fused bead was accelerated by heating the beaker on a hotplate with constant agitation. The resultant solution was subsequently filtered into a 100 mL volumetric flask and diluted to the mark with 2% v/v HNO₃. The diluted solution was transferred into 50 mL graduated polypropylene vials and stored in a refrigerator till further analysis. Each CRM was prepared in triplicate with a procedural blank carried out after each set of triplicate fusions. Platinum crucibles were cleaned between each fusion by melting potassium bisulphate in the crucible over a Bunsen burner. The melt was swirled, covering the inner surface of the crucible and allowed to cool before dissolving the residue in boiling water. The crucible subsequently was boiled in a dilute HNO₃ acid solution and rinsed with Millipore water before use.

4.4 HPLC Separation of REE

4.4.1 HPLC Instrumentation

The HPLC instrumentation employed in this study comprised principally of Shimadzu Prominence series components. These included an online degassing unit (DGU -20A5); a pump equipped with a low pressure gradient valve enabling ternary gradient elution (LC-20AT), a pump for the post-column derivatisation reagent (LC-20AD); an autosampler with variable (0.1 – 50 μL) injection volume (SIL-20A); photo diode array detector (SPD-M20A); a system controller enabling automatic control of the flow rate and gradient elution programme (CBM-20A); and an automated fraction collector (FRC-10A).

4.4.1.1 HPLC post-column derivatisation

The application of post-column derivatisation required the following modifications to the HPLC setup:

- To accommodate an additional pump within HPLC instrument setup, the pump used to deliver eluents was connected to the instrument via a 150 cm \times 1/16 in. \times 0.010 in. polytetrafluoroethylene (PTFE) capillary tubing.
- The post-column derivatisation system involved connecting the capillary tubing from the pump which supplied the derivatisation reagent and the column outlet tubing to a stainless steel mixing tee (Valco ZT1: zero dead volume for connecting 1/16 in., bore size 0.75 mm). The mixed eluent and derivatisation reagent solution was routed from the mixing tee through a coiled stainless steel capillary tubing (30 cm \times 1/16 in. \times 0.010 in.) prior to reaching the photo diode array detector.

4.4.2 Samples and Standards

The standards used for optimisation of separation conditions were prepared in 2% HNO₃ by dilution of a 50 mg L⁻¹ multi-element REE standard solution (Sigma-Aldrich). Retention times of individual REE were established by analysis of individual standards (1 mg L⁻¹) prepared by dilution of 10 g L⁻¹ standards of each REE (Inorganic Ventures). A multi-element standard containing REE concentrations representative of those found in geological samples was prepared by appropriate dilution of 10 g L⁻¹ individual REE standards (Inorganic Ventures). The concentrations of respective REE in this standard are presented in Table 4.2. Samples used for analysis were solutions obtained after lithium metaborate fusion of investigated CRMs. Fused CRM solutions were spiked with 20 mg L⁻¹ of each REE prior to analysis. This was carried out to improve sensitivity, particularly for analytes present in ng g⁻¹ concentrations.

All samples and standards were filtered through 0.45 µm filters and subsequently transferred to 2 mL autosampler vials prior to analysis.

Table 4.2 Concentrations of REE in standard representative of those found in geological materials

Analyte	Concentration/ mg L⁻¹
Sc	0.2
Y	6.0
Lu	0.1
Yb	0.4
Tm	0.1
Er	0.6
Ho	0.3
Dy	1.5
Tb	0.5
Gd	5.0
Eu	1.5
Sm	7.0
Nd	60
Pr	25
Ce	250
La	200

4.4.3 Ion Pair Chromatographic (IPC) Separation of REE

4.4.3.1 Analytical column

A 5- μm Kinetex C₁₈ 150 mm \times 4.6 mm (Phenomenex Inc.) analytical column was applied for REE separation.

4.4.3.2 Reagents

All solutions were prepared using Millipore purified water (18 M Ω). High purity reagents ($\geq 99\%$) were used. These were purchased from Sigma-Aldrich, unless otherwise indicated.

The eluents used for separation include α -hydroxyisobutyric acid (HIBA) and sodium 1-octanesulfonate solutions. A mass of 41.6 g of HIBA (Alfa Aesar) was dissolved in water to give 500 mL of 0.8 M HIBA. The pH was then adjusted to 3.8 with concentrated ammonium hydroxide. A 250 mL solution of 0.05 M sodium 1-octanesulfonate was prepared by the dissolution of 2.93 g of sodium 1-octanesulfonate monohydrate in water. The post-column derivatisation reagent (0.15 mM arsenazo III) was prepared by dissolving 0.11 g arsenazo III in 1.0 L water.

Prepared solutions were filtered through Millipore 0.2 μm filters and subsequently degassed by sparging with helium gas prior to usage. For storage periods greater than eight hours, prepared reagents and eluents were stored in a refrigerator.

4.4.3.3 HPLC separation

Initial and optimised chromatographic separation conditions are summarised in Table 4.3 and Table 4.4 respectively. The initial conditions are adopted from C. H. Knight *et al.* and E. A. Gautier *et al.*^{120, 128}.

Table 4.3 Initial chromatographic conditions for IPC separation of REE^{120, 128}

Sample-loop volume	50 μ L
Analytical column	Kinetex C ₁₈ , 5- μ m (150 mm \times 4.6 mm)
Column temperature	30 $^{\circ}$ C
Eluent 1: 1-octanesulfonate	0.1 M 1-octanesulfonate
Eluent 2: HIBA	0.3 M HIBA
Eluent 3 : Water	18 M Ω Millipore water
Eluent flow rate	0.8 mL min ⁻¹
Post-column reagent	0.15 mM Arsenazo III
Reagent flow rate	1.2 mL min ⁻¹
Detector wavelength	658 nm
Gradient program	

Time/ min.	Eluent 1: 1-octanesulfonate	Eluent 2: HIBA	Eluent 3: Water
0.0	10	10	80
15.0	10	90	0
35.0	10	90	0

Table 4.4 Optimised chromatographic conditions for IPC separation of REE

Sample-loop volume	15 μ L
Analytical column	Kinetex C ₁₈ , 5- μ m (150 mm \times 4.6 mm)
Column temperature	30 $^{\circ}$ C
Eluent 1: 1-octanesulfonate	0.05 M 1-octanesulfonate
Eluent 2: HIBA	0.8 M HIBA (pH 3.8)
Eluent 3 : Water	18 M Ω Millipore water
Eluent flow rate	0.8 mL min ⁻¹
Post-column reagent	0.15 mM Arsenazo III
Reagent flow rate	1.2 mL min ⁻¹
Detector wavelength	658 nm
Gradient program	

Time/ min.	Eluent 1: 1-octanesulfonate	Eluent 2: HIBA	Eluent 3: Water
0.0	25	4	71
16.0	25	37.5	37.5
20.0	25	75	0
35.0	25	75	0

Prior to analysis, the HPLC system was flushed with 60% v/v acetone, followed by water to remove traces of organic solvents from previous usage. The removal of organic solvents is essential to prevent the precipitation of sodium 1-octanesulfonate¹⁵³. Equilibration of the column with the starting composition of the mobile phase was carried out for 45 minutes, followed by the analysis of a 2% HNO₃ (blank) solution to facilitate the elution of any contaminants adsorbed on the column. To ascertain the performance of the HPLC system and of the analytical column, a 1 mg L⁻¹ REE multi-element standard was analysed. The resultant chromatogram was inspected for any changes in separation efficiency, peak shape or retention times that may result from contamination of the mobile phase, blocked column frits, air trapped in the system or inadequate column equilibration. The pressure of the HPLC system was carefully monitored throughout the analysis to prevent backflow of the derivatisation reagent into the analytical column.

Spiked CRM sample solutions were directly injected into the HPLC system for analysis *i.e.* no matrix removal or REE group separation was performed prior to injection. Sample analysis was carried out in triplicate. Under the optimised separation conditions, the chromatographic system was operated from 0.03 – 0.30 M HIBA over 15 minutes, followed by 0.30 – 0.60 M HIBA from 15 – 20 minutes at a flow rate of 0.8 mL min⁻¹. The concentration of sodium 1-octanesulfonate of the mobile phase was maintained at 0.0125 M throughout the analysis. The temperature of the column was kept constant at 30 °C. Separated REE ions eluted from the column were reacted with 0.15 mM arsenazo III (supplied at a flow rate of 1.2 mL min⁻¹) via a mixing tee. REE ions were subsequently detected at 658 nm.

After each separation, the sample loop of the autosampler was rinsed. The column was equilibrated with the starting composition of the mobile phase for 10 minutes between chromatographic runs. The analytical column was stored in 0.05 M sodium 1-octanesulfonate when not in use.

4.4.3.4 Fraction collection of separated REE ions

Fraction collection of separated REE ions was performed on CRM solutions obtained after lithium metaborate fusion and multi-element REE standards. The concentration ranges of REE present in these standards are provided (Table 4.5).

Table 4.5 Concentration ranges of REE present in standards used for fraction collection

Analyte	Concentration range/ mg L ⁻¹
Sc	0.02 – 0.20
Y	0.10 – 6.00
Lu	0.01 – 0.10
Yb	0.02 – 0.40
Tm	0.01 – 0.10
Er	0.02 – 0.60
Ho	0.01 – 0.30
Dy	0.05 – 1.50
Tb	0.02 – 0.50
Gd	0.20 – 5.00
Eu	0.05 – 1.50
Sm	0.50 – 7.00
Nd	5.00 – 60.0
Pr	2.50 – 25.0
Ce	25.0 – 250
La	10.0 – 200

- *Fraction collection of REE in CRM solutions*

To establish retention times required to program the Shimadzu FRC10-A for fraction collection, each spiked CRM solution were analysed in triplicate. The mean peak start and end times obtained from the chromatographic data of these runs were used to pre-set the fraction collector.

With respect to fraction collection in order to perform sample analysis, each CRM replicate solution obtained from lithium metaborate procedure (un-spiked) was analysed in triplicate. The retrieved separated REE fractions from all three runs were combined and transferred into 2.0 mL Eppendorf micro-centrifuge vials. The same procedure was followed for lithium metaborate blank solutions. Collected fractions were stored in refrigerator till further analysis.

- *Fraction collection of REE in multi-element standard solutions*

A 1 mg L⁻¹ multi-element REE standard was analysed in triplicate. The mean peak start and end times obtained from the chromatographic data of these runs were used to pre-set the Shimadzu FRC10-A fraction collector.

Fraction collection of standards was performed by analysis of each multi-element standard in triplicate. The procedure was repeated for fraction collection of a blank standard solution. The retrieved separated REE fractions from all three runs were combined and transferred into 2.0 mL Eppendorf micro-centrifuge vials. Collected fractions were stored in refrigerator till further analysis.

4.4.4 Ion Exchange Chromatographic (IEC) Separation of REE

4.4.4.1 Analytical column

Separation of REE was effectuated by use of a Dionex CS5A (250 mm × 4.0 mm) bifunctional quaternary ammonium-sulfonate ion exchange analytical column. This was preceded by application of a Dionex CG5A (50 mm × 4.0 mm) guard column.

4.4.4.2 Reagents

All solutions were prepared using Millipore purified water (18 M Ω). High purity reagents (≥ 99%) were used. These were purchased from Sigma-Aldrich, unless otherwise indicated. The eluents applied for separation include 2,6-pyridinedicarboxylic acid (PDCA), oxalic acid and diglycolic acid.

Preparation of an eluent solution containing 6 mM PDCA, 50 mM sodium acetate and 50 mM acetic acid was carried out by dissolving 1.025 g of sodium acetate and 0.250 g of PDCA in 125 mL of water. Dissolution of PDCA was accelerated by heating the solution on a hot plate with constant stirring. Once cooled to room temperature, 0.715 mL of glacial acetic acid was added to the solution and diluted to a final volume of 250 mL with water. A 500 mL solution of 300 mM oxalic acid and 570 mM lithium hydroxide was prepared by dissolving 9.45 g of oxalic acid dihydrate and 5.98 g of lithium hydroxide monohydrate in water. A 250 mL solution of 300 mM diglycolic acid and 570 mM lithium hydroxide was prepared by the dissolution of 10.05 g of diglycolic acid (Alfa Aesar) and 5.98 g of lithium hydroxide monohydrate in water. The post-column derivatisation reagent solution comprised of 0.2 mM 4-(2-pyridylazo)resorcinol (PAR), 3 M ammonium hydroxide and 1 M acetic acid was prepared by dissolving 0.025 g of PAR in 250 mL of water. A volume of 100 mL of 30% v/v ammonium hydroxide was added to the solution, followed by the dropwise addition of 28.5 mL of glacial acetic acid. The resultant solution was diluted to a final volume of 500 mL with water.

Prepared solutions were filtered through Millipore 0.2 μm filters and subsequently degassed by sparging with helium gas prior to usage. For storage periods greater than eight hours, prepared reagents and eluents were stored in a refrigerator. PAR solutions that had exceeded its shelf life of two weeks (due to oxidation) were discarded and re-prepared.

4.4.4.3 HPLC separation

Initial and optimised chromatographic separation conditions are summarised in Table 4.6 and Table 4.7 respectively. The initial conditions were adopted from a Dionex Corporation technical note^{125, 154}.

Before analysis, the guard and analytical column were flushed the eluent solution comprised of 6 mM PDCA, 50 mM sodium acetate and 50 mM acetic acid for 15 minutes, followed by water for an additional 30 minutes. This was performed to facilitate the removal of impurities and metal ions that were retained on the column from previous use. The guard and analytical column were equilibrated with the starting composition of the mobile phase for 45 minutes.

Similar to IPC separation, separation of a blank solution was performed after column equilibration, followed by the analysis of a 5 mg L⁻¹ REE multi-element standard. Furthermore, spiked CRM sample solutions were also directly injected into HPLC system and analysed in triplicate. Under the optimised separation conditions, separation of REE was effectuated by isocratic elution of oxalic acid followed by gradient elution of both oxalic and diglycolic acids (Table 4.6). Separated REE ions were reacted with post-column derivatisation reagent (0.2 mM PAR) prior to detection at 530 nm.

After analysis of each sample, the guard and analytical column were flushed with PDCA for 15 minutes, followed by water for another 30 minutes. This was performed due to the retention of select transition metal ions on the column which would not elute under the optimised separation conditions. After flushing of the column, the gradient elution program returned to initial conditions. Once the baseline was stable, the next sample was analysed. The guard and analytical column was stored in 0.5 M NaOH when not in use.

Table 4.6 Initial chromatographic conditions for IEC separation of REE^{125, 154}

Sample-loop volume	50 μ L			
Guard column	Dionex CG5A (50 mm \times 4.0 mm)			
Analytical column	Dionex CS5A (250 mm \times 4.0 mm)			
Eluent 1: Water	18 M Ω Millipore water			
Eluent 2: PDCA	6 mM PDCA, 50 M sodium acetate, 50 mM acetic acid			
Eluent 3 : Oxalic acid	100 mM oxalic acid, 190 mM lithium hydroxide			
Eluent 4: Diglycolic acid	100 mM diglycolic acid, 190 mM lithium hydroxide			
Eluent flow rate	0.8 mL min ⁻¹			
Post-column reagent	0.2 mM PAR, 3 M ammonium hydroxide, 1 M acetic acid			
Reagent flow rate	0.56 mL min ⁻¹			
Detector wavelength	530 nm			
Gradient program				
Time/min.	Eluent 1:	Eluent 2:	Eluent 3:	Eluent 4:
	Water	PDCA	Oxalic acid	Diglycolic acid
0.00	0	100	0	0
12.0	0	100	0	0
12.1	100	0	0	0
17.0	100	0	0	0
17.1	40	0	60	0
21.0	40	0	60	0
21.1	20	0	80	0
30.0	51	0	26	23

Table 4.7 Optimised chromatographic conditions for IEC separation of REE

Sample-loop volume	15 μ L
Guard column	Dionex CG5A (50 mm \times 4.0 mm)
Analytical column	Dionex CS5A (250 mm \times 4.0 mm)
Eluent 1: Water	18 M Ω Millipore water
Eluent 2 : Oxalic acid	300 mM oxalic acid, 570 mM lithium hydroxide
Eluent 3: Diglycolic acid	300 mM diglycolic acid, 570 mM lithium hydroxide
Eluent flow rate	0.8 mL min ⁻¹
Post-column reagent	0.2 mM PAR, 3 M ammonium hydroxide, 1 M acetic acid
Reagent flow rate	0.56 mL min ⁻¹
Detector wavelength	530 nm
Gradient program	

Time/min.	Eluent 1: Water	Eluent 3: Oxalic acid	Eluent 4: Diglycolic acid
0.00	100	0	0
1.00	90	10	0
4.00	67	33	0
7.10	67	33	0
7.20	10	90	0
12.10	57	23	20
18.10	70	14	16
30.00	67	33	0

4.5 ICP-MS Analysis of REE

4.5.1 ICP-MS Instrumentation

The ICP-MS instrumentation employed in this study was a standard PerkinElmer NexION 300Q ICP-MS fitted with a concentric nebuliser and a cyclonic spray chamber. Instrument operation conditions and isotopes selected for analysis are summarised (Tables 4.8 and 4.9 respectively). Isotopes that were free of spectral interferences were given preference. In the event that this was not feasible, the NexION software provided default corrections for isobaric interferences. ICP-MS analysis was performed on fused CRM solutions (before separation) and their corresponding separated REE fractions obtained after IPC separation. Indium and Re were used as internal standards to correct for matrix interferences and instrumental drift. The rinse solution used between run comprised of 2% HNO₃.

Table 4.8 ICP-MS instrument operation conditions

ICP- MS instrument	Perkin Elmer NexION 300Q	
Plasma power	1 400 kW	
Plasma gas	Argon	
Plasma gas flow rate	17 L min ⁻¹	
Auxiliary gas flow rate	1.4 L min ⁻¹	
Nebuliser gas flow rate	0.75 L min ⁻¹	
Acquisition parameters:		
Data acquisition mode	Peak hopping	
Sample uptake rate	0.8 mL min ⁻¹	
	CRM solutions after fusion	IPC separated CRM REE fractions
Acquisition time	100 s	70 s
Washout time	120 s	180 s
Number of replicates	3	3

Table 4.9 Isotopes selected for ICP-MS analysis

Element	Mass/ amu
In	114.90
Re	186.96
Sc	44.95
Y	88.90
La	138.91
Ce	139.90
Pr	140.91
Nd	145.91
Sm	146.91
Eu	150.92
Tb	158.92
Gd	159.93
Dy	162.92
Ho	164.93
Er	166.93
Tm	168.93
Yb	173.94
Lu	174.94

4.5.2 ICP-MS analysis of CRM solutions after lithium metaborate fusion

Prior to analysis, sample and skimmer cones (Ni) were removed from the instrument and cleaned with 1% HNO₃ solution. This was followed by calibration of the instrument using multi-element REE standards. Calibration standards were prepared in 2% HNO₃ by dilution of 10 g L⁻¹ standards of each REE (Inorganic Ventures). Each standard also included 10 µg L⁻¹ of Re and In as internal standards. The concentration ranges of REE present in these standards are provided (Table 4.10).

Table 4.10 Concentration ranges of REE present in standards used ICP-MS instrument calibration

Analyte	Concentration range/ mg L ⁻¹
Sc	$1.0 \times 10^{-3} - 1.0 \times 10^{-2}$
Y	$5.0 \times 10^{-3} - 3.0 \times 10^{-1}$
Lu	$5.0 \times 10^{-4} - 5.0 \times 10^{-3}$
Yb	$1.0 \times 10^{-3} - 2.0 \times 10^{-2}$
Tm	$5.0 \times 10^{-4} - 5.0 \times 10^{-3}$
Er	$1.0 \times 10^{-3} - 3.0 \times 10^{-2}$
Ho	$5.0 \times 10^{-4} - 1.5 \times 10^{-2}$
Dy	$2.5 \times 10^{-3} - 7.5 \times 10^{-2}$
Tb	$1.0 \times 10^{-3} - 2.5 \times 10^{-2}$
Gd	$1.0 \times 10^{-2} - 2.5 \times 10^{-1}$
Eu	$2.5 \times 10^{-3} - 7.5 \times 10^{-2}$
Sm	$2.5 \times 10^{-2} - 3.5 \times 10^{-1}$
Nd	$2.5 \times 10^{-1} - 3.5 \times 10^0$
Pr	$1.3 \times 10^{-1} - 1.3 \times 10^0$
Ce	$1.3 \times 10^0 - 1.3 \times 10^1$
La	$5.0 \times 10^{-1} - 1.0 \times 10^1$

Each CRM solution obtained from lithium metaborate fusion including procedural blanks were subject to a 20x dilution factor, due to the addition of In and Re as internal standards. All CRM and blank solutions were diluted with 2% HNO₃ and possessed a final In and Re concentration of 10 µg L⁻¹.

The measurement sequence employed consisted of a blank, calibration standards, a quality control check solution containing known amounts of REE, a fusion procedural blank and replicate solutions of a particular CRM. Each blank and CRM replicate solution were analysed in duplicate. This sequence was repeated prior to analysis of each of the five CRMs.

4.5.3 ICP-MS analysis of IPC separated REE fractions of CRM solutions

ICP-MS analysis was performed on separated REE fractions obtained after IPC separation of fused CRM and standard solutions. These fractions were subject to a 20x dilution factor, due to the addition of Re and In as internal standards as similarly conducted for ICP-MS analysis of CRM solutions after fusion.

The diluted REE fractions of standard solutions were used to calibrate the instrument. The concentrations of REE corresponding to these solutions are comparable to that presented in Table 4.10.

The analysis was performed for a single analyte at a time. The measurement sequence consisted of a blank, fraction collected standards, a quality control check solution containing known amounts of REE and replicate solutions of separated analyte fractions corresponding to all CRMs. Each blank and CRM REE fraction were analysed in duplicate. After analysis, sample and skimmer cones of the instrument were cleaned with 2% HNO₃ solution. This sequence was repeated prior to analysis of the next analyte.

CHAPTER 5 - RESULTS AND DISCUSSION

5.1 ICP-MS Analysis of REE after Lithium Metaborate Fusion

Lithium metaborate fusion was selected for sample preparation due to the presence of acid resistant minerals in the mineralogical composition of selected CRMs. These included chromite, zircon, pyrochlore and fluorite, in which at least one of these minerals were present in each CRM. The resultant fused CRM solutions were subjected to ICP-MS analysis, prior to separation. This was performed in order to validate the fusion procedure, identify potential sources of error and establish a basis of comparison for REE results obtained after separation.

5.1.1 Limits of detection (LOD) and limits of quantification (LOQ)

Limits of detection (LOD) and limits of quantification (LOQ) of the procedure were calculated (Table 5.1). The LOD was calculated as three times the standard deviation from 24 determinations of four procedural blanks, divided by the sensitivity or slope of respective calibration curves (Appendix B). LOD values denotes the smallest analyte concentration that generates a signal which is statistically distinguishable from the blank¹¹⁷. These values indicate the extremity of an instrument's detection capabilities for an analyte and cannot be used a reliable indicator for quantification¹¹⁷. Consequently, LOQ need to be evaluated in order to assess the smallest analyte concentration that can measured with certainty¹¹⁷. LOQ values of the procedure were calculated using ten times the standard deviation of procedural blanks, divided by the sensitivity. These values further take into account the dilution factor (4000) arising from sample dissolution procedure and introduction of internal standards prior to ICP-MS analysis.

Table 5.1 Limits of detection (LOD) and limits of quantification (LOQ) of lithium metaborate fusion procedure

Analyte	LOD/ng L ⁻¹	LOQ/ng g ⁻¹
Sc	1.933×10^{-2}	2.557×10^{-1}
Y	75.11×10^{-2}	1.002×10^0
La	1.164×10^0	15.52×10^0
Ce	4.957×10^{-1}	6.609×10^0
Pr	1.770×10^{-1}	2.360×10^0
Nd	2.043×10^0	27.24×10^0
Sm	4.637×10^{-2}	6.184×10^{-1}
Eu	7.694×10^{-3}	1.026×10^{-1}
Gd	9.011×10^{-1}	12.01×10^0
Tb	3.023×10^{-3}	3.751×10^{-2}
Dy	3.023×10^{-2}	4.031×10^0
Ho	7.998×10^{-3}	1.066×10^{-1}
Er	1.194×10^{-2}	1.591×10^{-1}
Tm	8.099×10^{-3}	1.080×10^{-1}
Yb	1.466×10^{-2}	1.955×10^{-1}
Lu	6.032×10^{-3}	8.042×10^{-2}

Calculated LOQ values ranged from $1.026 \times 10^{-1} - 27.24 \times 10^0$ ng g⁻¹ for LREE and $8.042 \times 10^{-2} - 4.031 \times 10^0$ ng g⁻¹ for HREE, indicating the applicability of the procedure to analyse REE concentrations associated with geological materials. Despite the large dilution factor, a great number of LOQ values were below 1.00 ng g⁻¹, allowing quantification of corresponding REE at sub-ppb levels.

5.1.2 Precision

Precision of the fusion procedure, characterised as percent relative standard deviation (% RSD), was evaluated by replicate analysis of CRMs. CRMs were fused in triplicate with each resultant solution analysed in duplicate by ICP-MS. The precision indicates variation of data obtained from repeated measurements and contributes to the uncertainty which accompany the mean. Low RSD values are associated with high precision, whilst high RSD values are associated with poor precision. The mean (\bar{x}), standard deviation (s) and % RSD of the data are presented (Appendix C).

The precision of replicate data varied between each CRM and were within the range of 0.485 – 10.4%. CGL-111 exhibited poorest precision of investigated CRMs, possessing the highest RSD values for all REE (2.34-10.4%). Conversely, RSD values obtained for AMIS CRMs were all below 5%. It was apparent that RSD values were independent of REE concentrations. This was rationalised by taking into consideration RSD data obtained for AMIS0356, which exhibited the highest precision despite possessing the lowest concentrations of most REE. Furthermore, precision amongst REE within an individual CRM also did not display any distinct trend with concentration, as elements of both high and low concentrations exhibited ranges of RSD values that coincide.

5.1.3 Accuracy

Accuracy of the fusion procedure was assessed by comparison of measured concentration values with certified and provisional concentrations provided in CRM certificates of analysis. Informational values were excluded as they did not accompany an uncertainty range and therefore did not fulfil the requirements for assessing accuracy of the procedure.

Measured and certified/provisional concentrations with corresponding 95% confidence intervals for each REE were calculated (Table 5.2 – 5.5). The 95% confidence interval represents the range in which the true mean value is found with a 95% probability⁵¹. The agreement between measured concentration values and those provided in CRM certificates are established by whether the 95% confidence intervals between these two values overlap.

An effective way of illustrating this agreement is to normalise the measured concentrations (C_{measured}) to the corresponding certified/provisional concentrations of the CRM ($C_{\text{certified}}$)¹³⁴. The resultant ratios of $C_{\text{measured}}/C_{\text{certified}}$ and their uncertainty ranges are plotted against each analyte (Figures 5.1 – 5.4). The closeness of the resultant ratio of $C_{\text{measured}}/C_{\text{certified}}$ to the value of one (represented by a dashed line) gives an indication of how well the measured and certified/provisional values correlate. Furthermore, the uncertainty range which accompanies $C_{\text{measured}}/C_{\text{certified}}$ ratios indicate whether the 95% confidence intervals of these values overlap. The 95% confidence intervals are designated within the figures by solid lines at values 0.95 and 1.05 respectively.

Differences in the degree of REE characterisation amongst each investigated CRM exist. As a result, not all REE concentrations were available for comparison. With respect to AMIS0185, certified/provisional values were not provided for Sc, Gd, Tb, Er, Yb and Lu. However, for the remaining REE, all measured concentrations were in in good agreement with certified/provisional concentrations (Fig 5.1).

AMIS0304 was the least characterised of investigated CRMs with certified/provisional values stated particularly for Y and La-Sm. Of these values, only the measured concentration of Pr fell just below the lower 95% confidence interval limit. The remaining measured concentrations corresponded well with the provided certified/provisional values (Fig 5.2)

AMIS0356 was the sole CRM for which Sc is characterised (Table 5.4). A large discrepancy was observed for the measured Sc concentration ($110 \pm 5.14 \mu\text{g g}^{-1}$) in relation to the provisional value provided ($28 \pm 6 \mu\text{g g}^{-1}$). This may be attributed to a calibration error, as the expected concentration did not generate the same instrument response as a Sc standard solution of a similar concentration. This difference in the instrument response may also be explained in terms of polyatomic isobaric interferences. Si forms oxide and hydroxide molecular species ($^{29}\text{SiO}^+$ and $^{28}\text{SiOH}^+$), which possess the same nominal m/z as monoisotopic $^{45}\text{Sc}^+$. Since Si is present at much greater concentrations than Sc in geological materials, the degree of this interference is significant⁹². This predicament may be compensated by using matrix matched standards, the method of standard addition or using CRMs of similar sample composition to calibrate the instrument for Sc. Another analyte which did not agree with the certified value for AMIS0356 is Pr, which fell just below the lower 95% confidence interval limit. The remaining REE (Y, La, Ce, Nd, Sm, Eu, Dy, Ho and Tm) certified/provisional values were in good agreement for AMIS0356 (Fig 5.3).

Table 5.2 Comparison of ICP-MS measured and certified* REE concentrations for AMIS0185 from fusion procedure ($n = 6$, $P = 0.95$)

Analyte	Measured Concentration/ $\mu\text{g g}^{-1}$	Certified Concentration/ $\mu\text{g g}^{-1}$	$C_{\text{measured}}/C_{\text{certified}}$
Sc	77.8 ± 3.24	—	—
Y	64.8 ± 1.54	62 ± 7.7	1.05 ± 0.13
La	$28\ 896 \pm 493$	$29\ 760 \pm 2\ 720$	0.97 ± 0.09
Ce	$38\ 913 \pm 791$	$40\ 750 \pm 4\ 610$	0.95 ± 0.11
Pr	$3\ 108 \pm 49.8$	$3\ 471 \pm 343$	0.89 ± 0.09
Nd	$9\ 412 \pm 143$	$9\ 238 \pm 1\ 033$	1.02 ± 0.11
Sm	554 ± 9.83	556 ± 48	0.99 ± 0.09
Eu	96.8 ± 2.05	<i>94.2 ± 12.1</i>	1.03 ± 0.13
Gd	435 ± 8.74	—	—
Tb	40.5 ± 0.914	—	—
Dy	32.8 ± 0.608	<i>27.1 ± 5.1</i>	1.21 ± 0.23
Ho	3.82 ± 0.0681	<i>3.2 ± 0.5</i>	1.19 ± 0.19
Er	5.55 ± 0.118	—	—
Tm	0.506 ± 0.0113	<i>0.43 ± 0.08</i>	1.16 ± 0.22
Yb	3.73 ± 0.0811	—	—
Lu	0.418 ± 0.0116	—	—

* Provisional concentrations are italicised

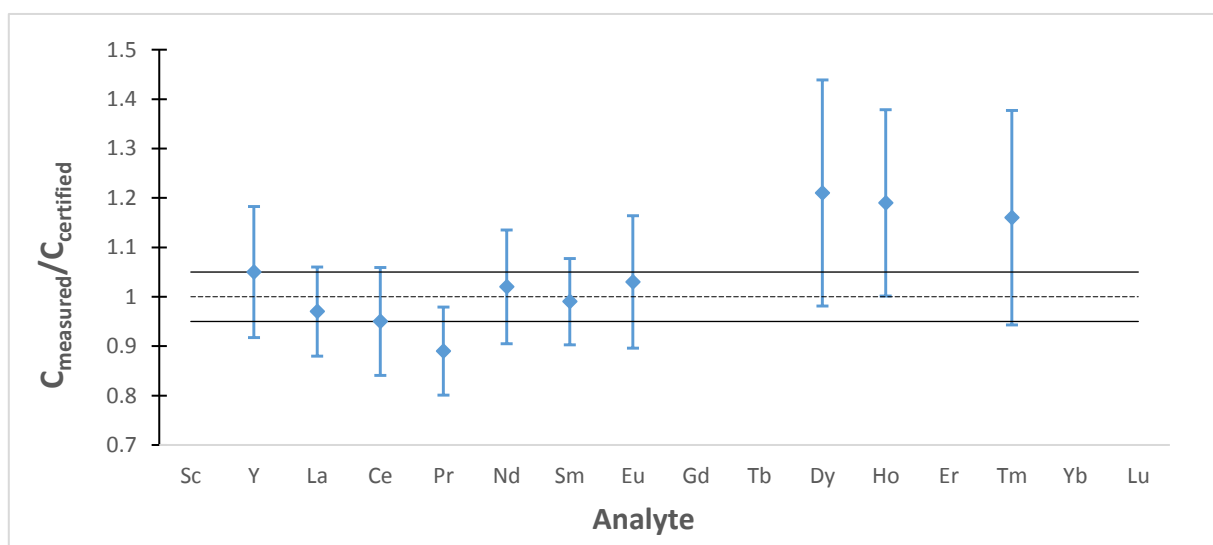


Figure 5.1 Agreement of measured (C_{measured}) and certified concentrations ($C_{\text{certified}}$) within the 95% confidence interval for AMIS0185 from fusion procedure

Table 5.3 Comparison of ICP-MS measured and certified* REE concentrations for AMIS0304 from fusion procedure ($n = 6, P = 0.95$)

Analyte	Measured Concentration/ $\mu\text{g g}^{-1}$	Certified Concentration/ $\mu\text{g g}^{-1}$	$C_{\text{measured}}/C_{\text{certified}}$
Sc	160 ± 5.26	—	—
Y	417 ± 4.88	410 ± 39	1.02 ± 0.10
La	3 251 ± 30.0	3 610 ± 311	0.90 ± 0.08
Ce	7 756 ± 131	8 090 ± 692	0.96 ± 0.08
Pr	868 ± 8.97	1 007 ± 89	0.86 ± 0.08
Nd	3 806 ± 37.9	3 875 ± 442	0.98 ± 0.11
Sm	576 ± 7.18	<i>575 ± 70</i>	1.00 ± 0.12
Eu	147 ± 2.04	—	—
Gd	349 ± 5.24	—	—
Tb	34.1 ± 0.639	—	—
Dy	138 ± 1.79	—	—
Ho	19.6 ± 0.271	—	—
Er	33.8 ± 0.441	—	—
Tm	3.79 ± 0.0548	—	—
Yb	18.6 ± 0.313	—	—
Lu	2.41 ± 0.0508	—	—

* Provisional concentrations are italicised

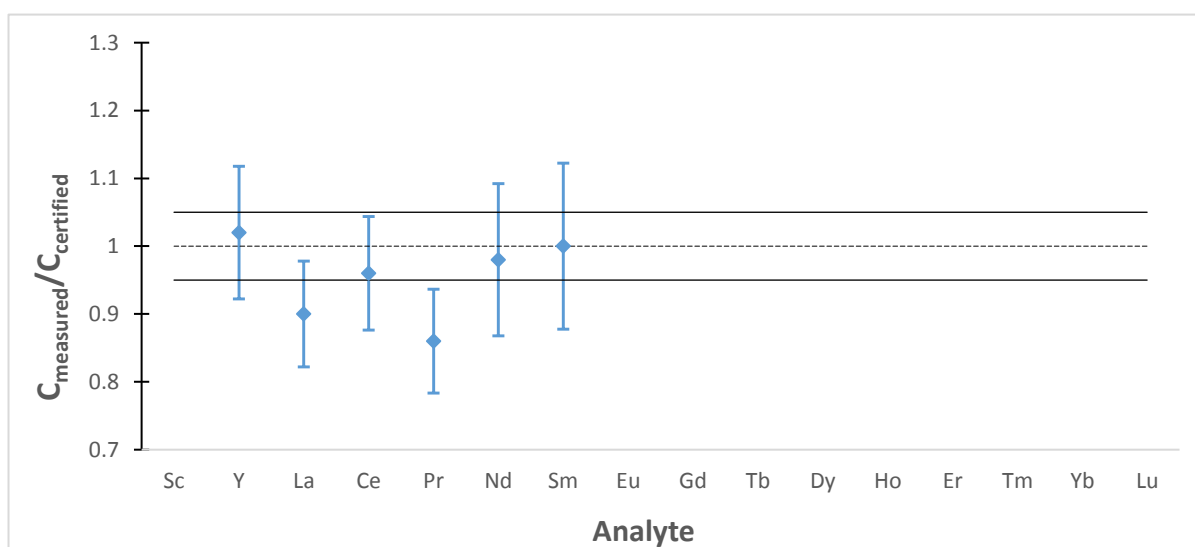


Figure 5.2 Agreement of measured (C_{measured}) and certified concentrations ($C_{\text{certified}}$) within the 95% confidence interval for AMIS0304 from fusion procedure

Table 5.4 Comparison of ICP-MS measured and certified* REE concentrations for AMIS0356 from fusion procedure ($n = 6, P = 0.95$)

Analyte	Measured Concentration/ $\mu\text{g g}^{-1}$	Certified Concentration/ $\mu\text{g g}^{-1}$	$C_{\text{measured}}/C_{\text{certified}}$
Sc	110 \pm 5.14	28 \pm 6	3.93 \pm 4.72
Y	38.2 \pm 0.194	35 \pm 4	1.09 \pm 0.12
La	8 465 \pm 45.2	8 533 \pm 731	0.99 \pm 0.08
Ce	11 190 \pm 66.4	11 160 \pm 705	1.00 \pm 0.06
Pr	819 \pm 4.99	942 \pm 73	0.87 \pm 0.07
Nd	2 449 \pm 17.6	2 419 \pm 240	1.01 \pm 0.10
Sm	162 \pm 0.962	159 \pm 10	1.02 \pm 0.06
Eu	31.1 \pm 0.197	29 \pm 2.1	1.07 \pm 0.08
Gd	122 \pm 1.26	—	—
Tb	11.6 \pm 0.0961	—	—
Dy	14.0 \pm 0.0936	13 \pm 1.5	1.08 \pm 0.12
Ho	1.90 \pm 0.280	1.6 \pm 0.3	1.19 \pm 0.22
Er	3.19 \pm 0.0322	—	—
Tm	0.368 \pm 0.00640	0.31 \pm 0.04	1.19 \pm 0.16
Yb	2.18 \pm 0.0211	—	—
Lu	0.269 \pm 0.0125	—	—

* Provisional concentrations are italicised

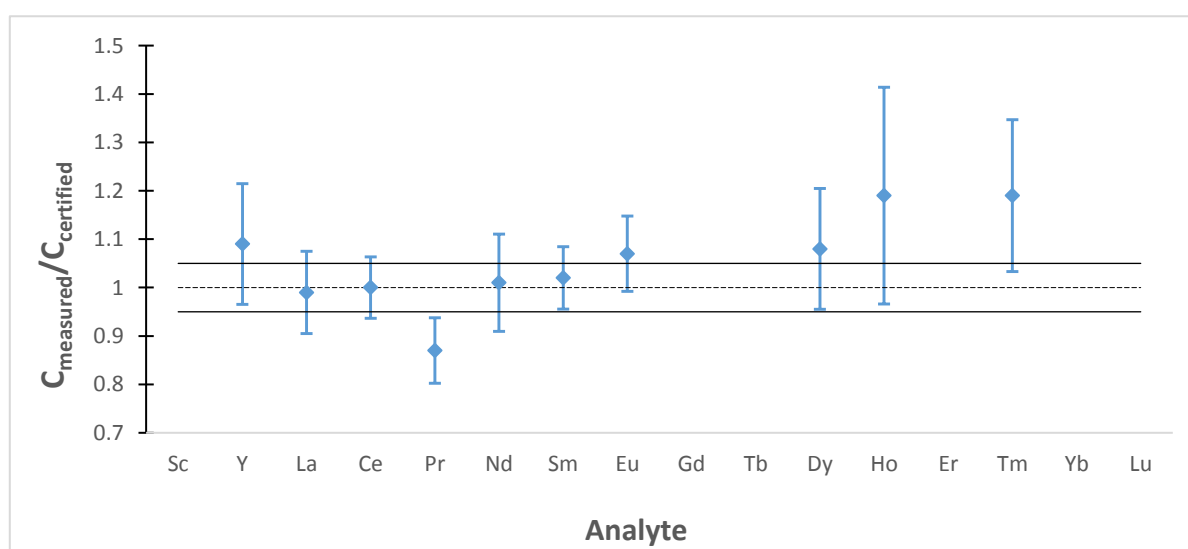


Figure 5.3 Agreement of measured (C_{measured}) and certified concentrations ($C_{\text{certified}}$) within the 95% confidence interval for AMIS0356 from fusion procedure

Table 5.5 Comparison of ICP-MS measured and certified REE concentrations for CGL-111 from fusion procedure ($n = 6$, $P = 0.95$)

Analyte	Measured Concentration/ $\mu\text{g g}^{-1}$	Certified Concentration/ $\mu\text{g g}^{-1}$	$C_{\text{measured}}/C_{\text{certified}}$
Sc	47.5 ± 2.46	—	—
Y	986 ± 67.6	959 ± 40	1.03 ± 0.08
La	$16\,174 \pm 1\,504$	$19\,300 \pm 1\,000$	0.84 ± 0.09
Ce	$14\,979 \pm 368$	$29\,000 \pm 1\,200$	0.52 ± 0.02
Pr	$2\,119 \pm 223$	$2\,800 \pm 300$	0.76 ± 0.11
Nd	$7\,370 \pm 771$	$8\,900 \pm 800$	0.83 ± 0.11
Sm	741 ± 73.3	900 ± 300	0.82 ± 0.28
Eu	174.8 ± 17.2	211.6 ± 8.5	0.83 ± 0.09
Gd	473 ± 51.6	553 ± 83	0.85 ± 0.16
Tb	46.6 ± 4.68	54.6 ± 14.2	0.85 ± 0.24
Dy	158 ± 16.0	206 ± 32	0.77 ± 0.14
Ho	28.1 ± 2.80	36.6 ± 7.4	0.77 ± 0.17
Er	63.2 ± 6.08	79.5 ± 8.5	0.79 ± 0.11
Tm	8.17 ± 0.831	—	—
Yb	43.06 ± 4.01	54.52 ± 5.24	0.79 ± 0.10
Lu	5.47 ± 0.547	7.64 ± 1.08	0.72 ± 0.12

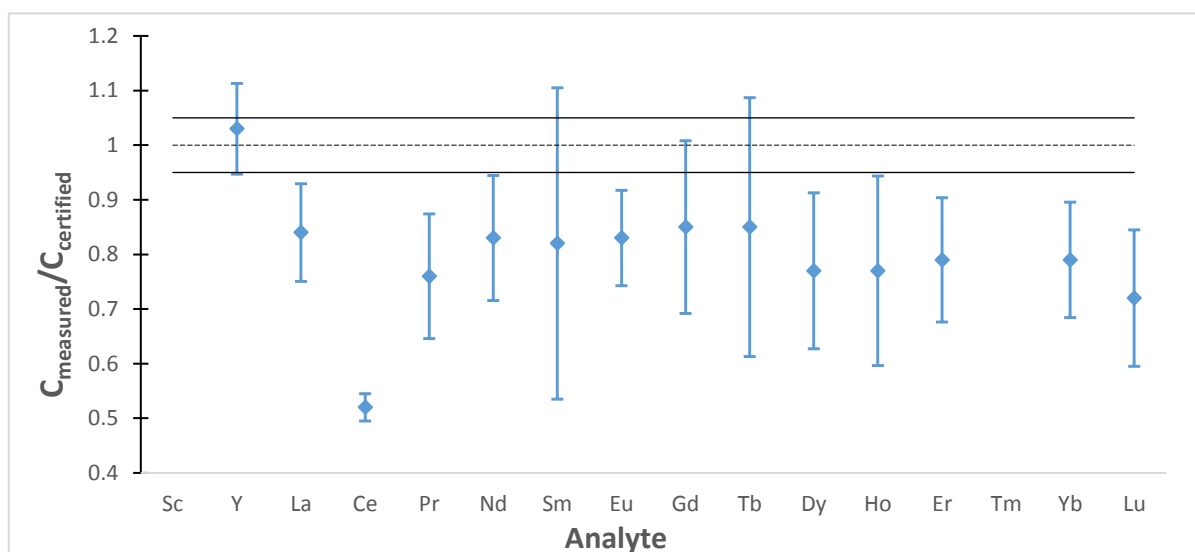


Figure 5.4 Agreement of measured (C_{measured}) and certified concentrations ($C_{\text{certified}}$) within the 95% confidence interval for CGL-111 from fusion procedure

Measured concentrations for CGL-111 were consistently lower than the stated certified concentrations (Fig 5.4). Y, Nd, Sm, Gd, Tb and Ho were the only analytes in which the measured concentrations were in agreement with corresponding certified values. A considerable deviation between the measured and certified values of Ce was evident (Fig 5.4). The measured value of $14\,979 \pm 368 \mu\text{g g}^{-1}$ was significantly lower than the corresponding certified value of $29\,000 \pm 1\,200 \mu\text{g g}^{-1}$. Other REE concentrations which were well below the 95% confidence interval included La and Pr. Remaining REE (Eu, Dy, Er, Yb and Lu) were lower than the 95% confidence limit by less than $4.0 \mu\text{g g}^{-1}$, implying that sample loss during sample decomposition was highly probable. However, this did not justify the significant loss of Ce which may be due to incomplete sample decomposition.

The differences in the agreement of measured and certified/provisional values amongst the investigated CRMs can be rationalised by taking into consideration their mineralogical characteristics. AMIS0185, AMIS0304 and AMIS0356 were all bastnäsite rich carbonatite materials for which the fusion procedure exemplified good accuracy. Furthermore, the procedure was capable of accurately determining trace concentrations in these materials as low as $0.368 \mu\text{g g}^{-1}$ and $1.90 \mu\text{g g}^{-1}$ for Tm and Ho, respectively (Table 5.4). The poor recovery of Ce in CGL-111 may be attributed to incomplete decomposition. However, the exact source of this partial decomposition is unclear, as there are many potential causes. A possible rational is due to the high content of apatite and related secondary phosphate minerals of CGL-111 (combined 60.2 wt.%), which contain Ce as a major constituent¹⁵. The high content of these REE bearing minerals may require a higher flux: sample ratio to promote complete decomposition. Another is due to the presence of a “few particles” of pyrite (FeS_2) as indicated in the mineral composition of CGL-111. Lithium metaborate is a basic flux predominantly used for the decomposition of minerals which contain high concentrations of metal oxides (acidic minerals)⁵¹. Due to its non-oxidising nature, lithium metaborate is not capable of converting sulfides into equivalent oxides and therefore, is not suitable for the decomposition of these minerals¹⁰⁵. As a result, the occurrence of pyrite may have contributed to the incomplete dissolution of this CRM, despite being present in minute quantities.

The occurrence of sulfide minerals such as pyrite (FeS_2) and galenite (PbS) also resulted in the unsuitability of the fusion procedure to decompose CGL-124. This was the only CRM for which the fusion procedure did not effectuate sample decomposition. The ineffectiveness of the fusion procedure was verified by ICP-MS analysis, in which REE signals were below that of the blank used to calibrate the instrument. Consequently, the data obtained for this CRM are not presented.

The applicability of the fusion procedure for REE analysis was highly dependent on the mineralogical composition of the materials analysed. Satisfactory accuracy and precision of REE measurements for AMIS CRMs was attained, indicating the suitability of the procedure for decomposition of bastnäsitite rich carbonatite materials. However, the procedure is limited with respect to materials which contain sulfide minerals. This is justified by the inadequate decomposition of CGL-124 and unsatisfactory accuracy and precision of measured REE concentrations for CGL-111. The occurrence of Si in fused CRM solutions resulted in the formation of polyatomic isobaric interferences that affected quantification of Sc. Despite these limitations, the procedure demonstrated the capability of accurately quantifying remaining REE (Y and La-Lu). Furthermore, the procedure accommodated sample solutions with high TDS, as no disturbance to the nebulisation efficiency, high contribution to the background signal or reduced sensitivity was observed. This is further substantiated by the low LOQ values calculated for the procedure, which allowed for the determination of trace REE concentrations (ng g^{-1} levels) present in geological materials.

5.2 Evaluation of Chromatographic Methods for REE Separation

Two well established HPLC methods were evaluated on their proficiency to separate REE in geological matrices without sample pre-treatment. The selected methods involved ion pair and ion exchange chromatographic modes of separation. Separation conditions of both methods were optimised using synthetic REE standards prior to their application on lithium metaborate fused CRM solutions. A comparison of the selected methods was subsequently performed, in order to establish which of the two was most suitable for REE separation prior to ICP-MS analysis.

5.2.1 Ion Pair Chromatographic (IPC) Separation of REE

The IPC method investigated in this study entailed separation of REE on a C₁₈ reverse phase column using an ion pair reagent (sodium 1-octanesulfonate) and a complexing agent (HIBA) as the mobile phase^{120, 128, 130}. Separation was effectuated by adsorption of ions on sulfonate groups of the ion pair reagent, followed by gradient elution with HIBA. Elution order of REE was from Lu-La. Separated REE ions were reacted with a post-column derivatisation reagent (arsenazo III) prior to detection at 658 nm.

5.2.1.1 Optimisation of chromatographic separation conditions

Initial separation conditions, as prescribed in previous studies are summarised (Table 4.3). The chromatogram exemplifying the separation of REE under these conditions are presented (Fig 5.5a).

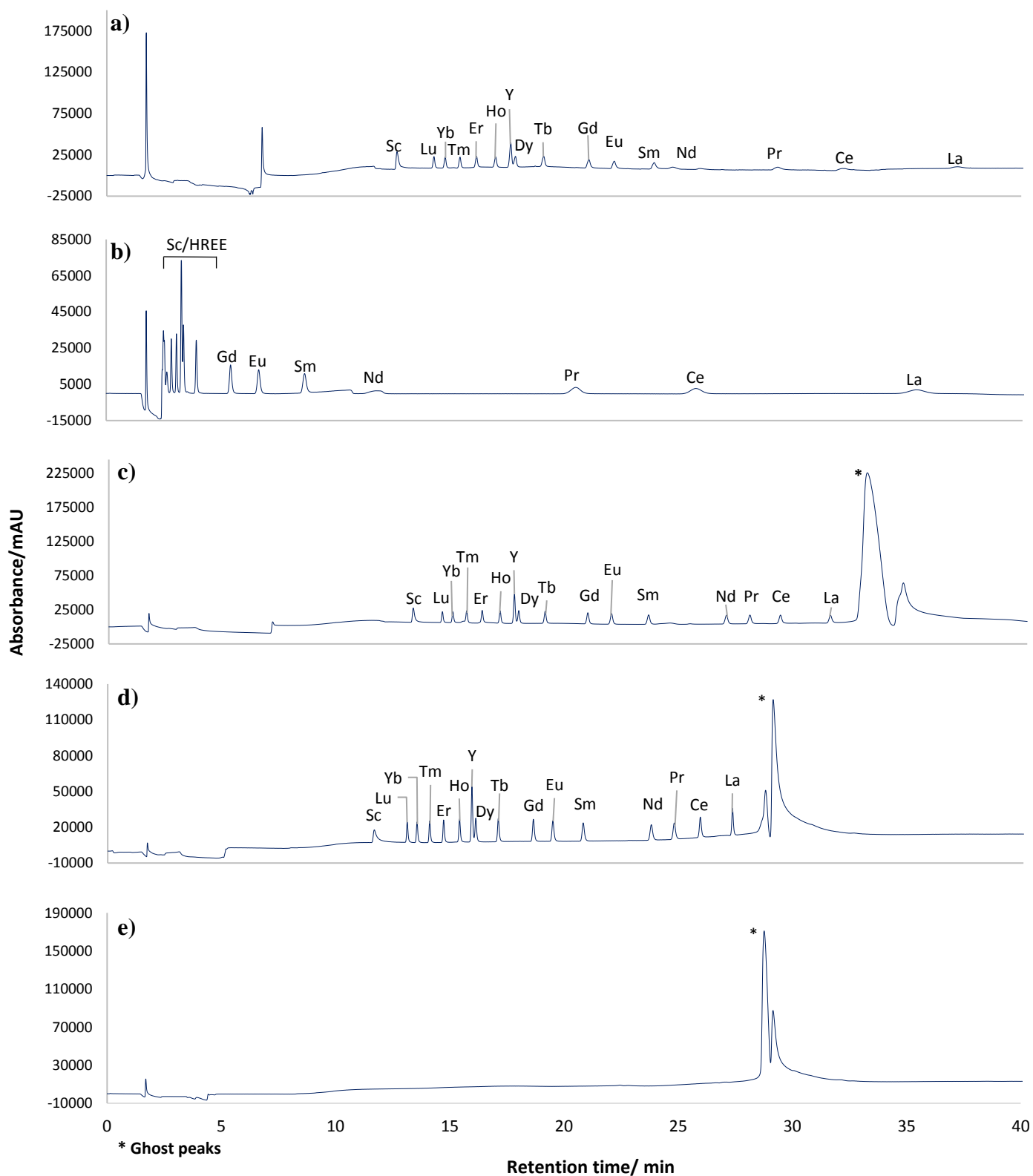


Figure 5.5 Optimisation of IPC separation conditions. **a – d)** Separation of 1 mg L⁻¹ REE (50 µL) at 0.8 mL min⁻¹. **e)** Separation of blank (50 µL). Separation conditions are presented in Table 5.6.

Table 5.6 IPC separation conditions accompanying Fig 5.5

		Concentration of HIBA (pH 3.8)/ mol L ⁻¹				Concentration of 1-octanesulfonate/ mol L ⁻¹
Figure 5.5	Time	0 min	15 min	20 min	40 min	
a)	Initial conditions	0.03	0.30	0.30	0.30	0.0100
b)	Isocratic elution	0.30	0.30	0.30	0.30	0.0100
c)	Gradient Elution	0.03	0.30	0.60*	0.60	0.0100
d)	Optimised conditions	0.03	0.30	0.60	0.60	0.0125
e)	Optimised conditions	0.03	0.30	0.60	0.60	0.0125

*HIBA concentration increased until 26 minutes

Efficient separation of early eluting peaks (Sc, Y and Lu-Sm) was attained. The elution peaks corresponding to these elements were adequately resolved, with the exception of Dy and Y in which baseline resolution was not achieved. The effectiveness of the initial separation conditions deteriorated for late eluting peaks *i.e.* Nd, Pr, Ce and La. The peaks corresponding to these elements exhibited band broadening with a resultant decrease in peak height and sensitivity. This suggested that the eluent strength of the mobile phase was not sufficient in lowering the affinity of these ions for the column, resulting in slow migration rates and lengthy retention times.

To effect better separation, the influence of changes to the concentration of mobile constituents (HIBA and 1-octanesulfonate) as well as changes to the gradient elution program on the retention behaviour of REE were studied.

- *Optimisation of HIBA concentration*

The eluent strength at the highest concentration of HIBA (0.30 M) employed in the initial separation conditions was investigated (Fig 5.5b). This was performed by separating REE at 0.30 M HIBA under isocratic elution conditions to identify whether poor separation was due to the inadequate eluent strength of mobile phase or due to the rate at which HIBA concentration varied during separation (gradient elution program). Rapid elution of Sc, Y and Lu-Tb was achieved (0 – 5 minutes) followed by Gd-Sm (5 – 10 minutes). However, the rate of elution decreased substantially for Nd-La with retention times in the range of 12 – 36 minutes. This confirmed that eluent strength of the mobile phase under the initial conditions was not adequate for the separation of Nd-La, which were still strongly retained relative to the other REE.

To promote the separation of Nd, Pr, Ce and La within reasonable time, an increase in the elution rates of these elements were required. This was achieved by increasing the concentration of HIBA in the gradient elution program. Since the separation of Sc, Y and Sm-Lu were satisfactory under initial separation conditions, the first step of the gradient program (0.03 – 0.30 M HIBA over 15 minutes) was maintained. Nonetheless, an additional step was introduced to the gradient program to facilitate the separation of Nd-La.

This involved an increase in HIBA concentration from 0.30 to 0.60 M over 15 – 26 minutes. The impact of these modifications resulted in the separation of all REE within 32 minutes with adequate resolution (Fig 5.5c). The separation of Sc, Y and Lu-Sm is comparable to that presented in Figure 5.5a as the gradient elution program was maintained. However, the additional step of the elution program resulted in a significant improvement in separation of Nd-La.

The decrease in retention time of Nd-La (26 – 32 minutes) and resultant improvement in peak shape and resolution was effectuated solely by the increase in HIBA concentration of the mobile phase. This observation can be substantiated by the equilibrium which exists between REE ions adsorbed onto sulfonate groups of the ion pair reagent on the column stationary phase, and dissociated HIBA ions of the mobile phase (Eqn 5.1)



An increase in HIBA concentration leads to an increase in concentration of dissociated HIBA ions in the mobile phase. This shifts the equilibrium, favouring the formation of REE-HIBA complexes, lowering the affinity of REE ions for the column and resulting in faster elution and a decrease in retention times¹³².

- *Optimisation of 1-octanesulfonate concentration*

REE peak resolution was enhanced due to an increase in ion pair reagent concentration (1-octanesulfonate) from 0.01 M to 0.0125 M (Fig 5.5d). By increasing the concentration of the ion pair reagent, the number of sulfonate groups available for ion exchange is also increased. This raises the ion exchange capacity of the column contributing to the observed improvement in resolution¹¹⁷.

- *Optimisation of gradient elution program*

The gradient elution program was modified by increasing the rate at which HIBA concentration was ramped from 0.30 – 0.60 M (15 – 20 minutes instead of 15 – 26 minutes) (Fig 5.5d). This reduced the retention times of Nd, Pr, Ce and La such that complete separation of all REE was achieved within 30 minutes.

The separation of REE under optimised separation conditions are presented (Fig 5.5d). REE peaks are narrow and symmetrical indicating that the migration rates of individual REE were successfully optimised to effect separation and reduce band broadening. The efficiency of the optimised separation conditions was also evident in the difference in retention times of each REE (Table 5.7).

Table 5.7 Retention times of REE under optimised IPC separation conditions

Analyte	Retention Time/ Minutes
Sc	12.18
Lu	13.26
Yb	13.68
Tm	14.23
Er	14.84
Ho	15.53
Y	16.07
Dy	16.27
Tb	17.25
Gd	18.80
Eu	19.66
Sm	21.00
Nd	24.00
Pr	24.98
Ce	26.07
La	27.43

The separation of REE under optimised chromatographic conditions also illustrated unfavourable features concerning the separation of Y and Dy as well as the presence of ghost peaks towards the end of the chromatographic run. These are discussed in further detail:

- *Separation of Y and Dy*

Baseline resolution of Y and Dy could not be attained due to their highly comparable retention times of 16.07 and 16.27 minutes respectively (Fig 5.5d). The inadequate separation of these elements are attributed to the use of HIBA as an eluent, rather than inefficiency of the chromatographic separation conditions. This is due to the marked similarity of stability constants ($\log \beta$) of Dy- and Y-HIBA aqueous complexes which are 8.49 and 8.61 respectively¹⁵⁵. Since separation of REE is achieved due to the differences of their relative REE-HIBA stability constants, the similarity of Dy- and Y-HIBA $\log \beta$ values justifies why complete separation of these elements were not achievable using HIBA¹¹⁵.

- *Ghost peaks*

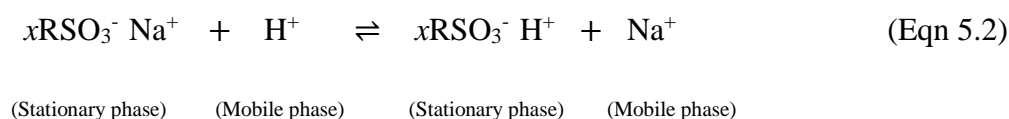
The increase in HIBA concentration during optimisation accompanied the formation of large broad peaks toward the end of the chromatographic run (Fig 5.5c and 5.5d). The retention times of these ghost peaks occurred at ~29.0 and 29.5 minutes respectively (Fig 5.5d) and were present at the same retention time during the analysis of blank solutions (Fig 5.5e).

Rinsing of autosampler injection system, flushing of the analytical column, re-preparation of mobile phase eluents and standards used for optimisation, ruled out the possibility of contaminants from these sources as determinants. To ensure that the origin of these ghost peaks were not due strong retention of REE ions on the column, the ghost peaks were fraction collected and analysed by ICP-MS. The results revealed that Sc, Y and Pr-Lu were absent, whilst La and Ce concentrations were negligible ($< 10 \mu\text{g L}^{-1}$).

The only remaining metal ion present in the chromatographic system that is capable generating a detector response is Na^+ . The presence of Na, is attributed to the ion pair reagent, whose counter ions are Na^+ (sodium 1-octanesulfonate). Na reacts with the post-column derivatisation reagent (arsenazo III) resulting in formation of coloured complexes that absorb light at the detection wavelength. This was confirmed by UV-Vis spectrophotometric analysis.

Fractions before, during and after the formation of the ghost peaks were analysed for Na. Results indicated that the Na concentration increased by ~15 ppm during the formation of these peaks, implicating Na as the determinant of these peaks.

The increase in Na concentration is attributed to the absorption of the ion pair reagent on the column, which results in the immobilisation of its sulfonate groups and corresponding Na⁺ counter ions. This interaction, indirectly results in the pre-concentration of exchangeable Na⁺ counter ions on the column. The mass transfer of these ions from the sulfonate groups into the mobile phase can be effectuated indirectly by an increase in HIBA concentration. Since the pH of HIBA in the mobile phase is maintained at 3.8 (greater than its pKa value of 3.77), dissociation of HIBA occurs, resulting in HIBA⁻ and H⁺ ions respectively¹³². Consequently, an increase in HIBA concentration of the mobile phase also results in an increase of H⁺ ions. These H⁺ ions are capable of exchanging with Na⁺ counter ions of the ion pair sulfonate groups, which is illustrated in the following equilibrium equation:



Eqn 5.2 substantiates that an increase of H⁺ ions can displace Na⁺ ions into the mobile phase. This displacement results in Na⁺ elution, increasing the Na concentration of the mobile phase significantly. Eluted Na⁺ ions are capable of forming complexes with arsenazo III, giving rise to the large peaks present (Fig 5.5c and 5.5d). This rationale justifies why these ghost peaks were only visible once concentration of HIBA was increased from 0.30 M to 0.60 M. It also explains the presence of these peaks in blank chromatographic runs, as its formation is due to interaction of the mobile phase reagents with the stationary phase and is unrelated to REE standard or blank solutions.

5.2.1.2 *Optimisation of injection volume and equilibration time*

Appropriate injection volumes and equilibration times were determined by analysis of a synthetic standard representative of the natural concentrations of REE in geological materials. A minimum equilibration time of 10 minutes between runs was deemed acceptable as no REE peaks were detected on chromatograms of blank solutions after separation. Injection volumes of 10 μL , 15 μL , 25 μL and 50 μL were investigated. The influence of these volumes on the chromatograms obtained are presented (Fig 5.6).

An increase in injection volume from 10-50 μL resulted in an increase in peak height until column overload conditions were observed. This distorted the elution of REE and is exemplified in chromatograms corresponding to 25 μL and 50 μL (Figs 5.6c and 5.6d respectively). Elution peaks corresponding to Nd-La in these chromatograms exhibited peak broadening which was intensified with an increase in injection volume. These analytes were particularly affected due to their large concentrations relative to remaining REE. The chromatogram corresponding to an injection volume of 50 μL also demonstrated peak splitting, suggesting that at this particular injection volume the sample solvent (2% HNO_3) was not compatible with the mobile phase (Fig 5.6d). As a result, 25 μL and 50 μL injection volumes were not suitable for analysis as they affect the elution of REE, resolution between analyte peaks and the overall separation efficiency of the column. Of the remaining injection volumes investigated, 15 μL (Fig 5.6b) was selected as the optimum over 10 μL (Fig 5.6a) as it demonstrated a greater peak height and thus, greater sensitivity. It was also the highest injection volume investigated that did not exemplify a deterioration in peak shape due to column overload.

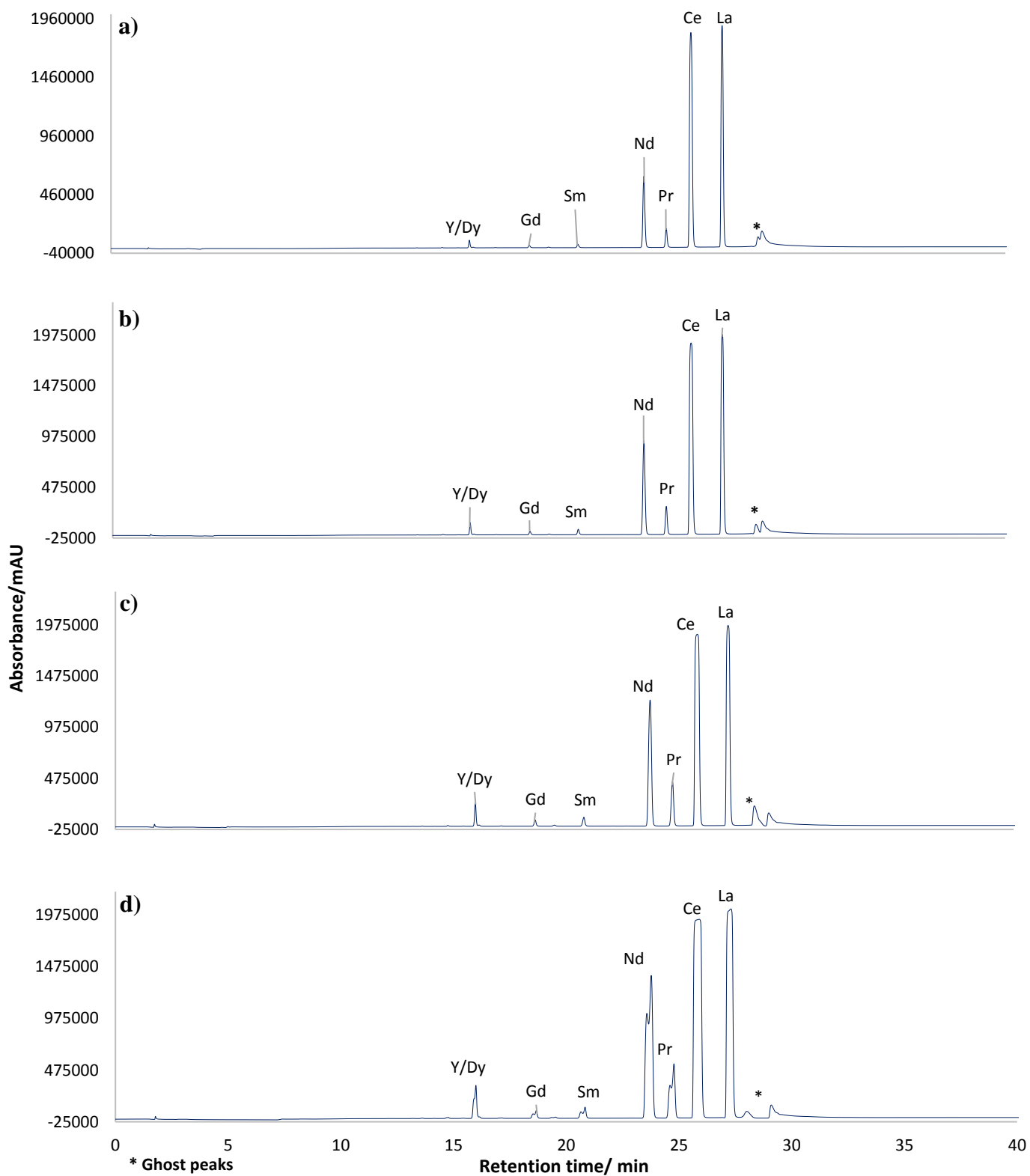


Figure 5.6 Optimisation of injection volume under optimised IPC separation conditions. **a)** 10 µL, **b)** 15 µL, **c)** 25 µL, **d)** 50 µL

5.2.1.3 Interference from matrix ions

The effect of matrix ions Fe, Ba, Al, Si and Mg on the separation of REE was investigated. These specific ions were selected as they are frequently present at significantly greater concentrations in geological matrices relative to REE. Their impact on the separation of REE was assessed by analysing 20 mg L⁻¹ standard solutions of each of these elements and determining their retention times under optimised separation conditions. Their potential interference on REE separation was established on whether matrix ion retention times overlap with that of REE. The results of which are presented (Table 5.8 and Appendix D).

Table 5.8 Potential interference of selected matrix ions on REE separation by IPC

Matrix Element	Retention Time/ min.	Possible Interference
Fe	3.673	—
Al	14.92	Er and Ho
Ba	38.03	—
Si	*ND	—
Mg	*ND	—

*ND = Not detected

The retention time of Fe corresponded to the start of the chromatographic run, suggesting that it was not retained under the optimised separation conditions. As a result, Fe eluted before the REE and does not interfere with their separation. On the contrary, the retention time of Al (14.92 minutes) coincided with that of Er and Ho (~14.5 and 15.5 minutes respectively). This implies that the presence of Al can impair the separation of Er and Ho, particularly in samples that possess significant amounts of this element. Barium eluted after the most retained REE ion (La) with a retention time of 38.03 minutes. Consequently, Ba was effectively isolated from the REE and hence does not impact their separation. The influence of Mg and Si on REE separation could not be determined as elution peaks of these elements were not observed at the concentrations analysed.

5.2.1.4 *IPC separation of REE in geological matrices*

The proficiency of the optimised IPC conditions for separation of REE in geological matrices was investigated by the analysis of lithium metaborate fused CRM solutions. These solutions were directly analysed, without matrix removal or REE group separation procedures. This was performed to identify the influence of sample matrix components on separation and establish the necessity of sample pre-treatment procedures prior to analysis.

To effectively demonstrate the separation efficiency of the IPC method, fused CRMs were spiked with 20 mg L⁻¹ of each REE to improve sensitivity. The direct injection of fused CRM solutions into the chromatographic system were feasible, as samples were compatible with the eluent composition of the mobile phase. Furthermore, precipitation of sample components during separation was not observed, contradictory to that reported in literature¹³⁰.

The efficiency of the optimised separation conditions was evident in chromatograms obtained for each fused CRM solution (Fig 5.7). The suitability of the sample injection volume (15 µL) was verified as column overloading was not demonstrated. However, peak tailing was observed (Figs 5.7c and 5.7d). This is attributed to the separation of REE ions on a non-uniform stationary phase. The separation of REE takes place on sulfonate groups of the ion pair reagent, which is adsorbed on the column. Consequently, peak tailing was a result of inadequate equilibration times provided between chromatographic runs for the adsorption of the ion pair reagent with the column stationary phase¹⁵⁶. Nevertheless, REE were adequately resolved possessing discrete, sharp and narrow peaks. No interference from matrix ions were identified, indicating that matrix removal prior to separation is not necessary.

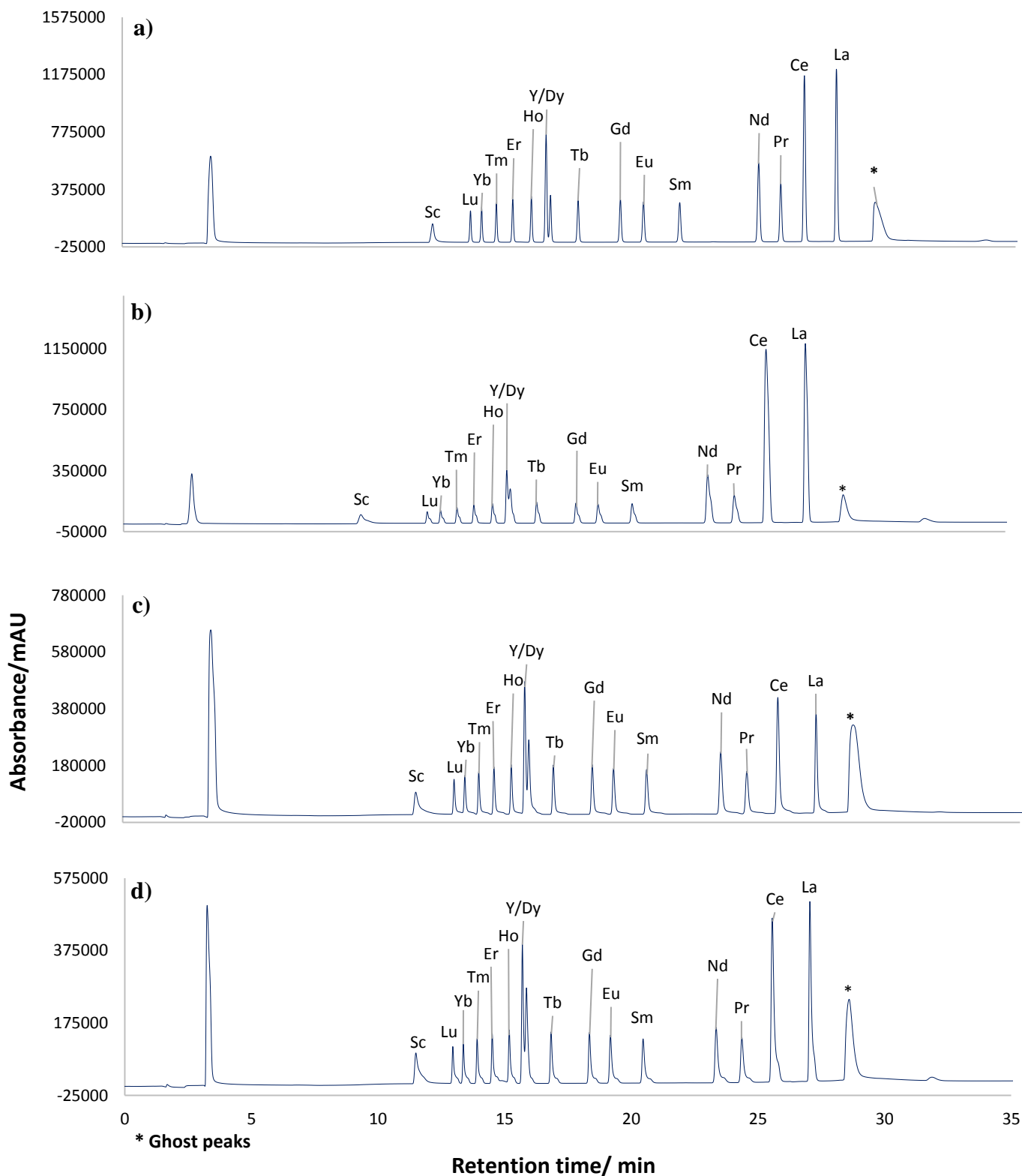


Figure 5.7 Separation of REE in alkali fused CRMs under optimised IPC separation conditions:
a) CGL-111 **b)** AMIS0185 **c)** AMIS0304 **d)** AMIS0356

The chromatograms further illustrate that the separation of REE was unaffected by the presence of sample matrix components (Fig 5.7). However, previous studies involving IPC methods for REE separation in geological matrices employed matrix removal as a pre-requisite^{118, 130, 157}. This was performed in order to avoid possible matrix interferences due to the non-specific nature of the detection method (post-column derivatisation reaction prior to detection by UV-Vis absorbance detector). Post-column derivatisation reagents are not specific to REE and thus can also form complexes which generate a detector response for sample matrix components. This raises uncertainty of whether peaks are attributed to REE only, complicating interpretation of chromatograms obtained.

Nevertheless, matrix separation procedures results in the removal of Sc in addition to matrix ions, precluding its analysis. As a result, previous HPLC studies did not account for the separation of Sc or whether the separation methods studied were capable of resolving this element from the remaining REE. The influence of Sc on REE separation was recently discussed in a study involving the IPC separation of Sc and REE in red mud (a by-product during production of Al_2O_3 from bauxite)¹⁵⁸. Although the sample matrix is different to geological samples, chromatograms presented for synthetic standard solutions demonstrated appreciable peak overlap between Sc and Lu. The efficiency of matrix removal procedures are also questionable. Even after the implementation of these procedures for rock standards, matrix interferences on REE separation were still exemplified¹¹⁸.

In chromatograms obtained from fused CRM solutions in this study (Fig 5.7), Sc and Lu were well resolved with no observed interferences from matrix ions. The chromatograms are comparable with those presented by other research studies, even though matrix removal was not performed prior to separation^{130, 157}. However, the run times required for complete REE separation were not similar with that presented in literature. Previous studies indicate that separation of REE can be performed under 20 minutes using IPC methods in comparison to 30 minutes presented in this study^{118, 120, 128, 130, 157}. The additional time was due to the length of the connection tubing from the pump to the column. This affected the rate at which the mobile phase enters the column impacting the rate of REE separation. Consequently, a reduction in the length of this connection, can achieve REE separation within a shorter period of time.

5.2.2 Ion Exchange Chromatographic (IEC) Separation of REE

The IEC method selected for investigation achieved simultaneous separation of REE and transition metals on a bifunctional quaternary ammonium-sulfonate ion exchange column (Dionex IonPac CS5A)^{68, 125, 135, 149, 154, 159}. The presence of anion and cation exchange sites of the column stationary phase, permitted the application of both ion exchange mechanisms to achieve separation. The eluents applied include oxalic acid, diglycolic acid and 2,6-pyridinedicarboxylic acid (PDCA). Elution order of REE was from La-Lu. Separated ions were reacted with a post-column derivatisation reagent (PAR) prior to detection at 530 nm.

5.2.2.1 *Optimisation of chromatographic separation conditions*

Initial separation conditions, as presented in previous studies are summarised (Table 4.6). The gradient elution program employed consisted of four principal steps:

- Application of PDCA under isocratic conditions to promote the separation of transition metals from REE. PDCA forms stable mono- and di-valent anionic complexes with transition metals, whilst forming stable trivalent anionic complexes with REE. The differences in valence between these complexes permits the separation of transition metals, whilst REE remain strongly retained on the column.
- Flushing the column with water, providing sufficient time for elution of separated transition metals and removal of un-complexed PDCA.
- Introduction of oxalic acid under isocratic elution conditions.
- Gradient elution with both oxalic and diglycolic acids to effectuate REE separation.

Flushing of the column between the application of PDCA and oxalic acid was essential in minimising the formation of reaction products which absorb light at the detection wavelength⁶⁸. These reaction products were present during the analysis of blank solutions (Fig 5.8a) which gave rise to pronounced peaks at ~22.5 minutes. Additional peaks present at the beginning of the chromatogram (~2.5 minutes) were attributed to mobile phase composition, during which PDCA was used as the eluent.

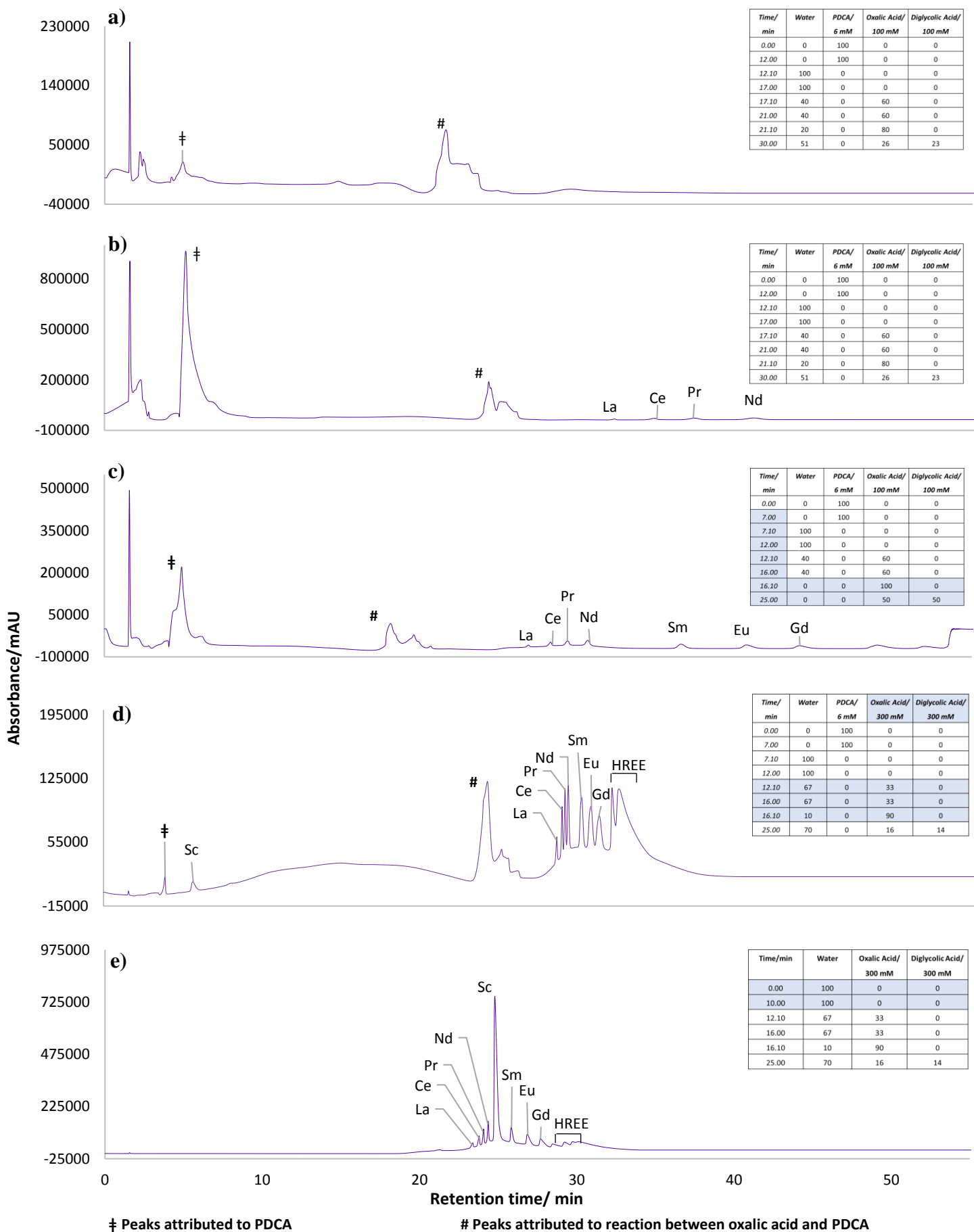


Figure 5.8 Optimisation of IEC separation conditions. **a – e)** Separation of 5 mg L⁻¹ REE standard at (50 µL) at 1.0 mL min⁻¹. Changes to gradient program are highlighted

The separation of REE under the initial separation conditions is presented (Fig 5.8b). Retention times of REE ions were expected between 28 – 42 minutes^{68, 125, 135, 149, 154, 159}. However, only four of the total REE were present during this period. The elution peaks found correspond to La, Ce, Pr and Nd and were broad and poorly distinguished. A late eluting peak at ~57 minutes suggested that elution of remaining REE were still in progress. This demonstrated that the initial separation conditions was ineffective in eluting strongly retained REE ions, resulting in slow elution rates and poor peak shape. The inefficiency of these conditions was further evident as separation of all REE within reasonable time was not achieved.

To effect better separation the gradient elution program, concentrations of oxalic and diglycolic acids and the rate at which these concentrations change during separation were optimised. Furthermore, the influence of PDCA on REE separation was also investigated.

- *Optimisation of gradient elution program*

The inadequacy of the initial separation conditions was contributed to the length of the connection tubing from the pump to the column. This impacted the rate at which relative compositions of the mobile phase were introduced into the column, affecting REE separation. Its effect was substantial in complex gradient elution programs in which the mobile phase was comprised of multiple eluents or when there was a rapid change over from one eluent to the next. Preliminary investigations revealed that the time in which the mobile phase reached the column at the required composition, exceeded the programmed time by ~5 minutes (flow rate of 1.0 ml min⁻¹). Consequently, each step of gradient elution program was reduced by 5 minutes to compensate for this effect (Figure 5.8c).

- *Optimisation of oxalic acid and diglycolic acid concentrations*

To further improve REE separation, oxalic acid and diglycolic acids concentrations were increased in the last two steps of elution program. At 16.10 minutes into the chromatographic run, oxalic acid concentration was increased from 80 – 100 mM. In addition, the concentration of oxalic and diglycolic acids were increased from 26 – 50 mM and 23 – 50 mM respectively at 25.00 minutes. The effect of changes to the mobile phase composition as well as gradient program times is presented (Figure 5.8c). The elution of all REE was achieved within 55 minutes. Peaks corresponding to La, Ce, Pr and Nd, exhibited a decrease in retention time (26 – 31 minutes) resulting in improved peak shape and resolution. The elution peaks of Sm, Gd and Eu, which were not previously observed, possessed retention times between 36 – 45 minutes. Nevertheless, separation conditions were not able to resolve these ions into discrete peaks. The separation efficiency decreased considerably for HREE (retention times 48 – 53 minutes) in which significant band broadening resulted in peak overlap and co-elution of Tb-Lu. This revealed that the eluent strength of mobile phase was not able to promote the elution of these strongly retained ions.

To increase the eluent strength of mobile phase, oxalic and diglycolic eluents were re-prepared to a final concentration of 300 mM, instead of 100 mM as previously used. Consequently, the relative compositions of the gradient elution program were adequately adjusted such that mobile phase constituted the same concentration of these eluents as in previous investigations.

- *Optimisation of the rate of oxalic acid concentration change*

To enhance separation efficiency, the rate at which concentration of oxalic acid changes during separation was increased. From 12.00 – 16.00 minutes the oxalic acid concentration was increased from 0 – 99 mM, followed by 99 – 270 mM from 16.00 – 16.10 minutes. These modified conditions resulted in a significant improvement in REE separation (Fig 5.8d). Sc elution peak corresponded to a retention time of ~6 minutes indicating that PDCA was capable of eluting this element at the beginning of the chromatographic run.

This presented a challenge as transition metals were expected to elute in this region. Sc is present in trace concentrations relative to transition metals in geological matrices, as a result the elution of Sc amongst these ions can affect its separation and analysis. The elution peaks corresponding to La-Sm were sharp, symmetrical and adequately resolved with retention times between 28 – 32 minutes. However, the separation conditions were not capable of resolving Y and Tb-Lu which co-eluted as one large peak (retention time ~33 minutes). The unstable baseline observed is due to rapid replacement of eluents which constitute gradient program. For example, from 7.00 – 7.10 minutes PDCA was replaced with water and between 12.00 – 12.10 minutes, water was rapidly changed to a high concentration of oxalic acid (99 mM). This is expected to generate an unstable baseline as the column is not given sufficient time to equilibrate to these eluent changes. The change in eluent composition was due to the application of PDCA and the required rinsing prior to the introduction of oxalic acid. This is because interaction of PDCA and oxalic acid generates products which absorb light at the detection wavelength⁶⁸. This justifies the occurrence prominent peaks at 25.00 minutes, which was due to the interaction of oxalic acid and traces of PDCA which still remained in the column or HPLC lines after rinsing.

- *Influence of PDCA on REE separation*

The influence of PDCA and subsequent rinsing step on the separation of REE was investigated by eliminating PDCA from the gradient program. The gradient elution program times were maintained to ensure that separation was attributed to PDCA only and not the period of time in which REE ions were retained on the column. Composition of oxalic and diglycolic acids were the same as that previously used. The chromatogram obtained under these conditions is presented (Figure 5.8e).

The impact of PDCA on the separation of REE was clearly established by comparison of figures 5.8d and 5.8e. The removal of PDCA, results in greater stability of the baseline, making easier to distinguish baseline resolution between La-Sm. However, peaks corresponding to Gd and Eu, despite being adequately resolved exhibited peak tailing. This is due to the cation and anion exchange sites of the column, both of which are able to retain free REE³⁺ ions and trivalent anionic REE-oxalate and REE-diglycolate complexes¹³⁵.

The difference in retention mechanisms generates a difference in migration rates, resulting in the observed peak tailing. A small improvement in separation of Y and Tb-Lu were attained owing to a decrease in the extent of peak overlap of these elements. However, peaks corresponding to these elements were still not adequately resolved. The removal of PDCA permitted the separation of Sc amongst the REE. Sc eluted after Nd with a retention time of ~25 minutes. The height of the peak is not a reflection of its concentration, but rather a higher molar absorptivity of Sc complexes with the post-column derivatisation reagent (PAR) relative to other REE¹⁶⁰. Due to the improvement in REE separation, enhanced baseline stability and change in retention time of Sc, PDCA was excluded from further separation optimisation.

- *Separation of REE using oxalic acid and diglycolic acid*

The elimination of PDCA and accompanied rinsing steps required adjustment of the gradient elution program. However the relative composition of oxalic acid and diglycolic acid in the mobile phase and the rate at which their concentrations changed during the chromatographic run were maintained. The removal of PDCA accomplished separation of REE within 24 minutes in comparison to the previous run time of 31 minutes. As a result, the retention of REE ions on the column were not as prolonged as in previous separation conditions, resulting in an improvement in peaks and resolution (Fig 5.9a). This was evident in the peak shapes of Eu and Gd in which peak tailing was no longer observed. The complete separation of Sc, La-Gd and Er was achieved. However a broad peak at 19.5 minutes corresponded to Tb, Y, Dy and Ho which co-eluted under these separation conditions. Incomplete separation of Tm, Yb and Lu was also observed in which peak overlap of these elements were present at ~22 minutes (Fig 5.9a).

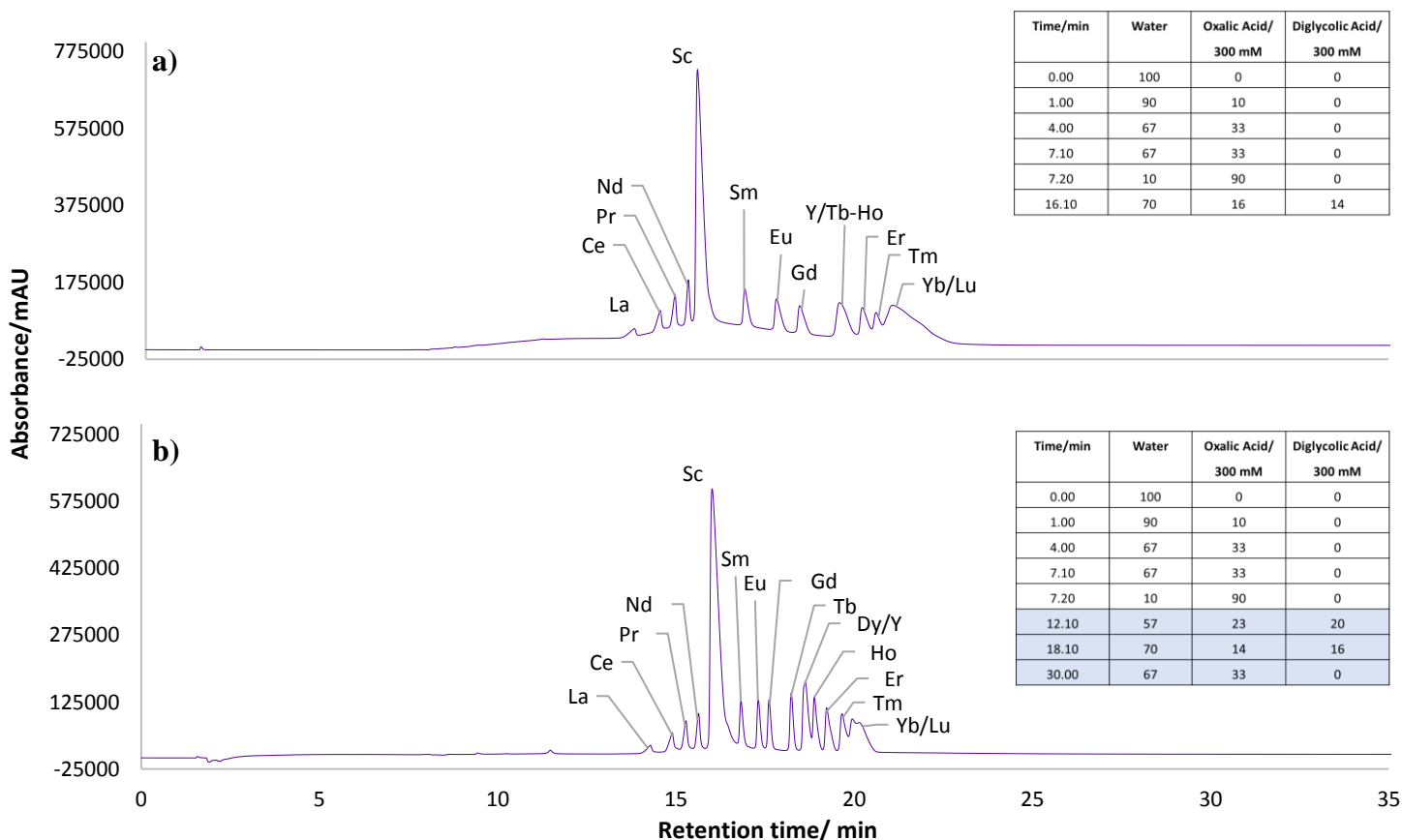


Figure 5.9 Optimisation of IEC conditions using oxalic and diglycolic acids: Separation of 5 mg L⁻¹ REE standard (50 μ L) at 1.0 mL min⁻¹. **a)** Separation with oxalic and diglycolic acid **b)** Optimised separation conditions.

- *Optimisation of the rate of diglycolic acid concentration change*

The separation of Tb-Lu was considerably improved by increasing the concentration of diglycolic acid in the mobile phase¹³⁵. This was due to ineffectiveness of oxalic acid to reduce the affinity of HREE ions for the column, necessitating the use of a stronger complexing agent (*i.e.* diglycolic acid) to improve separation. Consequently, the gradient elution program was modified such that concentration of diglycolic acid was increased from 0 – 60 mM between 7.20 – 12.10 minutes followed by a steady decrease in concentration from 0.60 – 0.42 mM over the next 6.0 minutes (12.10 – 18.10 minutes). These changes to the elution program represent the optimised conditions in which REE separation was attained within 22 minutes (Figure 5.9b). The separation of Dy and Ho was affected by Y, which was observed to co-elute with Dy, impairing the baseline resolution between Dy/Y and Ho (~19 minutes).

Complete separation of Tm, Yb and Lu was also not acquired. This observation can be substantiated in literature whereby resolution of Yb and Lu could not be attained using gradient elution of oxalic and diglycolic acids^{68, 125, 135, 149, 154, 159}. Regardless, changes in pH, flow rate and column temperature were investigated in attempt to improve resolution of Dy, Y, Ho as well as Tm-Lu without any success. The separation of Sc, La-Tb and Er was achieved with satisfactory resolution. Peaks corresponding to these elements were sharp and narrow in shape indicating the efficiency of these chromatographic conditions for the separation of these elements. The retention times of individual REE are presented (Table 5.9).

Table 5.9 Retention times of REE under optimised IEC separation conditions

Analyte	Retention Time/ Minutes
La	14.28
Ce	14.89
Pr	15.28
Nd	15.63
Sc	16.01
Sm	16.82
Eu	17.31
Gd	17.61
Tb	18.23
Dy	18.63
Y	18.71
Ho	18.88
Er	19.23
Tm	19.65
Yb	19.95
Lu	20.14

5.2.2.2 *Optimisation of injection volume*

Optimisation of injection volumes was performed by analysis of a synthetic solution representative of the natural concentrations of REE in geological materials. Injection volumes corresponding to 10, 15, 25 and 50 μL was investigated to establish its influence on the separation efficiency of the IEC method.

The chromatograms obtained (Fig 5.10) demonstrated a trade-off between sensitivity and resolution. HREE which are frequently present at trace concentrations required high injection volumes to improve the sensitivity of the detection method. However, peaks corresponding to Eu, Gd, and Tm-Lu were inadequately distinguished from the baseline at the volumes investigated.

An increase in injection volume from 10 – 50 μL , accompanied a deterioration of the separation efficiency of La-Nd. This was particularly observed for an injection volume of 25 μL (Fig 5.10c), in which significant peak overlap of Ce-Nd was demonstrated. The resolution of these peaks further deteriorated by increasing the injection volume to 50 μL , in which co-elution of La-Nd was observed at ~ 14.5 minutes (Fig 5.10d). The decrease in resolution of these elements with an increase in injection volume is attributed to the relative concentrations at which REE are present in geological matrices in addition to the poor sensitivity of the detection method. Neighbouring REE elements frequently possess unequal concentrations (due to the odd-even effect) resulting in adjacent REE chromatographic peaks to possess unequal sizes¹⁴. This presents a challenge as a higher degree of resolution is required to prevent peak overlap in comparison to the separation of peaks that possess similar sizes. This justifies the difference in separation efficiency demonstrated for standard solutions possessing equal REE concentrations (Fig 5.9b) in comparison to that representative of the natural REE concentrations in geological materials (Fig 5.10). An injection volume of 15 μL was selected as optimum as it provided an adequate compromise between sensitivity and resolution. It also exemplified the greatest resolution of the investigated injection volumes as it is only chromatogram in which separation of Ce and Pr peaks were observed (Fig 5.10b).

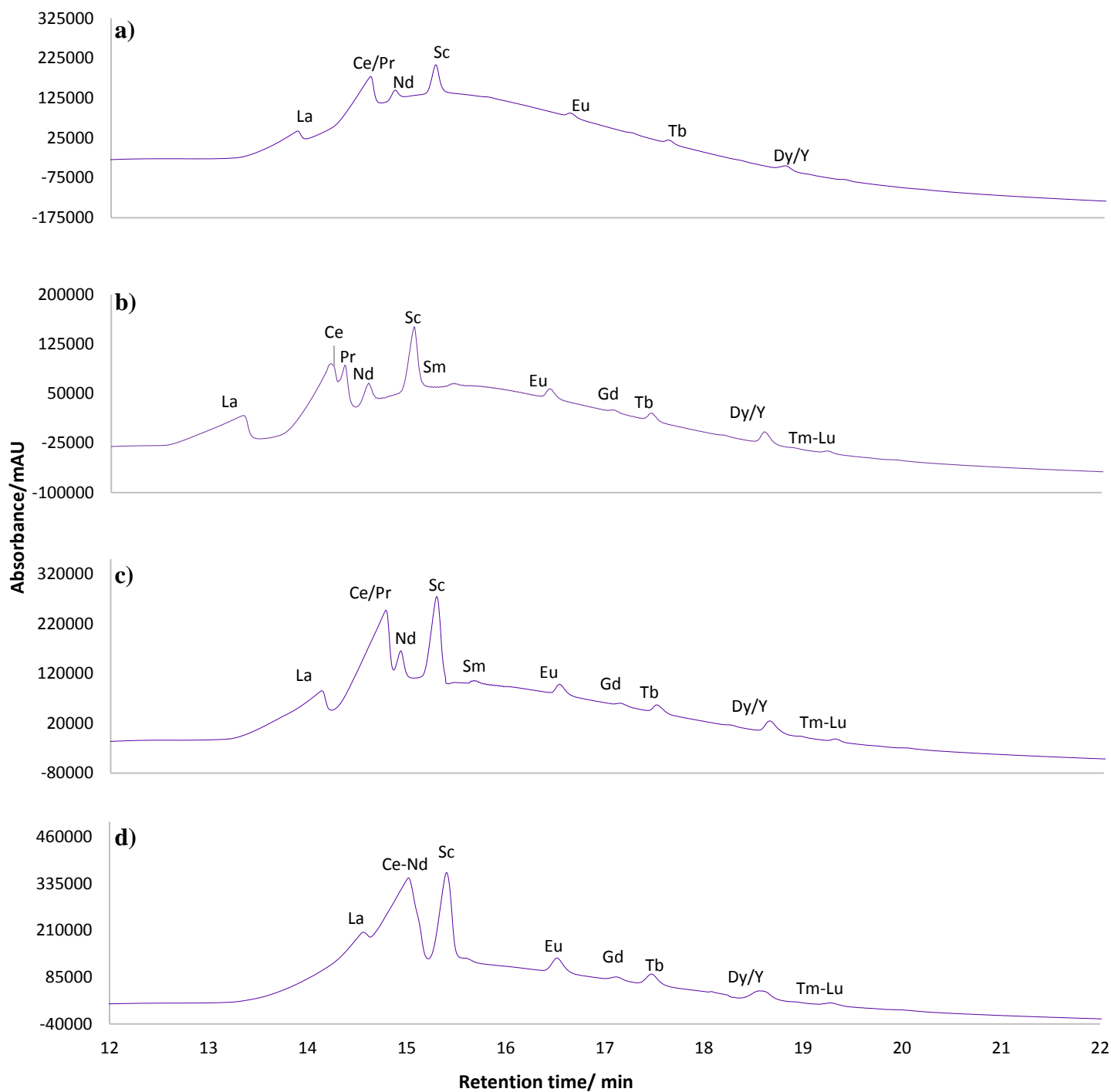


Figure 5.10 Optimisation of injection volumes under optimised IEC separation conditions. **a)** 10 µL **b)** 15 µL **c)** 25 µL **d)** 50 µL

5.2.2.3 Interference from matrix ions

The effect of matrix ions Fe, Ba, Al, Si and Mg on the separation of REE was investigated (similarly to that performed for IPC). The potential of these matrix ions to interfere with REE separation was determined by whether matrix ion retention times overlapped with that of REE. The results of which are presented (Table 5.10 and Appendix E).

Table 5.10 Potential interference of selected matrix ions on REE separation by IEC

Matrix Element	Retention time/ min.	Possible Interference
Fe	*ND	—
Al	*ND	—
Ba	15.52	Sc and Sm
Si	18.24	Dy, Y and Ho
Mg	15.25	Sc and Sm

*ND = Not detected

The retention times of Ba, Si and Mg coincided with the time range in which REE ions elute. Ba and Mg peaks both eluted between Sc and Sm peaks, affecting the resolution of these analytes. The high molar absorptivity of Sc made it difficult to establish whether co-elution was present as peaks from these interferents were not pronounced and can be easily overshadowed by Sc.

The elution peak of Si corresponded to the retention times of Dy, Y and Ho. Co-elution of Y with Dy and poor resolution between Dy/Y and neighbouring Ho, also made it difficult to identify interferences from Si, as baseline resolution was not achieved under optimised separation conditions (Fig 5.9b). As a consequence, Si can elute in this region without significantly distorting the chromatogram. The potential rise in baseline due to presence of Si can be easily misinterpreted as the peak overlap which already exists between Dy/Y and Ho.

The use of oxalic acid together with a Dionex IonPac CS5A column is also capable of eluting transition metals other than those investigated in this study^{125, 161-163}. These include Cu, Pb, Co, Mn, Zn and Ni suggesting that interferences from these ions are highly probable.

The retention times of Al and Fe could not be determined at the concentrations analysed however, previous studies have indicated that Fe³⁺ and Al³⁺ ions were strongly retained on the column under the separation conditions investigated^{68, 149, 154, 162}. The accumulation of these ions on the column can significantly deteriorate REE separation efficiency since it reduces the number of ion exchange sites that are available to effect separation. To prevent this, cleaning of the column with PDCA between each chromatographic run is advised. This additional step in the procedure considerably impacts the period of time required for analysis. After flushing the column with PDCA, a minimum of 30 minutes is required for the column to equilibrate with the starting eluent composition prior to separation^{68, 154}. This is due to the reaction of PDCA and oxalic acid which forms reaction products that absorb light at the detection wavelength. As a result sufficient time needs to be allocated to allow the exit of these products from the HPLC system prior to the commencement of the next chromatographic run.

5.2.2.4 IEC separation of REE in geological matrices

The efficiency of the IEC method to separate REE in geological matrices was investigated by the direct analysis of spiked lithium metaborate fused CRM solutions (20 mg L⁻¹ of each REE)..

Chromatograms corresponding to the IEC separation of REE in fused CRMs (Fig 5.11) demonstrated the potential of sample matrix components to impair REE separation efficiency, especially that of La and Ce. These interferences were evident in chromatograms attained for CGL-111 and AMIS0185 respectively (Fig 5.11a and 5.11b). Separation of La was affected by the presence of an unassigned interferent ion which possessed a similar retention time of ~ 12.35 minutes, resulting in significant peak overlap. The poor peak shape of Ce also suggested co-elution with an interferent ion, as its peak width was broader in comparison to the remaining REE ions (Fig 5.11b). No interferences were observed during the elution of Sc, Pr-Tb and Er. However, a distortion in peak shape of Dy/Y during analysis of AMIS0304 (Fig 5.11c) could be attributed to Si which also elutes in this region. The poor resolution of Tm-Lu under optimised conditions made it difficult to identify possible interferents on their separation. As a result, matrix removal prior to REE separation is essential to ensure that detected peaks are attributed to REE in to addition to improving the separation efficiency of this method.

The application of matrix removal procedures however, results in the removal of Sc as demonstrated in previous HPLC studies^{14, 68, 149, 159}. As a result, these studies did not account for Sc during REE separation. Rapid changes of the mobile phase composition also compromised baseline resolution of Ce and Pr as well as Y, Dy-Er. Chromatograms obtained during analysis of alkali fused CRMs under optimised IEC separation conditions in this study (Fig 5.11), demonstrated the capability of separating Sc amongst the remaining REE. The observed drift in baseline (Fig 5.11) is attributed to the gradient elution program and is comparable with chromatograms presented in literature^{14, 68, 149, 159}. The method was particularly efficient for the separation of Pr-Tb and Er as the elution peaks corresponding to these elements were sharp, symmetrical and sufficiently resolved. However, the presence of matrix interferences and incomplete separation of Y, Dy, Ho, Tm, Yb and Lu represent the shortcomings of this method.

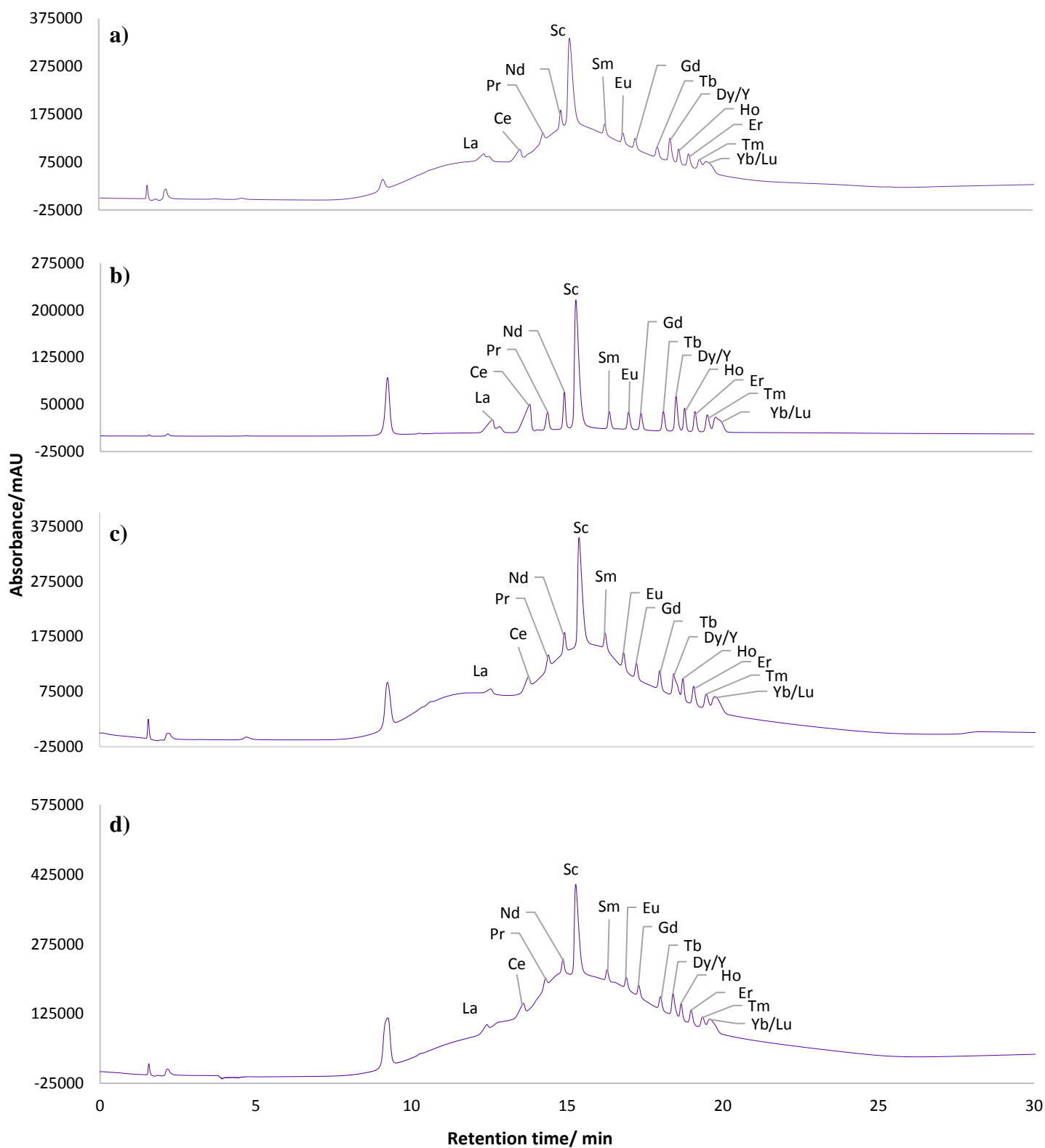


Figure 5.11 Separation of REE in alkali fused CRMs under optimised IEC separation conditions:
 a) CGL-111 b) AMIS0185 c) AMIS0304 d) AMIS0356

5.2.3 Comparison of IPC and IEC Methods for REE Separation

A comparison of IPC and IEC methods was performed to establish which of the two was most suitable for REE separation prior ICP-MS analysis. The separation of REE is expected to eliminate the occurrence of interferences on their quantification by ICP-MS, as the interferences are essentially removed before REE detection. As a result, to determine which chromatographic method was most applicable, a comparison based on the following factors was carried out:

5.2.3.1 Separation of REE

The capability of a chromatographic method to completely separate individual REE is not only a reflection of the efficiency of the separation method, but it is also essential for the avoidance of ICP-MS spectroscopic interferences that REE impose on each other.

Complete separation of all REE was achieved by IPC, with the exception of Dy and Y in which baseline resolution was not attained. Nevertheless, Y does not generate any spectral interferences that affect the analysis of Dy or vice versa. Consequently, IPC is capable of eliminating the potential of any mutual REE interferences that may occur during ICP-MS analysis.

On the other hand, REE separation by the application of IEC resulted in the incomplete separation of Y, Dy, Ho and Tm-Lu. Of these elements, the most significant is the inadequate separation of Yb and Lu. This is attributed to the elemental isobaric interference of $^{176}\text{Yb}^+$ on $^{176}\text{Lu}^+$, which affects the accurate quantification of this analyte by ICP-MS.

5.2.3.2 *Influence of matrix ions on REE separation*

The occurrence of matrix ions during the separation of REE are capable of inducing both spectroscopic and matrix interferences on the ICP-MS analysis of these elements. Since geological matrices are comprised of a number of elemental constituents that are present at significantly higher concentrations relative to REE, chromatographic methods must separate REE from sample matrix components in addition to individual REE group members.

To investigate the capability of the IPC and IEC methods to achieve this, the influence of Fe, Al, Mg, Si and Ba on REE separation was performed using standard solutions. Although these elements do not represent all of the sample matrix components that may affect separation, Fe, Al, Mg and Si were chosen as they constitute the major elemental components in geological matrices. The selection of Ba was due to its capability of generating a number of polyatomic interferences on REE analysis by ICP-MS.

With respect to the IEC separation of REE, Mg, Ba and Si were observed to possess similar retention times as REE (Table 5.10). Mg and Ba have retention times amidst that of Sc and Sm, whilst the retention time of Si corresponded to elution between Dy/Y and Ho. The occurrence of Mg and Si does not generate any spectroscopic interferences on the respective REE. However, the elution of Ba in the vicinity of Sm can contribute to polyatomic isobaric interferences. Ba is capable of forming oxide and hydroxide molecular species which overlap the two most abundant isotopes of Sm ($^{152}\text{Sm}^+$ and $^{154}\text{Sm}^+$ respectively). The impact of matrix interferences on the separation of REE by IEC were further evident in chromatograms obtained during analysis of fused CRM solutions (Fig 5.11). Here, unassigned matrix ions affected the separation of La and Ce. As a result, the IEC method is not capable of separating REE from matrix elements in addition to individual REE.

On the contrary, the IPC method may be affected by high concentrations of Al which elutes between Er and Ho. Regardless, Al does not possess any elemental or polyatomic isobaric interferences which overlap the mass range of Er and Ho isotopes.

5.2.3.3 Requirement of matrix removal

The influence of sample matrix components on the separation of REE determined the necessity of performing matrix removal prior to the separation of these elements. The application of matrix removal procedures are inconvenient as they increase the time required for analysis and also introduce additional sources of error to the analytical method. These include sample loss and introduction of contaminants from reagents used to effect matrix removal. Previous studies have also pointed out the ineffectiveness of these procedures for complete matrix removal, as Ba^{2+} , Al^{3+} and Fe^{3+} are not adequately eliminated and co-elute with REE^{63, 64, 115, 118, 122, 130}. The application of these procedures also result in the removal of Sc amongst sample matrix components, precluding its analysis. Consequently, the capability of the chromatographic method to separate REE without the requirement of matrix removal is preferable. In addition, the direct injection of samples into the HPLC system results in higher sample throughput and also confers additional confidence to the analytical method.

Chromatograms obtained from IPC separation of fused CRM solutions indicated the capability of the method to accommodate direct injection of samples without any observed interferences of matrix ions on REE separation (Fig 5.7). As a consequence, matrix removal prior to separation by IPC is not required.

On the contrary, IEC conditions resulted in the inadequate separation of REE from matrix components (particularly Ba). As a result, the formation of spectroscopic interferences which affect REE analysis is still possible. Due to the influence of matrix ions on the IEC separation efficiency and its implications during analysis of REE, matrix removal prior to REE separation is necessitated.

5.2.3.4 *Analysis time*

An additional factor that needs to be taken into consideration is time required for separation. Although this does not provide an indication of the effectiveness of the separation procedure, it is a significant factor in determining the applicability of the method for routine analysis. Apart from actual time of the chromatographic run, other factors such as equilibration times need to be taken into account as they also impact the number of samples which can be analysed within a given time.

With respect to the IEC method, a run time of 22 minutes was required for REE separation. However, these separation conditions were not capable of eluting Fe^{3+} and Al^{3+} which were retained on the column. This required cleaning of the column between chromatographic runs, followed by equilibration of the column starting composition of the mobile phase prior to the next run (an additional 45 minutes). Consequently, the time required for analysis of a single sample was ~67 minutes, which is unsuitable for routine analysis.

In comparison, the IPC method required a longer run time to achieve complete separation (30 minutes), however the equilibration time between samples was 10 minutes, bringing the total time required for each sample to ~40 minutes.

On the basis of these factors, IPC was selected as the separation method of preference. The method allowed the direct analysis of geological matrices without the need of sample pre-treatment methods such as matrix removal. The separation of REE in lithium metaborate fused CRMs did not exhibit interference from matrix ions including that of Ba. Furthermore, IPC achieved separation in a shorter period in comparison of that required for IEC. The method also demonstrated a greater REE separation efficiency in comparison to IEC, as exhibited in chromatograms obtained during separation of alkali fused CRMs (Fig 5.7 and Fig 5.11). IPC also possesses an added benefit in which the ion exchange capacity of the column can be varied by adjusting the concentration of the ion pair reagent. As a result, more variables are available to fine tune the separation conditions to meet separation requirements of a specific application^{117, 120}.

5.3 Influence of Ion Pair Chromatographic Separation on ICP-MS analysis of REE

The influence of ion pair chromatographic separation (IPC) on the analytical performance of ICP-MS was investigated. This was accomplished by analysis of IPC separated REE fractions of CRMs and comparison of ICP-MS REE data obtained before and after separation. The impact of separation reagents (mobile phase constituents) on ICP-MS REE data, serves as a significant indicator of the potential of these two techniques to be coupled. Furthermore, it provides insight to the challenges that may be encountered and factors that need to be addressed before combining these techniques. Since detection of separated REE was aided by post-column derivatisation with arsenazo III, fractions analysed by ICP-MS also contained this reagent. As a consequence, results presented may be affected by combination of arsenazo III with IPC separation reagents. In addition, the application of Re and In as internal standards was ineffective for correcting matrix interferences during analysis.

5.3.1 Limits of detection (LOD) and limits of quantification (LOQ)

The impact of separation reagents on analysis was evident in the high background signal obtained for replicate blank fractions. The high background signal considerably limited the REE concentration range that can be measured with certainty and is evident with respect LOD and LOQ data (Table 5.11). The LOQ values clearly indicate the requirement of high concentrations ($\mu\text{g g}^{-1}$ levels) to generate a response which is distinguishable from the blank. As a consequence, quantification of REE present at trace concentrations cannot be achieved. This was apparent for Sc, Dy, Tm, Yb and Lu, in which the instrument response corresponding to their concentrations in calibration standards were indistinguishable from the background signal. Consequently, LOD and LOQ data corresponding to these elements are not presented. For the remaining REE, LOQ values ranged from 11.90 – 603.8 $\mu\text{g g}^{-1}$ for LREE, whilst values for Y, Tb, Ho, and Er ranged from (16.74 – 26.57 $\mu\text{g g}^{-1}$).

These LOQ values are significantly greater than that obtained for ICP-MS analysis of fused CRMs prior to separation, in which LOQ values were in ng g⁻¹ levels for all REE (Table 5.1). The decrease in sensitivity of the analysis could also be attributed the absolute REE concentrations that were measured by the ICP-MS after separation. Separated REE were subjected post-column derivatisation (effectively diluting the REE fraction), followed by further dilution due to the introduction of internal standards prior to ICP-MS analysis. As a result, it is highly probable that REE initially present in ng g⁻¹ concentrations were diluted to the extent at which they could not be measured with confidence.

Table 5.11 Limits of detection (LOD) and limits of quantification (LOQ) of ICP-MS analysis of separated REE fractions

Analyte	LOD/ $\mu\text{g L}^{-1}$	LOQ/ $\mu\text{g g}^{-1}$
Sc	—	—
Y	1.993	26.57
La	30.36	404.8
Ce	45.28	603.8
Pr	6.725	89.67
Nd	29.58	394.4
Sm	4.871	64.95
Eu	0.8930	11.90
Gd	2.338	31.18
Tb	1.942	25.89
Dy	—	—
Ho	1.256	16.74
Er	1.603	21.37
Tm	—	—
Yb	—	—
Lu	—	—

5.3.2 Precision

Precision of the analysis was evaluated by replicate analysis of separated CRM REE fractions. Each fused CRM solution was subjected to the separation and fraction collection procedure in triplicate with resultant REE fractions analysed in duplicate by ICP-MS. The mean (\bar{x}), standard deviation (s) and % RSD of the data are presented (Appendix G)

Precision of replicate measurements of CRM REE fractions were observed to be dependent on the analyte concentration, in which poor precision (high RSD values) were associated with low concentrations. Measurements performed in proximity to the respective LOQ values exhibited the poorest precision. The range of RSD values amongst the various CRMs ranged from 1.64 – 36.5%, with majority of values above 5.00%. This poor precision is attributed to a drift in instrument response between replicate measurements, which further intensified over the duration of the analysis. The variation in response is possibly due to the organic content of the separation reagents, in which combustion of organic compounds results in carbon formation. Carbon is capable of depositing on the sample and skimmer cones inducing signal suppression and changes in the analytical signal intensity over time⁷⁰. A similar effect is also caused by the presence of sodium which is the counter ion of the ion pair reagent, sodium octanesulfonate.

Aside from its sodium constituent, 1-octanesulfonate may also contribute signal drift due to its surfactant properties. This is apparent in the sample introduction system of the ICP-MS. The presence of 1-octanesulfonate increases the wetting properties of sample solutions, contributing to its adherence to the walls of the spray chamber. As a result, lengthy rinse times between samples are required to prevent carry overs from the previous sample solution¹⁶⁴. Although this was recognised and consequently corrected during analysis, it presents a challenge when coupling the IPC chromatographic separation method to an ICP-MS. This is because rinse times are dependent on intervals between each analyte peak as they exit the column.

The presence of separation reagents in REE fractions (particularly sodium 1-octanesulfonate) can significantly contribute to its TDS concentration. Solutions of high TDS (> 2%) can disrupt nebulisation efficiency affecting the rates at which sample solutions are introduced to the spray chamber. If nebulisation rates vary between sample replicates due to momentary clogging of the nebuliser, the precision of the analysis is impaired⁷⁰.

5.3.3 Accuracy

Accuracy of the analysis was evaluated by comparison of measured concentrations of separated CRM REE fractions with results obtained from the fusion procedure prior to IPC separation (section 5.1). The comparison of values before and after separation allows for identification of errors that may have incurred during the separation procedure.

Measured concentrations of separated CRM REE fractions and their corresponding concentrations from fused CRM solutions prior to separation are provided (Tables 5.12 – 5.15). The 95% confidence intervals accompanying these concentrations are also presented. The agreement between these two values are established by whether their 95% confidence intervals overlap. This is illustrated by normalising the measured concentrations of separated REE fractions (C_{measured}) with that obtained from the fusion procedure prior to separation (C_{fusion}). The resultant $C_{\text{measured}}/C_{\text{fusion}}$ ratios and their uncertainty ranges are plotted against each analyte (Figures 5.12 – 5.15) as similarly presented in section 5.1.

Only fusion results that were previously compared to certified/provisional CRM values were selected for comparison. Assessment of the accuracy of analysis was further limited to analytes which have exemplified concentrations greater than their respective LOQ. These analytes include Y and La-Gd which represent only a segment of the total REE.

With respect to AMIS0185, REE concentrations that were compared include that of Y and La-Eu (Table 5.12). Of these elements, La, Ce and Pr were consistent with values obtained prior to separation (Fig 5.12). These elements were present at high concentrations ($3\,108 - 38\,913 \mu\text{g g}^{-1}$) relative to the remaining REE. The exception was Nd, which exemplified poor accuracy despite possessing a high concentration of $9\,412 \pm 143 \mu\text{g g}^{-1}$. The measured concentration of Nd was significantly lower than that obtained prior to separation and corresponded to an absolute error of $1\,654 \mu\text{g g}^{-1}$. This denotes that sample loss during separation was highly probable. Poor accuracy was also demonstrated for Y, Sm and Eu, which were present at lower concentrations relative to La-Nd ($64.8 - 554 \mu\text{g g}^{-1}$). The poor correlation of their concentrations before and after separation was demonstrated by their $C_{\text{measured}}/C_{\text{fusion}}$ values which were below 0.95. This indicated that the 95% confidence intervals of these two values did not overlap.

Table 5.12 Comparison of measured REE concentrations of separated REE fractions with concentrations obtained from fusion procedure for AMIS0185 ($n = 6$, $P = 0.95$)

Analyte	Measured Concentration/ $\mu\text{g g}^{-1}$	Fusion Concentration/ $\mu\text{g g}^{-1}$	$C_{\text{measured}}/ C_{\text{fusion}}$
Y	52.1 ± 2.86	64.8 ± 1.54	0.80 ± 0.05
La	$28\ 810 \pm 910$	$28\ 896 \pm 493$	1.00 ± 0.04
Ce	$38\ 226 \pm 2\ 876$	$38\ 913 \pm 791$	0.98 ± 0.08
Pr	$3\ 287 \pm 271$	$3\ 108 \pm 49.8$	1.06 ± 0.09
Nd	$7\ 758 \pm 468$	$9\ 412 \pm 143$	0.82 ± 0.05
Sm	424 ± 40.8	554 ± 9.83	0.76 ± 0.07
Eu	65.2 ± 6.93	96.8 ± 2.05	0.67 ± 0.07

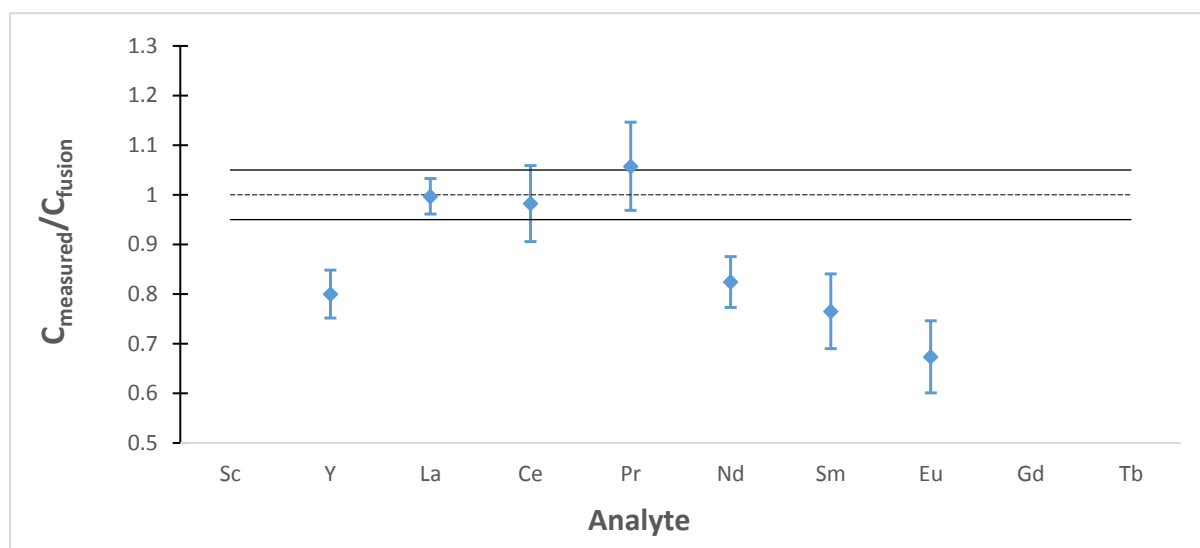


Figure 5.12 Agreement of measured concentrations of separated REE fractions (C_{measured}) and concentrations obtained from fusion procedure (C_{fusion}) within the 95% confidence interval for AMIS0185

Table 5.13 Comparison of measured REE concentrations of separated REE fractions with concentrations obtained from fusion procedure for AMIS0304 ($n = 6$, $P = 0.95$)

Analyte	Measured Concentration/ $\mu\text{g g}^{-1}$	Fusion Concentration/ $\mu\text{g g}^{-1}$	$C_{\text{measured}}/ C_{\text{fusion}}$
Y	363 ± 6.24	417 ± 4.88	0.87 ± 0.02
La	$2\,407 \pm 186$	$3\,251 \pm 30.0$	0.74 ± 0.06
Ce	$6\,120 \pm 420$	$7\,756 \pm 131$	0.79 ± 0.05
Pr	827 ± 29.7	868 ± 8.97	0.95 ± 0.04
Nd	$2\,686 \pm 322$	$3\,806 \pm 37.9$	0.70 ± 0.08
Sm	372 ± 37.4	576 ± 7.18	0.64 ± 0.06

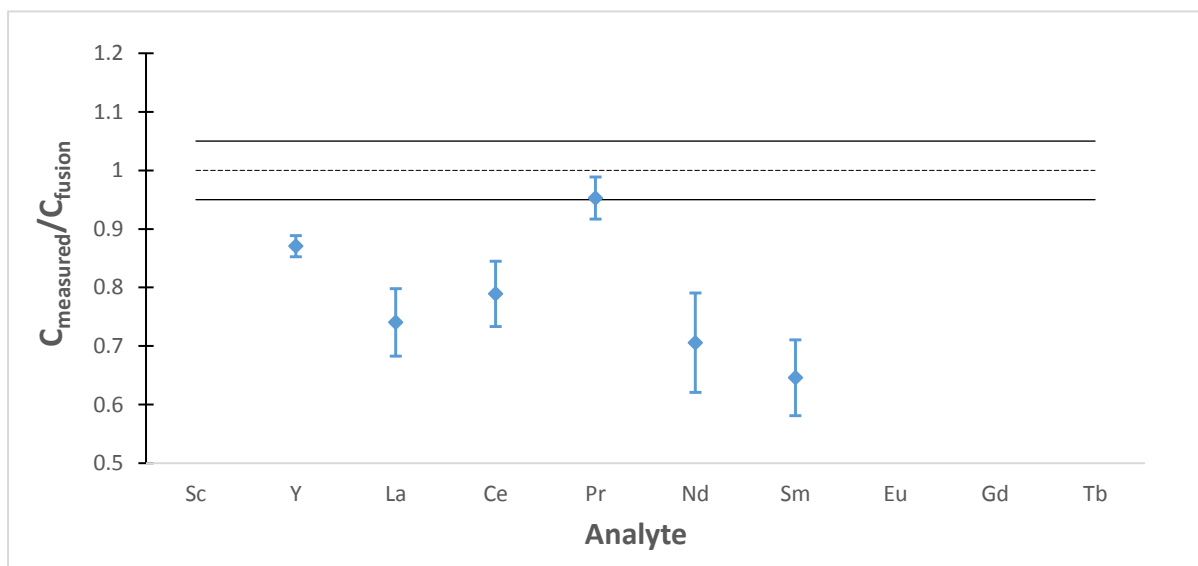


Figure 5.13 Agreement of measured concentrations of separated REE fractions (C_{measured}) and concentrations obtained from fusion procedure (C_{fusion}) within the 95% confidence interval for AMIS0304

Table 5.14 Comparison of measured REE concentrations of separated REE fractions with concentrations obtained from fusion procedure for AMIS0356 ($n = 6$, $P = 0.95$)

Analyte	Measured Concentration/ $\mu\text{g g}^{-1}$	Fusion Concentration/ $\mu\text{g g}^{-1}$	$C_{\text{measured}}/C_{\text{fusion}}$
Y	27.8 ± 1.39	38.2 ± 0.194	0.71 ± 0.04
La	$6\ 515 \pm 714$	$8\ 465 \pm 45.2$	0.77 ± 0.08
Ce	$9\ 487 \pm 705$	$11\ 190 \pm 66.4$	0.85 ± 0.06
Pr	925 ± 107	819 ± 4.99	1.13 ± 0.13
Nd	$1\ 693 \pm 187$	$2\ 449 \pm 17.6$	0.69 ± 0.08
Sm	—	162 ± 0.962	—
Eu	15.2 ± 3.21	31.1 ± 0.197	0.48 ± 0.10

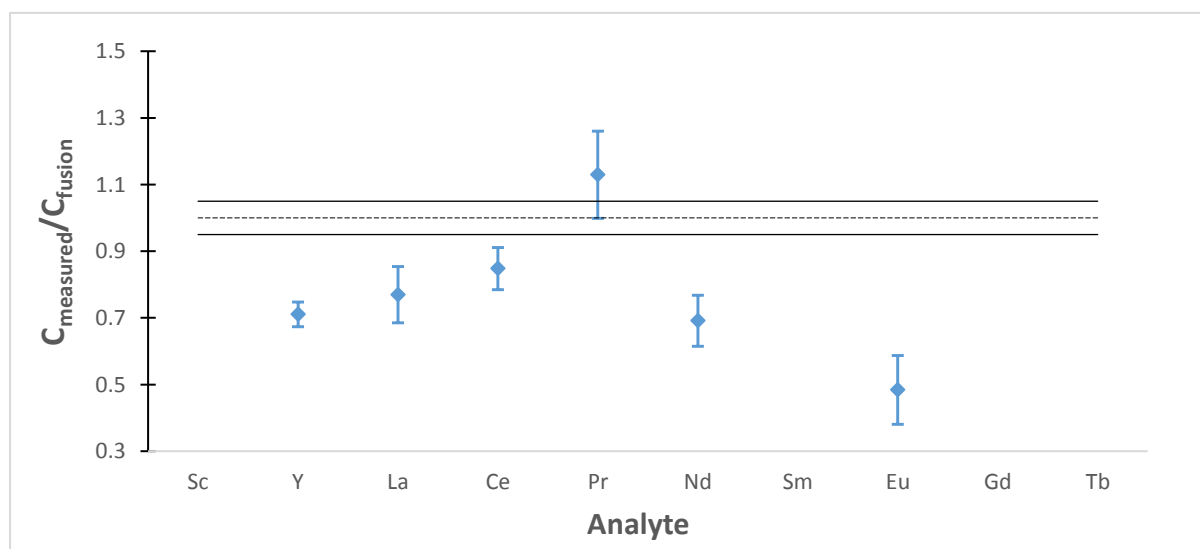


Figure 5.14 Agreement of measured concentrations of separated REE fractions (C_{measured}) and concentrations obtained from fusion procedure (C_{fusion}) within the 95% confidence interval for AMIS0356

Table 5.15 Comparison of measured REE concentrations of separated REE fractions with concentrations obtained from fusion procedure for CGL-111 ($n = 6$, $P = 0.95$)

Analyte	Measured Concentration/ $\mu\text{g g}^{-1}$	Fusion Concentration/ $\mu\text{g g}^{-1}$	$C_{\text{measured}}/C_{\text{fusion}}$
Y	885 ± 41.5	986 ± 67.6	0.90 ± 0.07
La	$15\,421 \pm 825$	$16\,174 \pm 1\,504$	0.95 ± 0.10
Ce	$16\,248 \pm 1192$	$14\,979 \pm 368$	1.08 ± 0.08
Pr	$2\,336 \pm 240$	$2\,119 \pm 223$	1.10 ± 0.16
Nd	$6\,269 \pm 414$	$7\,370 \pm 771$	0.85 ± 0.10
Sm	584 ± 49.0	741 ± 73.3	0.79 ± 0.10
Eu	126 ± 21.2	174.8 ± 17.2	0.72 ± 0.14
Gd	142 ± 54.5	473 ± 51.6	0.30 ± 0.12

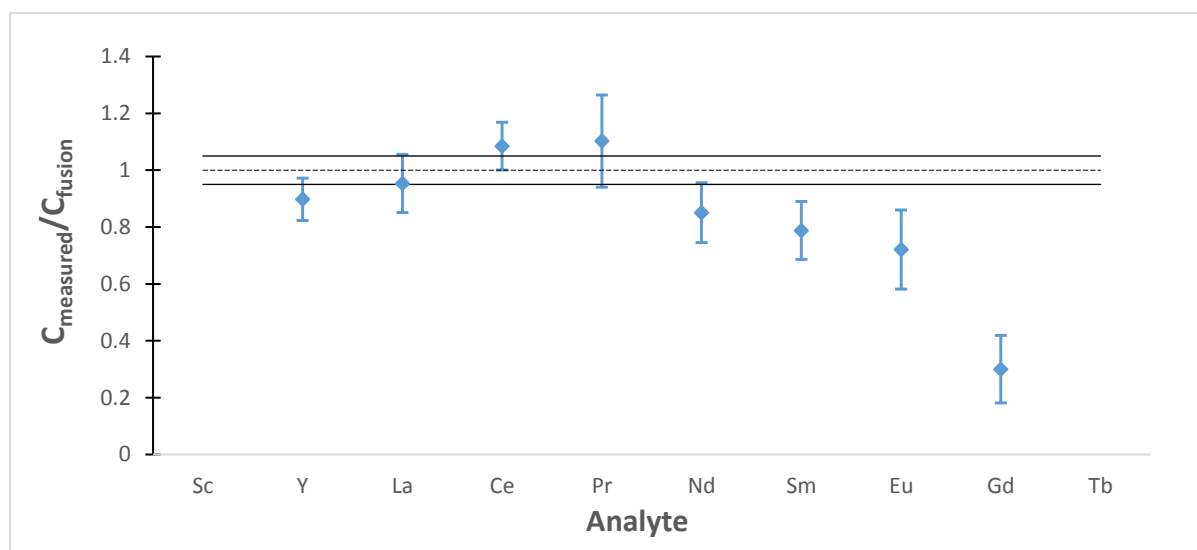


Figure 5.15 Agreement of measured concentrations of separated REE fractions (C_{measured}) and concentrations obtained from fusion procedure (C_{fusion}) within the 95% confidence interval for CGL-111

Measured REE concentrations in AMIS0304 comprised that of Y, La-Sm. Poor agreement between concentrations obtained before and after separation were demonstrated for Y, La, Ce, Nd and Sm (Fig 5.13). These elements were well below the lower 95% confidence interval, possessing $C_{\text{measured}}/C_{\text{fusion}}$ values in the range of 0.64 – 0.87 (Table 5.13). The poor accuracy of these elements may be related to their concentrations. AMIS0304 exemplified the lowest concentration of La and Ce in the CRMs investigated ($3\,251$ and $7\,756\ \mu\text{g g}^{-1}$ respectively) whilst Y, Nd and Sm were present at $417\ \mu\text{g g}^{-1}$, $3\,806\ \mu\text{g g}^{-1}$ and $576\ \mu\text{g g}^{-1}$ respectively. The measured concentration of Pr was the only value consistent with the fusion concentration obtained prior to separation.

With regard to AMIS0356, Y, La, Ce, Nd and Eu were well below the 95% confidence interval with $C_{\text{measured}}/C_{\text{fusion}}$ values between 0.48 – 0.85 (Table 5.14). The accuracy of measured concentrations corresponding to these elements depreciated with a decrease in concentration (Fig 5.14). This was particularly demonstrated by Eu, which had the lowest concentration ($31.1 \pm 0.197\ \mu\text{g g}^{-1}$), as well as the poorest correlation of concentrations before and after separation with a $C_{\text{measured}}/C_{\text{fusion}}$ value of 0.48. Measured concentration of Pr was the sole value that was in agreement with that obtained prior to separation.

For CGL-111, measured concentrations of Y and La-Nd were in good agreement with values obtained prior to separation (Fig 5.15). These elements were present at high concentration than the remaining REE within the CRM and were within the range of 844 – $17\,440\ \mu\text{g g}^{-1}$. The remaining REE which included Sm, Eu and Gd displayed poor accuracy with $C_{\text{measured}}/C_{\text{fusion}}$ values between 0.30 – 0.79 (Table 5.15). Concentrations corresponding to these were the lowest exhibited and were within 175 – $741\ \mu\text{g g}^{-1}$. The measured concentration of Gd ($142 \pm 54\ \mu\text{g g}^{-1}$) is considerably lower than that obtained prior to separation ($473 \pm 51.6\ \mu\text{g g}^{-1}$) with an absolute error of $331\ \mu\text{g g}^{-1}$.

The agreement of measured REE values before and after separation was highly dependent on the concentration at which each analyte was present. Results demonstrated the capability of the method to accurately analyse Y and La-Nd. However, this was only observed for AMIS0185 and CGL-111, which had the highest concentrations of these elements. Pr was the exception to this observation, as good accuracy was exemplified for all CRMs. This is justified as there are no extreme high or low concentrations of Pr in the CRMs investigated. The requirement of high concentrations for accurate quantification makes the method unsuitable for the analysis of Sm, Eu and Gd which are present at lower concentrations than La-Nd.

On the basis of measured REE values of CRMs after separation, the lowest concentrations of Y, La-Pr that can be measured with certainty are presented (Table 5.16). These concentrations indicate that the applicability of the method is limited to geological materials which contain a significant proportion of REE oxides of Y and La-Pr.

Table 5.16 REE and corresponding lowest concentrations that can be measured with certainty by ICP-MS after IPC separation

Analyte	Concentration/ $\mu\text{g g}^{-1}$
Y	885 \pm 41.5
La	15 421 \pm 825
Ce	16 248 \pm 1 192
Pr	827 \pm 29.7

The lowest concentration of Nd that can be accurately quantified requires further verification. This is because CGL-111 was the only CRM for which Nd was in agreement with compared values, although it did not possess the highest concentration of this analyte amongst the investigated CRMs.

Poor accuracy of REE present at low concentrations are possibly attributed to errors which accompany the number of steps carried out prior to ICP-MS analysis. These steps included: IPC separation of REE; post-column derivatisation of separated REE before UV-Vis detection and collection of separated REE fractions. Furthermore, collected REE were also subject to dilution due to the introduction of internal standards prior to ICP-MS analysis.

Possible errors at any of these stages are additive and significantly impacts the overall accuracy of the method. For example, separation of sample replicates may exhibit small variations in analyte peak area, shape and retention times. The use of a mixing tee and a reaction coil for post-column derivatisation increases the path length that separated REE peaks have to travel before they reach the detector. As a result, the potential for band spreading of separated REE peaks increases, intensifying these variations.

The reproducibility of post-column derivatisation reaction can also be affected by temperature changes as well as pressure fluctuations of the pump used to deliver the derivatisation reagent¹³⁹. As a result, each of these factors can affect the separation and detection of REE such that reproducibility of analyte retention times and peak areas are impaired. This significantly influences efficiency of the fraction collection procedure, as separated REE peaks are collected based on the consistency of peak start and end times. Consequently any deviations in peak elution can result in unsatisfactory recoveries and analyte loss.

The resultant loss of analyte negatively impacts the accuracy of the analysis. This was exemplified by Nd in AMIS0185, in which peak tailing during separation affected the performance of the fraction collection procedure. This substantiates the large absolute error of concentrations measured before and after separation. Potential losses of analytes present at low concentrations are more critical due to the magnification of analytical errors. This justifies the poor accuracy demonstrated for Sm, Eu and Gd, as well as the measurements corresponding to AMIS0304 and AMIS0356 as they possessed low concentrations of REE relative to the remaining CRMs.

Matrix interferences caused by separation reagents not only impacted the precision of the analysis, as aforementioned, but also the accuracy of measurements by ICP-MS. The deposition of carbon and sodium on interfacial cones can result in orifice clogging which induces suppression of the analyte signal^{73, 78}. This limits the sensitivity of the analysis including the concentration range that can be measured with certainty, as only a fraction of analyte ions are detected. Consequently, the poor correlation of measured concentrations before and after separation can also be contributed to the separation reagents present in separated REE fractions.

Overall, the REE data obtained from ICP-MS analysis of separated REE fractions exemplified a degradation in sensitivity of the analysis in comparison to that obtained prior to separation. The decreased sensitivity was attributed to the mobile phase constituents of the IPC separation procedure, which generated a high background signal during analysis. The influence of the separation reagents was further substantiated by the high calculated LOQ values ($\mu\text{g g}^{-1}$ levels) which precluded the determination of REE present at trace concentrations (Sc and HREE).

The drift in instrument response between sample replicates considerably impaired the precision of the analysis. This may be due to sodium and carbon constituents of the separation reagents which are capable of depositing on the sample and skimmer cones of the ICP-MS instrumentation. The contribution of the separation reagents to the TDS concentration of analysed samples as well as surfactant properties of the ion pair reagent (1-octanesulfonate) were also identified as a potential sources of variations in instrument response.

The number of steps carried out prior to ICP-MS analysis including the separation procedure itself contributed to the overall potential error of the procedure. These errors affected the accuracy of measured REE concentrations after separation, in which poor accuracy was obtained for REE present at low concentrations. Accuracy of the analysis may also be affected by the occurrence of matrix interferences generated by separation reagents. Both these factors limits the analyte concentration range that can be measured with confidence. Nevertheless, the ICP-MS analysis of REE after IPC separation demonstrated the capability to accurately determine Y, La, Ce, Pr and Nd that are present at high concentrations.

CHAPTER 6 - CONCLUSION AND IMPROVEMENTS TO STUDY

Validation of the lithium metaborate fusion procedure by ICP-MS analysis of CRM solutions revealed that its efficiency was highly dependent on the mineralogical composition of the materials analysed. The applicability of the sample decomposition method was demonstrated for CRMs which comprised of bastnäsite rich carbonate materials but was unable to effectuate complete decomposition of reference materials which consisted of sulfide minerals. The selective nature of this prevalent decomposition method indicates its potential to introduce errors at the beginning of analytical methodology commonly applied for the determination of REE. These errors are attributed to non-oxidising nature of lithium metaborate which is unable to convert sulfides into their equivalent oxides required for their decomposition. The limitation associated with the use of lithium metaborate can be overcome the addition of an oxidising agent such as sodium, potassium or ammonium nitrite to the sample prior to fusion¹⁶⁵. Results of CRM analysis also established errors on the quantification of Sc attributed to formation of polyatomic molecular species of Si ($^{29}\text{SiO}^+$ and $^{28}\text{SiOH}^+$). However, the concentration of Sc was characterised for only one of the CRMs investigated. As a result, the impact of these polyatomic isobaric interferences on Sc determination requires further verification. With exception of Sc, the fusion procedure exhibited accurate and precise quantification of remaining REE (Y and La-Lu) with LOQ values applicable for trace determination of these elements in geological materials (ng g^{-1} levels).

Evaluation of IPC and IEC methods for separation of individual REE revealed that IPC was the most efficient method. Furthermore, IPC demonstrated the proficiency to separate individual REE from sample matrix components such that the direct separation of REE in geological materials can be achieved. Therefore, the application of IPC prior to ICP-MS analysis has potential to eliminate spectroscopic interferences (arising from sample matrix components and REE as a group itself), since separation of analytes from interferent ions was accomplished. The avoidance of sample pre-treatment procedures allows for direct introduction of sample solutions for analysis.

This limits errors attributed to sample loss, introduction of interferences from reagents used to execute these procedures and removal of Sc, conferring the analytical method greater speed and accuracy. It is due to these proficiencies, which were not exemplified by IEC, that IPC was selected as the most suitable method for REE separation prior to ICP-MS analysis.

The influence of the IPC mobile phase composition on the analytical performance of ICP-MS was assessed by analysis of separated REE fractions of CRMs. The resultant REE data was compared with validated CRM data obtained prior to separation to provide a credible evaluation of errors attributed to the separation procedure. Results revealed that the IPC mobile phase constituents impact the ICP-MS analysis of REE in the following manner:

- Carbon and sodium constituents (attributed to HIBA and sodium 1-octanesulfonate) are capable of affecting both the precision and sensitivity of the analysis due to deposition of these constituents on the interfacial cones of the ICP-MS
- Surfactant properties of sodium 1-octanesulfonate increases the wetting properties of the sample solutions increasing its adherence to walls of the spray chamber such that carry over from previous sample solutions are evident. This affects both the precision and accuracy of the ICP-MS analysis.
- The high TDS content of the mobile phase (attributed to sodium 1-octanesulfonate) impairs nebulisation efficiency resulting in variations of the rate of sample introduction. This also affects precision of the analysis.

Overall, the IPC mobile phase composition contributed to instrument background signal/suppression of analyte signal such that REE concentration ranges that can be measured with confidence may be limited. Calculated LOQ values were at $\mu\text{g g}^{-1}$ levels, significantly higher than those obtained prior to separation, precluding the analysis of REE present at trace concentrations. It must be taken into account that factors other than IPC mobile phase constituents may have also contributed to the results obtained. These include the inclusion of arsenazo III (post-column derivatisation reagent) in the separated REE fractions analysed, errors attributed to the fraction collection procedure and manual introduction of internal standards prior to ICP-MS analysis. However each of these factors can be addressed by the coupling of the IPC separation method directly to an ICP-MS. This is justified as post-column derivatisation and fraction collection will not be required and the introduction of internal standards can be performed online.

The ICP-MS analysis of separated REE fractions obtained after IPC separation provided insight to the challenges that will be encountered by integration of this method with ICP-MS as a detector. As a result the following improvements to the study can be made:

- The application of both helium and oxygen for the conversion of a sample solutions into an aerosol (nebuliser gas). The addition of oxygen into the gas stream permits its reaction with organic constituents of the mobile phase forming carbon dioxide. This eliminates the deposition of carbon on the sample and skimmer cones and its associated influence on the ICP-MS analysis⁷⁰. However, the addition of oxygen also promotes formation of REE oxide and hydroxide polyatomic species. As a result the use of oxygen to overcome carbon deposition requires further evaluation.
- Replacement of sodium 1-octanesulfonate with ammonium octanesulfonate as the ion pair reagent for REE separation by IPC¹⁶⁶. The use of ammonium octanesulfonate is not expected to generate any changes in separation efficiency of the IPC method as octanesulfonate is the main component that effectuates the separation of REE and not its counter ion. The exclusion of sodium will significantly reduce the TDS content of the mobile phase in addition to minimising the deposition of this component on the interfacial cones of the ICP-MS.
- The surfactant properties of 1-octanesulfonate and its influence on the behaviour of sample solutions within the spray chamber necessitates further investigation. Different spray chamber designs may increase drainage characteristics of sample solutions such that sample carry over between runs are minimised¹⁶⁷.
- The influence of sample matrix components on IPC separation of REE requires further investigation. Not all matrix ions are capable of forming stable complexes with the derivatisation reagent (arsenazo III), necessary for generating a UV-Vis detector response during HPLC separation.

Provided that these improvements are addressed, it is expected that the influence of IPC mobile phase composition will be minimised such that accurate and precise quantification of REE can be achieved by coupling of IPC separation with ICP-MS detection.

IPC possesses a high potential to be coupled to an HPLC-ICP-MS due to its high efficiency for REE separation. The successful integration of this chromatographic method with HPLC-ICP-MS for direct separation of REE in geological materials will provide a highly efficient means of overcoming interferences which afflict REE determination by ICP-MS analysis alone. Furthermore it will permit the disuse of sample pre-treatment procedures which frequently accompany the determination of REE in complex matrices, eliminating errors associated with these procedures. These advantageous attributes will revolutionise REE analyses as it will allow the accurate quantification of these elements at concentrations of several orders of magnitude in complex matrices. This makes it suitable for analysis of REE in geological materials required for quantification of these elements in mined REE ores and for future REE mineral exploration.

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APPENDICES

Appendix A –CRM Certificates of Analysis



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D1 Isando Business Park, 11 Gewel Street (off Hulley Rd), Isando, P.O. Box 856, Isando, 1600, South Africa.
A Division of Set Point Industrial Technology (Pty) Ltd. Reg.No. 1989/000201/07.

AMIS0185

Certified Reference Material

Rare Earth Elements
Wigu Carbonatite Complex, Tanzania

Certificate of Analysis

Recommended Concentrations and Limits^{1, 2}
(at two Standard Deviations)

Certified Concentrations³

Ce M/ICP	4.075	±	0.461	%
La XRF	3.003	±	0.171	%
La M/ICP	2.976	±	0.272	%
Nd M/ICP	9238	±	1033	ppm
Pr M/ICP	3471	±	343	ppm
Sm M/ICP	556	±	48	ppm
Specific Gravity	3.28	±	0.08	

Provisional Concentrations³

Ce XRF	4.154	±	0.618	%
Dy M/ICP	27.1	±	5.1	ppm
Eu M/ICP	94.2	±	12.1	ppm
Ho M/ICP	3.2	±	0.5	ppm
Tm M/ICP	0.43	±	0.08	ppm
Y M/ICP	62.0	±	7.7	ppm
Y XRF	56.9	±	14.2	ppm

Informational Means

Er M/ICP	4.24	ppm
Gd M/ICP	244	ppm
Lu M/ICP	0.56	ppm
Sc M/ICP	15.4	ppm
Tb M/ICP	15.3	ppm
Yb M/ICP	2.75	ppm

1. Manufacturers recommended limits for use of the material as control samples, based on two standard deviations, calculated using "Between Laboratory" statistics for treatment of the data for trivial, non-trivial and technically invalid results. See sections 1, 9 and 12.
2. See Appendix 2 for the oxide conversions.
3. There is additional certified major element data presented on p2 and uncertified trace element data presented as an appendix.

Director: G.J Horsfield (CEO), MD Evers (CFO)(British), S.J Ingram, K Gerber,
M McWha, N Robinson, MH Snelling, J Vassiloudis, D Williams

**Major Element
Recommended Concentrations and Limits
(at two Standard Deviations)**

Certified Concentrations

Al ₂ O ₃	2.22	±	0.12	%
CaO	11.48	±	0.36	%
Fe ₂ O ₃	5.29	±	0.28	%
LOI	20.69	±	0.64	%
MgO	4.65	±	0.20	%
P ₂ O ₅	1.74	±	0.10	%
S Combustion / LECO	1.93	±	0.14	%
SiO ₂	21.53	±	0.82	%

Provisional Concentrations

K ₂ O	0.10	±	0.02	%
MnO	1.09	±	0.16	%
TiO ₂	0.081	±	0.024	%

Informational Means

Cr ₂ O ₃	0.026	%
Na ₂ O	0.17	%

1. Intended Use: AMIS0185 can be used to check analysis of samples of rare earth element bearing rocks with a similar grade and matrix.

It is a matrix matched Certified Reference Material, fit for use as control samples in routine assay laboratory quality control when inserted within runs of samples and measured in parallel to the unknown. Its purpose is to monitor inter-laboratory or instrument bias and within lab precision. It can be used, indirectly, to establish the traceability of results to an SI system of units.

The recommended concentrations and limits for this material are property values based on a measurement campaign (round robin) and reflect consensus results from the laboratories that participated in the round robin.

Slight variations in analytical procedures between laboratories will reflect as slight biases to the recommended concentrations (see 19). Good laboratories will report results within the two standard deviation levels with a failure rate of <10 %.

The material can also be used for method development and for the calibration of equipment.

2. Origin of Material: AMIS0185 is a commissioned CRM made up of material supplied by Montero Resources Ltd. from the Wigu Carbonatite Complex located 200km WSW of Dar es Salaam. Wigu Hill is underlain by Paleoproterozoic metasediments consisting of well foliated high grade gneisses and amphibolites. These rocks have been intruded by a swarm of carbonatite dykes on the southern edge of the Uluguru Mountains where the Uluguru massif is truncated by a major Karoo aged rift. The intrusions have resulted in strong carbonate alteration of the gneisses and amphibolites adjacent to the dykes and a more pervasive fenitisation and weaker carbonate alteration halo away from the dykes.

3. Mineral and Chemical Composition: The carbonatite material selected for this sample is fresh, compact and tightly and finely crystalline. It is bastnasite-rich with minor amounts of

synchisite, parasite and monazite, with traces of apatite. The carbonatite is dolomitic with a significant proportion of Rare Earth Oxide minerals (REO's) and lesser associated quartz, barite, strontianite, iron oxides and minor manganese.

Regional sampling to date has identified that the main rare earth minerals present in the Wigu carbonatites are the light rare earths, namely Cerium, Lanthanum, Neodymium, Praseodymium, and Samarium. Minor amounts of Europium and Gadolinium are present, but the other heavy rare earth elements are present in trace amounts only.

4. **Appearance:** The material is a very fine Pale Red powder (Corstor colour chart – 10R 6/2).

5. **Handling instructions:** The material is packaged in Laboratory Packs and Explorer Packs that must be shaken or otherwise agitated before use. Normal safety precautions for handling fine particulate matter are suggested, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

6. **Method of Preparation:** The material was crushed, dry-milled and air-classified to <54µm. Wet sieve particle size analysis of random samples confirmed the material was 98.5% <54µm. It was then blended in a bi-conical mixer, systematically divided and then sealed into 1kg Laboratory Packs. Explorer Packs are subdivided from the Laboratory packs as required. Samples were randomly selected for homogeneity testing and third party analysis. Statistical analysis of both homogeneity and consensus test results were carried out by an independent statistician.

7. **Methods of Analysis requested:**

1. Multi-acid digest, including HF, ICP- OES or ICP-MS. Multi element scan to include REE, Y & Sc.
2. Fusion, ICP- OES or ICP-MS. Multi element scan to include REE, Y & Sc.
3. XRF. Light & Heavy Rare Earth Elements, Y & Sc.
4. XRF fusion. Majors (Al₂O₃, CaO, Cr₂O₃, Fe₂O₃, K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, TiO₂. LOI.)
5. S. Combustion analysis.
6. SG (gas pycnometer).

8. **Information requested:**

1. State and provide brief description of analytical techniques used.
2. State aliquots used for all determinations.
3. Results for individual analyses to be reported (not averages)
4. All results for Rare Earth Elements to be reported in ppm (not as oxides).
5. All results for multi-element scans to be reported in ppm.
6. All results for major elements to be reported in %, as oxides.
7. Report all QC data, to include replicates, blanks and certified reference materials used.

9. **Method of Certification:** Nineteen laboratories were each given eight packages, comprising eight samples scientifically selected from throughout the batch. Eighteen laboratories reported results in time for certification of the economic elements. Eight of these laboratories reported results for the major elements.

Final limits were calculated after first determining if all data was compatible within a spread normally expected for similar analytical methods done by reputable laboratories. Data from any one laboratory was then removed from further calculations when the mean of all analyses from that laboratory failed a "t test" of the global means of the other laboratories. The means and standard deviations were then re-calculated using all remaining data. Any analysis that fell outside of the new two standard deviations was removed from the ensuing data base. The mean and standard deviations were again calculated using the remaining data.

Assay data (cont)

Lab Code	Al2O3 XRF %	CaO XRF %	Cr2O3 XRF %	Fe2O3 XRF %	K2O XRF %	MgO XRF %	MnO XRF %	Na2O XRF %	P2O5 XRF %	S LECO %	SiO2 XRF %	TiO2 XRF %	LOI %	SG pycnometer
K	2.22	10.60	0.02		0.10	4.59		0.20	1.67	1.93	20.40	0.07	20.40	3.24
K	2.16	10.40	0.02		0.10	4.50		0.20	1.64	1.90	19.95	0.06	20.50	3.23
K	2.11	10.10	0.01		0.10	4.37		0.19	1.59	1.90	19.40	0.06	20.30	3.21
K	2.24	10.65	0.03		0.10	4.61		0.21	1.70	1.88	20.60	0.07	20.50	3.21
K	2.13	10.20	0.01		0.10	4.41		0.19	1.61	1.92	19.65	0.06	20.40	3.21
L	2.34	11.40	0.10	5.40	0.11	4.52	1.15	0.26			21.30	0.10	20.74	3.32
L	2.30	11.50	0.10	5.31	0.12	4.48	1.12	0.39			21.20	0.10	20.68	3.29
L	2.28	11.50	0.09	5.42	0.14	4.53	1.13	0.28			21.40	0.11	20.71	3.30
L	2.35	11.50	0.10	5.36	0.19	4.54	1.14	0.28			21.10	0.10	20.81	3.31
L	2.28	11.50	0.12	5.39	0.12	4.54	1.12	0.27			21.00	0.11	20.56	3.29
L	2.36	11.90	0.18	5.50	0.13	4.74	1.16	0.33			21.90	0.12	20.94	3.32
L	2.31	11.50	0.10	5.36	0.12	4.52	1.13	0.28			21.40	0.11	20.20	3.31
L	2.31	11.60	0.10	5.45	0.20	4.51	1.14	0.33			21.30	0.11	20.79	3.31
M	2.21	11.35	0.05		0.10	4.69	1.03	0.19	1.73	1.89	21.10	0.08	21.00	3.06
M	2.23	11.40	0.05		0.10	4.70	1.03	0.19	1.73	1.88	21.10	0.07	20.90	3.06
M	2.20	11.20	0.05		0.10	4.62	1.02	0.19	1.71	1.88	20.80	0.08	21.00	3.08
M	2.22	11.40	0.06		0.10	4.71	1.04	0.20	1.74	1.90	21.10	0.08	20.90	3.03
M	2.24	11.55	0.05		0.10	4.74	1.05	0.20	1.76	1.90	21.30	0.07	20.90	3.05
M	2.25	11.55	0.05		0.10	4.74	1.04	0.20	1.75	1.89	21.30	0.07	20.90	3.06
M	2.25	11.45	0.05		0.10	4.72	1.04	0.19	1.74	1.86	21.20	0.07	20.90	3.12
M	2.22	11.50	0.05		0.10	4.71	1.04	0.20	1.74	1.89	21.20	0.07	20.90	3.07
N	2.22	11.70		5.47	0.12	4.75	1.16	0.04			21.90	0.08	20.50	
N	2.22	11.80		5.53	0.12	4.79	1.17	0.03			22.00	0.09	20.50	
N	2.21	11.70		5.49	0.12	4.77	1.16	0.04			21.90	0.09	20.50	
N	2.23	11.80		5.48	0.12	4.79	1.16	0.04			22.00	0.09	20.50	
N	2.23	11.70		5.47	0.12	4.78	1.15	0.05			22.00	0.09	20.50	
N	2.24	11.70		5.49	0.12	4.77	1.16	0.04			21.90	0.09	20.50	
N	2.22	11.70		5.50	0.12	4.77	1.16	0.05			21.90	0.09	20.60	
N	2.24	11.70		5.47	0.12	4.77	1.15	0.04			21.90	0.09	20.60	
O	2.24	11.70		5.33	0.11	4.62	1.20	0.21	1.81		22.20	0.07	21.20	3.31
O	2.24	11.70		5.39	0.11	4.67	1.17	0.23	1.82		21.90	0.08	21.20	3.29
O	2.21	11.60		5.39	0.11	4.65	1.18	0.26	1.80		22.10	0.08	21.20	3.33
O	2.20	11.60		5.44	0.10	4.62	1.19	0.20	1.82		22.00	0.09	21.20	3.29
O	2.24	11.70		5.47	0.11	4.65	1.16	0.23	1.83		22.10	0.08	21.10	3.36
O	2.27	11.70		5.43	0.11	4.68	1.18	0.27	1.82		22.00	0.09	21.10	3.40
O	2.21	11.70		5.48	0.11	4.66	1.18	0.22	1.80		22.00	0.08	21.20	3.33
O	2.25	11.70		5.47	0.11	4.62	1.19	0.15	1.83		22.00	0.09	21.20	3.34
P	2.37	11.70	0.01	5.40	0.12	4.83	1.16	0.10	1.87	1.85	23.90	0.09	20.40	
P	2.41	11.50	0.01	5.35	0.13	4.71	1.02	0.20	1.58	1.85	23.90	0.08	20.50	
P	2.26	11.10		5.29	0.11	4.59	1.07		1.70	1.91	23.20	0.08	20.40	
P	2.28	11.30		5.18	0.10	4.64	1.10		1.77	1.84	23.70	0.08	20.50	
P	2.32	11.30		5.17	0.10	4.66	1.10	0.10	1.79	1.83	23.80	0.08	20.50	
P	2.34	11.60		5.31	0.10	4.72	1.12		1.73	1.86	24.10	0.08	20.50	
P	2.31	11.60		5.28	0.11	4.73	1.12	0.10	1.76	1.85	24.20	0.09	20.50	
P	2.40	11.90		5.44	0.12	4.77	1.15	0.10	1.81	1.85	24.60	0.09	20.50	

12. **Measurement of Uncertainty:** The samples used in the certification process were selected in such a way as to represent the entire batch of material and were taken from the final packaged units; therefore all possible sources of uncertainty (sample uncertainty and measurement uncertainty) are included in the final combined standard uncertainty determination.

The uncertainty measurement takes into consideration the between lab and the within lab variances and is calculated from the square roots of the variances of these components using the formula:

$$\text{Combined standard uncertainty} = \sqrt{(\text{between lab. var/no of labs}) + (\text{mean square within lab. var/no of assays})}$$

These uncertainty measurements may be used, by laboratories, as a component for calculating the total uncertainty for method validation according to the relevant ISO guidelines.

Analyte	Method	Unit	S ¹	σ_L ²	SW ³	CSU ⁴
Ce	M/ICP	%	2304	2169	687	727
La	XRF	%	856	889	285	338
La	M/ICP	%	1361	1252	515	422
Nd	M/ICP	ppm	516	464	145	148
Pr	M/ICP	ppm	171	130	73	38
Sm	M/ICP	ppm	23.9	17.9	11.0	5.3
SG	pycnometer		0.048	0.038	0.031	0.014
Al2O3	XRF	%	0.064	0.052	0.030	0.017
CaO	XRF	%	0.181	0.136	0.101	0.044
Cr2O3	XRF	%	0.019	0.018	0.005	0.006
Fe2O3	XRF	%	0.139	0.122	0.062	0.041
K2O	XRF	%	0.011	0.008	0.005	0.002
LOI		%	0.319	0.256	0.096	0.075
MgO	XRF	%	0.104	0.077	0.045	0.023
MnO	XRF	%	0.080	0.066	0.017	0.019
Na2O	XRF	%	0.093	0.075	0.021	0.022
P2O5	XRF	%	0.054	0.043	0.021	0.013
S	LECO	%	0.068	0.061	0.026	0.020
SiO2	XRF	%	0.406	0.352	0.134	0.112
TiO2	XRF	%	0.012	0.009	0.004	0.003
Ce	XRF	%	3088	3496	450	1323
Dy	M/ICP	ppm	2.75	2.34	0.78	0.71
Eu	M/ICP	ppm	7.08	5.97	2.26	1.82
Ho	M/ICP	ppm	0.251	0.199	0.107	0.061
Tm	M/ICP	ppm	0.044	0.028	0.030	0.009
Y	M/ICP	ppm	3.86	2.89	1.31	0.81
Y	XRF	ppm	7.10	9.34	2.10	4.19
Er	M/ICP	ppm	1.72	1.81	0.25	0.64
Gd	M/ICP	ppm	90.1	79.9	7.8	24.1
Lu	M/ICP	ppm	0.339	0.293	0.072	0.089
Sc	M/ICP	ppm	3.45	2.99	1.69	1.02
Tb	M/ICP	ppm	5.24	4.40	0.53	1.27
Yb	M/ICP	ppm	1.33	1.13	0.12	0.33

1. S - Std Dev for use on control charts.
2. σ_L - Betw Lab Std Dev, for use to calculate a measure of accuracy.
3. SW - Within Lab Std Dev, for use to calculate a measure of precision.
4. CSU - Combined Standard Uncertainty, a component for use to calculate the total uncertainty in method validation.

13. **Certified values:** The Certified, Provisional and Informational values listed on p1 and p2 of this certificate fulfill the AMIS statistical criteria regarding agreement for certification and have been independently validated by Dr Barry Smee.

14. **Metrological Traceability:** The values quoted herein are based on the consensus values derived from statistical analysis of the data from an inter laboratory measurement program. Traceability to SI units is via the standards used by the individual laboratories, the majority of which are accredited, who have maintained measurement traceability during the analytical process.

15. **Certification:** AMIS0185 is a new material.

16. **Period of validity:** The certified values are valid for this product, while still sealed in its original packaging, until notification to the contrary. The stability of the material will be subject to continuous testing for the duration of the inventory. Should product stability become an issue, all customers will be notified and notification to that effect will be placed on the www.amis.co.za website.

17. **Minimum sample size:** The majority of laboratories reporting used a 0.5g sample size for the ICP. This is the recommended minimum sample size for the use of this material.

18. **Availability:** This product is available in Laboratory Packs containing 1kg of material and Explorer Packs containing custom weights (from 50g to 250g) of material. The Laboratory Packs are sealed bottles delivered in sealed foil pouches. The Explorer Packs contain material in standard geochem envelopes, vacuum sealed in foil pouches.

19. Recommended use: The data used to characterize this CRM has been scrutinized using outlier treatment techniques. This, together with the number of participating laboratories, should overcome any "inter-laboratory issues" and should lead to a very accurate measure for the given methods, notwithstanding the underlying assumption that what the good inter-laboratory labs reported was accurate. However an amount of bad data might have had an effect, resulting in limits which in some situations might be too broad for the effective monitoring of a single analytical method, laboratory or production process. Users should set their own limits based on their own data quality objectives and control measurements, after determining the performance characteristics of their own particular method, using a minimum of 20 analyses using this CRM. User set limits should normally be within the limits recommended on p1 and 2 of this certificate.

20. Legal Notice: This certificate and the reference material described in it have been prepared with due care and attention. However AMIS, Set Point Technology (Pty) Ltd, Mike McWha, Dr Barry Smee and Smee and Associates Ltd; accept no liability for any decisions or actions taken following the use of the reference material.

14 December 2010

(Appendix 2 added; and minor corrections made to Sections 8 & 9, 3: 8 March 2011)

Certifying Officers:



African Mineral Standards: _____

Mike McWha
BSc (Hons), FGSSA, MAusIMM, Pr.Sci.Nat



Geochemist: _____

Barry W. Smee
BSc, PhD, P.Geo, (B.C.)

19. Recommended use: The data used to characterize this CRM has been scrutinized using outlier treatment techniques. This, together with the number of participating laboratories, should overcome any "inter-laboratory issues" and should lead to a very accurate measure for the given methods, notwithstanding the underlying assumption that what the good inter-laboratory labs reported was accurate. However an amount of bad data might have had an effect, resulting in limits which in some situations might be too broad for the effective monitoring of a single analytical method, laboratory or production process. Users should set their own limits based on their own data quality objectives and control measurements, after determining the performance characteristics of their own particular method, using a minimum of 20 analyses using this CRM. User set limits should normally be within the limits recommended on p1 and 2 of this certificate.

20. Legal Notice: This certificate and the reference material described in it have been prepared with due care and attention. However AMIS, Set Point Technology (Pty) Ltd, Mike McWha, Dr Barry Smee and Smee and Associates Ltd; accept no liability for any decisions or actions taken following the use of the reference material.

14 December 2010

(Appendix 2 added; and minor corrections made to Sections 8 & 9, 3: 8 March 2011)

Certifying Officers:



African Mineral Standards: _____

Mike McWha
BSc (Hons), FGSSA, MAusIMM, Pr.Sci.Nat



Geochemist: _____

Barry W. Smee
BSc, PhD, P.Geo, (B.C.)



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11 Gewel Street (off Hulley Road), D1 Isando Business Park, Kempton Park, 1609
P.O. Box 856, Isando, 1600, Gauteng, South Africa, a division of the Set Point Group

AMIS0304

Certified Reference Material

**Rare Earth Elements
Glenover Carbonatite Complex, South Africa**

Certificate of Analysis

Recommended Concentrations and Limits^{1, 2.}
(at two Standard Deviations)

Certified Concentrations

Ce M/ICP	8090	±	692	ppm
La M/ICP	3610	±	311	ppm
Nd M/ICP	3875	±	442	ppm
Pr M/ICP	1007	±	89	ppm
U M/ICP	24	±	1.7	ppm
Y M/ICP	410	±	39	ppm
Al M/ICP	8070	±	676	ppm
Ca M/ICP	20.11	±	1.34	%
Fe M/ICP	14.73	±	0.93	%
Mg M/ICP	1.67	±	0.18	%
P M/ICP	7.88	±	0.35	%
P XRF	7.99	±	0.32	%
Si M/ICP	5.81	±	0.34	%
Specific gravity	3.37	±	0.10	

Provisional Concentrations

Sm M/ICP	575	±	70	ppm
Th M/ICP	437	±	67	ppm
Th XRF	450	±	71	ppm

1. *Manufacturers recommended limits for use of the material as control samples, based on two standard deviations, calculated using "Between Laboratory" statistics for treatment of the data for trivial, non-trivial and technically invalid results. See sections 1, 9 and 12.*
2. *There is additional certified major element data presented on p2 and uncertified trace element data presented as an appendix.*

Major Element Recommended Concentrations and Limits (at two Standard Deviations)

Certified Concentrations

Al ₂ O ₃	1.52	±	0.08	%
CaO	28.50	±	0.72	%
Fe ₂ O ₃	20.93	±	1.00	%
K ₂ O	0.28	±	0.02	%
MgO	2.87	±	0.12	%
MnO	0.46	±	0.03	%
P ₂ O ₅	18.35	±	0.74	%
SiO ₂	12.31	±	0.40	%
TiO ₂	1.80	±	0.08	%
LOI	7.45	±	0.66	%

Indicated Means

Cr ₂ O ₃	0.01	%
Na ₂ O	0.09	%

1. Intended Use: AMIS0304 can be used to check analysis of samples of rare earth element bearing rocks with a similar grade and matrix.

It is a matrix matched Certified Reference Material, fit for use as control samples in routine assay laboratory quality control when inserted within runs of samples and measured in parallel to the unknown. Its purpose is to monitor inter-laboratory or instrument bias and within lab precision. It can be used, indirectly, to establish the traceability of results to an SI system of units.

The recommended concentrations and limits for this material are property values based on a measurement campaign (round robin) and reflect consensus results from the laboratories that participated in the round robin.

Slight variations in analytical procedures between laboratories will reflect as slight biases to the recommended concentrations (see 19). Good laboratories will report results within the two standard deviation levels with a failure rate of <10 %.

The CRM can also be used for method development and for the calibration of equipment.

2. Origin of Material: AMIS0304 is a commissioned CRM made up of material supplied by Fer-Min-Ore (Pty) Ltd from the Glenover Phosphate Mine on the Glenover Carbonatite Complex. This deposit is located 88km north of Thabazimbi, Limpopo Province, South Africa. The Glenover complex is an irregular pipe like carbonatite body approximately at the centre of a large biotite pyroxenite plug with cone sheets and irregular intrusions of carbonatite emanating from the pipe. Rare Earth Elements are associated with this Carbonatite.

An apatite bearing hematite breccia body, which has been exploited for its phosphate content, is situated at the centre of the biotite pyroxenite, immediately north of the central carbonatite pipe.

3. Mineral and Chemical Composition: The central body of the carbonatite is composed of beforosite, an ankerite rich rock with crystallographic and physical characters resembling dolomite and siderite. The pyroxenite was an earlier event and comprises mainly decomposed biotite-phlogopite. The pyroxenite has been intruded by carbonatite dykes, sills and cone sheets and, where cut by the carbonatite, it has undergone carbonatisation and is veined with beforosite and sovite.

4. **Appearance:** The material is a very fine powder. It is colored a Moderate Red (Corstor 5R 4/8).

5. **Handling instructions:** The material is packaged in Laboratory Packs and Explorer Packs that must be shaken or otherwise agitated before use. Normal safety precautions for handling fine particulate matter are suggested, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

6. **Method of Preparation:** The ore is crushed, then dry-milled and air classified to 100% <54 μ . This fine powder is mixed in a blender for 14 hours and then split down into numbered 1 kg tubs. These lots are sampled for quality control and for round robin analysis. Quality control will typically comprise sampling 30 tubs selected from the whole stream. Round robin samples are selected the same way, so that one laboratory will receive samples from the beginning, end, and from throughout the batch.

7. **Methods of Analysis requested:**

1. Multi-acid digests, including HF, ICP- OES or ICP-MS. Multi element scan.
2. Fusion, ICP- OES or ICP-MS. Multi element scan to include REE's, Nb, Y, Al, Mg, Si, P, Fe, Ca, U and Th.
3. XRF. Multi element scan to include REE's, Nb, Y, Al, Mg, Si, P, Fe, Ca, U and Th.
4. XRF fusion. Majors (Al₂O₃, CaO, Cr₂O₃, Fe₂O₃, K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, TiO₂, LOI.)
5. SG (gas pycnometer

8. **Information requested:**

1. State and provide brief description of analytical techniques used.
2. State aliquots used for all determinations.
3. Results for individual analyses to be reported (not averages)
4. All results for Rare Earth Elements to be reported in ppm (not as oxides).
5. All results for multi-element scans to be reported in ppm.
6. All results for major elements to be reported in %, as oxides.
7. Report all QC data, to include replicates, blanks and certified reference materials used.

9. **Method of Certification:** Twenty one laboratories were each given eight packages, comprising eight samples scientifically selected from throughout the batch. Sixteen laboratories reported results in time for certification of the economic elements. Fourteen of these laboratories reported results for the major elements.

Final limits were calculated after first determining if all data was compatible within a spread normally expected for similar analytical methods done by reputable laboratories. Data from any one laboratory was then removed from further calculations when the mean of all analyses from that laboratory failed a "t test" of the global means of the other laboratories. The means and standard deviations were then re-calculated using all remaining data. Any analysis that fell outside of the new two standard deviations was removed from the ensuing data base. The mean and standard deviations were again calculated using the remaining data.

The "between-laboratory" standard deviation is used in the calculation to eliminate technically and statistically invalid data. Upper and lower limits are based on the standard deviation of the remaining data, which reflect individual analyses and can be used to monitor accuracy in routine laboratory quality control. This is different to limits based on standard deviations derived from grouped set of analyses (see 12), which provide important measures for precision and trueness, but which are less useful for routine QC.

Standards with an RSD of near or less than 5 % are termed "Certified", RSD's of between near 5 % and 15 % are termed "Provisional", and RSD's over 15 % are termed "Informational

Assay data (cont) - Major Oxides and Specific Gravity

Lab Code	Al2O3 XRF %	CaO XRF %	Cr2O3 XRF %	Fe2O3 XRF %	K2O XRF %	MgO XRF %	MnO XRF %	Na2O XRF %	P2O5 XRF %	SiO2 XRF %	TiO2 XRF %	LOI %	SG pyc %
U	1.52	28.73		20.36	0.28	2.77	0.44	0.07	18.67	12.67	1.83	7.88	3.30
U	1.51	28.82		20.42	0.28	2.81	0.44		18.79	12.67	1.82	7.95	3.29
U	1.52	28.45		20.14	0.29	2.76	0.43	0.05	18.67	12.51	1.81	7.90	3.32
U	1.51	28.43		20.18	0.28	2.76	0.43	0.06	18.52	12.46	1.80	7.82	3.29
U	1.54	28.69		20.29	0.29	2.79	0.43	0.09	18.63	12.67	1.83	8.04	3.33
U	1.46	28.51		20.13	0.28	2.77	0.43	0.06	18.68	12.62	1.81	7.94	3.30
U	1.53	28.57		20.14	0.28	2.78	0.43	0.06	18.65	12.52	1.80	7.86	3.31
U	1.54	28.87		20.42	0.29	2.79	0.44	0.07	18.74	12.64	1.83	7.83	3.30

12. Measurement of Uncertainty: The samples used in the certification process were selected in such a way as to represent the entire batch of material and were taken from the final packaged units; therefore all possible sources of uncertainty (sample uncertainty and measurement uncertainty) are included in the final combined standard uncertainty determination.

The uncertainty measurement takes into consideration the between lab and the within lab variances and is calculated from the square roots of the variances of these components using the formula:

$$\text{Combined standard uncertainty} = \sqrt{(\text{between lab.var/no of labs}) + (\text{mean square within lab.var / no of assays})}$$

These uncertainty measurements may be used, by laboratories, as a component for calculating the total uncertainty for method validation according to the relevant ISO guidelines.

Analyte	Method	Unit	S ¹	σ _L ²	Sw ³	CSU ⁴
Ce	M/ICP	ppm	346.3	242.7	208.1	76.57
La	M/ICP	ppm	155.3	111.6	89.50	35.01
Nd	M/ICP	ppm	220.9	151.2	114.5	43.47
Pr	M/ICP	ppm	44.31	29.63	22.16	8.529
Sm	M/ICP	ppm	35.05	25.38	14.96	7.195
Th	M/ICP	ppm	33.50	25.57	14.63	7.530
Th	XRF	ppm	35.50	36.13	15.03	13.81
U	M/ICP	ppm	0.832	0.458	0.635	0.155
Y	M/ICP	ppm	19.66	16.40	7.708	5.261
Al	M/ICP	ppm	337.9	247.5	184.4	77.25
Ca	M/ICP	ppm	6716	5620	2943	1808
Fe	M/ICP	ppm	4849	3659	2071	1125
Mg	M/ICP	ppm	877.2	714.9	303.6	218.1
P	M/ICP	ppm	1761	1127	1391	436
P	XRF	ppm	1590	1435	347.0	455.5
Si	M/ICP	ppm	1716	1225	1091	406.5
Al2O3	XRF	%	0.037	0.030	0.017	0.010
CaO	XRF	%	0.356	0.281	0.139	0.086
Cr2O3	XRF	%	0.002	0.001	0.001	0.001
Fe2O3	XRF	%	0.501	0.408	0.142	0.119
K2O	XRF	%	0.009	0.007	0.006	0.002
LOI		%	0.327	0.285	0.064	0.086
MgO	XRF	%	0.059	0.045	0.024	0.013
MnO	XRF	%	0.013	0.012	0.005	0.004
Na2O	XRF	%	0.020	0.017	0.010	0.006
P2O5	XRF	%	0.367	0.331	0.079	0.105
SiO2	XRF	%	0.202	0.159	0.090	0.049
TiO2	XRF	%	0.043	0.037	0.013	0.012
SG	pyc	%	0.046	0.044	0.025	0.017

1. S - Std Dev for use on control charts.
2. σ_L - Betw Lab Std Dev, for use to calculate a measure of accuracy.
3. Sw - Within Lab Std Dev, for use to calculate a measure of precision.
4. CSU - Combined Standard Uncertainty, a component for use to calculate the total uncertainty in method validation.

13. Certified values: The Certified, Provisional and Indicated values listed on p1 of each certificate fulfill the AMIS statistical criteria regarding agreement for certification and have been independently validated by Dr Barry Smees, BSc, PhD, P.Geo, (B.C.).

14. Metrological Traceability: The values quoted herein are based on the consensus values derived from statistical analysis of the data from an inter laboratory measurement program. Traceability to SI units is via the standards used by the individual laboratories, the majority of which are accredited, who have maintained measurement traceability during the analytical process.

15. Certification: AMIS0304 is a new material.

16. **Period of validity:** The certified values are valid for this product, while still sealed in its original packaging, until notification to the contrary. The stability of the material will be subject to continuous testing for the duration of the inventory. Should product stability become an issue, all customers will be notified and notification to that effect will be placed on the www.amis.co.za website.

17. **Minimum sample size:** The majority of laboratories reporting used a 0.5g sample size for the ICP. This is the recommended minimum sample size for the use of this material.

18. **Availability:** This product is available in Laboratory Packs containing 1kg of material and Explorer Packs containing custom weights (from 50g to 250g) of material. The Laboratory Packs are sealed bottles delivered in sealed foil pouches. The Explorer Packs contain material in standard geochem envelopes, vacuum sealed in foil pouches.

19. **Recommended use:** The data used to characterize this CRM has been scrutinized using outlier treatment techniques. This, together with the number of participating laboratories, should overcome any "inter-laboratory issues" and should lead to a very accurate measure for the given methods, notwithstanding the underlying assumption that what the good inter-laboratory labs reported was accurate. However an amount of bad data might have had an effect, resulting in limits which in some situations might be too broad for the effective monitoring of a single analytical method, laboratory or production process. Users should set their own limits based on their own data quality objectives and control measurements, after determining the performance characteristics of their own particular method, using a minimum of 20 analyses using this CRM. User set limits should normally be within the limits recommended on p1 and 2 of this certificate.

20. **Legal Notice:** This certificate and the reference material described in it have been prepared with due care and attention. However AMIS, Set Point Technology (Pty) Ltd, Mike McWha, Dr Barry Smee and Smee and Associates Ltd; accept no liability for any decisions or actions taken following the use of the reference material.

10 May 2012

Certifying Officers:



African Mineral Standards: _____

Mike McWha
BSc (Hons), FGSSA, MAusIMM, Pr.Sci.Nat



Geochemist: _____

Barry W. Smee
BSc, PhD, P.Geo, (B.C.)



African Mineral Standards

MATRIX REFERENCE MATERIALS

Tel: +27 (0) 11 923 0800, Fax: +27 (0) 11 392 4715, web: www.amis.co.za
11 Gewel Street (off Hulley Road), D1 Isando Business Park, Kempton Park, 1609
P.O. Box 856, Isando, 1600, Gauteng, South Africa, a division of the Set Point Group

AMIS0356

Certified Reference Material

Rare Earth Elements
Wigu Carbonatite Complex, Tanzania

Certificate of Analysis

Recommended Concentrations and Limits^{1, 2}
(at two Standard Deviations)

Certified Concentrations

Ce FUS	1.116	±	0.0705	%
Dy FUS	13	±	1.5	ppm
Eu M/ICP	29	±	2.1	ppm
La FUS	8533	±	731	ppm
Nd FUS	2482	±	171	ppm
Nd M/ICP	2419	±	240	ppm
Pr FUS	942	±	73	ppm
Sm FUS	159	±	12	ppm
Sm M/ICP	159	±	10	ppm
Sr FUS	1.848	±	0.127	%
Sr M/ICP	1.803	±	0.131	%
Th FUS	84	±	7	ppm
Th M/ICP	84	±	10	ppm
Tm M/ICP	0.31	±	0.04	ppm
U FUS	4.3	±	0.5	ppm
U M/ICP	4.2	±	0.5	ppm
Y FUS	35	±	4	ppm
Specific Gravity	2.99	±	0.20	

Provisional Concentrations

Dy M/ICP	12.8	±	2.9	ppm
Eu FUS	29.7	±	3.6	ppm
Ho FUS	1.7	±	0.4	ppm
Ho M/ICP	1.6	±	0.3	ppm
La M/ICP	8226	±	1066	ppm
Nb FUS	214	±	42	ppm
Pr M/ICP	894	±	169	ppm
Sc M/ICP	28	±	6	ppm
Y M/ICP	35	±	5	ppm



Directors: GJ Horsfield (CEO), MD Evers (CFO)(British), A Buddingh, W Erasmus, Gerber, SJ Ingram
M McWha, N Robinson, V Singh, MH Snelling, D Steenkamp (Alt), J Vassiloudis

Indicated Means

Er FUS	2.9	ppm
Er M/ICP	3.2	ppm
Gd FUS	72.5	ppm
Gd M/ICP	58	ppm
Lu FUS	0.24	ppm
Lu M/ICP	0.28	ppm
Nb XRF	166	ppm
Nb M/ICP	173	ppm
Tb FUS	5	ppm
Tb M/ICP	4	ppm
Tm FUS	0.32	ppm
Y XRF	27	ppm
Yb FUS	1.9	ppm
Yb M/ICP	1.9	ppm

1. Manufacturers recommended limits for use of the material as control samples, based on two standard deviations, calculated using "Between Laboratory" statistics for treatment of the data for trivial, non-trivial and technically invalid results. See sections 1, 9 and 12.
2. There is additional certified major element data presented on p2 and uncertified trace element data presented as an appendix.
3. CREO = $(Nd+Eu+Tb+Dy+Y)_2O_3 = 0.314\%$ (see Appendix 2)

Major Element Recommended Concentrations and Limits (at two Standard Deviations)

Certified Concentrations

Al ₂ O ₃	5.84	±	0.10	%
CaO	15.69	±	0.42	%
Fe ₂ O ₃	8.02	±	0.40	%
K ₂ O	0.51	±	0.04	%
MgO	6.00	±	0.14	%
MnO	0.92	±	0.04	%
Na ₂ O	2.75	±	0.10	%
P ₂ O ₅	2.58	±	0.12	%
SiO ₂	28.86	±	0.60	%
TiO ₂	0.33	±	0.02	%
LOI	20.22	±	0.52	%

Indicated Mean

Cr ₂ O ₃	0.02	%
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1. **Intended Use:** AMIS0356 can be used to check analysis of samples of rare earth element bearing rocks with a similar grade and matrix.

It is a matrix matched Certified Reference Material, fit for use as control samples in routine assay laboratory quality control when inserted within runs of samples and measured in parallel to the unknown. Its purpose is to monitor inter-laboratory or instrument bias and within lab precision. It can be used, indirectly, to establish the traceability of results to an SI system of units.

The recommended concentrations and limits for this material are property values based on a measurement campaign (round robin) and reflect consensus results from the laboratories that participated in the round robin.

Slight variations in analytical procedures between laboratories will reflect as slight biases to the recommended concentrations (see 19). Good laboratories will report results within the two standard deviation levels with a failure rate of <10 %.

The material can also be used for method development and for the calibration of equipment.

2. Origin of Material: AMIS0356 is a commissioned CRM made up of material supplied by Montero Resources Ltd. from the Wigu Carbonatite Complex located 200km WSW of Dar es Salaam. Wigu Hill is underlain by Paleoproterozoic metasediments consisting of well foliated high grade gneisses and amphibolites. These rocks have been intruded by a swarm of carbonatite dykes on the southern edge of the Uluguru Mountains where the Uluguru massif is truncated by a major Karoo aged rift. The intrusions have resulted in strong carbonate alteration of the gneisses and amphibolites adjacent to the dykes and a more pervasive fenitisation and weaker carbonate alteration halo away from the dykes.

3. Mineral and Chemical Composition: The carbonatite material selected for this sample is fresh, compact and tightly and finely crystalline. It is bastnasite-rich with minor amounts of synchisite, parasite and monazite, with traces of apatite. The carbonatite is dolomitic with a significant proportion of Rare Earth Oxide minerals (REO's) and lesser associated quartz, barite, strontianite, iron oxides and minor manganese.

Regional sampling to date has identified that the main rare earth minerals present in the Wigu carbonatites are the light rare earths, namely Cerium, Lanthanum, Neodymium, Praseodymium, and Samarium. Minor amounts of Europium and Gadolinium are present, but the other heavy rare earth elements are present in trace amounts only.

4. Appearance: The material is a very fine Pale Yellowish Brown powder (Corstor colour chart – 10YR 6/4).

5. Handling instructions: The material is packaged in Laboratory Packs and Explorer Packs that must be shaken or otherwise agitated before use. Normal safety precautions for handling fine particulate matter are suggested, such as the use of safety glasses, breathing protection, gloves and a laboratory coat.

6. Method of Preparation: The material was crushed, dry-milled and air-classified to <54µm. Wet sieve particle size analysis of random samples confirmed the material was 98.5% <54µm. It was then blended in a bi-conical mixer, systematically divided and then sealed into 1kg Laboratory Packs. Explorer Packs are subdivided from the Laboratory packs as required. Samples were randomly selected for homogeneity testing and third party analysis. Statistical analysis of both homogeneity and consensus test results were carried out by an independent statistician.

7. Methods of Analysis requested:

1. Multi-acid digest, including HF, ICP- OES or ICP-MS. Multi element scan.
2. Fusion, ICP- OES or ICP-MS. Multi element scan to include REE's, Nb, Y, Sr, U and Th.
3. XRF. Multi element scan to include REE's, Nb, Y, Sr, U and Th.
4. XRF fusion. Majors (Al₂O₃, CaO, Cr₂O₃, Fe₂O₃, K₂O, MgO, MnO, Na₂O, P₂O₅, SiO₂, TiO₂, LOI.)
5. SG (gas pycnometer).

8. Information requested:

1. State and provide brief description of analytical techniques used.
2. State aliquots used for all determinations.
3. Results for individual analyses to be reported (not averages)
4. All results for Rare Earth Elements to be reported in ppm (not as oxides).
5. All results for multi-element scans to be reported in ppm.
6. All results for major elements to be reported in %, as oxides.
7. Report all QC data, to include replicates, blanks and certified reference materials used.

9. Method of Certification: Twenty three laboratories were each given eight randomly selected packages of sample. Twenty one of the laboratories submitted results in time for certification.

Final limits were calculated after first determining if all data was compatible within a spread normally expected for similar analytical methods done by reputable laboratories. Data from any one laboratory was then removed from further calculations when the mean of all analyses from that laboratory failed a "t test" of the global means of the other laboratories. The means and standard deviations were then re-calculated using all remaining data. Any analysis that fell outside of the new two standard deviations was removed from the ensuing data base. The mean and standard deviations were again calculated using the remaining data.

The "between-laboratory" standard deviation is used in the calculation to eliminate technically and statistically invalid data. Upper and lower limits are based on the standard deviation of the remaining data, which reflect individual analyses and can be used to monitor accuracy in routine laboratory quality control. This is different to limits based on standard deviations derived from grouped set of analyses (see 12), which provide important measures for precision and trueness, but which are less useful for routine QC.

Standards with an RSD of near or less than 5 % are termed "Certified", RSD's of between near 5 % and 15 % are termed "Provisional", and RSD's over 15 % are termed "Informational".

10. Participating Laboratories: The 21 out of 23 laboratories that provided results timeously were (not in same order as in the table of assays):

1. ACME Analytical Laboratories Ltd CA
2. Activation Laboratories Pty Ltd (ActLabs) CA
3. ALS Ammtec (Australia)
4. ALS Chemex Laboratory Group Perth WA
5. ALS Chemex Laboratory Group Vancouver CA
6. ALS OMAC (Ireland)
7. ANSTO Minerals Laboratory (Australia)
8. Bureau Veritas (Namibia)
9. Bureau Veritas (USA)
10. BV Amdel (Australia)
11. Genalysis Laboratory Services (W Australia P)
12. Intertek Utama Services (Indonesia)
13. Labtium Inc Finland
14. Set Point Laboratories (Isando) SA
15. SGS Australia Pty Ltd (Newburn) WA
16. SGS Geosol Laboratories Ltda (Brazil)
17. SGS Mineral Services Lakefield (Canada)
18. SGS South Africa (Pty) Ltd - Booyens JHB
19. SGS Toronto (Canada)
20. SGS Townsville (Australia)
21. Ultra Trace (Pty) Ltd WA

Assay data Major Oxides (cont)

Lab Code	Al ₂ O ₃ XRF %	CaO XRF %	Cr ₂ O ₃ XRF %	Fe ₂ O ₃ XRF %	K ₂ O XRF %	MgO XRF %	MnO XRF %	Na ₂ O XRF %	P ₂ O ₅ XRF %	SiO ₂ XRF %	TiO ₂ XRF %	LOI %	SG pyc
Q	5.83	15.5	0.03	8.34	0.52	5.86	0.95		2.52	28.7	0.34	20.5	2.96
Q	5.82	15.5	0.03	8.37	0.53	5.90	0.95		2.53	28.7	0.34	20.4	2.97
Q	5.80	15.5	0.02	8.35	0.50	5.88	0.96		2.52	28.6	0.34	20.4	2.97
Q	5.77	15.5	0.03	8.39	0.50	5.79	0.94		2.49	28.3	0.33	20.5	2.98
Q	5.80	15.5	0.03	8.37	0.50	5.85	0.95		2.51	28.5	0.34	20.5	2.96
Q	5.79	15.6	0.03	8.35	0.50	5.90	0.96		2.52	28.6	0.34	20.4	2.97
Q	5.81	15.5	0.03	8.37	0.51	5.84	0.95		2.51	28.4	0.34	20.5	2.98
Q	5.83	15.6	0.04	8.38	0.50	5.91	0.95		2.52	28.8	0.34	20.4	2.97
R	5.77	15.8	0.02	8.13	0.52	6.10	0.94	2.78	2.68	29.0	0.33	20.0	
R	5.78	15.8	0.02	8.13	0.51	6.08	0.95	2.78	2.66	29.0	0.34	20.0	
R	5.75	15.8	0.02	8.15	0.52	6.05	0.94	2.79	2.59	29.0	0.34	20.0	
R	5.75	15.7	0.02	8.16	0.52	6.06	0.94	2.79	2.52	29.1	0.34	20.0	
R	5.76	15.8	0.02	8.16	0.52	6.10	0.94	2.75	2.66	28.9	0.34	20.0	
R	5.76	15.7	0.01	8.14	0.51	6.04	0.94	2.80	2.66	29.0	0.33	20.0	
R	5.77	15.8	0.02	8.13	0.51	6.07	0.94	2.78	2.68	29.0	0.33	20.0	
R	5.77	15.7	0.02	8.14	0.52	6.05	0.94	2.79	2.61	29.0	0.34	20.0	
T													3.13
T													3.16
T													3.13
T													3.13
T													3.14
T													3.12
T													3.11
T													3.13
U	5.66	15.4	0.03	7.65	0.49	5.90	0.89	2.55	2.53	28.3	0.38	20.7	2.88
U	5.63	15.3	0.02	7.58	0.49	5.85	0.88	2.49	2.50	28.0	0.37	20.6	2.94
U	5.61	15.4	0.03	7.64	0.49	5.87	0.89	2.55	2.55	28.4	0.38	20.6	2.89
U	5.65	15.4	0.02	7.68	0.49	5.95	0.90	2.54	2.52	28.4	0.39	20.6	2.92
U	5.61	15.4	0.03	7.66	0.49	5.91	0.89	2.54	2.54	28.4	0.38	20.6	2.92
U	5.70	15.4	0.03	7.67	0.50	5.89	0.89	2.53	2.54	28.3	0.38	20.6	2.87
U	5.64	15.4	0.03	7.68	0.50	5.91	0.89	2.57	2.53	28.3	0.39	20.7	2.88
U	5.62	15.2	0.03	7.56	0.50	5.85	0.87	2.55	2.49	28.1	0.38	20.7	2.87
V													3.06
V													3.06
V													3.06
V													3.07
V													3.07
V													3.06
V													3.07
V													3.05
W	5.82	15.4	0.02	7.93	0.57	5.89	0.90		2.54	28.4	0.34	20.0	2.87
W	6.03	16.2	0.02	8.28	0.60	6.16	0.94		2.68	29.4	0.36	19.9	2.88
W	5.93	15.7	0.02	8.08	0.58	6.00	0.92		2.58	28.9	0.35	20.1	2.88
W	5.90	15.9	0.02	8.14	0.56	6.05	0.92		2.58	28.9	0.35	20.1	2.87
W	5.91	15.8	0.02	8.13	0.57	6.03	0.92		2.61	29.0	0.34	20.0	2.89
W	6.02	15.9	0.02	8.24	0.60	6.08	0.93		2.61	29.3	0.34	20.0	2.88
W	5.87	15.8	0.02	8.14	0.59	6.01	0.92		2.58	28.9	0.33	20.0	2.88
W	6.07	16.1	0.02	8.29	0.62	6.14	0.93		2.67	29.6	0.34	20.1	2.81

12. Measurement of Uncertainty : (ref Dr Hugh Bartlett, Hugh Bartlett Consulting CC.)

The samples used in the certification process were selected in such a way as to represent the entire batch of material and were taken from the final packaged units; therefore all possible sources of uncertainty (sample uncertainty and measurement uncertainty) are included in the final combined standard uncertainty determination.

The uncertainty measurement takes into consideration the between lab and the within lab variances and is calculated from the square roots of the variances of these components using the formula:

$$\text{Combined standard uncertainty} = \sqrt{(\text{between lab.var/no of labs}) + (\text{mean square within lab.var /no of assays})}$$

These uncertainty measurements may be used, by laboratories, as a component for calculating the total uncertainty for method validation according to the relevant ISO guidelines.

Analyte	Method	Unit	S ¹	σ _L ²	Sw ³	CSU ⁴
Ce	Fusion	ppm	352	300	177	102
Dy	Fusion	ppm	0.77	0.50	0.54	0.17
Dy	M/ICP	ppm	1.46	1.27	0.64	0.43
Er	Fusion	ppm	0.54	0.46	0.24	0.16
Er	M/ICP	ppm	1.14	1.25	0.33	0.48
Eu	Fusion	ppm	1.82	1.39	0.91	0.43
Eu	M/ICP	ppm	1.06	0.87	0.64	0.32
Gd	Fusion	ppm	17.3	15.0	3.08	4.54
Gd	M/ICP	ppm	33.3	34.2	3.94	12.10
Ho	Fusion	ppm	0.18	0.18	0.07	0.06
Ho	M/ICP	ppm	0.14	0.11	0.07	0.04
La	Fusion	ppm	365	284	122	83.1
La	M/ICP	ppm	533	421	277	137
Lu	Fusion	ppm	0.05	0.04	0.02	0.01
Lu	M/ICP	ppm	0.07	0.07	0.02	0.03
Nb	XRF	ppm	56.2	68.6	4.81	28.0
Nb	Fusion	ppm	21.2	17.6	6.47	5.37
Nb	M/ICP	ppm	36.5	31.5	13.68	10.1
Nd	Fusion	ppm	85.6	63.7	44.14	19.8
Nd	M/ICP	ppm	142	127	83.3	49.3
Pr	Fusion	ppm	36.3	24.6	18.8	7.07
Pr	M/ICP	ppm	84.6	75.2	34.4	25.4
Sc	M/ICP	ppm	3.00	2.69	0.73	0.85
Sm	Fusion	ppm	5.99	4.01	3.25	1.16
Sm	M/ICP	ppm	5.22	4.48	3.23	1.75
Sr	Fusion	ppm	636	564	385	219
Sr	M/ICP	ppm	655	638	470	295
Tb	Fusion	ppm	1.48	1.37	0.17	0.44
Tb	M/ICP	ppm	2.31	2.27	0.25	0.76
Th	Fusion	ppm	3.44	2.47	2.01	0.77
Th	M/ICP	ppm	5.07	4.15	2.25	1.34
Tm	Fusion	ppm	0.050	0.039	0.030	0.014
Tm	M/ICP	ppm	0.017	0.012	0.014	0.005
U	Fusion	ppm	0.25	0.13	0.20	0.05
U	M/ICP	ppm	0.23	0.14	0.15	0.04
Y	XRF	ppm	8.46	11.45	4.17	5.77
Y	Fusion	ppm	2.06	1.58	0.83	0.46
Y	M/ICP	ppm	2.40	1.70	1.273	0.507
Yb	Fusion	ppm	0.3	0.2	0.2	0.08
Yb	M/ICP	ppm	0.55	0.53	0.13	0.18
Al ₂ O ₃	XRF	%	0.054	0.038	0.030	0.011
CaO	XRF	%	0.208	0.153	0.084	0.043
Cr ₂ O ₃	XRF	%	0.005	0.004	0.003	0.001
Fe ₂ O ₃	XRF	%	0.205	0.150	0.067	0.041
K ₂ O	XRF	%	0.015	0.012	0.006	0.003
LOI		%	0.280	0.220	0.070	0.067
MgO	XRF	%	0.075	0.045	0.046	0.013
MnO	XRF	%	0.023	0.019	0.007	0.005
Na ₂ O	XRF	%	0.046	0.037	0.026	0.013
P ₂ O ₅	XRF	%	0.057	0.040	0.026	0.012
SiO ₂	XRF	%	0.305	0.203	0.168	0.059
TiO ₂	XRF	%	0.011	0.008	0.005	0.002
SG	pyc		0.098	0.069	0.033	0.018

1. S - Std Dev for use on control charts.
2. σ_L - Betw Lab Std Dev, for use to calculate a measure of accuracy.
3. Sw - Within Lab Stc Dev, for use to calculate a measure of precision.
4. CSU - Combined Standard Uncertainty, a component for use to calculate the total uncertainty in method validation.

13. Certified values: The Certified, Provisional and Informational values listed on p1 and p2 of this certificate fulfill the AMIS statistical criteria regarding agreement for certification and have been independently validated by Dr Barry Smee.

14. Metrological Traceability: The values quoted herein are based on the consensus values derived from statistical analysis of the data from an inter laboratory measurement program. Traceability to SI units is via the standards used by the individual laboratories, the majority of which are accredited, who have maintained measurement traceability during the analytical process.

15. Certification: AMIS0356 is a new material.

16. Period of validity: The certified values are valid for this product, while still sealed in its original packaging, until notification to the contrary. The stability of the material will be subject to continuous testing for the duration of the inventory. Should product stability become an issue, all customers will be notified and notification to that effect will be placed on the www.amis.co.za website.

17. Minimum sample size: The majority of laboratories reporting used a 0.5g sample size for the ICP. This is the recommended minimum sample size for the use of this material.

18. Availability: This product is available in Laboratory Packs containing 1kg of material and Explorer Packs containing custom weights (from 50g to 250g) of material. The Laboratory Packs are sealed bottles delivered in sealed foil pouches. The Explorer Packs contain material in standard geochem envelopes, vacuum sealed in foil pouches.

19. Recommended use: The data used to characterize this CRM has been scrutinized using outlier treatment techniques. This, together with the number of participating laboratories, should overcome any "inter-laboratory issues" and should lead to a very accurate measure for the given methods, notwithstanding the underlying assumption that what the good inter-laboratory labs reported was accurate. However an amount of bad data might have had an effect, resulting in limits which in some situations might be too broad for the effective monitoring of a single analytical method, laboratory or production process. Users should set their own limits based on their own data quality objectives and control measurements, after determining the performance characteristics of their own particular method, using a minimum of 20 analyses using this CRM. User set limits should normally be within the limits recommended on p1 and 2 of this certificate.

20. Legal Notice: This certificate and the reference material described in it have been prepared with due care and attention. However AMIS, Set Point Technology (Pty) Ltd, Mike McWha, Dr Barry Smee and Smee and Associates Ltd; accept no liability for any decisions or actions taken following the use of the reference material.

3 August 2013

Certifying Officers:



African Mineral Standards: _____
Mike McWha
BSc (Hons), FGSSA, MAusIMM, Pr.Sci.Nat



Geochemist: _____
Barry W. Smee
BSc, PhD, P.Geo, (B.C.)

MONGOLIA
CENTRAL GEOLOGICAL LABORATORY



CERTIFICATE OF ANALYSIS

Certified Reference Material "TRM-2"
Silver-bearing complex ore "CGL 111"

Certified values (CV) and their confidence interval ($\pm\Delta_A$)

No.	Oxides/ Elements	Unit	CV	$\pm\Delta_A$	N
1.	SiO ₂	%	14.86	0.17	21
2.	TiO ₂	%	0.15	0.04	20
3.	Al ₂ O ₃	%	2.47	0.10	21
4.	Fe ₂ O ₃	%	13.45	0.26	21
5.	FeO	%	0.14	0.03	13
6.	CaO	%	25.51	0.50	21
7.	MgO	%	0.50	0.02	22
8.	MnO	%	0.14	0.01	22
9.	Na ₂ O	%	0.92	0.05	19
10.	K ₂ O	%	0.91	0.08	17
11.	P ₂ O ₅	%	19.26	0.28	19
12.	SO ₃	%	4.58	0.32	24
13.	Loss on ignition	%	6.78	0.22	14
14.	CO ₂	%	1.04	0.07	6
15.	As	mg/kg	155.83	26.58	12
16.	Ba	mg/kg	917	58	12
17.	Ce	%	2.90	0.12	19
18.	Co	mg/kg	32.46	6.03	16
19.	Cu	mg/kg	147	58	20
20.	Dy	mg/kg	206	32	9
21.	Eu	mg/kg	211.60	16.20	11
22.	Er	mg/kg	79.50	8.50	9
23.	Ho	mg/kg	36.60	7.40	9
24.	Gd	mg/kg	553	83	11
25.	La	%	1.93	0.10	25
26.	Lu	mg/kg	7.64	1.08	6
27.	Nd	%	0.89	0.08	20

No.	Oxides/ Elements	Unit	CV	$\pm\Delta_A$	N
28.	Ni	mg/kg	70.80	11.20	14
29.	Pb	%	0.11	0.014	16
30.	Pr	%	0.28	0.03	17
31.	Rb	mg/kg	43	10	10
32.	Sm	%	0.09	0.03	12
33.	Sr	%	2.24	0.095	11
34.	ΣTR_2O_3	%	7.56	0.25	13
35.	Tb	mg/kg	54.60	14.20	8
36.	Th	mg/kg	217.58	40.42	15
37.	V	mg/kg	138.6	18.9	8
38.	Y	mg/kg	959	40	14
39.	Yb	mg/kg	54.52	5.24	10
40.	Zn	%	0.06	0.004	21

Information values (IV)

No.	Oxides/ Elements	Unit	IV
1	H ₂ O	%	0.67
2	F	%	1.89
3	CaF ₂	%	32.90
4	Mo	mg/kg	23.86

Classification criteria

CV – certified value satisfying certification criteria

IV - not certified value not satisfying certification criteria

Description of the sample

The material is a reference material taken from the Mushgia khudag deposit in the Umnogobi area of Mongolia. The material consists of a homogeneous powder (particles have passed a sieve with apertures smaller than 63 μ m).

The mineral composition of the material has been determined to be:

Minerals	Percentage, % m/m
Apatite	48.6
secondary phosphate	11.6
Hydrous ferric oxide	16.8

quartz	10.1
Gypsum	5.5
Calcite	2.1
sericite	3.4
celestine	1.5
Fluorite	0.8
epidote, pyrite	few particles

Instructions for Storage and Use

The recommended minimum sample intake is 100 mg. If there is a need of sample intake below 100 mg for an analytical method (e.g. the optic emission spectrometry), weigh more than 100 mg and mix in an agate mortar. Then weigh necessary weight.

Taken portions should not be poured back in a bottle as it may contaminate the material.

The reference material is stored in a polyethylene bottle of 100 g. The bottle should be stored preferably in a dry place at the room temperature, protected from an effect of chemical reagents.

The reference material can be transported by any kind of transport means.

Validity of the Certificate

The date of production is December, 1998. The date of reattestation is December, 2006. Duration of use is 20 years.

Availability of Material

This reference material will be classified as "CGL 111" in the future in accordance with CGL CRM classification system.

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Participating Laboratories

Preparation, homogeneity and stability testing:

- Central Geological Laboratory

Certification analyses:

- Laboratory of Methods, Standards, Control and Metrology of the Central Geological Laboratory, Ulaanbaatar, Mongolia
- Laboratory of Chemical & Physical Techniques of the Central Geological Laboratory, Ulaanbaatar, Mongolia
- Spectral Laboratory of the Central Geological Laboratory, Ulaanbaatar, Mongolia
- Technological Testing Laboratory of the Central Geological Laboratory, Ulaanbaatar, Mongolia
- Geological and Investigation Company "Gurvan gol", Ulaanbaatar, Mongolia
- Nuclear Research Centre, Mongolian State University, Ulaanbaatar, Mongolia
- Chemical and Technological Centre for New Materials, Mongolian State University, Ulaanbaatar, Mongolia
- Institute of Physics and Technology, Mongolian Academy of Science, Ulaanbaatar, Mongolia
- Scientific-production Company "Erdes", Ulaanbaatar, Mongolia
- Amdel laboratories, Australia
- Shimadzy Corporation, Analytical group, Kyoto, Japan
- Institute for Earth crust SO RAN, Irkutsk, Russia
- Federal Institute for Geosciences and Natural Resources (BGR), RFA-Laboratory, Hannover, Germany
- Institute de Tecnologia Ceramica, Chemical Analysis Unit, Spain
- Geoscience Laboratories, Ontario, Canada
- The Geological Survey of Israel, Israel
- Geological Institute of Hungary, Hungary
- National Research Center for Geoanalysis, China
- Beijing Research Institute of Uranium Geology, China
- State Geological Institute of Dionyz Stur, Geoanalytical Laboratories, Slovak
- Eurotest Control JSC, Bulgaria

Methods used

Methods of final determination were:

- Atomic absorption spectrometry MgO, MnO, As, Co, Ni, Cu, Zn, Pb, Rb
- X-ray fluorescence spectrometry SiO₂, TiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, MnO, Na₂O, K₂O, P₂O₅, LoI, F, Ba, As, Co, Ni, Cu, Zn, Pb, Rb, Mo, Sr, Th, La, Ce, Pr, Nd, Dy, Er, Eu, Ho, Gd, Sm, Tb, Lu, Yb, Y
- flame photometry Na₂O, K₂O, Rb
- photometry SiO₂, TiO₂, Al₂O₃, Fe₂O₃, P₂O₅, F, As, Mo, Th, ΣTR₂O₃
- ICP spectrometry SiO₂, TiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, MnO, Na₂O, K₂O, P₂O₅, LoI, F, Ba, As, Co, Ni, Cu, Zn, Pb, Rb, Mo, Sr, Th, La, Ce, Pr, Nd, Dy, Er, Eu, Ho, Gd, Sm, Tb, Lu, Yb, Y

- gravimetric SiO_2 , CaO, SO_3 , LOI , H_2O , $\Sigma\text{TR}_2\text{O}_3$
- volumetric Fe_2O_3 , FeO, CaO, CaF_2 , CO_2

Certification

This reference material was confirmed and given the number USZ 25-2006 by the National Center for Standardization and Metrology.

Note

A detailed technical report on the analysis procedure and the treatment of the analytical data is supplied with each sample.

MONGOLIA
CENTRAL GEOLOGICAL LABORATORY

CERTIFICATE OF ANALYSIS



Certified Reference Material "TRLK"

Rare earth ore "CGL 124"

Certified values (CV) and their confidence interval ($\pm\Delta_A$)

No.	Oxides/ Elements	Unit	CV	$\pm\Delta_A$	N
1.	SiO ₂	%	11.86	0.15	28
2.	TiO ₂	%	0.20	0.012	30
3.	Al ₂ O ₃	%	2.72	0.13	30
4.	Fe ₂ O ₃	%	5.71	0.17	28
5.	CaO	%	32.68	0.40	29
6.	MgO	%	2.78	0.05	26
7.	MnO	%	1.67	0.05	28
8.	Na ₂ O	%	0.25	0.03	25
9.	K ₂ O	%	1.55	0.05	23
10.	P ₂ O ₅	%	0.22	0.01	26
11.	Loss on ignition	%	30.56	0.12	22
12.	CO ₂	%	29.00	0.33	15
13.	As	mg/kg	224	24	11
14.	Ba	mg/kg	307	10	10
15.	Ce	%	2.76	0.05	16
16.	Co	mg/kg	7.89	0.81	10
17.	Cu	mg/kg	27.37	6.43	18
18.	Dy	mg/kg	57.63	11.63	8
19.	Eu	mg/kg	87.22	8.68	9
20.	Ho	mg/kg	7.86	1.72	7
21.	La	%	2.11	0.11	17
22.	Li	mg/kg	21.78	2.23	9
23.	Mo	mg/kg	34.40	3.41	10
24.	Nb	mg/kg	31	4.54	8
25.	Nd	%	0.65	0.03	16
26.	Ni	mg/kg	13.18	3.50	14
27.	Pb	%	0.16	0.007	23

No.	Oxides/ Elements	Unit	CV	$\pm\Delta_A$	N
28.	Pr	%	0.23	0.03	14
29.	Rb	mg/kg	67.12	3.91	17
30.	Sm	mg/kg	539	62	15
31.	Sr	%	0.49	0.04	22
32.	Th	mg/kg	946	51	14
33.	V	mg/kg	115	14.92	10
34.	Y	mg/kg	167	20	11
35.	Yb	mg/kg	17.85	1.92	8
36.	Zn	mg/kg	469	21	24
37.	ΣTR_2O_3	%	8.27	0.25	10

Information values (IV)

No.	Oxides/ Elements	Unit	IV
1	FeO	%	0.08
2	SO ₃	%	0.14
3	H ₂ O ⁻	%	0.19
4	H ₂ O ⁺	%	2.03
5	F	%	1.61
6	Au	mg/kg	0.46
7	Bi	mg/kg	8.7
8	Cr	mg/kg	33.56
9	Cs	mg/kg	54.55
10	Er	mg/kg	23.88
11	Gd	mg/kg	295
12	Sc	mg/kg	15.17
13	Tb	mg/kg	45
14	U	mg/kg	51.4
15	W	mg/kg	18.71
16	Zr	mg/kg	136

Classification criteria

CV – certified value satisfying certification criteria

IV - not certified value not satisfying certification criteria

Description of the sample

The bulk for a reference material is taken from the Lugin gol deposit of the Khatanbulag sum of the Dornogobi province of Mongolia. The material consists of a homogeneous powder (particles have passed a sieve with apertures smaller than 63 μm).

The mineral composition of the material has been determined to be:

Minerals	Percentage, % m/m
Synchisite-bastnaesite	20.2
Orthite	0.8
Quartz	27.3
Sericite	2.2
Muscovite	11.2
Calcite, celestine, dolomite	18.4
Potassium feldspar	13.3
Plagioclase	1.6
Biotite	1.5
Clay minerals	2.0
Fluorite	0.3
Hydrogeothite	0.7
Zircon, apatite, pyrite, goethite, ilmenite, rutile, agnetite, leucoxene, galenite and others	0.5

Instructions for Storage and Use

The recommended minimum sample intake is 100 mg. If there is a need of sample intake below 100 mg for an analytical method (e.g. the optic emission spectrometry), weigh more than 100 mg and mix in an agate mortar. Then weigh necessary weight.

Taken portions should not be poured back in a bottle as it may contaminate the material.

The reference material is stored in a polyethylene bottle of 100 g. The bottle should be stored preferably in a dry place at the room temperature, protected from an effect of chemical reagents.

The reference material can be transported by any kind of transport means.

Validity of the Certificate

Duration of production is 2002-2006. Duration of use is 20 years.

Availability of Material

This reference material will be classified as "CGL 124" in the future in accordance with CGL CRM classification system.

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Participating Laboratories

Preparation, homogeneity and stability testing:

Central Geological Laboratory

Certification analyses:

- Laboratory of Methods, Standards, Control and Metrology of the Central Geological Laboratory, Ulaanbaatar, Mongolia
- Laboratory of Chemical & Physical Techniques of the Central Geological Laboratory, Ulaanbaatar, Mongolia
- Nuclear Research Centre, Mongolian State University, Ulaanbaatar, Mongolia
- Laboratory of Precious Metals, the Faculty of Chemistry, Mongolian State University, Ulaanbaatar, Mongolia
- Chemical and Technological Centre for New Materials, Mongolian State University, Ulaanbaatar, Mongolia
- Exploitation and Investigation Center of Technology of Mineral Resources, Ulaanbaatar, Mongolia
- Research-Scientific Laboratory of the Institute for Medicine, Ulaanbaatar, Mongolia
- Food Biotechnology School, Mongolian University of Science and Technology, Mongolia
- Institute of Physics and Technology, Mongolian Academy of Science, Ulaanbaatar, Mongolia
- SGS Mongolia Minerals, Ulaanbaatar, Mongolia
- SGS Welshpool Minerals, Australia
- Federal Institute for Geosciences and Natural Resources (BGR), RFA-Laboratory, Hannover, Germany
- Institute de Tecnologia Ceramica, Chemical Analysis Unit, Spain
- Geoscience Laboratories, Ontario, Canada
- The Geological Survey of Israel, Israel
- Geological Institute of Hungary, Hungary
- National Research Center for Geoanalysis, China
- Beijing Research Institute of Uranium Geology, China
- State Geological Institute of Dionyz Stur, Geoanalytical Laboratories, Slovak
- Eurotest Control JSC, Bulgaria

Methods used

Methods of final determination were:

- Atomic absorption spectrometry	TiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , MnO, MgO, Na ₂ O, K ₂ O, As, Au, Ba, Co, Cs, Cu, Li, Mo, Ni, Pb, Rb, Sr, Zn
- X-ray fluorescence spectrometry	SiO ₂ , TiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , CaO, MnO, MgO, Na ₂ O, K ₂ O, P ₂ O ₅ , SO ₃ , LOI, H ₂ O ⁻ , SO ₃ , H ₂ O ⁺ , F, As, Ba, Bi, Ce, Co, Cr, Cs, Cu, Eu, Gd, La, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sm, Sr, Th, U, V, W, Y, Zn, Zr, \sum TR ₂ O ₃
- flame photometry	Na ₂ O, K ₂ O, Rb
- photometry	SiO ₂ , TiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , MnO, Na ₂ O, K ₂ O, P ₂ O ₅ , F, As, Co, Cr, Ni, Th, V, W, Zr
- ICP spectrometry	SiO ₂ , TiO ₂ , Al ₂ O ₃ , Fe ₂ O ₃ , CaO, MnO, MgO, Na ₂ O, K ₂ O, P ₂ O ₅ , SO ₃ , H ₂ O ⁻ , CO ₂ , H ₂ O ⁺ , F, As, Ba, Bi, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Gd, Ho, La, Li, Mo, Nb, Nd, Ni, Pb, Pr, Rb, Sc, Sm, Sr, Tb, Th, U, V, W, Y, Yb, Zn, Zr, \sum TR ₂ O ₃
- gravimetric	SiO ₂ , Al ₂ O ₃ , CaO, H ₂ O ⁻ , SO ₃ , H ₂ O ⁺ , LOI, Au, \sum TR ₂ O ₃
- volumetric	Al ₂ O ₃ , Fe ₂ O ₃ , FeO, CaO, MgO, CO ₂ , H ₂ O ⁺ , F, Pb
- Fire Assay -AAS	Au

Certification

This reference material was confirmed and given the number USZ 42-2006 by the Mongolian National Center for Standardization and Metrology.

Note

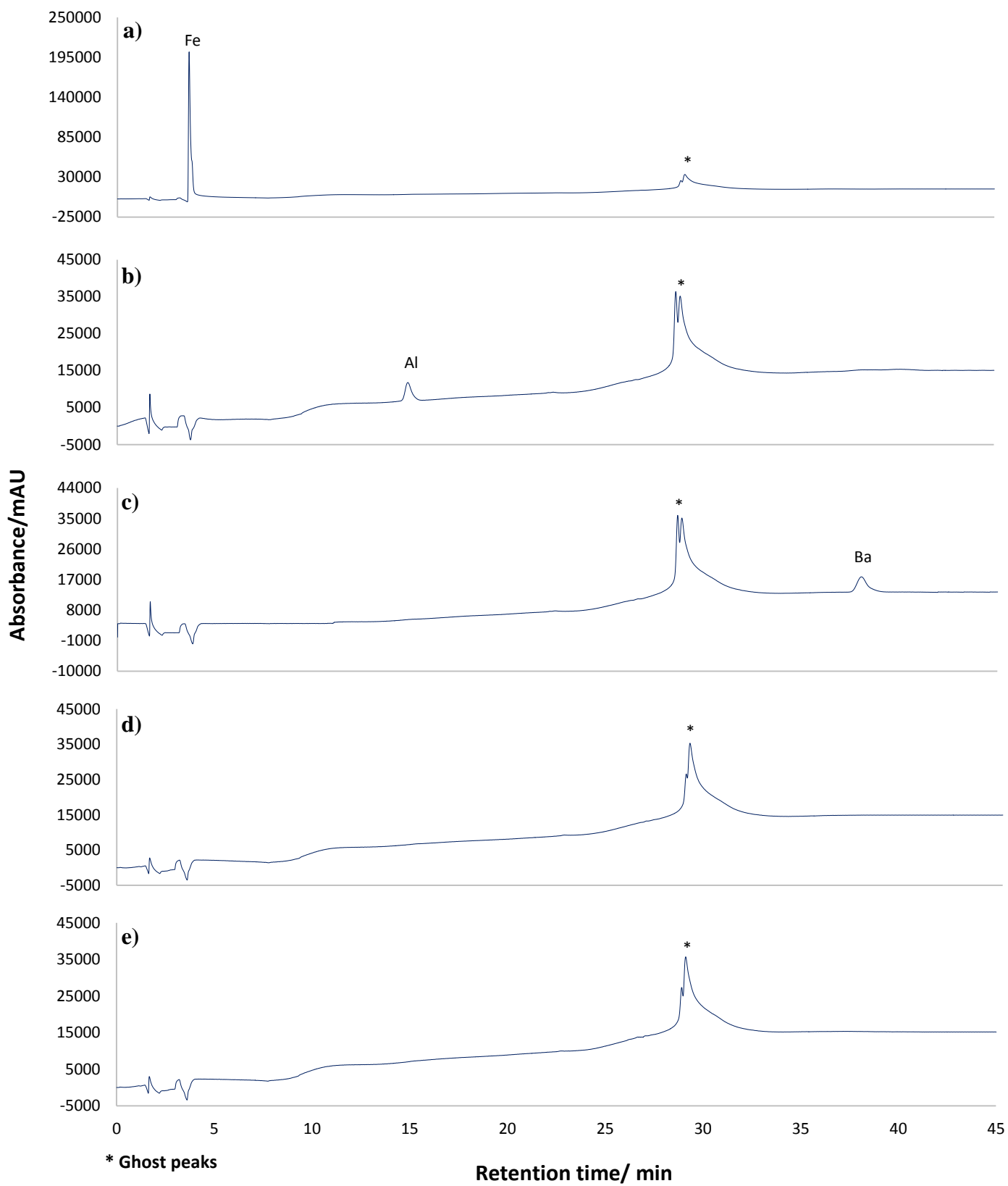
A detailed technical report on the analysis procedure and the treatment of the analytical data is supplied with each sample.

Appendix B. Standard deviation and equation of the calibration curve used to calculate the limits of detection (LOD) and limits of quantification (LOQ) of lithium metaborate fusion procedure

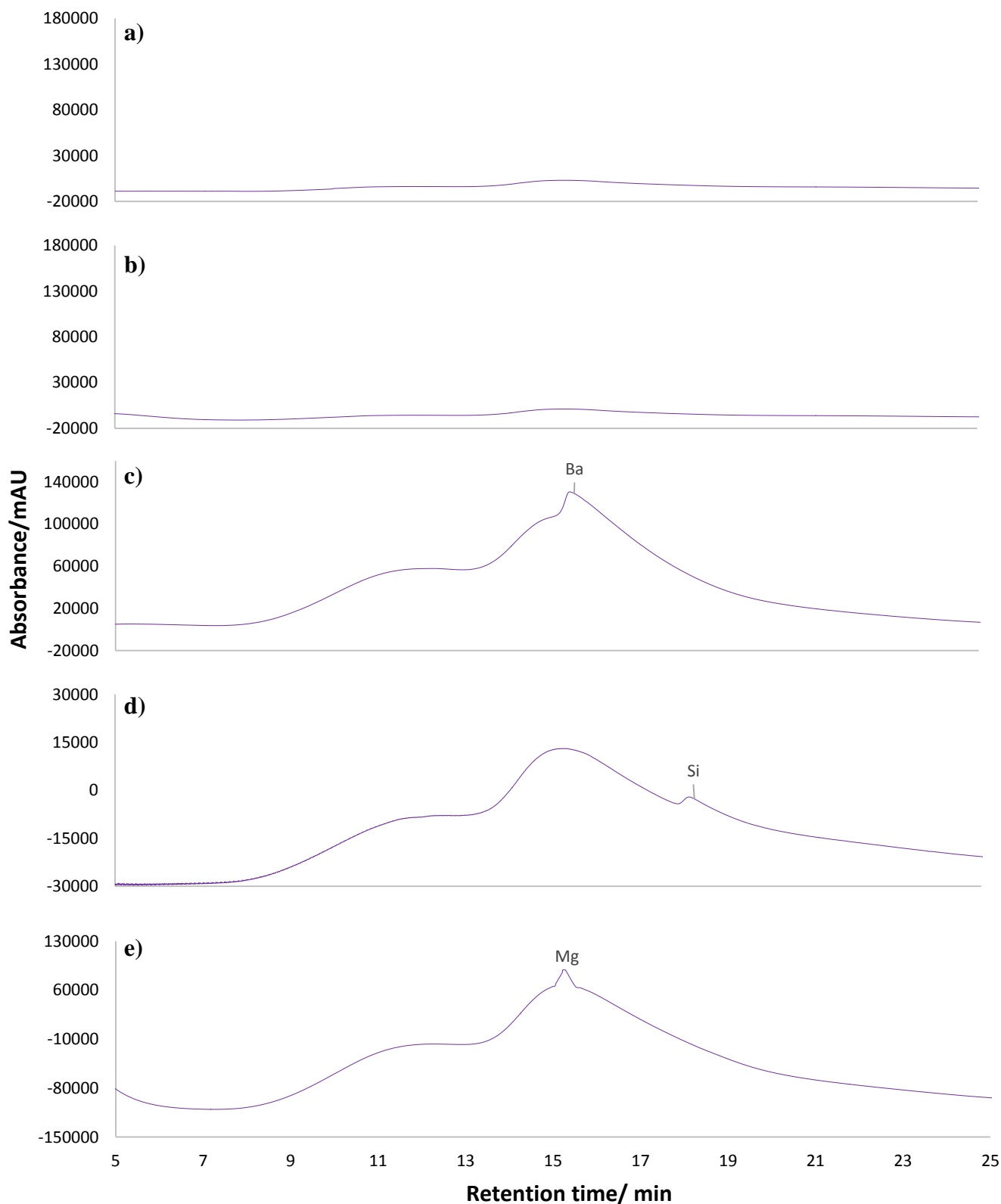
Analyte	s/ $\mu\text{g L}^{-1}$	Equation ($y = mx + c$)
Sc	0.1702	$y = 26412x + 4720.7$
Y	0.1589	$y = 6348.6x + 4923$
La	1.931	$y = 4975.4x + 62863$
Ce	0.7761	$y = 4697.8x - 39149$
Pr	0.3727	$y = 6317.4x - 20270$
Nd	0.6051	$y = 888.49x + 15728$
Sm	0.08897	$y = 5755.3x + 10256$
Eu	0.04494	$y = 17524x + 2530.9$
Gd	0.4324	$y = 1439.5x + 17843$
Tb	0.05307	$y = 56601x + 64840$
Dy	0.8702	$y = 8635.7x + 3208.8$
Ho	0.08997	$y = 33745x + 5915.3$
Er	0.05613	$y = 14109x + 400.96$
Tm	0.09362	$y = 34677x + 1015.2$
Yb	0.06989	$y = 14302x + 1766.5$
Lu	0.08277	$y = 41167x - 3074.4$

Appendix C. ICP-MS REE data of various CRMs obtained from fusion procedure

	AMIS0185			AMIS0304			AMIS0356			CGL-111		
	$\bar{x}/\mu\text{g g}^{-1}$	$s/\mu\text{g g}^{-1}$	%RSD	$\bar{x}/\mu\text{g g}^{-1}$	$s/\mu\text{g g}^{-1}$	%RSD	$\bar{x}/\mu\text{g g}^{-1}$	$s/\mu\text{g g}^{-1}$	%RSD	$\bar{x}/\mu\text{g g}^{-1}$	$s/\mu\text{g g}^{-1}$	%RSD
Sc	77.81	3.084	3.963	160.5	5.016	3.125	109.7	4.908	4.475	47.53	2.347	4.938
Y	64.83	1.474	2.275	416.7	4.652	1.116	38.22	0.1852	0.4846	985.7	64.46	6.539
La	28 896	470.0	1.626	3 251	28.61	0.8801	8 464	43.11	0.5083	16 174	1434	8.864
Ce	38 913	754.2	1.938	7 756	124.8	1.610	11 190	63.33	0.5659	14 979	350.7	2.342
Pr	3 108	47.49	1.528	867.8	8.552	0.9854	818.7	4.758	0.5842	2 119	212.7	10.03
Nd	9 413	136.7	1.452	3 806	36.15	0.9500	2 488	16.82	0.6871	7 370	735.1	9.973
Sm	554.0	9.369	1.691	576.3	6.842	1.187	161.6	0.9176	0.5678	741.5	69.91	9.428
Eu	95.76	1.957	2.044	146.9	1.945	1.325	31.07	0.1875	0.6036	174.8	16.35	9.356
Gd	434.9	8.338	1.917	348.9	4.994	1.431	122.1	1.198	0.9808	473.2	49.26	10.41
Tb	40.54	0.8713	2.149	34.07	0.6088	1.786	11.65	0.09160	0.7866	46.64	4.457	9.556
Dy	32.83	0.5797	1.766	138.4	1.702	1.230	14.03	0.08920	0.6358	158.2	15.25	9.636
Ho	3.824	0.06500	1.699	19.59	0.2591	1.322	1.898	0.02667	1.405	28.15	2.668	9.479
Er	5.480	0.1124	2.051	33.83	0.4205	1.243	3.192	0.03072	0.9622	63.23	5.799	9.172
Tm	0.506	0.01079	2.134	3.795	0.05200	1.376	0.3680	0.006091	1.656	8.169	0.7920	9.695
Yb	3.735	0.07735	2.071	18.56	0.2982	1.606	2.179	0.02012	0.9232	43.06	3.827	8.887
Lu	0.418	0.01106	2.648	2.410	0.04840	2.008	0.2699	0.01192	4.414	5.474	0.5222	9.538



Appendix D. Separation of 20 mg L⁻¹ of selected matrix ions under optimised IPC separation conditions: **a)** Fe **b)** Al **c)** Ba **d)** Si **e)** Mg



Appendix E. Separation of 20 mg L⁻¹ of selected matrix ions under optimised IEC separation conditions: **a)** Fe **b)** Al **c)** Ba **d)** Si **e)** Mg

Appendix F. Standard deviation and equation of the calibration curve used to calculate the limits of detection (LOD) and limits of quantification (LOQ) of ICP-MS analysis of separated REE fractions

Analyte	s/ $\mu\text{g L}^{-1}$	Equation ($y = mx + c$)
Sc	–	–
Y	0.6642	$y = 324.08x - 576.23$
La	10.12	$y = 22.061x + 5206.1$
Ce	15.09	$y = 23.502x + 3717.6$
Pr	2.242	$y = 504.81x + 256.25$
Nd	9.861	$y = 65.444x - 2189.2$
Sm	1.624	$y = 86.276x - 776.36$
Eu	0.2976	$y = 174.47x - 108.94$
Gd	0.7794	$y = 69.37x - 210.61$
Tb	0.6473	$y = 133.2x + 154.77$
Dy	–	–
Ho	0.4186	$y = 82.646x + 52.479$
Er	0.5342	$y = 80.894x + 9.7779$
Tm	–	–
Yb	–	–
Lu	–	–

Appendix G. ICP-MS data of various CRM REE fractions obtained after ion pair chromatographic separation

AMIS0185			AMIS0304			AMIS0356			CGL-111			
$\bar{x}/\mu\text{g g}^{-1}$	$s/\mu\text{g g}^{-1}$	% RSD	$\bar{x}/\mu\text{g g}^{-1}$	$s/\mu\text{g g}^{-1}$	%RSD	$\bar{x}/\mu\text{g g}^{-1}$	$s/\mu\text{g g}^{-1}$	% RSD	$\bar{x}/\mu\text{g g}^{-1}$	$s/\mu\text{g g}^{-1}$	% RSD	
Y	52.06	2.729	5.242	362.8	5.950	1.640	26.87	1.331	4.954	885.4	39.52	4.463
La	28 810	867.3	3.010	2 407	177.1	7.354	6 515	6809	10.45	15 421	786.6	5.101
Ce	38 226	2741	7.171	6 120	400.0	6.536	9 487	671.8	7.082	16 248	1136	6.991
Pr	3 287	258.5	7.862	826.9	28.29	3.421	925.2	102.2	11.04	2 336	228.4	9.777
Nd	7 759	445.9	5.747	2 686	306.8	11.42	1 693	178.7	10.55	6 269	394.3	6.289
Sm	423.5	38.91	9.187	372.5	35.62	9.560	—	—	—	584.0	46.71	8.998
Eu	65.20	6.609	10.13	14.86	2.916	19.61	15.17	3.059	20.17	126.5	20.25	16.01
Gd	118.9	7.871	6.620	273.3	15.44	5.651	—	—	—	142.2	51.95	36.53