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Determination of the geographical origin of green coffee beans via elemental and isotopic fingerprinting using ICPMS

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Langenzersdorf, September 2012

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I dedicate this work to my mum.

♫ Rock on! ♫

Abstract

The first cultivation of coffee plants can be traced back to Yemen in the beginning of the 13th century (ICO, 2011). From then on, coffee gained more and more importance all over the world. Nowadays, coffee is one of the most valuable products in world trade, especially a crucial export good for the least developed countries as it contributes to over 50 % of the foreign exchange earnings through exports. Therefore, it is clearly stated that coffee shows a great potential concerning geographical origin discrimination and avoiding fraud or misleading of the consumer.

The first part of this work was the establishment of an optimized sample preparation method using a rare earth element specific resin to separate the analytes from the sample matrix and to apply REE patterns to define elemental fingerprints of green coffee beans originating from Africa, Asia and America. The main aim of the separation procedure was the reduction of interfering matrix parts such as barium and iron. While these substances could be successfully separated, the resin did not show specific REE adhesion, resulting in high loss of original REE contents. Only a limited number of rare earth elements were above limits of detection and total combined uncertainties of measurements were quite high. Based on the results, the method was not adequate to solve the research question and requires further development.

The second part of the thesis puts a special emphasis on the combination of different elemental and isotopic data to define a unique fingerprint of green coffee beans and to classify their geographical origins. These patterns include rare earth element patterns determined by ICPQMS, multi-element patterns determined by ICPSFMS, strontium isotope ratios determined by HR-MC-ICPMS as well as light stable isotope ratios determined by IRMS. The data were evaluated statistically by use of principal component and canonical discriminant analysis. While rare earth patterns did not show satisfying results, strontium and light stable isotope ratios as well as the multi-element pattern did support successful origin classification up to 100%.

Zusammenfassung

Die Wurzeln der Kultivierung von Kaffee gehen zurück auf Yemen im 13. Jahrhundert (ICO, 2011). Von dieser Zeit an gewann Kaffee immer mehr an Bedeutung im globalen Handel. Heute ist Kaffee eines der wertvollsten Produkte im Welthandel und ein wichtiges Exportgut der wirtschaftlich weniger prosperierenden Länder, wo er bis zu 50% der Auslandsgeschäfte ausmacht. Aus diesem Grund ist klar ersichtlich, dass einer Herkunftsbestimmung von Kaffee besondere Bedeutung zukommt.

Der erste Teil dieser Arbeit beschäftigt sich mit der Entwicklung einer Methode zur Separation der Seltenen Erdelemente (REE) von der Matrix. Die REE-Verteilung soll letztendlich als Fingerabdruck für die geografische Herkunft dienen, um Kaffeebohnen aus Afrika, Asien und Amerika zu unterscheiden. Das Hauptziel der Trennmethode war die Abtrennung interferierender Elemente, in erster Linie Barium und Eisen. Obwohl diese Elemente abgetrennt werden konnten, zeigte das verwendete Harz keine Rückhaltung der Seltenen Erden, woraus sich ein hoher Verlust der Seltenerdmetalle ergab. Als Konsequenz lag nur eine beschränkte Anzahl an Seltenen Erden oberhalb der Nachweisgrenze, die Gesamtmessunsicherheit dieser Elemente war sehr hoch.

Als Resultat dieser Untersuchungen zeigte sich, dass die vorgeschlagene Methode nicht geeignet zur Lösung der Fragestellung war.

Im zweiten Teil der Arbeit wurde die Kombination der aus verschiedenen Quellen gewonnenen Daten von Elementverteilungen und Isotopenverhältnissen herangezogen, um grüne Kaffeebohnen gemäß ihres geografischen Ursprunges zu klassifizieren. Diese Verteilungen beinhalten Seltenerdmetalle, (gemessen mit ICPQMS), Multielementverteilungen (ICPQMS-Messungen), Sr Isotopen (MC-ICPMS-Messungen) und leichte stabile Isotope (C, H, O, gemessen mit IRMS). Diese Daten wurden mithilfe von Hauptkomponentenanalyse und kanonischer Diskriminanzanalyse untersucht. Die Seltenen Erden zeigten kein erfolgreiches Ergebnis, während Strontium und die leichten stabilen Isotope gemeinsam mit den Multielementverteilungen die Herkunft bis zu 100% richtig klassifizierten.

1 Introduction

The main goal of food authenticity studies is to protect consumers from fraud and wrong declarations. Moreover, tracing food through the production and distribution chain is important to identify risks and protect public health (EC, 2002). Consequently, food traceability is equally essential for the quality as well as for the safety of products.

More and more analytical methods regarding food authenticity are applied (see chapter 1.2). This thesis pursues the work with isotopic fingerprinting using inductively coupled plasma mass spectrometry (ICPMS), which is a fairly new but promising approach for determining the origin of food and has been proven in several studies dealing, for instance, with asparagus from the Marchfeld (Brunner, 2007; Swoboda et al. 2008), pumpkin see oil (Grabmann, 2009) and paprika (Brunner et al., 2010) amongst others.

The geology as well as environmental conditions (e.g. wind, precipitation, traffic) influence the elemental composition of food. Trace elements are taken up by plants through air, water or soil, allowing the determination of geographical origin and enabling traceability “from farm to fork” (Prohaska et al., 1999).

In this work’s research, special emphasis is put on the analysis of the rare earth element composition of green coffee beans, reflecting a possible specific geographical pattern. A pilot was carried out to test a newly developed rare earth resin, which was at the time of the project start to be launched on the market for its ability to minimize interferences via chromatographic separation during sample preparation in order to improve accuracy of obtained data. In future, the procedure would enable the development of an on-line measurement method for REE pattern.

An inter-disciplinary approach to confirm and fortify the determination of geographical origin of the samples under examination will be applied merging data

of multiple elemental and isotopic patterns to produce combined and significant results. The Centre for Environmental Biology, Stable Isotopes and Instrumental Analysis Facility (SIIAF), University of Lisbon, provided the latter data (Rodrigues et al., 2009; Rodrigues et al., 2011), which had been accomplished within a research project of the VIRIS laboratory and the SIIAF.

In the first part of this thesis, general information on the analytical substrate green coffee beans, methods, materials and instrumentation used will be given. The experimental section in part two contains details about the pilot study mentioned above, sample treatment, experimental setups and protocols as well as about the measurements. Part three deals with the interpretation of different data, which were derived within this study and parallel studies. Finally, a short overview as well as a prospective on geographical origin determination and the future of methods mentioned in the thesis will be given.

1.1 Objective of the pilot study

The aim of the work was to establish an optimized environment for newly developed rare earth elements resin, provided by Triskem International (Bruz, France). The resin was used to decrease isobaric interferences, which are a main contribution to inaccurate measurement results. Hence it is supposed to alleviate the determination of a rare earth fingerprint of green coffee beans within the scope of food traceability studies using ICPMS. By the end of all data acquisitions it should be possible to combine data from several different method approaches (e.g. REE composition, multielement pattern, Sr isotope ratios and stable light isotopes) to acquire a holistic and validated final result concerning the origin of the green coffee bean samples. Each approach will be discussed in detail in the following chapters and a summary of all methods and their ability to determine the exact origin of the samples will be given at the end of this section.

1.2 Food authenticity and traceability

Food authenticity has become a key issue for consumer protection. As more and more products are labeled PDO (Protected Denomination of Origin), PGI (Protected Geographical Indications) and TSG (Traditional Speciality Guaranteed), special focus is put on the traceability as well.

Food traceability is defined as *"the ability to track any food, feed, food-producing animal or substance that will be used for consumption, through all stages of production, processing and distribution"* (EC, 2002) and is meant to guarantee that food purchased by the consumer matches its description. While undeclared addition of cheap(er) materials or wrong amounts of ingredients mislead consumers, this thesis puts special emphasis on false statements concerning the geographical origin of food and food ingredients (FSA, 2011).

Recent publications deal with the optimization of food traceability systems (Dabenne et al., 2011, Zhang et al., 2011) and emphasize that they have to be based on accurate and reliable analytical techniques.
Many different approaches are applied to determine the geographical origin. Among these approaches, a number of analytical methods is applied which determine specific chemical compounds or the chemical composition of the investigated food compartment. Commonly used methods applied are biochemical, molecular and separation based as well as spectrometric methods and elemental analyses. In this particular content, elemental fingerprinting or specific isotopic patterns are among the most prominent and promising approaches. Advantages of isotopic fingerprints are their natural variation, the uniqueness of their analytical values and sample integrity. (Prohaska et al., 1998)

As this study focuses on the determination of the geographical origin of green coffee beans, the following table below gives a short overview of studies recently performed on green coffee beans:

Tab. 1 Overview of recent studies on (green) coffee beans

Aim	Method	Group
Effect of temperatures and rain on coffee berry disease caused by Colletotrichum kahawae	epidemiological study	Mouen et al., 2012
Green coffee extracts and their effect on the neurotoxicity induced by aluminium chloride	biomolecular study	Elsaid et al., 2011
Determination of iodine-like flavor-causing components in Brazilian coffee	GC, olfactometry	Kato et al., 2011
Determination of the best production model of a coffee plantation according to environmental performance	comparison of emergy indices	Giannetti et al., 2011
Analysis of radical activity, phenolic and volatile compounds of coffee beans	GC, MS	Somporn et al., 2011
Determination of melatonin and serotonin contents	HPLC, ESI-MS	Ramakrishna et al., in press
Geographical origin determination	Electronic noses	Sberveglieri et al., 2011
Detection of fungal contamination	Electronic noses, GC, MS	Sberveglieri et al., 2011
Determination of maturity of green coffee beans	FTIR	Craig et al., 2011
Feasibility of storing green beans in different kinds of packaging	Sensory analysis, photometric methods	Ribeiro et al., 2011
Determination of interaction between coffee plant and local environment	IRMS, ICPMS	Rodrigues et al., 2011
Dependence of roasting process and amount of bioactive components	GFC	Chen et al., 2011
Determination of chlorogenic acid content in green coffee (and their inhibitory effect on alpha-amylase)	HPLC	Narita et al., 2011
Discrimination between different coffee species	Raman spectroscopy, chemometric analysis	El-Abassy et al., 2011
Authenticity of coffee via Strontium and oxygen isotope fingerprints	MC-ICPMS, IRMS	Rodrigues et al., 2011
Quality evaluation of green coffee beans	IRMS, NIRS	Santos et al., 2012
Development of a tensiometric model for surface energy characterization of raw coffee beans	PFPE	Rossi et al., 2012

Pesticide analysis in green coffee beans	GC-MS, NCI-SIM	Pizzutti et al., 2012
Extraction of chlorogenic acids from green coffee beans	MAE	Tezotto et al., 2012
Impact of climatic factors on the organic compound fingerprint in green coffee beans	GC-MS	Bertrand et al., 2012
Discrimination of arabica coffee cultivars	Fourier transform ion cyclotron resonance mass spectrometry	Garrett et al., 2012 (in press)

1.3 General aspects of coffee

It is essential to gain knowledge about coffee to be able to develop feasible methods for authenticity studies on coffee plants as well as for the interpretation of the data. This chapter will therefore give a short description of the coffee plant itself, its nutritional value and its metabolism with focus on the green coffee bean, which will be under examination in the experimental section.

1.3.1 The coffee plant

The genus *Coffea* belongs to the family *Rubiaceae* and covers approximately 70 species, the two most important being *C. arabica L.* and *C. canephora Pierre* (commonly known as “Robusta”) both originating from Africa (N.N., 2007). Each coffee fruit (picture) contains two beans, which are elliptical and plane-convex (Eira et al., 2006)

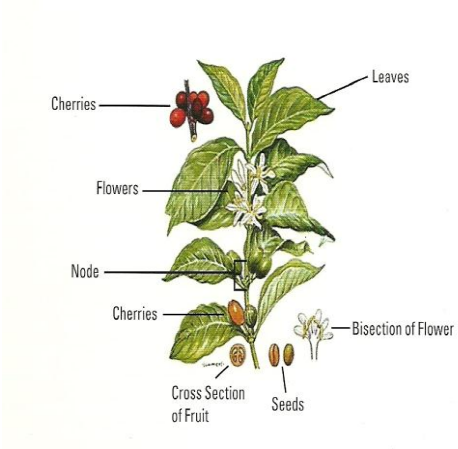

Fig. 1 Structure of a coffee plant (Rodrigues, 2010)

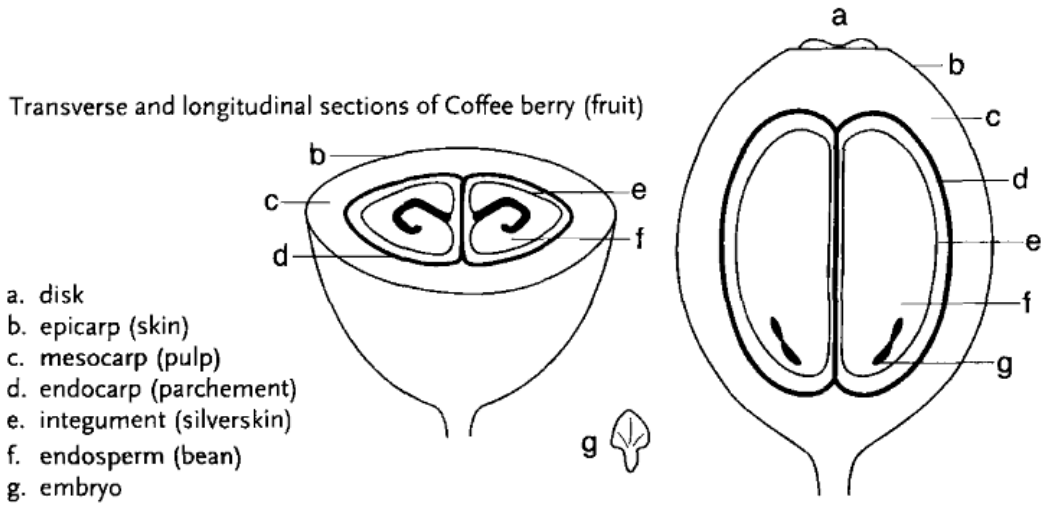

Fig. 2 Structure of a coffee berry (fruit) (Wintgens, 2004)

Fig. 3 Longitudinal cut (green coffee bean)

Fig. 4 Transverse cut (green coffee bean)

What is commonly known as bean is actually the endosperm of the coffee fruit. After self-pollination (Arabica) or cross-pollination (Robusta), the embryo (coffee bean) starts growing and gradually replaces the integument. Five weeks later, the beans are fully formed and start changing their color which signals the optimal point for harvest. Subsequently, the beans are processed, dried and roasted to varying degrees, depending on the desired flavor. Before consumption, they are grinded and brewed (National Coffee Association, 2011). Beans used for this research have not been processed further.

The roots of coffee plants can extend up to 25 km in length and about 30 cm below the surface. Their growth is strongly dependant on the composition of the soil, especially on its nitrogen, calcium and magnesium content (Nutman, 1993) which emphasizes the reciprocity of soil and plant and its potential for analytical interaction research.

1.3.2 Nutritional value

Although coffee is best known for its caffeine content, it offers far more (micro) nutrients like magnesium, potassium, niacin, vitamin E, and secondary plant products like chlorogenic and caffeinic acid expressing antioxidative effects on the human organism. The table below lists the main nutritional ingredients of coffee.

Tab. 2 Ingredients of Coffee (Souci et al., 2008)

Ingredients of roasted coffee (g /100 g) (mean values, depending on degree of roasting and breed)	
Dietary fiber	58,2
Carbohydrates	1,5
Protein	13,5
Fat	13,4
Mineral nutrients	4,16
Water	3,43
Chlorogenic acid	4,11
Caffeine	1,28

Moderate daily intake of coffee shows physiological benefits such as stimulation of the central nervous system resulting in higher awareness and concentration, reduction of cerebral apoplexy incidents or lower risk of liver and colorectal cancer (Binns et al. 2008; Lopez-Garcia et al. 2009; Nkondjock, 2009; WCR 2007).

1.4 Isotopic systems used in provenance studies

Even though there are numerous isotopic systems, only the ones relevant for this thesis will be explained in more detail. Stable isotopes are atoms with the same number of protons but different number of neutrons in the core. They do not undergo radioactive decay over time. Fractionation processes alter the isotopic composition during chemical and physical processes due to different atomic weights, e.g. the heavier the atom the more energy is needed to break bonds. These processes can either be controlled by kinetics or thermodynamics – therefore, kinetic fractionation can be distinguished from equilibrium fractionation.

1.4.1 The isotopic system of Strontium (Sr)

The isotopic patterns of the alkaline earth metal strontium are well established as a parameter for origin authentication, lately in the food traceability area as well. The element has four naturally occurring stable isotopes: ^{84}Sr (abundance 0.56%), ^{86}Sr (9.86%), ^{87}Sr (7.00%) and ^{88}Sr (82.58%). (International Union of Pure and Applied Chemistry, 2011). Due to the radioactive decay of ^{87}Rb into ^{87}Sr, the amount of ^{87}Sr increases with time and thus the ^{87}Sr/^{86}Sr ratio depends on the geochemical composition and the geological age of the maternal rock and is an indicator for the geographic location.

As a proxy for calcium, strontium can be incorporated into organisms similar to that trace element. (Capo et al., 1998) The natural variation of this heavy element due to radioactive processes results in significantly different distribution of the isotopes regarding the local weather and the geographical location, respectively. (Aggarwal et al., 2008) The ^{87}Sr/^{86}Sr ratio can be used for geographical

origin determination, because biological processes involved in plant metabolism do not fractionate strontium isotopes significantly. (Rodrigues et al., 2011)

1.4.2 Light stable isotopes: carbon, oxygen, nitrogen, hydrogen, sulfur

Light, stable isotopes include ^{12}C, ^{13}C; ^{16}O, ^{17}O, ^{18}O; ^{14}N, ^{15}N; ^{1}H, ^{2}H as well as the sulfur isotopes ^{32}S, ^{33}S, ^{34}S and ^{36}S. The Centre for Environmental Biology, Stable Isotopes and Instrumental Analysis Facility (SIIAF), University of Lisbon, has been researching in this field (Rodrigues et al., 2009; Rodrigues et al, 2011) and provided data for this thesis to allow a combination and connection of several isotopic fingerprints.

The specific proportions of the isotopes of hydrogen, oxygen and carbon depend on climatic and geographical environments as well as on the plant's metabolism – these influences are also referred to as isotopic fractionation, measured mainly by isotope ratio mass spectrometry (IRMS). (Rodrigues et al., 2011)

Tab. 3 Average terrestrial abundances of stable isotopes H, C, N, O, S (modif. Ehleringer, 2011)

Element	Isotope	Abundance (%)
Hydrogen	^{1}H	99.985
	^{2}H	0.015
Carbon	^{12}C	98.89
	^{13}C	1.11
Nitrogen	^{14}N	99.63
	^{15}N	0.37
Oxygen	^{16}O	99.759
	^{17}O	0.037
	^{18}O	0.204
Sulfur	^{32}S	95.00
	^{33}S	0.76
	^{34}S	4.22
	^{36}S	0.014

1.5 Multi-element patterns

Multi-elemental analysis allows the determination of specific geographical patterns as well as the discussion on nutritional values of coffee. The major focus of this work was the determination of rare earth element pattern. As the method

of determining other multi-elemental patterns via ICPMS has been well established, additional elements were included in this work to provide more parameters for the combined data evaluation. Additional Elements under examination were: Li, Be, B, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Mo, Ag, Cd, Te, Ba, Tl, Pb and Bi. Only elements which were above the detection limits according to a pilot study were selected.

1.5.1 Rare earth elements

The rare earth elements (listed in the table below) were used for the analysis of geochemical source fingerprints for instance of sea sediments (Alargasamy et al., 2009), soil (Aström et al, 2001) and to understand the formation of the Earth's crust mantle and the sedimentary system (Baker et al, 2002) as well as for water samples, ground and drinking waters (Dia et al, 2000; De Boer et al., 1996; Bahramifar et al, 2005) or otoliths of fish (Arslan et al., 2003). One main goal of this thesis is to apply rare earth element patterns for the analysis of green coffee beans, which is a promising approach.

Tab. 4 Rare earth elements and their natural abundances (modif. IUPAC, 2005 and University of Alberta, 2011)

Name	Z	Symbol	Mass of Atom (u)	Abundance (%)
Scandium	21	^{45}Sc	44.955910	100.00
Yttrium	39	^{89}Y	88.905848	100.00
Lanthanum	57	^{138}La	137.907107	0.09
		^{139}La	138.906348	99.91
Cerium	58	^{136}Ce	135.907144	0.19
		^{138}Ce	137.905986	0.25
		^{140}Ce	139.905434	88.45
		^{142}Ce	141.909240	11.11
Praseodymium	59	^{141}Pr	140.907648	100.00
Neodymium	60	^{142}Nd	141.907719	27.20
		^{143}Nd	142.909810	12.20
		^{144}Nd	143.910083	23.80
		^{145}Nd	144.912569	8.30
		^{146}Nd	145.913112	17.20
		^{148}Nd	147.916889	5.70
		^{150}Nd	149.920887	5.60

Promethium	61	^{145}Pm	144.912744	not present in nature
Samarium	62	^{144}Sm	143.911995	3.07
		^{147}Sm	146.914893	14.99
		^{148}Sm	147.914818	11.24
		^{149}Sm	148.917180	13.82
		^{150}Sm	149.917271	7.38
		^{152}Sm	151.919728	26.75
		^{154}Sm	153.922205	22.75
Europium	63	^{151}Eu	150.919846	47.81
		^{153}Eu	152.921226	52.19
Gadolinium	64	^{152}Gd	151.919788	0.20
		^{154}Gd	153.920862	2.18
		^{155}Gd	154.922619	14.80
		^{156}Gd	155.922120	20.47
		^{157}Gd	156.923957	15.65
		^{158}Gd	157.924101	24.84
		^{160}Gd	159.927051	21.86
Terbium	65	^{159}Tb	158.925343	100.00
Dysprosium	66	^{156}Dy	155.924278	0.06
		^{158}Dy	157.924405	0.10
		^{160}Dy	159.925194	2.34
		^{161}Dy	160.926930	18.91
		^{162}Dy	161.926795	25.51
		^{163}Dy	162.928728	24.90
		^{164}Dy	163.929171	28.18
Holmium	67	^{165}Ho	164.930318	100.00
Erbium	68	^{162}Er	161.928775	0.14
		^{164}Er	163.929197	1.61
		^{166}Er	165.930290	33.61
		^{167}Er	166.932045	22.93
		^{168}Er	167.932368	26.78
		^{170}Er	169.935460	14.93
Thulium	69	^{169}Tm	168.934211	100.00
Ytterbium	70	^{168}Yb	167.933894	0.13
		^{170}Yb	169.934759	3.04
		^{171}Yb	170.936322	14.28
		^{172}Yb	171.936378	21.83
		^{173}Yb	172.938207	16.13
		^{174}Yb	173.938858	31.83
		^{176}Yb	175.942568	12.76
Lutetium	71	^{175}Lu	174.940768	97.41
		^{176}Lu	175.942682	2.59

Additionally, REEs can be classified according to their mass into heavy (HREE, Terbium to Lutetium), middle (MREE, Neodymium to Gadolinium) and light (LREE, Scandium to Praseodymium) elements (Cao et al., 2001).

The most challenging aspect of REE determination studies is the similarity of their chemical properties, especially when dealing with REE mixtures in the analyte material due to numerous interferences as well as their low abundances, often ranging below limit of detection (LOD) levels of the instrumentation. Therefore, sample pretreatment in terms of preconcentration and separation is often applied to increase sensitivity and selectivity although time-consuming. The most common techniques for the analysis of REE are ICPMS, ICPOES, XRF as well as NAA.

Tab. 5 Review of analytical techniques used to analyze REE, adapted from (Zawisza et al., 2011)

Analytical Technique		**Analyzed material**	**Author**
ICPMS	ICPSFMS	Biological samples	Riondato et al., 2001
		Water	Zhu et al., 2010
		Sediments	Ardini et al., 2010
		Geological materials	Varga et al., 2010
		Nuclear materials	Isnard et al., 2005
	ICPQMS	Geological materials	Nakamura et al., 2007
	LA-ICPMS	Geological materials	Petrelli et al., 2007
	MC-ICPMS	Nuclear materials	Isnard et al., 2005
ICPOES		Biological samples	Li et al., 2010
		Water	Shariati et al., 2009
		Sediments	Ardini et al., 2010
		Geological materials	Jain et al., 2002
XRF		Geological materials	Baryshev et al., 2001
NAA	INAA	Water	Kayasth et al., 2004
		Sediments	Rezaee et al., 2010
		Geological materials	El-Taher, 2007
	RNAA	Geological materials	Minowa et al., 2003
Spectrophotometry UV-Vis		Water	Alaa et al., 2001
		Geological materials	El-Dessouky et al., 2007
PIXE		Geological materials	Hirokawa et al., 2001
SIMS		Polycristalline materials	Palcut et al., 2008

1.6 Inductively coupled plasma mass spectrometry (ICPMS)

ICPMS has developed to one of the most reliable techniques for the determination of elemental contents (as well REE) due to its high sensitivity, multi-element capability and the possibility to perform isotopic measurements as well as regarding its cost- and time-efficiency. (Zawisza et. al, 2011)

1.6.1 Principle

Inductively coupled plasma mass spectrometry (ICPMS) allows fast and reliable quantitative analysis of almost all (trace) elements along with isotope ratios. It is based on generating positively charged ions using a high temperature Ar plasma discharge, and subsequent separation of the ions in a mass separator according to their mass-to-charge (m/z) ratio. (Longerich, 2000). Liquid samples are converted into aerosols, injected into the plasma and dried, vaporized, atomized and ionized in the different heating zones of the plasma. Ions are transported to the mass separator of the instrument where they are separated and subsequently detected and translated into a signal output.

The three ICPMS instruments used in this thesis were a high resolution sector field ICPMS (ICPSFMS ELEMENT2, Thermo Scientific, Bremen, Germany), an ICP quadrupole MS instrument (ICPQMS ELAN DRC-e, PerkinElmer, Waltham, Massachusetts, USA) equipped with a dynamic reaction cell and a multiple collector sector field ICPMS (MC-ICPSFMS Nu Plasma, Nu Instruments Ltd., Wrexham, UK)

The basic structure of an ICPMS instrument is shown in the figure below, each part will be described in more detail.

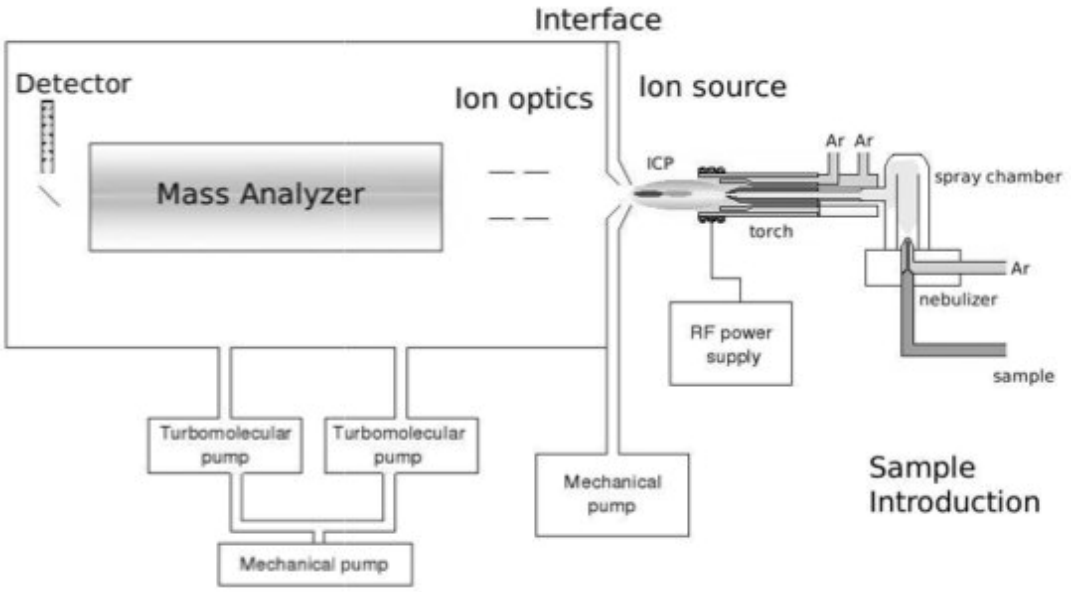

Fig. 5 Schematic View of ICPMS, adopted from (Horsky, 2010)

1.6.1.1 Sample introduction system

The first part of an ICPMS is the sample introduction system. As most samples analyzed by this analytical technique are liquids, the introduction system consists of a peristaltic pump, a nebulizer and a spray chamber. Solid samples can be analyzed directly using laser ablation systems. The liquid sample introduced into the nebulizer is converted into an aerosol with the help of nebulizer gas (argon). The two primarily applied nebulizer types are concentric and crossflow nebulizers. While concentric nebulizers are used for clean samples, provide excellent sensitivity and stability, but can face blockage problems at the occurrence of particles, crossflow nebulizers are the method of choice for samples with solid particles due to their larger diameter, but are not as efficient or sensitive.

The nebulizer is attached to a double pass or cyclonic spray chamber, where droplet selection according to droplet size and velocity takes place.

1.6.1.2 Ion source

The ICP torch in combination with an RF coil and RF power supply generates the plasma which serves as the ion source, converting the analyte atoms to ions through extremely high temperatures (up to 8000 K). Three different Ar gas flows contribute to the maintenance of the plasma, which consists of a mixture of argon atoms, ions and electrons: plasma gas, auxiliary gas and the nebulizer gas transporting the sample. (Thomas, 2001a)

As the atoms of the sample solution travel through the plasma, they absorb more energy from the plasma and eventually release one electron to form a singly charged ion. The singly charged ions exit the plasma and enter the interface region. (Hoffmann et al., 2007)

1.6.1.3 Interface

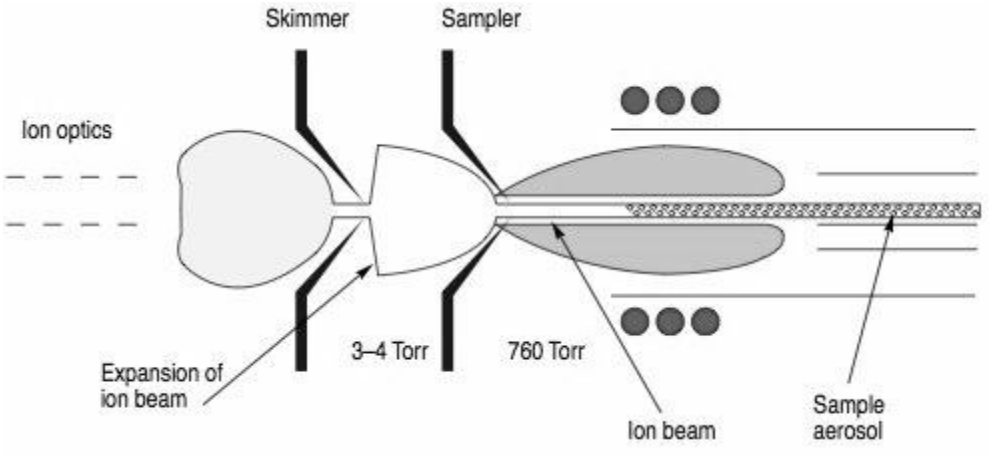

Fig. 6 Interface Region (Thomas, 2001)

An interface region links the atmospheric pressure outside the ICPMS to a vacuum ranging between 10^{-6} torr and 10^{-8} torr, which is needed due to the fact that ions do not move very far at atmospheric pressure before a collision occurs. The beginning of the interface is represented by a sampler cone and ends at a skimmer cone, both made of nickel in most cases. (Longerich, 2000)

1.6.1.4 Ion optics

The main aim of ion optics is to focus the analyte ions and guide them through the analyzing part of the system to the detector. Since the ions generated in the plasma are nearly all positively charged, they have a natural tendency to repel each other. Moreover, their different mass-to-charge ratios result in different kinetic energies. The lens of an ICPMS, a charged device, focuses ions into a beam for transmission into the analysis unit. Additionally, ion optics stop other particles such as photons from entering the analyzing unit as they would cause signal instability and degraded detection capabilities due to higher background levels.

The ICPQMS used for measurements in this work includes a dynamic reaction cell (DRC). The DRC is equipped with a quadrupole in a closed cell, where reaction gases can be applied. Gas phase reactions in the cell with e.g. highly reactive gas (e.g. NH_3) convert polyatomic interfering ions like $^{40}Ar^{16}O$ (interfering with ^{56}Fe) to non-disturbing species or – when using e.g. O_2 as reaction gas - changing the analyte itself by converting it to another mass or neutral shifted species takes place before ions enter the mass analyzing unit. Neutral atoms don't carry charges and are therefore not stable in the quadrupole resulting in their exclusion from the cell. Reaction cells remove interfering ions very effectively while preserving the analyte ions.

1.6.1.5 Mass analyzer

The analyzer represents the core part of an ICPMS enabling the separation of ions according to their mass-to-charge (m/z) ratio. Three types of mass analyzers are generally applied in ICPMS instruments: Quadrupole, double focusing magnetic sector and time-of-flight analyzers. The used instruments were equipped with either a quadrupole or magnetic sectorfield device and will be explained in more detail.

1.6.1.5.1 Quadrupole mass analyzer

The quadrupole analyzer consists of four rods arranged in a square. A DC voltage is applied resulting in the same charge of each pair of opposing rods which is then overlaid by an RF voltage. Ions enter the region between the four rods which act as a mass filter, only allowing ions with the selected mass to pass through. (Longerich, 2000)

A major problem present in this technique is the separation of analyte- and interfering masses due to the limitations in resolving power. Quadrupole based ICPMS instruments offer resolutions only ranging between 0.7 and 1.0 amu (low resolution, resolving power app. 300) – a fact that contributes to resolution related spectral interferences. (Thomas, 2001)

1.6.1.5.2 Magnetic sectorfield mass analyzer

A magnetic sectorfield device consists of a curved magnet for mass separation in general in combination with an electrostatic sectorfield in order to accomplish energy focusing. The magnetic and electrostatic sectorfield arranged subsequently in one curvature is mostly referred to Nier Johnson geometry (MC-ICPMS). The backward arrangement is called reverse Nier Johnson geometry and is found in single collector ICPSFMS instruments. In the magnetic field, the ions are separated according to their mass/charge ratio (Jakubowski, 2011). The introduction of a slit in the ion beam path allows accomplishing mass resolutions up to 12.000. Therefore, interfered elements such as Fe, K, As, V and Cr can be quantified. Higher resolutions always correlate with lower sensitivity - changing from low to high resolution can result in more than a 100-fold loss in sensitivity. (Longerich et al., 2000)

A multi collector device is generally equipped with a magnetic sector field.

1.6.1.6 Detector

Single collector ICPMS instruments are generally equipped with discrete dynode detectors. These detectors can convert the ion beam to an output either via pulse counting (PC) or digital mode (DC) depending on the number of in-

coming ions. Faraday detectors can be found in MC-ICPMS instruments which allow higher ion beam currents and are therefore used for higher concentrations. MC-ICPMS instruments preferably use faraday cups as their small geometry allows to arrange multiple cups adjacent to each other.

The ICPMS software finally translates the ion counts measured by the detector into counts per second. The concentration of each element is determined by comparing the counts measured for a selected isotope to an external calibration curve that was generated for that element.

1.6.2 Data correction in ICPMS: interferences, matrix effects and mass bias

1.6.2.1 Spectral interferences

Interferences can be classified either as spectral or non-spectral. Most present are spectral interferences which can further be divided into isobaric, polyatomic and molecular species. Their occurrence depends e.g. on the gas used, matrix components and temperature.

An isobaric interference is the result of equal mass isotopes of different elements present in the sample solution. Low resolution instruments cannot distinguish between these isotopes. Polyatomic interferences arise due to recombined sample and matrix ions, for instance $^{40}Ar^{16}O$ is formed in case of aqueous sample solutions and argon gas flow and competes with ^{56}Fe. The formation of oxides, hydroxides, hydrides or doubly charged species impairs with the outcome of certain analyte isotopes as well. Rare earth elements, for instance, tend to form molecular species and form doubly charged ions more easily than other elements. The complicated interferences concerning REEs results from overlap of the polyatomic ions (MO^+, MOH^+) of LREEs on MREEs and HREEs as well as of BaO^+ and $BaOH^+$ (Cao et al., 2001).

Possible interferences of REE with barium, argon and the REEs themselves are given in the appendix. The evaluation was made using an ICP Interference Determination Utility (Nu Instruments Ltd:, Wrexham, UK). Main components of coffee were taken into account. Single atom, double atom and doubly charge interferences were evaluated.

The table in the appendix indicates the importance of the separation of e.g. barium from the sample matrix to reduce interferences. Several solution strategies minimize the bias by interferences. The formation of doubly charged ions can be reduced via optimization and tuning of the ICPMS instrument with respect to plasma conditions, gas flow (the lower the gas flow the lower the interfering oxide species), RF power and sampling position. Isobaric interferences can be avoided by choosing alternatives of other, less interfered isotopes or mathematical interference correction equations (Jakubowski et al., 2011). Furthermore, spectral interferences can be overcome by adequate sample preparation before measurement, such as separation of possibly interfering substances with the support of e.g. chromatographic techniques. Another possibility of avoiding poly-atomic interferences is the use of dynamic reaction cells as present in the ELAN DRCe or the application of high mass resolution. (Baker et al., 2002; Prohaska et al., 1998)

1.6.2.2 Matrix effects

The classic way to compensate for the matrix effect, which is a physical interference emerging during measurement is to use internal standardization. With this method of correction, certain elements (usually at the parts-per-billion level) – in our lab ^{115}In is the mainly used isotope - are spiked to the samples, calibration standards, and blanks to correct for any variations in the response of the elements caused by the matrix. Moreover, they enable to compensate for long-term signal drift produced by matrix components slowly blocking the sampler and skimmer cone orifices. An internal standard needs to fulfill criteria such as non-presence in the sample, non-interfering with the analyte's mass as well as a similar ionization potential (Thomas, 2001).

1.6.2.3 Mass bias

The mass discrimination effect occurs due to the preferential transmission of heavier or lighter isotopes after ionization in the plasma, resulting in inaccurate measurements and inconsistent results especially in isotopic ratio measurements. This so called “space charge effect”, where ions of heavy masses stay closer to the beam center while ions of light masses are rather located on the outside of the ion beam, needs to be corrected through the application of standard or certified reference material to obtain the true isotopic composition of the sample (Longerich, 2000).

Several mathematical models have been established for correcting mass discrimination when dealing with ICPMS measurements, the four commonly used being the Exponential Law, the Linear Law, the Power Law and the Russel equation which are described in more detail elsewhere. Next to mathematical correction, the application of an isotope reference standard and internal normalization with an isotopic system relating to the sample system result in a decrease of the mass bias.

2 Experimental section

Sample preparation as well as all measurements were performed either in the VIRIS (Vienna Isotope Research Investigation Survey) laboratory at the University of Applied Life Sciences (Division of Analytical Chemistry, Muthgasse 18, 1190 Vienna) or in the VIRIS laboratory located at the University of Vienna (Althanstraße 14, 1090 Vienna). The latter location is equipped with a cleanroom (class 10 000 and 100 000, respectively).

2.1 Materials

2.1.1 Laboratory equipment

All parts used for sample preparation and treatment consisted of polyethylene material, were only used once and subjected to a washing procedure including 24 hours in a 10% nitric acid bath, followed by 24 hours in a 1% nitric acid bath and rinsing with purified water (resistivity > 18 MΩ cm, SG, Wasseraufbereitung und Regenerierstation GmbH, Barsbuttel, Germany) before air drying and use.

2.1.2 Reagents and Standards

All samples – unless otherwise stated - and standards were prepared gravimetrically in an approximately 2% nitric acid solution. Water used was subboiled in a purification system (MLS DuoPur, MLS, Leutkirch im Allgäu, Germany) beforehand. Similarly, p.a. grade nitric acid (Merck KGaA, Darmstadt, Germany) had to undergo a subboiling process (MLS DuoPur, MLS, Leutkirch im Allgäu, Germany) twice.

Reagents, standard solutions and Standard Reference Materials (SRMs) used for the methods explained in this thesis were:

- ICP Multi Element Solution Standard 1 (CertiPrep, Spex Industries, Middlesex, United Kingdom)
- ICP Multi Element Standard Solution VI (CertiPur, suprapure, Merck KGaA, Darmstadt, Germany)

- Indium ICP Standard, 1000 mg L^{-1} In (CertiPur, Merck KGaA, Darmstadt, Germany)
- HNO_3 (65 % w/w) (MERCK KGaA, Darmstadt, Germany)
- H_2O_2 (31 % w/w) (MERCK KGaA, Darmstadt, Germany)
- Indium ICP Standard: 1000 mg L^{-1} In (CertiPur, MERCK KGaA, Darmstadt, Germany)
- Rhodium ICP Standard: 1000 mg L^{-1} Rh (CertiPur, MERCK KGaA, Darmstadt, Germany)
- Rubidium ICP Standard 1000 mg L^{-1} Rb (CertiPur, MERCK KGaA, Darmstadt, Germany)
- Germanium ICP Standard: 1000 mg L^{-1} Ge (CertiPur, MERCK KGaA, Darmstadt, Germany)
- ICP Multi Element Standard VI (MERCK KGaA, Darmstadt, Germany)
- TM-28.3 and 25.3 Certified Reference Material (Beta-Analytik, Austria, 2007)
- SRM 987 $SrCO_3$ (NIST, Gaithersburg, MD, USA)

2.2 Measurement by using the ELAN DRCe

110 ppb ^{115}Indium were placed in a PE tube as internal normalization standard to reach a final concentration of 10 ppb ^{115}In in the sample solution. Afterwards 0.1 mL of the previously resin-separated sample was added to the tube filled up with 1% HNO_3 to reach the wanted dilution (f.e. 1:50 when dealing with the 10 ng g^{-1} REE standard) and thoroughly shaken. External calibration standards were also prepared with 10 ppb ^{115}In. Multi VI standards with concentrations of 1 ng g^{-1}, 50 ng g^{-1} and 100 ng g^{-1} were measured as well to calibrate the Ba and Fe concentrations. For external calibration, 10 REE standard solutions with the concentrations of 0.001 ng g^{-1}, 0.005 ng g^{-1}, 0.01 ng g^{-1}, 0.025 ng g^{-1}, 0.05 ng g^{-1}, 0.1 ng g^{-1}, 0.25 ng g^{-1}, 0.50 ng g^{-1}, 1.00 ng g^{-1} and 10.00 ng g^{-1} REE in 1% HNO_3 were prepared. For the surveillance of the measurement quality itself, a certified reference material (TM25.3) was added to the sample list. ^{140}Ce, ^{164}Dy, ^{166}Er, ^{153}Eu, ^{158}Gd, ^{165}Ho, ^{139}La, ^{175}Lu, ^{142}Nd, ^{141}Pr, ^{45}Sc, ^{152}Sm, ^{159}Tb, ^{169}Tm, ^{89}Y, ^{137}Ba, ^{138}Ba, ^{56}Fe and ^{57}Fe were measured with the ICPQMS, referring to the optimized selection of least interfered REEs from previous studies (Lang,

2010). The isotope ^{232}Th is not defined as rare earth element, but was also measured and used for the data evaluation.

After running the daily performance check on the ICPQMS (ELAN), measurement of the samples was started applying the following instrument parameters:

Tab. 6 ELAN DRC-e Settings

Mode	**DRC**	**standard**
RF power	1250 W	1250 W
nebuliser gas flow rate	1 L min^{-1}	1 L min^{-1}
auxiliary gas flow	0.6 L min^{-1}	0.6 L min^{-1}
plasma gas flow	15 L min^{-1}	15 L min^{-1}
sample cone	nickel	nickel
skimmer cone	nickel	nickel
nebulizer	PFA	PFA
spray chamber	cyclonic spray chamber	cyclonic spray chamber
sample uptake rate	100 µl min^{-1}	100 µl min^{-1}
Cell gas	O_2	-
cell gas flow	0.55 L min^{-1}	0
Rpq	0.25	0.25
Rpa	0	0
signal intensity	650 000-900 000 cps	650 000-1000 000 cps
number of sweeps	10	10
number of readings	1	1
number of replicates	5	5
lens settings	< 12 V	< 12 V
flush delay	60 sec	60 sec
wash time	120 sec	120 sec
pump velocity	20 rpm	20 rpm
measurement	dual mode	dual mode

2.2.1 Membrane desolvation nebulizer linked to the ELAN DRCe

The Apex (APEX IR, Elemental Scientific Inc., Omaha, USA) is a semipermeable membrane desolvation unit leading to dried aerosols, which are further transported to the plasma. Therefore, as water vapor us reduced, interfering oxides are supposed to be reduced significantly (Thomas et al., 1998)

Fig. 7 Measurement Setup ELAN DRCe with APEX and autosampler

The APEX (APEX IR, Elemental Scientific Inc., Omaha, USA) was used as sample introduction system to evaluate a possible difference to the single use of a conventional nebulizer used in previous measurement setups.

REE elements were also analyzed using external calibration and internal normalization. The applied standards are described below.

Tab. 7 Gravimetrically prepared standard solutions

c (ng g^{-1})	Std. 1	Std. 2	Std. 3	Std. 4	Std. 5	Std. 6	Std. 7	Std. 8	Std. 9
Ce	0,001	0,005	0,011	0,027	0,053	0,105	0,265	0,512	1,063
Dy	0,001	0,005	0,011	0,027	0,053	0,105	0,265	0,512	1,063
Er	0,001	0,005	0,011	0,027	0,053	0,105	0,264	0,510	1,059
Eu	0,001	0,005	0,011	0,027	0,053	0,105	0,265	0,512	1,063
Gd	0,001	0,005	0,011	0,027	0,053	0,105	0,265	0,511	1,060
Ho	0,001	0,005	0,011	0,027	0,053	0,105	0,265	0,512	1,062

La	0,001	0,005	0,011	0,027	0,052	0,104	0,262	0,506	1,050
Lu	0,001	0,005	0,011	0,027	0,053	0,104	0,264	0,509	1,056
Nd	0,001	0,005	0,011	0,027	0,053	0,105	0,264	0,510	1,059
Pr	0,001	0,005	0,011	0,027	0,053	0,105	0,265	0,512	1,063
Sc	0,001	0,005	0,011	0,027	0,053	0,105	0,265	0,512	1,063
Sm	0,001	0,005	0,011	0,027	0,052	0,104	0,262	0,506	1,050
Tb	0,001	0,005	0,011	0,027	0,053	0,105	0,265	0,512	1,063
Th	0,001	0,005	0,011	0,027	0,053	0,105	0,265	0,511	1,060
Tm	0,001	0,005	0,011	0,027	0,052	0,104	0,263	0,507	1,053
Y	0,001	0,005	0,011	0,027	0,053	0,105	0,264	0,510	1,057
Yb	0,001	0,005	0,011	0,027	0,053	0,105	0,265	0,512	1,063

2.3 Measurement by using the Element 2

The same calibration standards as used for ICPQMS measurements were measured by using a HR-ICPSFMS, as well. As a consequence, the final results of the ICPSFMS were taken for further data evaluation as this instrument shows higher sensitivity as compared to an ICPQMS.

The standard measurement parameter as given in the following table were applied.

Tab. 8 Element 2 Settings

RF power	1400 W
nebuliser gas flow rate	1.1 L min-1
auxiliary gas flow	0.6 L min-1
plasma gas flow	14 L min-1
sample cone	nickel
skimmer cone	nickel
nebulizer	PFA
spray chamber	cyclonic spray chamber
sample uptake rate	100 µl min-1

2.4 Method validation

Method validation, traceability and uncertainty are important aspects concerning the measurements and should therefore be taken into account. While validation leads to the conclusion if the method used fits the purpose, traceability enables

comparison with other results as well as relation to stated references. Uncertainty budgets show the reliability and knowledge of measured data.

Method validation is needed as a quality system ensuring consistently produced valid data. The ISO/IEC 17025:2005 guideline points out the “general requirements for the competence of testing and calibration laboratories” including parameters defined below to ensure validation, traceability and uncertainty of measurement results. It is a process of establishing a method’s performance characterization, scope and limitation of a measurement procedure as well as identification of influences and plays a key role concerning the confidence of measured and evaluated data.

2.4.1 Working range

The working or measurement range is defined by the lowest and highest standard concentration of the external calibration. Calibration curves are calculated using linear regression and correlation factors ranging between 0.78 (Eu) and 1.00 (Ce, Er, Ho) could be achieved.

Element concentrations prepared for the external calibration for each instrument used for measurements are shown in the table below. Calculations were made according to the stock solution certificates (see appendix).

2.4.2 Sensitivity

This parameter is expressed by the slope of the calibration curve and represents the change in the response of the ELAN divided by the corresponding change in stimulus. Sensitivity can be specified either as $cps \cdot ng^{-1} \cdot g \cdot int(In)^{-1}$ or $cps \cdot ng^{-1} \cdot g$ (Currie, 1999).

2.4.3 Limit of Detection (LOD) and Limit of Quantification (LOQ)

Two important figures supporting the decision of elements chosen for statistical evaluation. While the LOD is calculated as three times the standard deviation of

the method blank and defines the smallest amount detectable during measurement, the LOQ even uses ten times the SD of the same blanks and ensures proper quantification limits for the analyte. Measurement data ranging below LOD levels has to be excluded from further data reprocessing.

$$Y_{LOD} = Y_{bl} + 3\,s_{bl} \rightarrow LOD = (Y_{LOD} - b_0)/b_1$$
$$Y_{LOQ} = Y_{bl} + 10\,s_{bl} \rightarrow LOQ = (Y_{LOQ} - b_0)/b_1$$

Equ. 1 Calculation of LOD and LOQ (Prohaska, 2010)

2.4.4 Traceability

This validation marker is needed to guarantee a transparent traceability of all data produced. As all of the data mentioned in this thesis is expressed in units according to SI (système international d'unités), results are comparable and comprehensible.

2.4.5 Uncertainty budget

The calculation of uncertainty budgets is a main contribution to increase confidence of the measurement results. According to GUM (Guide to the Expression of Uncertainty in Measurement), uncertainty is defined as a parameter which characterizes the dispersion of measured values taking into account possible uncertainty sources such as sample preparation, dilution procedures, storage conditions, instrument effects, reagent purity, matrix effects or interferences. It also takes into account the recovery, robustness, repeatability and reproducibility of measurement results.

In this thesis, method validation was carried out according to GUM, CITAC and EURACHEM guidelines either by using the GUM Workbench Pro (Metrodata GmbH, Germany) or Microsoft Excel and the Kragten approach. A model equation was established to find all sources of uncertainty. The expanded uncertainty U is obtained by multiplying the standard uncertainty u by a coverage factor k (=2, confidence level equals to 95%).

2.4.6 Selectivity

This parameter refers to the extent to which the method can be used to determine a specific analyte in a certain matrix without interferences from other components which might behave similarly.

2.4.7 Recovery

Recoveries represent the percentage of measured analyte amounts compared to expected and certified values, respectively. The closer recoveries are to 100%, the smaller is the bias in the procedure applied. Recoveries higher than 100% refer to successful preconcentration of the REE during sample preparation or – on the downside - to interfering substances or contamination resulting in higher detection values. The main contribution to recoveries close to 0% is loss of analytes. Recoveries are calculated using the following equation:

$$Recovery\ (\%) = {}^{c_{measured}}/_{c_{reference}} \times 100$$

Equ. 2 Calculation of Recovery (%)

2.5 Methods: REE Resin experiments

For all trials, the REE resin (Eichrom RE Resin, Triskem, Bruz, France) was used as agent to separate REEs from interfering substances and to preconcentrate the REEs under examination. Preconcentration steps are necessary when determining analytes in the ppb range to ensure proper measurement results. The resin was slurred in 2% nitric acid 24 hours before usage, stored at room temperature in a PE vessel and only used once. REE standard solutions containing each of the occurring REEs with the concentration of either 0.03 ng g^{-1}, which equals the expected range in coffee beans (Dietz et al., 1992) or 10 ng g^{-1} (for better sensitivity of the measurements) were prepared and enriched with a multi element standard containing Ba and Fe. Due to isobaric interferences, the washing step should eliminate Ba, while REEs are meant to be held back in the resin until elution. Coffee contains a fairly high amount of iron (Dietz et al., 1992) compared to its REE content and might result in interferences as well.

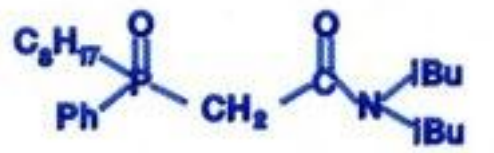

Fig. 8 Structure of CMPO (Triskem, 2011)

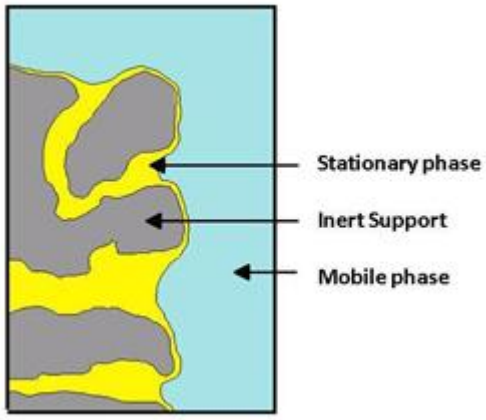

Fig. 9 Scheme of Resin Particle (Triskem, 2011)

The principle of this extraction chromatography is based on a combination of Octyl(phenyl)-N,N-di-isobutylcarbamoyl-methylphosphine oxide (CMPO), which

is the main component of this separation aid, and tributyl phosphate (TBP). All REEs ought to show similarly good retention and affinity to the resin in HNO_3, although acidities above 4M HNO_3 increase the affinity of heavy REEs to the resin, but decrease it for light REEs (Triskem, 2010). It should be taken into account that in previous studies iron shows an increasing retention in correlation with higher molarities of nitric acid and can be found in the matrix to be analyzed, the green coffee beans. If yttrium is found to be interfered in later data evaluation, it is most likely that the interfering substance is iron. (Dietz et al., 1992) On the other hand, it has to be mentioned that the resin might enhance the REE concentration, resulting in better sensitivity during the measurement (Esser et al., 1994). Moreover, when dealing with the original coffee bean digests, resin separation clears the sample solution, which later avoids blockage of the measurement instruments. Advantages of the use of the REE resin are the simple and cost efficient separation process which can be accomplished in a batch process in parallel vials as well as the resin's selectivity.

The first approach in this study was the optimization of separation conditions in a batch process to fully investigate the resin's potential for separation.

2.5.1 Offline setup with PP frits

The first offline setup – as can be seen in the figure below - consisted of 3 mL PP frits equipped with filters (10 µm pore size), previously washed in 5 % w/w and then stored in 1 % w/w nitric acid.

Fig. 10 Schematic overview of

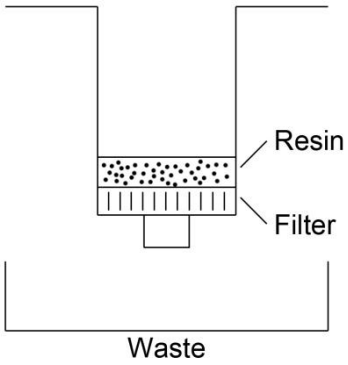

Fig. 11 Scheme of frit used for resin trials

The separation procedure was divided into the following steps:

- Conditioning with HNO_3 to prepare the resin for the separation process. Volumes used were 0.750 mL, 1.125 mL, 1.500 mL and 1.875 mL.
- The REE standard solution had to be diluted to the same molarity of HNO_3 used for the conditioning. Subsequently, the resin was coated with 2 mL of the sample (10 ng g^{-1} REE solution), added slowly drop by drop. Along with each sample batch, a blank using 2 % HNO_3 was prepared.
- Washing steps were always carried out using the same molarities as well as volumes as the HNO_3 used for conditioning.
- Three equal fractions, altogether summing up to the same volume used for conditioning or washing, were always eluted and collected separately.

After completion of the separating procedure, frits were flushed with 2 % HNO_3 and stored in 10 % HNO_3 for at least 24 hours and rinsed with HQ water before reuse. Filters were cleaned in an ultrasonic bath (Transsonic T80, Elma Hans Schmidbauer GmbH & Co. KG, Singen, Germany) for five to ten minutes and then stored in 5 % HNO_3.

This setup is very time-consuming due to the fact that all steps need to be monitored and executed manually. Also, setup conditions are hard to be kept consistent, as the bias is already quite high during the setup preparation concerning for instance the same amount of resin in the frits, the speed of manually applying the solutions etc.

2.5.2 Offline setup with resin column and peristaltic pump

The second offline setup was connected to a peristaltic pump (Perimax 12, Spetec, Erding, Germany), which was supposed to simulate parts of the online sample injection system. All resin columns were prepared at the laboratories of the Vienna University of Technology (TU Wien, Institute of Chemical Technologies and Analytics). PE tubes were primarily cut into approximately 10 cm pieces and equipped with punched out filters (10 µm pore size). Afterwards, different amounts of resin ranging between 100 µL and 200 µL were added to the columns with the help of a vacuum pump to enable dense packing. Finally, an-

other fitting filter was added on top of the resin to avoid percolation of the resin. To keep the resin damp, 1% HNO_3 was filled into the tubes. Columns were then stored in the fridge. The flow rate of the peristaltic pump was consistently maintained at 150. As offline systems and sample pretreatments are often very complicated, expensive and time-consuming, this setup was seen as first step towards the development of an online, automated preparation procedure. Previous studies showed that with online systems, up to 80% of sample preparation time could be saved (Zawisza et al., 2011).

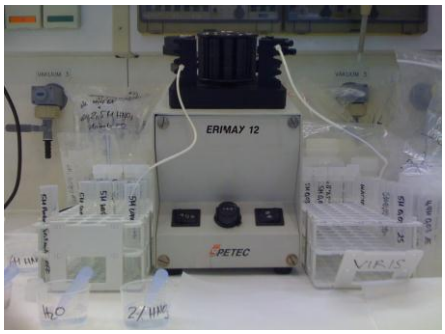

Fig. 12 Peristaltic Pump Experimental Setup

Volumes used for the separation process were 1.5 mL HNO_3 for conditioning, 2.0 mL sample solution, 1.5 mL HNO_3 for washing, 1.5 mL reagent for elution. When dealing with this setup, every single separation step output was collected to be able to determine whether REEs get lost during application of the sample solution or during the washing step. The second setup is still time consuming, as the columns need to be placed manually into the particular test tubes. The same column and therefore the same resin is used several times. Even though washing steps are included, the resin might lose its effectiveness. Advantages are the continuous flowrate and the approach to an automated online sample separation setup.

2.5.3 Online setup experiment

The third separation setup was an approach to an online ELAN DRC-e setup with a transient signal, but was not a main focus of this work. It would need further development to be usefully applied in this matter. In this case, the same columns used for the peristaltic pump setup were used.

For this special on-line testing procedure, a second internal standard consisting of 1ppb Ge and Rh was used additionally to Indium to monitor the effect of the sample solution, directly diluted prior to being injected to the spray chamber. Also, all reagents as well as the sample solutions used needed to be adjusted to approximately 6M to be comparable and to avoid damage of the measurement instrument caused by too high acidities. The setup can be seen in the pictures below. The hydride generator was used as additional mixing device of the solutions.

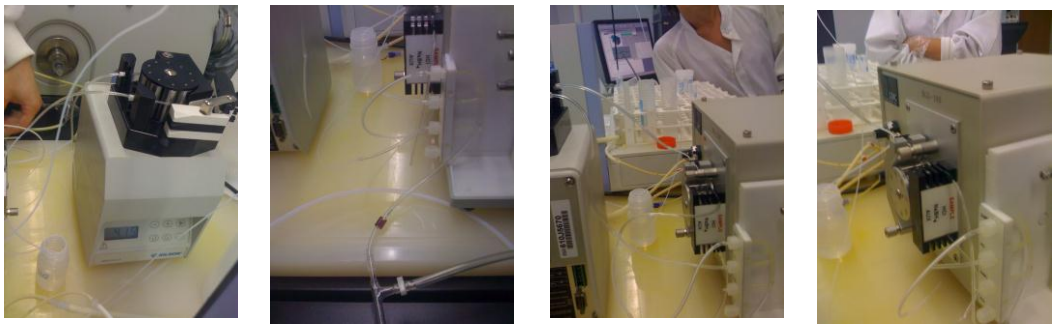

Fig. 13 Online setup

The commonly used PFA nebulizer was not working with this setup due to the high pressure resulting from the sample and internal standard solution mixture. A groovy nebulizer was applied instead with the downside being a loss of sensitivity. As the volume of this nebulizer was not sufficient either, the 2nd internal standard had been removed from the setup with only one internal standard remaining and no further dilution of the samples taking place. Another problem was the lack of impermeability of the filters in the resin columns, resulting in a nebulizer blockage due to resin particles. The online setup trial was stopped at this point and would need further development.

2.6 Analysis of Green Coffee Beans

Overall, 27 green coffee bean samples from three different continents were provided by the Center for Environmental Biology, Science Faculty of the University of Lisbon, Portugal for further analysis.

Tab. 9 Index and Origin of Samples

Assigned No.	Origin	Part of plant
1B	Ethiopia	Bean
1P	Ethiopia	Pulp
2	India	Bean
3	Ethiopia	Bean
4	Ethiopia	Bean
5B	Ethiopia	Bean
5H	Ethiopia	Husk
ICAT 253	Congo	Bean
ICAT 254	Vietname	Bean
ICAT 255	Ethiopia	Bean
ICAT 256	Guatemala	Bean
ICAT 257	Tanzania	Bean
ICAT 258	Hawaii Maui	Bean
ICAT 259	Timor	Bean
ICAT 260	Ethiopia	Bean
ICAT 261	Peru	Bean
ICAT 262	Ethiopia (Lake Tane)	Bean
ICAT 263	Laos	Bean
ICAT 264	India	Bean
ICAT 265	Hawaii Kona	Bean
ICAT 266	Colombia	Bean
ICAT 267	Brasil	Bean
ICAT 268	New Caledonia	Bean
ICAT 269	Uganda	Bean
ICAT 270	Peru	Bean
ICAT 271	Galapagos (Santa Cruz)	Bean
ICAT 272	Costa Rica	Bean

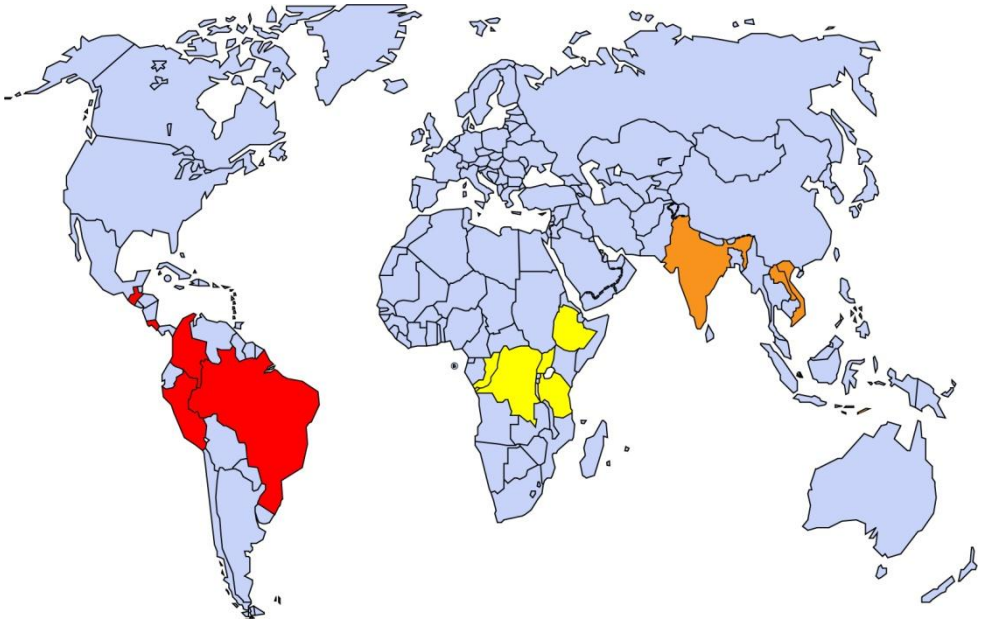

Fig. 14 Origin of Samples: Highlighted Countries

After indexing the samples, about 2 g of each bean sample were grinded in a ball mill between 30 and 60 minutes to obtain a homogenous powder, dried at 50°C (cabinet dryer, WTB Binder Labortechnik GmbH, Tuttlingen, Germany) over night and stored in petri dishes.

2.6.1 Microwave Digestion

All coffee samples were digested with a high performance microwave digestion unit (MLS 1200 mega, Leutkirch im Allgäu, Germany). 0.5 g of the grinded coffee samples was weighed into teflon bombs. 6 mL HNO_3 (65 % w/w) and 1 mL H_2O_2 (31 % w/w) were added until the coffee powder was fully soaked. The microwave digestion program consisted of the following time and heat levels:

Tab. 10 Microwave Digestion Program

Time	Power
2 min	250 W
2 min	0 W
6 min	250 W
5 min	400 W
5 min	600 W

10 min	Vented

After cooling of the samples, the now clear and transparent to yellowish colored digests were transferred into 50 mL PE bottles and gravimetrically weighed up to 20 g with sub boiled H_2O and then stored at room temperature.

The Teflon bombs were filled with 3 mL concentrated doubly sub boiled HNO_3 (65 % w/w) and had to undergo the same microwave program for cleaning reasons before reapplication.

Subsequently, 5 mL of each coffee bean digest were filtered (0.45 µm filters, Minisart RC 25, non-sterile, RC membrane, PP-housing) into PE tubes using a 5 mL syringe to avoid blocking of the measuring instrument due to solid particles remaining in the coffee digest.

Each sample was prepared in a two-fold determination and digestion blanks with 2 % HNO_3 instead of coffee powder were prepared with each digestion batch.

During multi-elemental analysis of the coffee bean samples by the ELAN, the following isotopes were screened: ^{7}Li, ^{9}Be, ^{10}B, ^{11}B, ^{23}Na, ^{24}Mg, ^{26}Mg, ^{27}Al, ^{39}K, ^{42}Ca, ^{43}Ca, ^{44}Ca, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{57}Fe, ^{59}Co, ^{58}Ni, ^{60}Ni, ^{63}Cu, ^{65}Cu, ^{66}Zn, ^{68}Zn, ^{69}Ga, ^{75}As, ^{77}Se, ^{82}Se, ^{85}Rb, ^{88}Sr, ^{98}Mo, ^{107}Ag, ^{109}Ag, ^{111}Cd, ^{114}Cd, ^{115}In (internal standard), ^{128}Te, ^{130}Te, ^{137}Ba, ^{138}Ba, ^{203}Tl, ^{205}Tl, ^{207}Pb, ^{208}Pb, ^{209}Bi, ^{238}Bi.

2.6.2 Sr/Rb separation

A Rb/Sr separation had to be accomplished for Sr isotope ratio measurements due to the fact that ^{87}Rb interferes with ^{87}Sr and therefore has to be eliminated in a separation procedure to minimize this bias. Additionally, other possibly interfering matrix elements will be removed, as well (e.g. Ca)

A Sr specific resin (EiChrom Industries, Inc., Darien, IL, USA) containing 4,4'(5')-di-t-butylcyclohexano 18-crown-6 in 1-octanol immobilized on an inert substrate with a pore size of 100 µm to 150 µm is used for solid phase extraction.

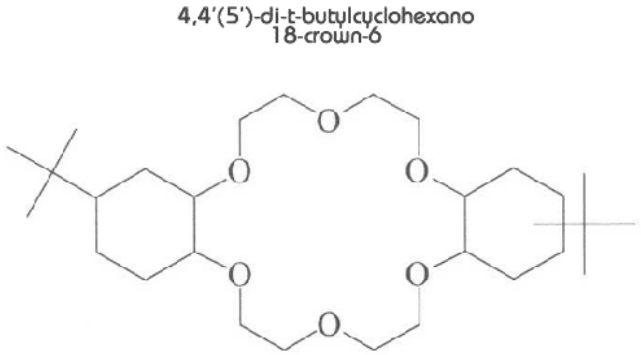

Fig. 15 Resin Structure (Eichrom Technologies Inc., 2010)

The separation procedure has been adapted from Brunner 2007, Swoboda et al. 2008 and Lang 2010 for the matrix used in this thesis. The resin was stored in 1% HNO_3 in the refrigerator. Before use, it was washed four times with sub boiled H_2O. The setup consistedof 3 mL PE frits equipped with 10 µm pore sized filters. The final bed volume of the resin summed up to approximately 0.5 mL per frit.

At the beginning of the separation procedure, the resin was conditioned with 0.5 mL 6M HNO_3 five times. Subsequently, 2 mL acidified coffee bean digests were added drop by drop manually to keep the flow rate below 1 mL min^{-1}. It is essential to proceed slowly to optimize the interaction between the resin and the Sr and to completely remove Rb. The sample application was followed by at least 16 times 0.5 mL 8M HNO_3 to wash out the unwanted matrix components. When working with coffee beans, numerous washing steps are necessary, as they contain a very high amount of Rb. Finally, the sample solution was eluted with four times 0.5 mL sub boiled H_2O and collected in previously cleaned PE tubes.

The achievement of sufficient Rb removal was confirmed by ICPQMS screening of the separated samples. Additional separation was applied if Rb residuals above 1% Rb (compared to the total Sr content) were detected. Satisfyingly separated sample solutions were diluted to a final Sr concentration ranging between 15 and 20 ng g^{-1} to provide optimal signal intensity and stability during HR-MC-ICPMS measurement. Determination of SRM 987 (certified $^{87}Sr/^{86}Sr$

ratio: 0.710263 ± 0.000016 ng g^{-1}) was performed every 6th sample to provide sufficient quality control of the measurement. Mass bias correction as well as correction of residual Rb traces were adopted from Ehrlich et al. (2001).
Total combined uncertainty budgets were calculated according to ISO/GUM and EURACHEM including blank correction, mass bias correction, Rb correction and the error of the measured ratio.

Sr isotope ratios analysis was performed with an MC-ICPSFMS equipped with 12 Faraday cups, a membrane desolvation unit and a PFA nebulizer for sample introduction. Instrumental parameters for the measurement are shown in the table below.

Tab. 11 Nu Plasma and Nebulizer settings

Nu Plasma settings	
Rf power	1,300 W
Auxiliary gas flow rate/cooling gas flow rate	0.75mL min^{-1}/13.0 mL min^{-1}
Sample uptake rate	100 µL min^{-1}
Sample/skimmer cone	Ni
Nebulizer	Perfluoralkoxy nebulizer
Sampling mode	6 blocks of 10 measurements
Measurement time	10 min per sample
Mass analyser pressure	<10-8 mbar
Background/baseline determination	HNO_3 (1% w/w)
Washout time	3 min
Axia mass/mass separation	86.05/0.5
Detection system	12 Faraday collectors
Cups L5 L4 L3 L2 L1	Ax H1 H2 H3 H4 H5 H6
Isotope ^{82}Kr ^{83}Kr ^{84}Sr ^{85}Rb	^{86}Sr ^{87}Sr ^{88}Sr
DSN-100 nebulizer settings	
Nebulizer pressure	2 bar (30 psi)
Hot gas flow	0.7 – 0.9 L min^{-1}
Membrane gas flow	4 L min^{-1}
Spray chamber temperature	112 °C

Membrane temperature	122 °C

2.6.3 Statistical data evaluation

Statistical data evaluation was performed using SPSS version 18.0 (SPSS Inc., Chicago). An anti-image correlation matrix with a measure of sampling adequacy (MSA) was applied to corroborate the results of the principal component analysis (PCA). Also, a univariate ANOVA analysis was done to ensure the significant separation of the variables/elements. Scree plots were produced to determine significant factors, although only factor one and two were considered.

In addition to the PCA, the data was classified by maximizing the variance between groups as well as minimizing the variance within groups via canonical discriminant analysis (DA) using the U-method.

The Eigenvalue – expressing the variance – was set ‘above 1’ in all cases. Values below the LOD were excluded from statistical analysis and all results are based on mean values of the twofold sample determination and of the different isotopes of an element respectively.

3 Results and Discussion

3.1 Optimization of the separation using Rare Earth Element resin

The aim of this investigation was to optimize the separation procedure using a newly developed rare earth elements resin. Aim of using the resin was the potential for:

- Matrix separation to remove possible interferences and reduce matrix effects
- Separation of REE into groups to avoid oxide interferences of REE on other REE
- Pre-concentration of REE in order to facilitate the measurement

As the resin was only classified for high concentration levels so far, the investigation of using REE levels as found in coffee digest was challenging and not predictable.

As a consequence, several parameters were examined in this progress, such as:

- The ideal amount of resin used for the separation procedure: Different bed volumes ranging from 50 µL to 200 µL of resin were put in the PP frits or the resin columns in the peristaltic pump setup, respectively.

Concerning the ideal amount of resin used for the separation procedure, no significant differences could be found when dealing with numerous amounts of resin, leading to the conclusion that at least 100 µg of resin (the least amount applied) should be sufficient enough to hold onto all REEs from the sample solution.

- The acidity of the solutions used for the conditioning, sample provision, washing as well as elution

- The acidity of HNO_3 used for the conditioning step: Throughout the sample preparation variations, acidities ranging from 0.015 molar HNO_3 to 10 molar HNO_3 were applied, all standard solutions gravimetrically diluted with subboiled H_2O.

- The acidity of the sample solution (prepared REE standard to be able to monitor and evaluate the results): If not mentioned otherwise – the sample solutions were pretreated to equal the acid concentration of HNO_3 used for the conditioning step.

- The acidity of HNO_3 for the washing step to wash out unwanted substances while keeping the wanted substances held back in the resin also varied between 0.015 and 10 molar HNO_3.

- The solution of choice for the elution step was chosen from subboiled water, 0.015 molar HNO_3 and 0.03 molar HNO_3.

The table below shows the recoveries of cerium as a representative for the group of rare earth elements. It can be concluded that the lower the HNO_3 molarity used in the separation process and the lower the acidity of the elution agent, the higher recoveries can be achieved. Therefore, when working with green coffee bean digests, they should be diluted to achieve lower acidities to improve measurement results. The solution of choice for the elution step turned out to be subboiled H_2O.

Tab. 12 Comparison of mean recoveries (%) of Ce in respect to molarity of HNO3 and elution agents

Elution with:	**H_2O**	**0.015M HNO_3**	**0.03M HNO_3**
M HNO_3 for conditioning and washing (below)	Recovery Ce [mean, %]	Recovery Ce [mean, %]	Recovery Ce [mean, %]
6M	32,75	26,16	19,30
8M	14,61	2,23	1,30
10M	0,18	0,18	0,08

Additional conclusions lead to the fact that even higher HNO_3 concentrations need to be tested as 10M HNO_3 approximately equals the molarity of digested coffee beans which should be subject of analysis in the future. ^{232}Th and ^{45}Sc showed lowest recoveries and could not be detected at all at some points due to interference problems.

- The capability of the resin to pre-concentrate REEs to subsequently enhance measurement sensitivity.

The capability of the used resin to preconcentrate REEs could not be proven as recoveries were always below 100%. The resin had no significant effect at the applied concentration levels.

- The capability of the resin to fractionate heavy (Er – Lu), middle (Eu – Gd) and light (La – Eu) REEs as suggested in the literature (Baker et al. 2002), whereas heavy REEs are supposed to elute earlier than middle and light REEs. To prove this hypothesis, three elution fractions were collected.

The capability of the resin to fractionate heavy, middle and light REEs could also not be observed. Regarding the fractionation of high, middle and light rare earth elements, one representative of each class was chosen for comparison. According to the table below, ^{175}Lu should be eluted first, followed by ^{164}Dy and ^{89}Y. No fractionated elution can be verified, as middle and light isotopes are eluted in the first fraction as well. There is no significant difference regarding the mass of the isotopes and their elution time.

Tab. 13 Results for a set of REE in subsequent fractions

	1st fraction 0.50M 0.25 ml	2nd fraction 0.50M 0.25 ml	3rd fraction 0.50M 0.25 ml	1st fraction 6.00M 0.25 ml	2nd fraction 6.00M 0.25 ml	3rd fraction 6.00M 0.25 ml
^{175}Lu (ng/g)	0,21	0,67	0,58	0,03	0,23	0,23
^{164}Dy (ng/g)	0,68	0,36	0,03	0,56	0,42	0,08
^{89}Y (ng/g)	0,13	0,04	0,00	0,33	0,13	0,02

- The capability of the resin to separate barium and iron from the REE solutions as these substances lead to interferences later on.

Barium separation could be achieved according to the calculated recoveries in the final elution solutions. There is no indication that the concentration of HNO_3 / the sample plays a significant role in this matter.

Tab. 14 Ba recovery in the elution solutions

HNO_3/ Sample concentration	**Ba Recovery (%)**
0.5 M	0.12
1.0 M	0,19
2.5 M	0.18
4.0 M	0.17
5.0 M	< 0.1
6.0 M	0.15

As a conclusive summary of the optimization procedure, it turned out that the resin was not suitable for the successful preparation of the green coffee bean digests in order to facilitate the REE measurements by ICPMS: As a consequence, the REE pattern were determined in the selected samples according to the applied standard procedure, i.e. direct REE analysis after digestion using external calibration and internal normalization.

3.2 Application of a membrane desolvation unit (APEX)

The method validation parameter (see. 3.3) were both evaluated for the regular setup (PFA nebulizer with cyclonic spray chamber) as well as with the APEX, also using a PFA nebulizer but with a cooled spray chamber and an additional membrane desolvation unit. The validation parameters did not show any significant difference and thus, the nebulizer cannot be seen of major advantage in common REE analysis. The validation parameters in the following chapter are derived by the common setup as the latter is used throughout the measurement of the green coffee bean samples.

3.3 REE analysis by ICPQMS - method validation

As already mentioned before, method validation is needed to indicate the suitability of a method.

3.3.1 Working range

Element concentrations of the REE standard solutions which were used for further evaluation ranged from 0.001 to 1.00 ng g^{-1}.

3.3.2 Sensitivity

The absolute sensitivity in cps for the ICPQMS system are given in table 14.
The sensitivity was calculated as slope of the non – normalized count rates and calculated for 100% abundance.

Tab. 15 Absolute sensitivity for REE measurements

Analyte	sensitivity (cps / ng g^{-1})
Ce	2.15E+05
Dy	2.24E+05
Er	2.16E+05
Eu	2.31E+05
Gd	2.20E+05
Ho	2.09E+05
La	2.02E+05
Lu	2.22E+05
Nd	2.50E+05
Pr	2.39E+05
Sc	6.70E+04

Sm	2.45E+05
Tb	2.16E+05
Th	2.86E+05
Tm	2.16E+05
Y	1.55E+05
Yb	2.36E+05

It is evident from the data that REE ranging from atomic number 58 – 71 show similar sensitivity in ICPMS.

3.3.3 LOD/LOQ

LOD/LOQ were determined according to the equations given in 2.3.3. and are shown in table 14.

Tab. 16 LOD and LOQ of REE measured by ICPQMS

Analyte	**Isotope mass**	**LOD** pg g^{-1}	**LOQ** pg g^{-1}
Ce	140	1.82	5.46
Dy	164	0.10	0.30
Er	166	0.17	0.50
Eu	153	0.06	0.17
Gd	158	0.14	0.42
Ho	165	0.05	0.15
La	139	0.05	0.16
Lu	175	0.03	0.09
Nd	142	1.00	3.00
Pr	141	0.01	0.02
Sc	45	15	45
Sm	152	0.18	0.55
Tb	159	0.04	0.13
Th	232	0.20	0.60
Tm	169	0.01	0.02
Y	89	0.06	0.18
Yb	174	0.06	0.18

3.3.4 Traceability

Traceability of the results was achieved by using reference standards as calibrants, which were certified for their REE content. All reference standards were traceable to SI according to their written description provided with the bottles. All sample preparation was accomplished by using a balance, which is gauged on a regular basis against a standard weight.

3.3.5 Uncertainty

Uncertainty estimations were calculated according to the following model equation:

$$C = \left[\frac{(I/I_{In}}{k} - C_{Blank}\right] x \frac{w_{Dil}}{ws}$$

Equ. 3 Model equation

where:
C = final concentration
I = measured intensity of the sample
I_{In} = measured ^{115}In intensity in the sample
k = slope of the calibration curve (forced through zero)
w_{Dil} = dilution weight
ws = weighted sample

The uncertainty contribution of the standard deviation of the single measurement intensities was calculated to be the major contributor to the uncertainty. Therefore the average RSD of REE measurements was taken as uncertainty estimate and is given in the following table.

Tab. 17 Uncertainty estimates for REE

Concentration range	Uncertainty estimation in % (RSU)
> 0.1 ng g^{-1}	5 %
0.5 pg g^{-1} – 0.1 ng g^{-1}	20%

3.4 Results of the analysis of the green coffee beans

The green coffee beans were analyzed for the REE content, which was the major task within this study. In addition, multi-element data were determined as described in chapter 2.5.1. along with Sr isotope ratios. In addition, light isotope data were provided by the University of Lisbon for increasing the information content of the data.

3.4.1 REE measurements

The REE data for the investigated coffee bean samples are given in the appendix (6.3.1). The measurements were accomplished using an Element 2 ICPSFMS as it provided higher sensitivity for the analysis of REE. It is evident,

that most of the concentrations were below the LOD and only a selected number of REE could be taken for further evaluation (chapter 3.5). These results show evidently, that a further development for pre-concentration and matrix separation has to be accomplished, which was unfortunately not successful within this work.

3.4.2 Multielement data

The multielement data, which were analyzed for the coffee samples are given in the appendix (6.3.2). Only data above the LOD were taken into account for further evaluation. It is evident from the data, that a number of elements vary significantly between the different regions. If these differences are reproducible and selective for a certain region cannot be defined exactly as statistical data are missing.

3.4.3 Sr isotope data

The Sr isotopic data measured within this study are given in the appendix (6.3.3). The data was taken for further evaluation in order to discriminate the samples for their geographic origin. It is evident from the data, that significant differences are seen depending on the growing region. In many cases, different adjacent regions show similar geological properties and therefore similar isotopic composition. Otherwise, small regional differences could be seen.

3.5 Statistical data evaluation

Statistical data evaluation was performed using SPSS version 18.0 (SPSS Inc., Chicago). An anti-image correlation matrix with a measure of sampling adequacy (MSA) was applied to corroborate the results of the principal component analysis (PCA). Also, a univariate ANOVA analysis was done to ensure the significant separation of the variables/elements. Scree plots were produced to determine significant factors, although only factor one and two were considered.

In addition to the PCA, the data was classified by maximizing the variance between groups as well as minimizing the variance within groups via canonical discriminant analysis (DA) using the U-method.

The Eigenvalue – expressing the variance – was set ‘above 1’ in all cases. Values below the LOD were excluded from statistical analysis and all results are based on mean values of the twofold sample determination and of the different isotopes of an element respectively.

3.5.1 Determination of the geographical origin with REE data

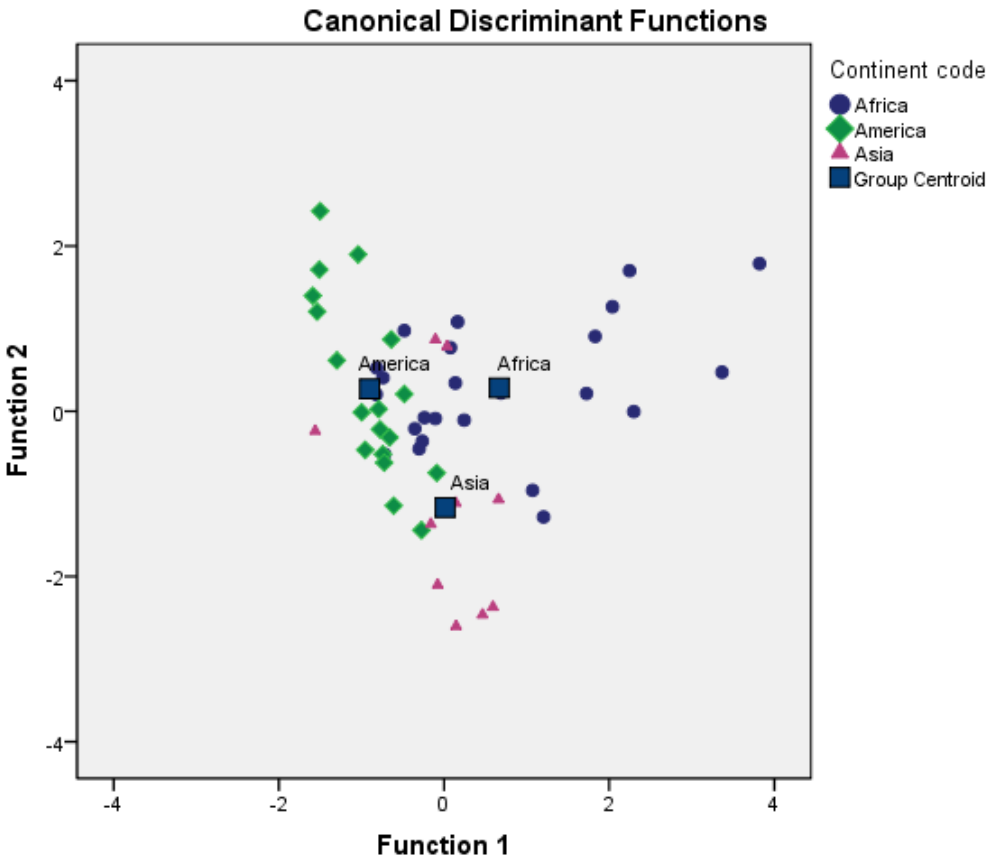

Fig. 16 Discriminant analysis of REE data

If only taking the REE element pattern into account, it was not possible to significantly distinguish between the continents of origin of the coffee bean samples. The major cause of the failure was the limited amount of information as most of

the elemental concentrations were below LOD. Only 67,3 % of the original samples could be classified correctly.

Tab. 18 Classification Results of REE data

Classification Results[b,c]

		Continent code	Predicted Group Membership			
			Africa	America	Asia	Total
Original	Count	Africa	13	7	4	24
		America	0	15	3	18
		Asia	2	1	7	10
	%	Africa	54,2	29,2	16,7	100,0
		America	,0	83,3	16,7	100,0
		Asia	20,0	10,0	70,0	100,0
Cross-validated[a]	Count	Africa	6	10	8	24
		America	1	12	5	18
		Asia	3	1	6	10
	%	Africa	25,0	41,7	33,3	100,0
		America	5,6	66,7	27,8	100,0
		Asia	30,0	10,0	60,0	100,0

a. Cross validation is done only for those cases in the analysis. In cross validation, each case is classified by the functions derived from all cases other than that case.

b. 67,3% of original grouped cases correctly classified.

3.5.2 Determination of the geographical origin with multi-element data

As the figure below indicates, it is possible to clearly distinguish the sample origins regarding the continents with Eigenvalues of the first two canonical discriminant functions of 15.879 and 21.350, respectively. As a consequence multi-element pattern are a straight forward and easily achievable factor for origin determination.

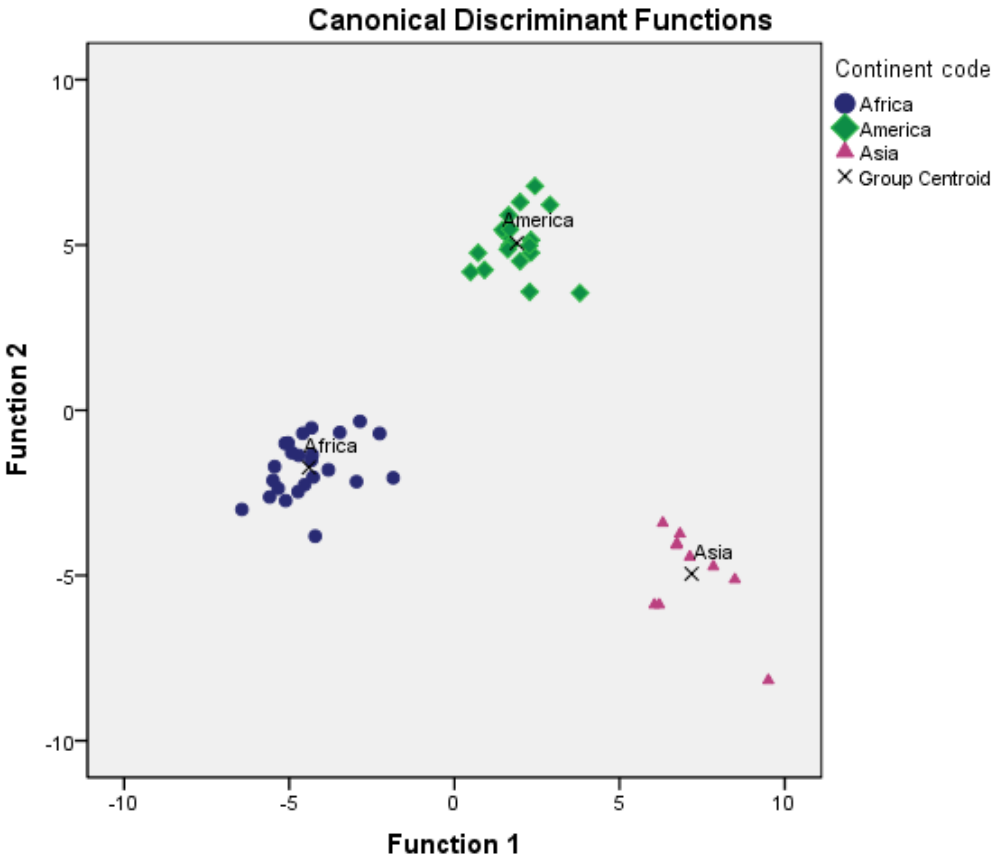

Fig. 17 Discriminant analysis of multielement data

It is evident, that 100% of the original samples could be classified correctly.

Tab. 19 Classification Results of multi-element data

		Continent code	Predicted Group Membership			
			Africa	America	Asia	Total
Original	Count	Africa	24	0	0	24
		America	0	18	0	18
		Asia	0	0	10	10
	%	Africa	100,0	,0	,0	100,0
		America	,0	100,0	,0	100,0
		Asia	,0	,0	100,0	100,0

3.5.3 Determination of the geographical origin combining multi-element, Sr isotope ratio and light stable isotope ratio data

In this statistical evaluation, all multi-element (this work), strontium isotope (this work) and light stable isotope ratios data (provided by the University of Lisbon) of the samples ICAT 253 to ICAT 272 were combined to show the potential to determine the geographical origin of green coffee beans by means of a multi-data approach. REE data were not used due to insufficient classification power.

The initial Eigenvalue regarding the multi-element data shows that the first component has the most influence with 19.56 % and the second 15.34 %. Taking the dataset with strontium isotope ratios and light stable isotope ratios into account, the influence of the first component was decreased to 18.12 % and the second component to 7.68 %. Strontium and the light stable isotope ratios express their influence at the second and third component. The scree plots of both approaches show the same drift of the affected components.

Tab. 20 Eigenvalues of the multi-element, light stable isotope and Sr ratio data

Eigenvalues

Function	Eigenvalue	% of Variance	Cumulative %	Canonical Correlation
1	18,117[a]	70,2	70,2	,973
2	7,681[a]	29,8	100,0	,941

a. First 2 canonical discriminant functions were used in the analysis.

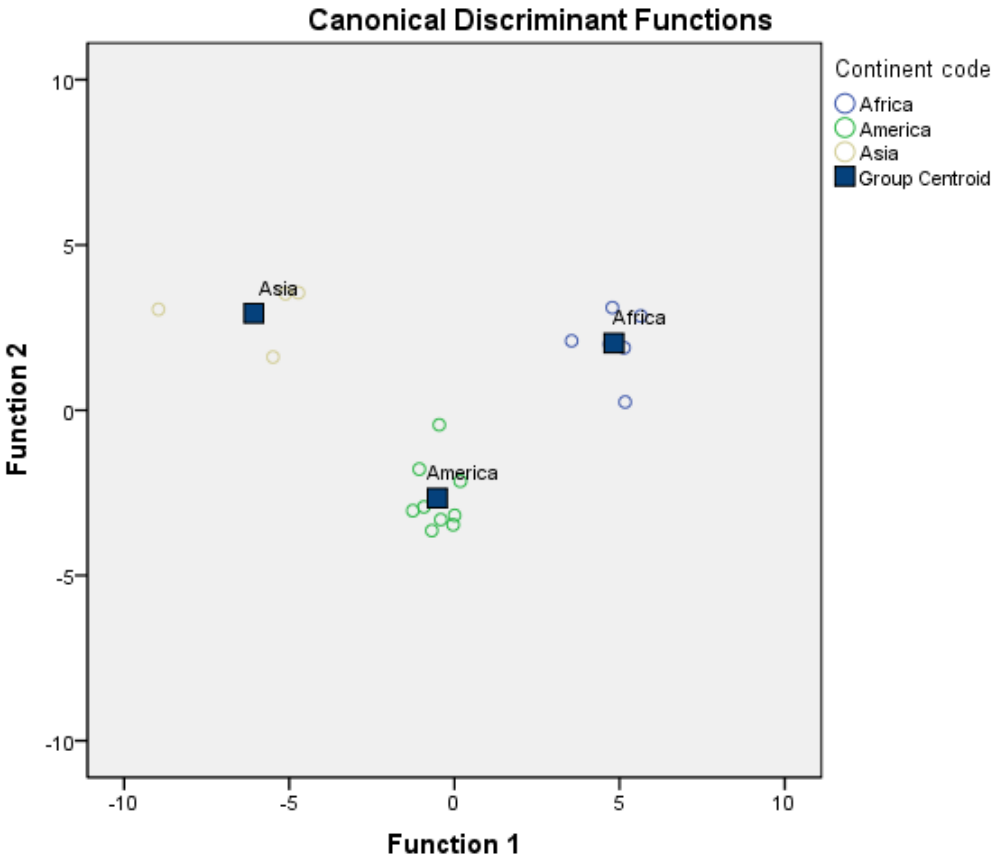

Fig. 18 Discriminant analysis of multielement, light stable isotope and Sr isotope ratio data

While coffees originating from Africa and America can still be classified satisfyingly, Asian samples don't show a clear grouping around their centroid. The grouping is expected and can easily be explained as a result of sample heterogeneity due to different growing regions within one continent.

4 Conclusive summary, Outlook and Future Perspectives

During this work, the time consuming development and full evaluation and validation of REE separation by means of a new resin clearly failed as the resin did not show the expected properties for the sample pretreatment of REE solutions in the low ng g^{-1} range and below. Whereas the resin showed satisfactory results for higher concentration levels, it clearly is not suitable to accomplish matrix separation and pre-concentration as a prerequisite for accurate REE determination at the < ng g^{-1} REE concentration levels as found in the green coffee digests. Therefore, the resin could not be applied for the further study. As a consequence, the investigated REE concentrations in the green coffee bean samples were too low in order to be used for origin discrimination. Nonetheless, REE still imply the potential to discriminate food commodities for their geographic origin. Therefore, further investigations have to be accomplished in order to develop or further optimize chromatographic separation procedures.
In addition, a special focus needs to be put on the development of appropriate reference materials for solid food such as coffee beans to ensure proper method validation.

It is nonetheless evident from the results, that multi-element data along with isotopic data give the best discriminators. It has to be seen clearly that a combination of data is the most adequate approach to trace the provenance of food.
In future approaches, collaborative efforts have to be undertaken in order to increase the statistical number of results in order to obtain satisfactory findings about sources. As a consequence, all obtained data should be consolidated within one database for future evaluation strategies. A holistic approach and the combination of various analysis approaches and data bases will lead to valid and confident results.

In order to successfully interpret the data, fractionation processes of elemental or isotopic uptake have to be conceived and to my understanding, further research is necessary in order to obtain reliable data. Therefore, many aspects besides the actual food matrix should be taken into account and compared when dealing with proof of origin, such as soil composition, precipitation or climate.

As the accomplished survey was performed on green coffee beans, it is definitely of interest to which extent various processing steps are influencing elemental or isotopic fingerprints. This consideration is even more important taking intensely processed food into account.

It can be concluded, that the establishment of elemental and isotopic fingerprints of food using ICPMS techniques is a very promising field and key to successful origin determination of food.

5 Bibliography

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6 Appendix

6.1 REE – isotopes and their interferences

REEs in coffee beans and their interfering species (asterisk (*) indicates isotopes selected for measurement due to their abundance and lowest interferences)

Symbol	Abundance (%)	Interferences	Interfering Mass
^{45}Sc*	100.00	$^{22}Ne^{23}Na$	44,981
		$^{9}Be^{36}Ar$	44,979
		$^{7}Li^{38}Ar$	44,978
^{89}Y*	100.00	$^{53}Cr^{36}Ar$	88,908
^{138}La	0.09	^{138}Ba	137,905
		^{138}Ce	137,906
^{139}La*	99.91	$^{9}Be^{130}Ba$	138,912
		$^{7}Li^{132}Ba$	138,921
^{136}Ce	0.19	^{136}Ba	135,905
		$^{100}Mo^{36}Ar$	135,875
		$^{98}Mo^{38}Ar$	135,868
		$^{6}Li^{130}Ba$	135,921
^{138}Ce	0.25	^{138}Ba	137,905
		^{138}La	137,907
		$^{100}Mo^{38}Ar$	137,870
		$^{98}Mo^{40}Ar$	137,867
		$^{6}Li^{132}Ba$	137,920
^{140}Ce*	88.45	$^{100}Mo^{40}Ar$	139,869
		$^{10}B^{130}Ba$	139,919
		$^{6}Li^{134}Ba$	139,920
^{142}Ce	11.11	^{142}Nd	141,908
		$^{10}B^{132}Ba$	141,918
		$^{7}Li^{135}Ba$	141,922
		$^{6}Li^{138}Ba$	141,920
^{141}Pr*	100.00	$^{11}B^{130}Ba$	140,916
		$^{9}Be^{132}Ba$	140,917
		$^{7}Li^{134}Ba$	140,920

		$^{6}Li^{135}Ba$	140,921
^{142}Nd*	27.20	^{142}Ce	141,909
		$^{10}B^{132}Ba$	141,918
		$^{7}Li^{135}Ba$	141,922
		$^{6}Li^{136}Ba$	141,920
^{143}Nd	12.20	$^{11}B^{132}Ba$	142,914
		$^{9}Be^{134}Ba$	142,917
		$^{7}Li^{136}Ba$	142,920
		$^{6}Li^{137}Ba$	142,921
^{144}Nd	23.80	^{144}Sm	143,912
		$^{10}B^{134}Ba$	143,917
		$^{9}Be^{135}Ba$	143,918
		$^{7}Li^{137}Ba$	143,922
		$^{6}Li^{138}Ba$	143,921
^{145}Nd	8.30	$^{109}Ag^{36}Ar$	144,873
		$^{107}Ag^{38}Ar$	144,868
		$^{11}B^{134}Ba$	144,914
		$^{10}B^{135}Ba$	144,919
		$^{7}Li^{138}Ba$	144,921
^{146}Nd*	17.20	$^{11}B^{135}Ba$	145,915
		$^{10}B^{136}Ba$	145,917
^{148}Nd	5.70	^{148}Sm	147,915
^{150}Nd	5.60	$^{11}B^{137}Ba$	147,915
		$^{10}B^{138}Ba$	147,918
^{145}Pm	not present in nature	-	-
^{144}Sm	3.07	^{144}Nd	143,910
		$^{10}B^{134}Ba$	143,917
		$^{9}Be^{135}Ba$	143,918
		$^{7}Li^{137}Ba$	143,922
		$^{6}Li^{138}Ba$	143,920
^{147}Sm	14.99	$^{109}Ag^{38}Ar$	146,867
		$^{107}Ag^{40}Ar$	146,867
		$^{11}B^{136}Ba$	146,914
		$^{10}B^{137}Ba$	146,919
		$^{9}Be^{138}Ba$	146,917
^{148}Sm*	11.24	^{148}Nd	147,917

		$^{11}B^{137}Ba$	147,915
		$^{10}B^{138}Ba$	147,918
^{149}Sm*	13.82	$^{113}In^{36}Ar$	148,872
		$^{109}Ag^{40}Ar$	148,867
		$^{11}B^{138}Ba$	148,915
^{150}Sm	7.38	^{150}Nd	149,921
^{152}Sm	26.75	^{152}Gd	151,920
^{154}Sm	22.75	^{154}Gd	153,921
		$^{24}Mg^{130}Ba$	153,891
^{151}Eu	47.81	$^{115}In^{36}Ar$	150,871
		$^{113}In^{38}Ar$	150,867
^{153}Eu*	52.19	$^{115}In^{38}Ar$	152,867
		$^{113}In^{40}Ar$	152,866
^{152}Gd	0.20	^{152}Sm	151,919
^{154}Gd	2.18	^{154}Sm	153,922
		$^{24}Mg^{130}Ba$	153,891
^{155}Gd	14.80	$^{115}In^{40}Ar$	154,866
		$^{25}Mg^{130}Ba$	154,892
^{156}Gd	20.47	^{156}Dy	155,924
		$^{120}Te^{36}Ar$	155,872
		$^{26}Mg^{130}Ba$	155,889
		$^{24}Mg^{132}Ba$	155,890
^{157}Gd	15.65	$^{27}Al^{130}Ba$	156,888
		$^{25}Mg^{132}Ba$	156,890
^{158}Gd*	24.84	^{158}Dy	157,924
		$^{122}Te^{36}Ar$	157,870
		$^{120}Te^{38}Ar$	157,867
		$^{28}Si^{130}Ba$	157,883
		$^{26}Mg^{132}Ba$	157,888
		$^{24}Mg^{134}Ba$	157,889
^{160}Gd	21.86	^{160}Dy	159,925
		$^{124}Te^{36}Ar$	159,870
		$^{122}Te^{38}Ar$	159,866

		$^{30}Si^{130}Ba$	159,880
		$^{28}Si^{132}Ba$	159,882
		$^{26}Mg^{134}Ba$	159,887
		$^{25}Mg^{135}Ba$	159,892
		$^{24}Mg^{136}Ba$	159,890
^{159}Tb*	100.00	$^{123}Te^{36}Ar$	158,782
		$^{29}Si^{130}Ba$	158,883
		$^{27}Al^{132}Ba$	158,887
		$^{25}Mg^{134}Ba$	158,890
		$^{24}Mg^{135}Ba$	158,891
^{156}Dy	0.06	^{156}Gd	155,922
		$^{120}Te^{36}Ar$	155,871
		$^{26}Mg^{130}Ba$	155,889
		$^{24}Mg^{132}Ba$	155,890
^{158}Dy	0.10	^{158}Gd	157,924
		$^{122}Te^{36}Ar$	157,870
		$^{120}Te^{38}Ar$	157,867
		$^{28}Si^{130}Ba$	157,883
		$^{26}Mg^{132}Ba$	157,888
		$^{24}Mg^{134}Ba$	157,889
^{160}Dy	2.34	^{160}Gd	159,925
		$^{124}Te^{36}Ar$	159,870
		$^{120}Te^{40}Ar$	159,866
		$^{30}Si^{130}Ba$	159,880
		$^{28}Si^{132}Ba$	159,882
		$^{26}Mg^{134}Ba$	159,887
		$^{25}Mg^{135}Ba$	159,892
		$^{24}Mg^{136}Ba$	159,890
^{161}Dy	18.91	$^{125}Te^{36}Ar$	160,872
		$^{123}Te^{38}Ar$	160,867
		$^{29}Si^{132}Ba$	160,882
		$^{27}Al^{134}Ba$	160,886
		$^{26}Mg^{135}Ba$	160,888
		$^{25}Mg^{136}Ba$	160,890
		$^{24}Mg^{137}Ba$	160,891
^{162}Dy	25.51	^{162}Er	161,929
		$^{126}Te^{36}Ar$	161,871
		$^{124}Te^{38}Ar$	161,866
		$^{30}Si^{132}Ba$	161,879
		$^{28}Si^{134}Ba$	161,881

		$^{27}Al^{135}Ba$	161,887
		$^{26}Mg^{136}Ba$	161,887
		$^{25}Mg^{137}Ba$	161,892
		$^{24}Mg^{138}Ba$	161,890
^{163}Dy*	24.90	$^{125}Te^{38}Ar$	162,867
		$^{123}Te^{40}Ar$	162,867
		$^{29}Si^{134}Ba$	162,881
		$^{28}Si^{135}Ba$	162,883
		$^{27}Al^{136}Ba$	162,886
		$^{26}Mg^{137}Ba$	162,888
		$^{25}Mg^{138}Ba$	162,891
^{164}Dy*	28.18	^{164}Er	163,930
		$^{30}Si^{134}Ba$	163,878
		$^{29}Si^{135}Ba$	163,882
		$^{28}Si^{136}Ba$	163,881
		$^{27}Al^{137}Ba$	163,887
		$^{26}Mg^{138}Ba$	163,888
^{165}Ho*	100.00	$^{125}Te^{40}Ar$	164,867
		$^{30}Si^{135}Ba$	164,879
		$^{29}Si^{136}Ba$	164,881
		$^{28}Si^{137}Ba$	164,883
		$^{27}Al^{138}Ba$	164,887
^{162}Er	0.14	^{162}Dy	161,927
		$^{30}Si^{132}Ba$	161,879
		$^{28}Si^{134}Ba$	161,881
		$^{26}Mg^{136}Ba$	161,887
		$^{25}Mg^{137}Ba$	161,891
		$^{24}Mg^{138}Ba$	161,890
^{164}Er	1.61	^{164}Dy	163,929
		$^{30}Si^{134}Ba$	163,878
		$^{29}Si^{135}Ba$	163,882
		$^{28}Si^{136}Ba$	163,881
		$^{27}Al^{137}Ba$	163,887
		$^{26}Mg^{138}Ba$	163,888
^{166}Er*	33.61	$^{130}Ba^{36}Ar$	165,874
		$^{128}Te^{38}Ar$	165,867
		$^{30}Si^{36}Ba$	165,878
		$^{29}Si^{137}Ba$	165,882
		$^{28}Si^{138}Ba$	165,882
^{167}Er*	22.93	$^{30}Si^{137}Ba$	166,880

		$^{29}Si^{138}Ba$	166,882
^{168}Er	26.78	^{168}Yb	167,933
		$^{132}Ba^{36}Ar$	167,873
		$^{130}Ba^{38}Ar$	167,869
		$^{128}Te^{40}Ar$	167,867
		$^{30}Si^{138}Ba$	167,879
^{170}Er	14.93	^{170}Yb	169,935
		$^{134}Ba^{36}Ar$	169,872
		$^{132}Ba^{38}Ar$	169,867
		$^{130}Te^{40}Ar$	169,868
		$^{130}Ba^{40}Ar$	169,869
		$^{40}K^{130}Ba$	169,870
		$^{40}Ca^{130}Ba$	169,869
		$^{38}Ar^{132}Ba$	169,868
^{169}Tm*	100.00	$^{39}K^{130}Ba$	168,869
^{168}Yb	0.13	^{168}Er	167,932
		$^{132}Ba^{36}Ar$	167,871
		$^{130}Te^{38}Ar$	167,872
		$^{130}Ba^{38}Ar$	167,868
		$^{128}Te^{40}Ar$	167,866
		$^{38}Ar^{130}Ba$	167,869
		$^{30}Si^{138}Ba$	167,879
^{170}Yb	3.04	^{170}Er	169,935
		$^{134}Ba^{36}Ar$	169,872
		$^{132}Ba^{38}Ar$	169,868
		$^{130}Te^{40}Ar$	169,869
		$^{130}Ba^{40}Ar$	169,869
		$^{40}Ar^{130}Ba$	169,869
		$^{40}K^{130}Ba$	169,870
		$^{40}Ca^{130}Ba$	169,869
		$^{38}Ar^{132}Ba$	169,868
^{171}Yb	14.28	$^{135}Ba^{36}Ar$	170,873
		$^{41}K^{130}Ba$	170,868
		$^{39}K^{132}Ba$	170,869
^{172}Yb*	21.83	$^{136}Ba^{36}Ar$	171,872
		$^{136}Ce^{36}Ar$	171,875
		$^{134}Ba^{38}Ar$	171,867
		$^{132}Ba^{40}Ar$	171,867
		$^{42}Ca^{130}Ba$	171,865
		$^{40}Ar^{132}Ba$	171,867

		$^{40}K^{132}Ba$	171,869
		$^{40}Ca^{132}Ba$	171,868
		$^{38}Ar^{134}Ba$	171,867
^{173}Yb	16.13	$^{137}Ba^{36}Ar$	172,873
		$^{135}Ba^{38}Ar$	172,868
		$^{43}Ca^{130}Ba$	172,865
		$^{41}K^{32}Ba$	172,867
		$^{38}K^{134}Ba$	172,868
		$^{38}Ar^{135}Ba$	172,868
^{174}Yb*	31.83	$^{138}Ba^{36}Ar$	173,873
		$^{138}La^{36}Ar$	173,875
		$^{138}Ce^{38}Ar$	173,874
		$^{134}Ba^{40}Ar$	173,867
		$^{44}Ca^{130}Ba$	173,862
		$^{42}Ca^{132}Ba$	173,864
		$^{40}Ar^{134}Ba$	173,867
		$^{40}K^{134}Ba$	173,869
		$^{40}Ca^{134}Ba$	173,867
		$^{39}K^{135}Ba$	173,869
		$^{38}Ar^{136}Ba$	173,867
^{176}Yb	12.76	^{176}Lu	175,943
		$^{140}Ce^{36}Ar$	175,873
		$^{138}Ba^{38}Ar$	175,868
		$^{138}La^{38}Ar$	175,870
		$^{138}Ce^{38}Ar$	175,869
		$^{46}Ca^{130}Ba$	175,860
		$^{44}Ca^{132}Ba$	175,860
		$^{41}K^{135}Ba$	175,867
		$^{40}Ar^{136}Ba$	175,867
		$^{40}K^{136}Ba$	175,869
		$^{40}Ca^{136}Ba$	175,867
		$^{39}K^{137}Ba$	175,870
		$^{38}Ar^{138}Ba$	175,868
^{175}Lu*	97.41	$^{139}La^{36}Ar$	174,874
		$^{137}Ba^{38}Ar$	174,868
		$^{135}Ba^{40}Ar$	174,868
		$^{45}Sc^{130}Ba$	174,862
		$^{43}Ca^{132}Ba$	174,864
		$^{41}K^{134}Ba$	174,866
		$^{40}Ar^{135}Ba$	174,868
		$^{40}K^{135}Ba$	174,870
		$^{40}Ca^{135}Ba$	174,868

		$^{39}K^{136}Ba$	174,868
		$^{38}Ar^{137}Ba$	174,867
^{176}Lu	2.59	^{176}Yb	175,943
		$^{140}Ce^{36}Ar$	175,941
		$^{138}Ba^{38}Ar$	175,873
		$^{138}La^{38}Ar$	175,868
		$^{138}Ce^{38}Ar$	175,869
		$^{136}Ce^{40}Ar$	175,870
		$^{46}Ca^{130}Ba$	175,860
		$^{44}Ca^{132}Ba$	175,861
		$^{42}Ca^{134}Ba$	175,863
		$^{41}K^{135}Ba$	175,867
		$^{40}Ar^{136}Ba$	175,867
		$^{40}K^{136}Ba$	175,868
		$^{40}Ca^{136}Ba$	175,867
		$^{39}K^{137}Ba$	175,870
		$^{38}Ar^{138}Ba$	175,868

6.2 Measurement results

6.2.1 REE data

REE data in ng g^{-1}, values 0.0 correspond to 0.1 ng g^{-1}

Origin	^{89}Y	^{139}La	^{140}Ce	^{141}Pr	^{147}Sm	^{149}Sm	^{143}Nd	^{145}Nd	^{146}Nd	^{151}Eu	^{153}Eu	^{165}Ho
Ethiopia	30.1	31.6	58.7	7.0	6.1	6.5	28.5	29.6	29.2	6.2	9.5	0.5
Ethiopia	27.5	29.4	54.1	6.5	5.8	5.9	26.7	26.8	26.6	6.5	9.7	0.3
Ethiopia	108.3	108.5	176.1	24.6	21.5	21.4	100.9	101.3	100.1	13.1	18.4	3.2
Ethiopia	194.0	184.1	301.8	42.0	37.6	36.7	171.0	176.0	173.1	24.1	33.3	6.1
India	5.6	12.3	19.3	1.8	1.4	1.5	7.4	7.2	8.1	5.0	8.3	0.0
India	6.2	11.8	20.6	2.0	1.6	1.6	8.0	7.8	8.3	4.8	8.3	0.0
Ethiopia	5.5	10.2	14.3	1.5	1.3	1.5	6.3	6.7	6.5	4.6	7.4	0.0
Ethiopia	5.8	63.8	16.8	1.5	1.4	1.3	6.3	6.0	6.9	4.6	7.8	0.0
Ethiopia	6.6	11.1	23.6	2.0	1.7	1.8	8.6	8.3	9.1	3.4	5.2	0.0
Ethiopia	5.8	10.8	23.2	1.9	1.6	1.9	9.1	8.2	8.2	3.7	5.6	0.0
Ethiopia	5.0	10.5	20.1	1.7	1.5	1.5	6.9	6.9	7.6	3.4	5.4	0.0
Ethiopia	5.4	10.2	19.1	1.7	1.4	1.3	6.9	6.8	7.7	3.6	5.5	0.0
Ethiopia	6.7	16.2	24.0	2.6	1.9	1.9	10.5	10.0	10.7	3.7	5.8	0.0
Ethiopia	6.9	16.1	23.9	2.6	1.9	2.0	10.6	10.4	10.9	3.5	5.7	0.0
Congo	35.0	76.3	150.0	15.2	10.5	10.7	56.4	56.7	56.6	9.2	13.8	0.7
Congo	34.1	87.1	168.9	17.1	11.6	11.6	63.0	64.0	63.6	5.9	8.5	0.7
Vietname	6.4	9.3	19.1	1.7	1.8	1.8	8.0	7.5	8.0	1.1	1.2	0.0
Vietname	6.2	8.9	19.1	1.7	1.8	1.9	7.9	7.4	8.1	1.2	1.4	0.0
Ethiopia	4.9	4.5	9.1	0.4	0.8	0.8	3.1	2.9	3.5	3.9	6.2	0.0
Ethiopia	3.5	4.4	7.6	0.5	0.6	0.8	3.0	2.8	3.2	3.4	5.6	0.0
Guatemala	1.3	1.6	1.7	0.0	0.3	0.4	1.3	0.8	1.5	1.2	1.7	0.0
Guatemala	2.8	3.0	3.6	0.2	0.5	0.5	2.4	2.3	2.5	2.4	3.9	0.0
Tanzania	33.6	53.4	65.7	9.4	6.9	6.8	38.0	39.0	38.7	10.8	17.0	0.4
Tanzania	31.8	47.7	56.9	8.8	6.4	6.8	36.6	35.7	35.3	10.6	17.4	0.2
Hawaii Maui	12.0	19.5	35.7	2.6	2.3	2.1	11.4	12.2	11.4	2.1	2.9	0.0
Hawaii Maui	14.0	12.3	20.0	2.0	2.5	2.2	9.7	10.0	9.7	6.5	10.5	0.0
Timor	3.8	6.8	14.7	1.3	1.3	1.6	6.0	5.7	6.3	0.9	1.0	0.0
Timor	3.4	5.4	11.8	0.9	1.2	1.2	4.5	4.7	4.8	0.7	0.8	0.0
Ethiopia	2.0	3.8	6.1	0.2	0.5	0.5	2.6	2.0	2.7	1.0	1.3	0.0
Ethiopia	4.2	9.5	15.4	1.2	0.9	0.9	5.5	4.9	5.8	2.3	3.5	0.0
Peru	2.8	4.0	8.6	0.6	0.9	0.9	4.0	3.9	4.1	2.0	2.9	0.0
Peru	2.8	5.0	10.9	0.7	0.7	0.8	4.5	3.8	4.3	1.8	2.6	0.0
Ethiopia (Lake Tane)	3.5	4.9	9.0	0.7	0.9	0.9	4.2	4.1	4.2	2.8	4.5	0.0
Ethiopia (Lake Tane)	3.4	4.8	8.7	0.8	0.9	0.9	4.5	3.9	4.3	3.2	4.8	0.0
Laos	9.4	14.6	27.7	2.8	2.6	2.9	12.9	12.3	12.9	1.3	1.5	0.0
Laos	9.5	17.3	35.5	3.1	3.0	3.0	13.7	13.0	13.3	1.3	1.5	0.0
India	5.9	12.4	13.8	1.4	1.1	1.2	6.1	5.9	6.3	2.2	3.0	0.0
India	5.5	14.4	14.8	1.6	1.1	1.2	6.4	6.2	6.7	2.0	3.1	0.0
Hawaii Kona	0.9	2.1	4.2	0.0	0.3	0.3	1.4	0.9	1.5	0.4	0.3	0.0

Hawaii Kona	1.2	10.0	17.9	0.7	0.4	0.4	4.0	2.9	3.4	0.5	0.4	0.0
Colombia	3.7	5.6	8.5	0.7	0.9	0.9	3.9	3.4	3.9	6.7	11.5	0.0
Colombia	3.6	7.5	11.9	1.2	1.1	1.2	5.7	5.0	5.6	6.8	11.1	0.0
Brasil	5.7	23.6	70.5	4.3	2.5	2.9	16.3	15.8	16.3	2.4	3.5	0.0
Brasil	4.9	23.9	68.9	4.1	2.4	2.6	16.7	15.7	16.4	2.4	3.2	0.0
Uganda	11.2	37.7	69.2	6.1	4.0	4.0	22.6	22.9	23.1	3.2	4.7	0.0
Uganda	12.1	31.7	59.5	5.4	3.7	3.5	20.6	19.2	20.8	3.4	5.3	0.0
Peru	3.4	1.6	3.1	0.0	0.5	0.6	1.7	1.5	1.8	2.0	3.2	0.0
Peru	3.5	1.5	3.1	0.0	0.4	0.7	1.4	1.4	1.6	2.0	3.2	0.0
Galapagos (Santa Cruz)	2.6	2.2	5.2	0.4	0.7	0.8	2.6	2.3	2.9	0.1	0.0	0.0
Galapagos (Santa Cruz)	2.6	2.1	5.1	0.3	0.6	0.8	2.2	2.5	2.7	0.2	0.0	0.0
Costa Rica	4.4	4.4	3.8	0.4	0.8	1.0	2.4	2.6	2.8	4.6	7.6	0.0
Costa Rica	4.3	4.4	3.6	0.3	0.6	0.7	2.7	2.2	3.0	5.0	8.1	0.0

Origin	**^{166}Er**	**^{167}Er**	**^{169}Tm**	**^{171}Yb**	**^{172}Yb**	**^{173}Yb**	**^{155}Gd**	**^{175}Lu**	**^{159}Tb**	**^{161}Dy**	**^{163}Dy**	**^{232}Th**
Ethiopia	2.7	3.1	0.0	0.0	0.0	0.0	56.1	0.0	0.5	5.6	5.0	5.4
Ethiopia	2.5	2.7	0.0	0.0	0.0	0.0	59.1	0.0	0.5	5.3	5.0	3.9
Ethiopia	10.2	10.0	0.9	0.6	0.9	0.4	110.5	0.8	3.0	20.8	19.4	11.9
Ethiopia	18.9	18.4	1.9	7.2	7.6	8.1	198.8	1.8	5.8	36.1	34.4	24.3
India	0.1	0.6	0.0	0.0	0.0	0.0	50.7	0.0	0.0	1.0	0.8	1.6
India	0.3	0.6	0.0	0.0	0.0	0.0	50.3	0.0	0.0	1.1	0.8	1.3
Ethiopia	0.1	0.6	0.0	0.0	0.0	0.0	46.8	0.0	0.0	0.9	0.7	0.0
Ethiopia	0.2	0.6	0.0	0.0	0.0	0.0	45.9	0.0	0.0	0.8	0.7	0.1
Ethiopia	0.3	0.7	0.0	0.0	0.0	0.0	34.2	0.0	0.0	3.8	1.0	0.0
Ethiopia	0.2	0.7	0.0	0.0	0.0	0.0	34.9	0.0	0.0	1.0	0.9	0.0
Ethiopia	0.2	0.5	0.0	0.0	0.0	0.0	35.1	0.0	0.0	1.1	0.8	0.0
Ethiopia	0.2	0.6	0.0	0.0	0.0	0.0	35.4	0.0	0.0	1.1	0.7	0.0
Ethiopia	0.3	0.7	0.0	0.0	0.0	0.0	37.9	0.0	0.0	1.3	1.0	0.4
Ethiopia	0.4	0.6	0.0	0.0	0.0	0.0	37.3	0.0	0.0	1.2	1.0	0.5
Congo	3.4	3.7	0.0	0.0	0.0	0.0	88.5	0.0	1.0	7.5	6.9	26.4
Congo	3.4	3.6	0.0	0.0	0.0	0.0	61.3	0.0	0.9	7.8	6.9	31.2
Vietname	0.3	0.6	0.0	0.0	0.0	0.0	10.0	0.0	0.0	1.5	1.1	0.1
Vietname	0.3	0.6	0.0	0.0	0.0	0.0	10.6	0.0	0.0	1.3	1.0	0.0
Ethiopia	0.0	0.7	0.0	0.0	0.0	0.0	36.9	0.0	0.0	0.6	0.5	0.0
Ethiopia	0.0	0.4	0.0	0.0	0.0	0.0	33.4	0.0	0.0	0.6	0.3	0.0
Guatemala	0.0	0.2	0.0	0.0	0.0	0.0	12.3	0.0	0.0	0.2	0.0	0.0
Guatemala	0.0	0.3	0.0	0.0	0.0	0.0	24.8	0.0	0.0	0.5	0.1	0.0
Tanzania	2.5	3.0	0.0	0.0	0.0	0.0	104.7	0.0	0.0	5.3	5.0	1.7
Tanzania	2.5	2.6	0.0	0.0	0.0	0.0	103.2	0.0	0.0	5.5	4.6	1.5
Hawaii Maui	0.5	0.9	0.0	0.0	0.0	0.0	20.3	0.0	0.0	2.2	1.7	0.0
Hawaii Maui	0.6	0.9	0.0	0.0	0.0	0.0	62.6	0.0	0.0	1.9	1.7	0.0
Timor	0.0	0.5	0.0	0.0	0.0	0.0	9.1	0.0	0.0	0.9	0.6	0.0
Timor	0.0	0.4	0.0	0.0	0.0	0.0	7.6	0.0	0.0	0.7	0.5	0.0
Ethiopia	0.0	0.3	0.0	0.0	0.0	0.0	11.2	0.0	0.0	0.3	0.2	0.0
Ethiopia	0.1	0.4	0.0	0.0	0.0	0.0	22.5	0.0	0.0	0.8	0.4	0.0
Peru	0.0	0.4	0.0	0.0	0.0	0.0	18.9	0.0	0.0	0.5	0.4	0.0

Peru	0.0	0.3	0.0	0.0	0.0	0.0	17.7	0.0	0.0	0.5	0.2	0.0
Ethiopia (Lake Tane)	0.0	0.4	0.0	0.0	0.0	0.0	27.9	0.0	0.0	0.6	0.4	0.0
Ethiopia (Lake Tane)	0.0	0.4	0.0	0.0	0.0	0.0	29.2	0.0	0.0	0.6	0.4	0.0
Laos	0.7	1.2	0.0	0.0	0.0	0.0	11.3	0.0	0.0	2.2	1.8	1.7
Laos	0.6	1.0	0.0	0.0	0.0	0.0	11.5	0.0	0.0	2.2	1.8	2.2
India	0.3	0.5	0.0	0.0	0.0	0.0	21.1	0.0	0.0	1.1	0.7	0.0
India	0.1	0.5	0.0	0.0	0.0	0.0	21.6	0.0	0.0	1.0	0.6	0.0
Hawaii Kona	0.0	0.1	0.0	0.0	0.0	0.0	4.6	0.0	0.0	0.1	0.0	0.0
Hawaii Kona	0.0	0.2	0.0	0.0	0.0	0.0	6.7	0.0	0.0	0.3	0.0	0.0
Colombia	0.0	0.3	0.0	0.0	0.0	0.0	65.4	0.0	0.0	0.6	0.3	0.0
Colombia	0.0	0.3	0.0	0.0	0.0	0.0	64.1	0.0	0.0	0.6	0.4	0.0
Brasil	0.3	0.6	0.0	0.0	0.0	0.0	25.7	0.0	0.0	1.3	1.1	8.1
Brasil	0.2	0.5	0.0	0.0	0.0	0.0	24.2	0.0	0.0	1.3	0.9	8.0
Uganda	1.0	1.2	0.0	0.0	0.0	0.0	35.0	0.0	0.0	2.5	2.1	7.0
Uganda	1.1	1.3	0.0	0.0	0.0	0.0	37.2	0.0	0.0	2.6	2.1	6.4
Peru	0.0	0.1	0.0	0.0	0.0	0.0	19.9	0.0	0.0	0.3	0.0	0.0
Peru	0.0	0.2	0.0	0.0	0.0	0.0	18.0	0.0	0.0	0.2	0.0	0.0
Galapagos (Santa Cruz)	0.0	0.4	0.0	0.0	0.0	0.0	1.3	0.0	0.0	0.5	0.3	0.0
Galapagos (Santa Cruz)	0.0	0.3	0.0	0.0	0.0	0.0	1.3	0.0	0.0	0.5	0.3	0.0
Costa Rica	0.0	0.4	0.0	0.0	0.0	0.0	45.4	0.0	0.0	0.6	0.3	0.0
Costa Rica	0.0	0.4	0.0	0.0	0.0	0.0	48.0	0.0	0.0	0.6	0.3	0.0

6.2.2 Multielement data

Sample	Origin	Li	Be	B	Na	Mg	Al	V	Mn	Fe
		ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
ICAT 253 A	Congo	<1	< 1	8.41E+03	2.28E+04	2.50E+06	9.00E+04	144.0	2.59E+04	2.50E+05
ICAT 254 A	Vietnam	4.0	6.3	1.33E+04	6.91E+03	2.16E+06	1.60E+04	< 1	2.10E+04	5.73E+04
ICAT 255 A	Ethiopia	4.5	< 1	1.16E+04	1.89E+04	2.44E+06	2.43E+03	4.0	2.18E+04	9.08E+04
ICAT 256 A	Guatemala	36.0	6.5	1.05E+04	2.47E+04	2.42E+06	1.85E+03	< 1	1.37E+04	4.32E+04
ICAT 257 A	Tanzania	3.7	7.2	1.02E+04	8.43E+03	2.20E+06	1.44E+04	< 1	4.32E+04	3.94E+04
ICAT 258 A	Hawaii Maui	16.2	< 1	1.68E+04	2.00E+05	3.22E+06	1.01E+04	15.0	3.64E+04	1.04E+05
ICAT 259 A	Timor	6.4	7.2	1.37E+04	8.13E+03	2.35E+06	8.18E+03	< 1	4.47E+04	4.42E+04
ICAT 260 A	Ethiopia	12.5	< 1	1.05E+04	1.86E+04	2.05E+06	5.59E+03	4.0	1.72E+04	8.37E+04
ICAT 261 A	Peru	11.9	< 1	1.13E+04	6.57E+03	2.18E+06	2.28E+04	28.0	7.24E+04	1.14E+05
ICAT 262 A	Ethiopia (Lake Tane)	3.6	7.8	2.80E+04	6.01E+03	2.29E+06	3.51E+03	< 1	1.51E+04	3.53E+04
ICAT 263 A	Laos	5.2	9.9	9.57E+03	8.03E+03	1.91E+06	2.46E+04	< 1	1.64E+04	6.02E+04
ICAT 264 A	India	8.9	< 1	1.28E+04	2.97E+04	2.11E+06	8.00E+03	5.0	1.70E+04	1.03E+05
ICAT 265 A	Hawaii Kona	5.6	< 1	1.12E+04	4.82E+04	2.64E+06	1.46E+03	9.0	2.99E+04	1.00E+05
ICAT 266 A	Colombia	6.3	5.6	1.11E+04	4.86E+03	2.44E+06	4.98E+03	< 1	4.11E+04	3.34E+04
ICAT 267 A	Brasil	4.9	< 1	8.90E+03	4.62E+03	2.45E+06	5.40E+04	62.0	2.98E+04	1.37E+05
ICAT 269 A	Uganda	13.5	< 1	1.52E+04	8.69E+03	2.47E+06	2.86E+04	33.0	1.86E+04	1.33E+05
ICAT 270 A	Peru	26.2	10.7	1.11E+04	6.16E+03	2.29E+06	1.09E+03	< 1	2.77E+04	3.40E+04
ICAT 271 A	Galapagos (Santa Cruz)	3.4	6.7	1.10E+04	1.04E+05	2.17E+06	2.17E+03	< 1	1.56E+04	3.70E+04
ICAT 272 A	Costa Rica	5.8	11.0	1.12E+04	1.10E+04	2.38E+06	2.58E+03	< 1	3.38E+04	3.99E+04

Sample	Origin	Co	Ni	Cu	Zn	Ga	As	Se	Rb	Mo
		ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
ICAT 253 A	Congo	2.30E+02	4.52E+03	1.70E+04	1.24E+04	3.44E+02	19.0	1.30E+02	1.90E+04	3.47E+02
ICAT 254 A	Vietnam	4.89E+02	3.52E+03	1.46E+04	6.60E+03	4.43E+01	< 1	2.03E+02	4.62E+04	5.35E+01
ICAT 255 A	Ethiopia	3.98E+01	2.61E+02	1.53E+04	7.62E+03	2.33E+02	10.0	2.25E+01	1.23E+04	3.84E+02
ICAT 256 A	Guatemala	5.99E+01	0.00E+00	1.53E+04	5.76E+03	2.02E+02	< 1	4.99E+01	5.81E+04	1.39E+02
ICAT 257 A	Tanzania	1.07E+02	1.89E+02	1.32E+04	6.75E+03	8.69E+02	< 1	1.55E+02	7.78E+04	1.09E+02
ICAT 258 A	Hawaii Maui	3.27E+02	1.16E+03	1.69E+04	7.31E+03	7.82E+01	18.0	6.09E+02	1.06E+04	1.25E+02
ICAT 259 A	Timor	4.47E+01	9.88E+02	1.69E+04	8.41E+03	3.27E+01	< 1	6.85E+01	2.87E+04	7.99E+01
ICAT 260 A	Ethiopia	4.75E+01	2.65E+02	1.46E+04	6.77E+03	1.11E+02	24.0	3.51E+02	2.27E+04	1.90E+02
ICAT 261 A	Peru	7.96E+01	3.42E+03	1.49E+04	1.17E+04	9.20E+01	12.0	5.13E+01	2.94E+04	2.11E+02
ICAT 262 A	Ethiopia (Lake Tane)	3.91E+01	3.41E+02	1.32E+04	7.55E+03	2.04E+02	< 1	1.40E+02	4.14E+04	1.19E+02
ICAT 263 A	Laos	4.73E+02	2.64E+03	1.14E+04	6.84E+03	2.81E+01	< 1	1.34E+02	4.29E+04	7.07E+01
ICAT 264 A	India	4.41E+02	3.61E+03	2.08E+04	8.46E+03	8.88E+01	11.0	1.49E+02	3.79E+04	1.05E+02
ICAT 265 A	Hawaii Kona	1.07E+02	6.38E+02	1.67E+04	8.65E+03	2.57E+01	24.0	9.36E-01	9.59E+03	5.58E+01

ICAT 266 A	Colombia	1.77E+02	4.30E+02	1.55E+04	8.41E+03	5.04E+02	< 1	1.57E+02	1.55E+04	8.45E+01
ICAT 267 A	Brasil	9.90E+01	1.78E+03	1.87E+04	7.31E+03	1.19E+02	19.0	5.92E+01	1.37E+04	9.87E+01
ICAT 269 A	Uganda	1.80E+02	1.10E+03	2.06E+04	8.89E+03	1.63E+02	16.0	2.24E+02	2.75E+04	4.96E+02
ICAT 270 A	Peru	2.95E+01	6.28E+02	1.66E+04	7.65E+03	1.39E+02	< 1	1.08E+02	9.77E+03	1.70E+02
ICAT 271 A	Galapagos (Santa Cruz)	4.28E+01	0.00E+00	1.71E+04	8.08E+03	0.00E+00	< 1	3.46E+02	9.93E+03	8.97E+01
ICAT 272 A	Costa Rica	1.90E+02	3.52E+02	1.69E+04	7.31E+03	3.66E+02	< 1	1.28E+02	2.34E+04	6.17E+01

Sample	**Origin**	**Ag**	**Cd**	**Te**	**Ba**	**Tl**	**Pb**	**Bi**	**Ca**	**Sr**
		ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	ng/g
ICAT 253 A	Congo	1.1	1.3	0.0	6.95E+03	0.76	31.4	15.6	6.34E+05	5.87E+03
ICAT 254 A	Vietname	1.3	4.7	2.9	1.26E+03	0.93	28.5	< 1	1.57E+06	3.73E+03
ICAT 255 A	Ethiopia	0.2	2.1	< 1	6.64E+03	<0.1	7.49	< 1	9.93E+05	4.94E+03
ICAT 256 A	Guatemala	2.3	5.5	3.2	4.28E+03	2.19	42.5	55.4	1.89E+06	9.77E+03
ICAT 257 A	Tanzania	1.7	3.0	< 1	1.74E+04	0.82	43.6	6.8	1.61E+06	9.83E+03
ICAT 258 A	Hawaii Maui	1.1	9.2	1.1	< 1.0E+3	0.68	22.4	16.0	8.51E+05	8.82E+03
ICAT 259 A	Timor	4.3	1.1	4.8	1.15E+03	0.67	40.2	2.9	1.43E+06	2.83E+03
ICAT 260 A	Ethiopia	161	1.1	2.2	3.44E+03	<0.1	17.2	< 1	1.10E+06	5.73E+03
ICAT 261 A	Peru	0.3	5.3	5.1	3.44E+03	0.91	35.9	< 1	9.00E+05	7.81E+03
ICAT 262 A	Ethiopia (Lake Tane)	2.1	2.4	2.5	4.26E+03	0.55	34.4	1.6	1.29E+06	4.38E+03
ICAT 263 A	Laos	3.3	6.2	< 1	8.90E+02	0.81	30.3	2.2	1.23E+06	2.92E+03
ICAT 264 A	India	< 1	7.2	8.0	3.00E+03	0.44	3.54	< 1	7.61E+05	3.53E+03
ICAT 265 A	Hawaii Kona	< 1	25.3	< 1	< 1.0E+3	0.61	28.2	15.7	7.49E+05	3.37E+03
ICAT 266 A	Colombia	3.8	9.0	0.4	1.01E+04	0.47	46.6	1.5	1.46E+06	8.96E+03
ICAT 267 A	Brasil	44.5	1.6	< 1	3.06E+03	0.33	27.1	< 1	7.03E+05	5.02E+03
ICAT 269 A	Uganda	< 1	5.5	< 1	4.79E+03	0.03	3.99	< 1	1.07E+06	8.20E+03
ICAT 270 A	Peru	28.8	20.1	0.3	3.21E+03	0.41	65.4	1.1	1.33E+06	2.79E+03
ICAT 271 A	Galapagos (Santa Cruz)	2.7	4.5	2.5	5.48E+01	0.16	36.7	< 1	8.94E+05	1.38E+03
ICAT 272 A	Costa Rica	31.1	4.9	1.0	7.30E+03	0.44	41.9	< 1	1.76E+06	1.34E+04

6.2.3 Sr isotope data

Sample No.	Origin	Continent code	87/86 corr	SU
1B A	Ethiopia	1	7.0856E-01	0.00035
1B B	Ethiopia	1	7.0822E-01	0.00035
1P A	Ethiopia	1	7.0384E-01	0.00035
1P B	Ethiopia	1	7.0498E-01	0.00035
3 A	Ethiopia	1	7.0879E-01	0.00035
3 B	Ethiopia	1	7.0876E-01	0.00035
4 A	Ethiopia	1	7.1375E-01	0.00035
4 B	Ethiopia	1	7.0900E-01	0.00035
5B A	Ethiopia	1	7.1089E-01	0.00035
5B B	Ethiopia	1	7.0926E-01	0.00035
5H A	Ethiopia	1	7.0744E-01	0.00035
5H B	Ethiopia	1	n.a.	
ICAT 253 A	Congo	1	7.2066E-01	0.00036
ICAT 253 B	Congo	1	7.0979E-01	0.00035
ICAT 255 A	Ethiopia	1	n.a.	
ICAT 255 B	Ethiopia	1	7.0697E-01	0.00035
ICAT 257 A	Tanzania	1	7.2296E-01	0.00036
ICAT 257 B	Tanzania	1	7.2260E-01	0.00036
ICAT 260 A	Ethiopia	1	7.0852E-01	0.00035
ICAT 260 B	Ethiopia	1	7.1001E-01	0.00036
ICAT 262 A	Ethiopia (Lake Tane)	1	7.0842E-01	0.00035
ICAT 262 B	Ethiopia (Lake Tane)	1	7.0998E-01	0.00035
ICAT 269 A	Uganda	1	7.2306E-01	0.00036
ICAT 269 B	Uganda	1	7.2518E-01	0.00036
ICAT 256 A	Guatemala	2	7.0665E-01	0.00035
ICAT 256 B	Guatemala	2	7.0587E-01	0.00035
ICAT 258 A	Hawaii Maui	2	7.0853E-01	0.00035
ICAT 258 B	Hawaii Maui	2	7.0919E-01	0.00035
ICAT 261 A	Peru	2	7.1252E-01	0.00035
ICAT 261 B	Peru	2	7.1151E-01	0.00036
ICAT 265 A	Hawaii Kona	2	7.1228E-01	0.00036
ICAT 265 B	Hawaii Kona	2	7.1024E-01	0.00036
ICAT 266 A	Colombia	2	7.0993E-01	0.00035
ICAT 266 B	Colombia	2	7.1031E-01	0.00036
ICAT 267 A	Brasil	2	7.1009E-01	0.00036
ICAT 267 B	Brasil	2	7.0961E-01	0.00035
ICAT 270 A	Peru	2	7.1153E-01	0.00036
ICAT 270 B	Peru	2	7.1114E-01	0.00036
ICAT 271 A	Galapagos (Santa Cruz)	2	7.0586E-01	0.00035
ICAT 271 B	Galapagos (Santa Cruz)	2	7.1669E-01	0.00036
ICAT 272 A	Costa Rica	2	7.0559E-01	0.00035
ICAT 272 B	Costa Rica	2	7.1413E-01	0.00036
2 A	India	3	7.2172E-01	0.00036

2 B	India	3	7.2339E-01	0.00036
ICAT 254 A	Vietname	3	7.1011E-01	0.00036
ICAT 254 B	Vietname	3	7.1873E-01	0.00036
ICAT 259 A	Timor	3	7.2454E-01	0.00036
ICAT 259 B	Timor	3	7.2541E-01	0.00036
ICAT 263 A	Laos	3	7.1496E-01	0.00036
ICAT 263 B	Laos	3	7.1527E-01	0.00036
ICAT 264 A	India	3	7.2404E-01	0.00036
ICAT 264 B	India	3	7.1894E-01	0.00036

6.2.4 C, N, O isotope data (source: C. Rodrigues, University of Lisbon)

Sample	Origin	Continentcode	$d^{13}C$	$d^{15}N$	$d^{18}O$
ICAT 253 A	Congo	1	-27	4.2	31.3
ICAT 254 A	Vietname	3	-27.9	2	32
ICAT 255 A	Ethiopia	1	-26.9	2.9	30.2
ICAT 256 A	Guatemala	2	-28.8	1.5	30
ICAT 257 A	Tanzania	1	-26.3	3.2	32
ICAT 258 A	Hawaii Maui	2	-28.1	1.1	32.2
ICAT 259 A	Timor	3	-28.9	1.5	26.4
ICAT 260 A	Ethiopia	1	-27.2	4.2	34.2
ICAT 261 A	Peru	2	-28.9	2.1	27.5
ICAT 262 A	Ethiopia (Lake Tane)	1	-28.6	3.5	36.9
ICAT 263 A	Laos	3	-28.2	2.1	24.1
ICAT 264 A	India	3	-28.2	3.1	28.8
ICAT 265 A	Hawaii Kona	2	-26.7	2.8	29.5
ICAT 266 A	Colombia	2	-28	2.5	26.7
ICAT 267 A	Brasil	2	-27.5	2.7	26.7
ICAT 269 A	Uganda	1	-27.1	4.1	32.8
ICAT 270 A	Peru	2	-30.9	3.6	20.5
ICAT 271 A	Galapagos (Santa Cruz)	2	-29	3	28.7
ICAT 272 A	Costa Rica	2	-28.2	1.8	24.7

6.3 Certificates of Analysis

6.3.1 SRM 987, Strontium Carbonate

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 987

Strontium Carbonate
(Isotopic Standard)

This Standard Reference Material (SRM) is certified for use as an isotopic reference material for the calibration of mass spectrometers. The material consists of highly purified strontium carbonate of high homogeneity. A unit of SRM 987 consists of 1 g of powder.

Certified Values: The certified values for the absolute strontium isotopic abundance ratios and the atom fractions of ^{88}Sr, ^{87}Sr, ^{86}Sr and ^{84}Sr are listed in Table 1. A NIST-certified value is a value for which NIST has the highest confidence in its accuracy, in that all known or suspected sources of bias have been investigated or accounted for by NIST. A certified value is the present best estimate of the true value based on the results of analyses performed at NIST and cooperating laboratories. Value assignment categories are based on the definition of terms and modes used at NIST for chemical reference materials [1]. The uncertainties listed with the values are expanded uncertainties (95 % confidence interval) and are calculated according to the methods in the ISO and NIST Guides [2].

Table 1. Certified Values for SRM 987 Strontium Carbonate

Absolute Abundance Ratios	$^{88}Sr/^{86}Sr = 8.378\ 61 \pm 0.003\ 25$
	$^{87}Sr/^{86}Sr = 0.710\ 34 \pm 0.000\ 26$
	$^{84}Sr/^{86}Sr = 0.056\ 55 \pm 0.000\ 14$
that yield atom percents of:	$^{88}Sr = 82.584\ 5 \pm 0.006\ 6$
	$^{87}Sr = 7.001\ 5 \pm 0.002\ 6$
	$^{86}Sr = 9.856\ 6 \pm 0.003\ 4$
	$^{84}Sr = 0.557\ 4 \pm 0.001\ 5$

This material was used as the reference sample in a determination of the absolute abundance ratios and atomic weight of strontium [3]. The atomic weight of strontium calculated from the absolute abundance ratios is 87.616 81 ± 0.000 12.

Expiration of Certification: The certification of this SRM is deemed to be indefinite within the stated uncertainties. However, certification is nullified if the SRM is contaminated or otherwise altered.

Maintenance of Certified Values: NIST will monitor this SRM and, if substantive changes occur in the certified values, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Stephen A. Wise, Chief
Analytical Chemistry Division

Gaithersburg, MD 20899
Certificate Issue Date: 19 June 2007
See Certificate Revision History on Last Page

Robert L. Watters, Jr., Chief
Measurement Services Division

SRM 987

Page 1 of 2

The overall direction and coordination of the technical measurements leading to the certification of this SRM were performed under the chairmanship of I.L. Barnes and W.R. Shields of the NIST Analytical Chemistry Division.

The characterization of this SRM was performed by G. Marinenko, E.E. Etz, D.G. Friend, I.L. Barnes, L.J. Moore, T.C. Rains, T.A. Rush, L.A. Machlan, T.J. Murphy, and P.J. Paulsen, all of the NIST Analytical Chemistry Division.

The support aspects involved in the preparation of this SRM were coordinated through the NIST Measurement Services Division. The current revised certificate was coordinated by Robert D. Vocke, Jr. of the Analytical Chemistry Division.

Storage and Handling: There are no special storage or handling instructions. While strontium carbonate is slightly hygroscopic (absorbing approximately 0.02 % moisture at 90 % humidity), this has no effect on the isotopic abundances.

The strontium carbonate used for this SRM was obtained from Spex Industries, Inc[1]. of Metuchen, NJ. The material, when received, was of high purity in relation to cationic impurities but assayed only 99.0 % due to moisture and other volatile impurities. The impurities reported in the strontium carbonate material are lithium, 4 mg/kg; sodium, 6 mg/kg; potassium, < 1 mg/kg; magnesium, < 2 mg/kg; calcium, 5 mg/kg; barium, < 15 mg/kg; copper, < 3 mg/kg; iron, < 3 mg/kg; aluminum, < 1 mg/kg; and silicon, < 1 mg/kg.

REFERENCES

[1] May, W.E.; Parris, R.M.; Beck II, C.M.; Fassett, J.D.; Greenberg, R.R.; Guenther, F.R.; Kramer; G.W.; Wise; S.A.; Gills, T.E.; Colbert, J.C.; Gettings, R.J.; MacDonald, B.S.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Spec. Pub. 260-136, U.S. Government Printing Office: Washington, DC (2000).

[2] ISO; *Guide to the Expression of Uncertainty in Measurement*; ISBN 92-67-10188-9, 1st ed., International Organization for Standardization: Geneva, Switzerland (1993); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297, U.S. Government Printing Office: Washington, DC (1994); available at http://physics.nist.gov/Pubs/.

[3] Moore, L.J.; Murphy, T.J.; Barnes, I.L.; Paulsen, P.J.; *Absolute Isotopic Abundance Ratios and Atomic Weight of a Reference Sample of Strontium*, J. of Res. (NBS) Vol. 87, No. 1, pp. 1–8 (1982).

Certificate Revision History: 19 June 2007 (Editorial change); 14 June 2007 (Editorial changes and revised as isotopic standard only); 01 May 2000 (Editorial changes); 01 October 1982 (Revision of certified values); 06 March 1972 (Editorial changes); 08 November 1971 (Original certificate date).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-6776; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

[1]Certain commercial equipment, instrumentation, or materials are identified in this certificate to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

6.3.2 TM-25.3

Environment Canada Environnement Canada

CERTIFIED REFERENCE MATERIAL

TM-25.3, lot 1107

A low level fortified standard for trace elements

Trace element standards are made in filtered and diluted Lake Ontario water and are preserved with 0.2% nitric acid. This fortified bulk CRM has concentrations in the low range and is designed for accuracy verification. Trace element standards are noted for their integrity and consistency, and are monitored in additional Proficiency Testing (PT) studies. "For Information" values indicate insufficient data exists to meet CRM certification criteria. The values and statistics for this CRM are derived from PT studies76, 78, 81, 84, and 88 dated March 2000, March 2001, September 2002, June 2004, and June 2006 respectively. A more detailed report on the methods used in our PT studies for specific parameters is available upon request. Please note that expiry dates of 1 year from the date of shipping are not indicative of sample stability, but rather of sample transport, handling and storage. We strongly recommend that the CRM be tightly capped and refrigerated immediately after use.

Measurand	Value[a] in µg/L	±2σ[b]	C.I.[c]	Studies / Results (N)
Aluminum	24.6	4.01	0.347	5 / 128
Antimony	23.7	3.22	0.298	5 / 144
Arsenic	27.6	4.47	0.372	5 / 139
Barium	26.8	2.35	0.193	5 / 142
Beryllium	26.0	2.97	0.259	5 / 127
Boron	32.4	5.83	0.779	3 / 56
Cadmium	24.0	2.5	0.189	5 / 168
Chromium	24.5	2.22	0.178	5 / 149
Cobalt	28.0	2.61	0.224	5 / 131
Copper	27.6	2.86	0.225	5 / 155
Iron	29.5	5.13	0.477	5 / 113
Lead	27.8	2.88	0.226	5 / 156
Lithium	25.6	2.72	0.303	5 / 79
Manganese	25.4	2.6	0.202	5 / 158
Molybdenum	28.8	3.2	0.283	5 / 123
Nickel	15.5	1.53	0.126	5 / 142
Selenium	27.9	4.08	0.369	5 / 120
Silver	22.0	2.41	0.225	5 / 112
Strontium	69.9	6.34	0.547	5 / 129
Thallium	29.9	3.29	0.351	5 / 86
Tin	24.4	3.63	0.472	5 / 59
Titanium	24.6	2.13	0.275	6 / 60
Uranium	27.4	2.8	0.283	5 / 96
Vanadium	26.3	2.51	0.212	5 / 134
Zinc	41.9	5.2	0.528	3 / 95

For information

Bismuth	22.4	47 results

[a] Outliers of > 3 std. dev. excluded and are calculated with 'Robust Analysis' Annex C, ISO DIS 13528:2005(E).
[b] 2-sigma limit for an individual measurement.
[c] 95% confidence interval on the population mean ($\sigma \div (1.96 \sqrt{N})$).

Last Updated: 19 November 2007

Canada

Certified Reference Materials (CRMs) are valuable and necessary tools for validating the analytical results in environmental research and monitoring programs.

These water reference materials are intended for the verification or development of analytical methods for environmental analysis.

Development and Certification

Reference waters are collected in bulk from various locations across North America. Waters are centrifuged, filtered and stored refrigerated. Certification is by means of large interlaboratory Proficiency Testing (PT) studies. This normally occurs over a minimum time span of 3 years, thus giving a good indication of sample stability and homogeneity.

Stability, Storage and Handling

The certification and stability of CRMs are subject to uncertainties. The inherently complex nature of natural water samples and environmental analyses should be observed as they may not be completely free of errors. CRMs should be handled by qualified personnel with good laboratory practices to ensure their integrity. In addition, CRMs are necessarily shipped by commercial couriers under non-controlled conditions and storage may be subject to foreign and unknown customs regulations.

CRMs should be stored refrigerated, well sealed and in the dark. Care should be taken when subsampling to avoid contamination of the sample bottle. It is recommended that users purchase new CRMs as required or as expiry dates are reached.

Disclaimer, Liability & Warranty

Certified values for these CRMs are based on performance based methods used by laboratories in Environment Canada's interlaboratory PT program. Environment Canada warrants that the materials conform to the certificate values. In the event of a breach of this warranty, Environment Canada will only be liable for a replacement sample, an equivalent substitute, or the invoice price of the CRM. In no event will Environment Canada be liable for direct, indirect, special, incidental or consequential damages arising from the use of or inability to use the material or documentation, or for the loss of revenue or profit, even if advised of the possibility of such damages.

Further Information

Environment Canada promotes its research and findings and makes them available to the scientific community. Additional information is available on request. Analytical results, any comments or suggestions will be most welcome. Difficulties or discrepancies arising with the certified standards should be communicated immediately.

Comments, concerns, or information inquiries may be addressed to:

Attention: CRM Sales
Environment Canada
National Laboratory for Environmental Testing
867 Lakeshore Road
Burlington, ON L7R 4A6
CANADA

Tel: +1 905-336-4653
Fax: +1 905-336-8914
E-mail: crmsales@ec.gc.ca
Website: English
http://www.nwri.ca/nlet-lnee/crm-mrc/crm-e.html
French
http://www.nwri.ca/nlet-lnee/crm-mrc/crm-f.html

Canada

6.4 List of Abbreviations

°C	degree Celsius
a	year
AAS	Atomic absorption spectrometry
AESA	Atomic emission spectral analysis
amu	atomic mass unit
c	concentration
cps	counts per second
CRM	certified reference material
DRC	dynamic reaction cell
EDXRF	Energy dispersive X-ray fluorescence spectrometry
equ.	equation
et al.	et alii
ETV	Electrothermal vaporization
FAAS	Flame atomic absorption spectrometry
fig.	figure
g	gram
HPLC	High-performance liquid chromatography
HR	high resolution
HREE	heavy rare earth elements
HR-ICPMS	High resolution inductively coupled plasma mass spectrometry
Hz	Hertz
ICP	inductively coupled plasma
ICPMS	Inductively coupled plasma mass spectrometry
ICPOES	Inductively coupled plasma optical emission spectrometry
ICPQMS	Inductively coupled plasma quadrupole mass spectrometry
ICPSFMS	Inductively coupled plasma sector-field mass spectrometry
ICPTOFMS	Inductively coupled plasma time of flight mass spectrometry
INAA	Instrumental neutron activation analysis
int	intensity
IRMS	isotope ratio mass spectrometry
IUPAC	International Union of Pure and Applied Chemistry
J	Joule
k	coverage factor
kcal	kilogram calorie
L	liter
LA	LASER ablation
LA-ICPMS	Laser ablation microprobe inductively coupled plasma MS
LOD	limit of detection
LREE	light rare earth elements
m	mass
M	molar
m/z	mass-to-charge ratio
MC	multiple collector
MC-ICPMS	Multiple-collector inductively coupled plasma mass spectrometry
MPT-OES	Microwave plasma torch-optical emission spectrometry

MREE	medium rare earth elements
MS	mass spectrometry
m-XRF	Micro X-ray fluorescence
n.c.	not certified
n.d.	not determined
NAA	Neutron activation analysis
p.a.	pro analysi
PCA	principal component analysis
PE	polyethylene
PFA	perfluoroalkoxy
PIXE	Particle-induced X-ray emission
PP	polypropylene
PTFE	polytetrafluoroethylene
QMS	quadrupole mass spectrometry
R	resolution
REE	rare earth elements
RM	reference material
RNAA	Radiochemical neutron activation analysis
rpm	revolutions per minute
RSU	relative standard uncertainty
SD	standard deviation
SF	sector field
SIMS	Secondary-ion mass spectroscopy
SPE	Solid-phase extraction
SU	standard uncertainty
subb.	subboiled
tab.	table
TIMS	Thermal ionization mass spectrometry
TXRF	Total-reflection X-ray fluorescence
U	voltage
UV	ultraviolet
UV-VIS	Ultraviolet-visible spectrophotometry
V	volt
VIRIS	Vienna Isotope Research, Investigation and Survey
W	watt
WC-OES	Tungsten coil optical emission spectrometry
XRF	X-Ray fluorescence spectrometry
z	charge

6.5 List of Figures

6.6 List of Tables

6.7 List of Equations

6.8 Curriculum vitae

Angaben zur Person

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