# DIPLOMARBEIT

Titel der Diplomarbeit

Provenance studies of wine, pumpkin seeds and pumpkin seed oil by element and isotope fingerprints using Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Verfasserin

Gerlinde Grabmann

angestrebter akademischer Grad

Magistra der Naturwissenschaften (Mag rer.nat.)

Wien, 2009

| | |
|---|---|
| Studienkennzahl lt. Studienblatt: | A 419 |
| Studienrichtung lt. Studienblatt: | Chemie |
| Betreuer: | ao. Univ. Prof. Dr. Prohaska Thomas (Universität für Bodenkultur, Wien) |

# Index

## Thanks:

**T**om Prohaska and his VIRIS team for giving me the opportunity to be part of their work group to broaden my horizon technically as well as socially.

**O**tti and Sepp, my parents, who encourage my free spirit and support me in everyday life

**W**hole department of analytical chemistry at BOKU for being smooth lab mates and supervisors

**H**oracek Micha, Martin Schmuckenschlager as well as David for providing me with sample material

**O**ma und Opa united forever

**M**&M, Moni and Magda who I could always share 'diploma thesis stuff' with

**I**ndia made it possible to have enough time for this thesis. Thx Stephan :* for proof-reading

**T**ina, Benji, Jot and Paul knowing them almost my whole life and being friends ever since; spread all over but no matter where we live there is always a way of catching up ☺

**M**y dear friends Christl and Pez, in good and bad times - during day and nite, talk talk talk and shake shake shake; luv ya gals

**A**lm hinterm Brunn, Hanni and Dietmar for financial support; happiest working place during three summer and one winter season and one more to come

**Y**eah

**C**ornelia, Fabian, Lilien, Nina and Amilie who bring joy to my life whenever I'm able to spend time with them; as well as my sister Daniela & Franz and my brother Christian & Barbara

**O**rder of appearance due to bold capital letters

**N**ot strawberry but Joananas

**C**hristoph, Rita and Aichi keeping me fit being boulder buddies, friends and study mates

**E**xcited

**R**ene, not only for sharing his laptop with me during writing but for always being there for me, i o u loads; simply best friend and flat mate

**N**elli for his C1 expertise, discussed on and off university as well as providing me with RM

# Abstract

Provenance studies of food and beverages have become key issues across Europe over the last few years. Various matrices have been under investigation so far to differentiate place of origin by different chemical parameters such as composition of elements and isotopes analyzed by ICP-MS. Stepwise authentication was performed on wine and pumpkin seed oil, in this thesis.

A full method validation was carried out for REE element pattern analysis using a quadrupole instrument (ICP-QMS) as well as a sector field instrument (ICP-SFMS). ICP-QMS provides equal quality compared to ICP-SFMS with respect to LoD/Q, recovery or quality control. However sensitivity of ICP-QMS was about one order of magnitude lower for all elements. Total combined uncertainty of ICP-QMS was up to 20 % higher. Moreover ICP-QMS analysis was optimized to measure P in plant matrices.

Authentic wine samples from different wine growing areas in Austria were investigated. All white wines could be distinguished from each other using multi-element pattern by B, Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Mo and U. However distribution of these samples among the vineyards was rather narrow. Furthermore 80% of red wine samples could be classified using discriminate analysis. Ga was measured in addition to the above mentioned elements as it was significantly above the LoD in red wine samples. Moreover, strontium isotope ratios and concentrations proved to be a promising discrimination tool as well.

Only traditionally manufactured pumpkin seed oil, pressed of seeds from certain regions in Austria, is protected through European Union and labeled PGI (protected geographical indication). Multi-element pattern, rare earth element concentration as well as a combination of both could clearly distinguish between oil from China, Lower Austria, and Serbia. However Slovenian oil was not significantly different to the region of Lower Austria. Nonetheless only a limited number of elements were above detection limit in pumpkin seed oil. Strontium isotope ratios in combination with respective concentration were applied as well. In addition any changes in composition of elements from seed to oil were investigated in detail. Detected elements in oil were below 10% of seed samples whereas chromium, lead and sodium showed significant contamination in oil. Only Ba, Rb, Sr and Mn did not show any contamination with respect to pressed oil. Rare element pattern were consistent from seed to oil and the concentration in oil was about one tenth compared to seed.

# Kurzfassung

Herkunftsstudien von Lebensmitteln und Getränken gewann in den letzten Jahren signifikante Bedeutung in ganz Europa. Verschiedene Proben wurden auf ihre chemischen Parameter analysiert und konnten z.B aufgrund der resultierenden Element- und Isotopenzusammensetzung ihrem Ursprungsort zugeordnet werden. Im Rahmen dieser Diplomarbeit wurden exemplarisch Wein und Kürbiskernöl untersucht.

Eine komplette Methodenvalidierung für die Analyse von Seltenen Erden mittels ICP-QMS und ICP-SFMS wurde durchgeführt. Beide Geräte zeigen ähnliche Resultate für LoD/Q und die Wiederfindung. Die Empfindlichkeit des ICP-QMS war jedoch um eine Zehnerpotenz geringer während die Messunsicherheit von einigen Elementen bei mehr als 20% lag. Daher liegen die Vorteile auf Seiten von ICP-SFMS wenn alle Parameter betrachtet werden.

Authentische Weinproben stammten aus diversen Weinbaugebieten Österreichs. Alle Weißweinproben konnten mittels Elementmuster der folgenden Elemente eindeutig zugeordnet werden: B, Mg, Ca, Mn, Fe, Co, Ni, Cu, Zn, Rb, Sr, Mo und U. Die Proben stammten allerdings aus sehr eng gefassten Regionen. Zusätzlich war eine Klassifizierung von 80% der Rotweinproben mittels Diskriminanzanalyse möglich. Hierbei wurden nicht nur die oben erwähnten Elemente verwendet, sondern auch Gallium, welches sich nur in Rotweinproben oberhalb der Quantifikationsgrenze befand. Strontium Isotopenverhältnisse und die zugehörigen Konzentrationen konnten ebenfalls als ein vielversprechendes Unterscheidungsmerkmal verwendet werden.

Nur Kürbiskernöl, welches den traditionellen Herstellungsverfahren entspricht sowie deren Kerne aus ausgewählten österreichischen Regionen stammen ist durch die EU geschützt. Dadurch erhält es die zusätzliche Bezeichnung g.g.A. (geschützte geographische Angabe). Durch die Verwendung von Elementmustern und Muster der Seltenen Erden war eine eindeutige Unterscheidung von extrahiertem Öl aus China, Niederösterreich, und Serbien möglich. Öl aus slowenischen Kernen konnte allerdings nicht eindeutig von jenem aus Niederösterreich unterschieden werden. $^{87}Sr/^{86}Sr$ haben sich für die Herkunftsbestimmung bewährt, jedoch war die Sr Konzentration in extrahiertem Öl viel niedriger als in gepresstem. Obwohl dieses auch an anderen Elementen höher konzentriert war konnte nur eine beschränkte Anzahl an Elementen (Rb, Sr, Ba und Mn) detektiert werden. Zusätzlich erfolgte eine Untersuchung der Veränderungen der Element- und Isotopenmuster während des Herstellungsprozesses von Öl aus den Kernen. Seltene Erden zeigen ein konstantes Muster mit einer Ausbeute von 10% von Kern zu Öl. Andere Elemente konnten nur zu weniger als 10% in das Öl gepresst werden. Außerdem zeigte das Öl eindeutige Spuren von Kontamination mit Blei, Chrom und Natrium. Alleine bei Ba, Rb, Sr und Mn konnte eine Verunreinigung ausgeschlossen werden.

# 1 Introduction

At the beginning of this thesis a general statement on food and beverage authentication is given and analytical methods regarding that matter are summarized. Improving traceability and authentication has been requested by law (government regulations (regulation (EC) No 178/2002) as well as consumers. One step in this direction is the use of European quality labels which declare determination of origin and will be explained in more detail. For a better understanding it is also important to get an overview of element composition in plants. Therefore element uptake by plants and application for provenance studies are mentioned. Concluding latest investigations on isotopic and element fingerprinting on foodstuff are summarized and listed in Table 4.

Chapter 3 deals with the experimental setup. This includes a short introduction of the used method, inductively coupled plasma mass spectrometry (ICP-MS), explanation of the sample preparation for measurement as well as a description of the applied method validation and the statistical evaluation.

One objective of this study is the routine analysis of wine samples from different winegrowing areas in Austria with ICP-MS. Results are evaluated using statistical software and conclusions concerning multi-element pattern and strontium isotope ratios are drawn. In addition optimization of the digestion of pumpkin seed and oil and further element and isotopic pattern determination for the identification of geographical origin and traceability from soil to seed to oil are described in detail. A full validation of the determination of rare earth elements using two different instruments was performed. Method validation is the prerequisite to guarantee that an analytical method is fit for purpose. Finally, the determination of phosphorus was under investigation. The challenges are interferences and low ionization potential. Producing a stable signal, with respect to different internal standards, was the main focus.

All results are presented and discussed in chapter four.

A final outlook is given on completing the validation process as well as authentication studies on wine and pumpkin seed oil. Additionally some thoughts are mentioned regarding further measurement procedures of phosphorus using a dynamic reaction cell.

# 2 Food and beverages authentication

Even though various analytical approaches have been known for food and beverages authentication, further development is still required and in progress. Depending on the studied matrix an appropriate method needs to be applied. In 2007 Peres et al. reviewed several analytical procedures which are grouped in physicochemical and biological techniques (Table 1). The first group includes spectroscopy, pyrolysis, variable radioactive isotope composition and the use of an electronic nose while the latter focuses on total bacterial flora analysis. In addition an outlook was given on two up-and-coming techniques: denaturing chromatography in high performance liquid phase (DHPLC) and DNA chips. All these methods are not discussed in further detail throughout this thesis. Even though stable isotope measurements using mass spectrometry was discussed, ICP-MS, the method which is employed in this study to asses element and isotopic fingerprints, was not mentioned at that time. (Peres et al., 2007). Table 1 gives an overview of mentioned methods and related analytes as well as used matrix.

| Analyte | Method | Matrix |
|---|---|---|
| fatty acids/$^{18}O$ | **NMR/MSIR** | milk, cheese, wine, |
| $^{90}Sr$, $^{234}U/^{238}U$ | **IEC-AAS, α-spectrometry** | cheese |
| D/H | **SNIF-NMR** | wine |
| inorganic molecules, sugar, anthocyanins | **MIRS-NIRS** | wine, fruit juice |
| cis and trans unsaturated fatty acids | **FT-MIRS** | cheese |
| aromatic amido acids, nucleic acids, | **FS** | cheese, meat, fish |
| carbohydrates, lipids, proteins, bacteria | **Cp-PyMS** | oyster |
| microbial interaction, androstenone and scatol | **Py-MS** | extra virgin oil, milk, tea, wine, cheese |
| volatile compounds | **EN** | olive oil, orange |
| DNA | **DGGE** | microbial flora in fresh water fish |
| DNA | **DHPLC** | not tested yet |
| DNA | **DNA chips** | not tested yet |
| Nuclear Magnet Resonance | NMR | |
| Mass Spectrometry of Isotope Ratio | MSIR | |
| Ion Exchange Chromatography | IEC | |
| Atomic Absorption Spectrometry | AAS | |
| Site-Specific Natural Isotope Fractionation | SNIF | |
| Mid and Near Infrared Spectroscopy | MIRS-NIRS | |
| Fourier Transform | Ft | |
| Fluorescence Spectroscopy | FS | |
| Curie point | Cp | |
| Pyrolysis | Py | |
| Electronic nose | EN | |
| Denaturant Gel Gradient Electrophoresis | DGGE | |

**Table 1: Analytical approaches concerning provenance studies (Peres et al., 2007)**

Since then, ICP-MS has been used on a broad range for food because it is able to detect a broad range of elements and isotopes in one run. This data can be fed to statistical programs in order

to determine characteristic element and/or isotopic pattern of food depending on their origin. More details on element and isotopic fingerprints used for food authentication are given in chapter 2.3. Nevertheless sample preparation can be time consuming and require statistical number of samples. Therefore further investigations are important for developing routine procedures, identifying elements that are most discriminating as well as creating databanks and mappings. Moreover it is essential to understand how tracer and environment are related (N. N., 2009(b)).

## 2.1 European Quality labels

In order to guarantee the provenience of a product, to avoid fraud but also to promote names and protect quality products the European Union established an agricultural product quality policy. As part of this policy three schemes are used to specify the products:

PDO (protected designation of origin)

PGI (protected geographical indication)

TSG (traditional speciality guaranteed)

Earlier regulations were revised in 2006 and the new regulation (EC) No 510/2006 for PDO and PGI as well as the new regulation (EC) No 509/2006 for TSG became effective on March 20th, 2006.

In order to obtain PDO certification all steps from production via processing to preparation have to take place in a certain geographical area. Furthermore recognized knowledge has to be used within the process. A PGI certification requires at least one of these steps to be geographically linked to a certain area. The above mentioned TSG is all about special and traditional characteristics that distinguish one product from another in obvious manner (European Commission, 2009(a)).

The European Union offers its citizens different databases in order to look up special products and the labels they are linked to. The European DOOR (database of origin and registration) provides all registered and applied product names and related quality schemes. Austria has eight certified PDO products; Vorarlberger Alpkäse, Tiroler Bergkäse, Vorarlberger Bergkäse, Gailtaler Almkäse, Tiroler Graukäse, Tiroler Almkäse(Alpkäse), Waldviertler Graumohn,

Wachauer Marille and 5 certified PGI products; Gailtaler Speck, Steirischer Kren, Tiroler Speck, Steirisches Kürbiskernöl, Marchfeldspargel. Mostviertler Birnmost applied in 2003 but has not been accepted yet (European Commission, 2009(b)).

In addition to the European DOOR another database, E-BACCHUS, is used for identification. It lists geographically protected wines originating in European Union member states and other countries (European Commission, 2009(c)).

Pumpkin seed oil as PGI and wine listed in E-BACCHUS were part of this investigation and are described in further detail.

### 2.1.1 **Cucurbita pepo L.**

Pumpkin is a common name for the species *Cucurbita pepo L.* which is part of the family *Cucurbitaceae* (ITIS, 2009). It is not known where pumpkins emanated from but evidence of the first pumpkin related seeds were found in Mexico between 7.000 and 5.500 years B.C. Some archaeologists even identified *Cucurbita* phytoliths originating from domesticated plants that were dated between 10.000 and 8.000 BC. Furthermore different species were domesticated in different South American areas independently (Piperno and Stothert, 2003). Nowadays pumpkins can be produced on all continents except Antarctica; Mexico, India, the United States and China are the biggest international growers. The main characteristics of a *Cucurbita pepo L* plant are the rambling vines, orange flowers that are shaped like trumpets and hairy stems as well as large, hairy, dark green leaves. The vines reach an expansion of up to ten meters. The yellow or orange fruit is round or longish and has a diameter between 15 and 40 cm. Therefore the berry can weigh up to 30 kg and is one of the largest fruits (Robinson and Decker-Walters, 1997).

#### *2.1.1.1 Cucurbita pepo var styriaca*

Pumpkin seeds, *pepitas*, are mainly used for producing pumpkin seed oil. 100 years ago a natural mutation in a single recessive gene took place in Styria. In addition after several 'man-made' mutations a dark green, pot-bellied, peel-less pumpkin seed was generated. The new subspecies was called *Cucurbita pepo var styriaca* (Fruhwirth and Albin Hermetter, 2007). Since the beginning of the 20$^{th}$ century the traditional styrian oilseed pumpkin has been cultivated and the extrected pumpkin seed oil has become a tradition in Austria. Due to predominantly continental climate as well as the soils favorable characteristics and some production secrets, high quality pumpkin seed oil can be produced in southeastern regions of Austria (N. N., 2009(c)).

Styrian pumpkin seed oil can be labeled PGI following specific production rules and is therefore protected throughout the European Union (European Commission, 2009(b)). Seeds may only be

grown in a specific area of Styria, Burgenland and Lower Austria. Nevertheless elimination of fraud is not an easy task. Thus trustworthy and fast analytical techniques are needed to distinguish between original and adulteration. Some efforts have been put on tocopherol patterns, phytosterols and fatty acid contents. As a result impure oil, due to adding of cheap sunflower oil or rape-seed oil, could be recognized (Mandl et al., 1999). Regarding rare earth elements pattern investigation lead to a forward-looking method for distinction of geographical origin with ICP-MS (Bandoniene, 2007). Protecting its unique taste along with the characteristic deep green shade is requested by/of local growers without price dumping due to seed imports.

### 2.1.2 Wine cultivation and determination of origin

About 50 thousand hectares of vineyards in eastern and southern parts of Austria are cultivated. They can be divided into four main groups: 'Weinland Österreich' including Lower Austria and Burgenland, 'Wien', 'Steiererland' counting all Styrian vineyards and 'Bergland Österreich' including the rest of Austria. Figure 1 shows all regions out of the first three main groups representing more than 99 % of total producing areas in Austria.


**Figure 1: Map of winegrowing regions in Austria (N. N. 2009(a)) modified**

Growing on different bedrocks but also due to differing climate conditions every wine region has its unique taste it is known for. However grape variety, special recipes and varying processes have an influence on a wine's grade, too. Therefore three quality labels have been established according to Austrian wine law namely 'table wine', 'wine of quality' and 'certified

wine'. In addition another appellation was introduced to the wine-system in 2002. DAC (Districtus Austriae Controllatus) comprises one specific varietal that represents a region at its best. Five DAC wines have been accepted yet which are Central-Burgenland DAC, Kamptal DAC, Kremstal DAC, Traisental DAC and Weinviertel DAC. Quality wine from that region with another grape variety is labeled with the specific main group instead. In 2010 Leithaberg DAC will be available as well (N. N., 2009(a)).

'Quality wine' and 'certified wine' are controlled twice by state laboratories, that is to say, chemical analysis and organoleptic tests are run to obtain an official control number as well as a red-white-red band document. Therefore different parameters are under investigation in order to guarantee highest quality (N. N., 2009(a)).

Nevertheless determination of geographical origin on a routine basis using inductively coupled plasma mass spectrometry has not been common in Austria up to now. However researchers around the world are trying to find the fittest way to identify different wine regions. Some parameters have been used individually so far but probably a combination of all will give the best results. Phenolic compounds, ethanol content, stable isotope ratios, heavy isotope ratios and multi-element pattern have been used to discriminate between different vineyards (e.g. (Almeida and Vasconcelos, 2001; Coetzee et al., 2005; Ogrinc et al., 2001; Pérez-Magariño et al., 2002)). Generally speaking analysis should be accurate, cheap, easy and fast.

Element and isotopic fingerprinting by ICP-MS is used for wine authentication as well. Since strontium rarely fractionates in plant uptake (see 2.2.3) wine represents the $^{87}Sr/^{86}Sr$ ratio of the bioavailable Sr in soil (Swoboda et al., 2008). Therefore it is used for determination of geographical origin. Other isotopic systems like boron or lead have been under investigation as well. While boron isotopic composition of wine can be used for characterization lead isotopic composition is altered probably due to industry and pollution (Coetzee and Vanhaecke, 2005; Mihaljevic et al., 2006). In addition multi-element and rare earth element pattern have been used for classification according to provenance in countries like Canada (Greenough et al., 2005; Taylor et al., 2003) , Germany (Gomez et al., 2004) , Portugal (Almeida and Vasconcelos, 2003), New Zealand (Angus et al., 2006), Italy (Galgano et al., 2008) or Spain (Baxter et al., 1997). However rare earth element pattern did not seem to work thoroughly (Angus et al., 2006; Jakubowski et al., 1999).

Nonetheless vinification processes as well as using additives of any kind might alter element composition (Suhaj and Korenovska, 2005; Taylor et al., 2003; Thiel et al., 2004). Therefore it is of analytical interest to trace source of contamination even though these might be specific for a production process.

## 2.2 Plant growth and element composition

Higher plants require different elements for growth. Main provider is soil but also ground water and precipitation. Soil consists of a certain composition of elements. Due to uptake by plants a soils pattern can be reflected in plants grown therein. Nevertheless ion uptake in higher plants is characterized by (Marschner, 1995):

- Selectivity
  - Some elements are taken up more likely whereas other elements are not taken up at all
- Accumulation
  - Plant cells can have a much higher concentration of mineral elements than provided by outer solutions
- Genotype
  - Uptake varies among plant species

Even though mineral element uptake by plants depends on several parameters they are strongly related to their origin. However soil samples from a given area are not always available for comparison regarding provenance studies. Therefore transfer from soil to the products of interest needs to be investigated more. Any alteration like contamination due to manufacturing processes or additives influences the element pattern of processed food. Therefore step by step investigations have to be carried out as has been done e.g. on wine (Castineira Gomez et al., 2004; Catarino et al., 2008).

The next chapters will give an overview of elements in plants. In addition rare earth elements, the strontium isotopic system and phosphorus are explained in more detail with respect to their behavior in plants as well as their use for provenance studies in general.

### 2.2.1 Multi-element pattern

**Most abundant elements in plants are hydrogen, carbon and oxygen (green in**

Figure 2). They are the key compounds of photosynthesis producing organic compounds which are the main frame for any further plant development. Nonetheless different factors play a role for a rise of a plant. Besides that, the isotopic composition of these three elements has been used for determination of origin in several food and beverages (Calderone et al., 2007; Camin et al., 2007; Donarski et al., 2008; Nakashita et al., 2008).

**Other essential elements are divided into macronutrients (dark blue in**

**Figure 2) and micronutrients (light blue in**

Figure 2). The first group contains the nonmetals nitrogen, phosphorus and sulfur but also the alkaline metal potassium and the earth alkaline metals magnesium and calcium. Whereas boron and chlorine as well as the transition metals manganese, iron, nickel, copper, zinc and molybdenum are considered to be micronutrients.

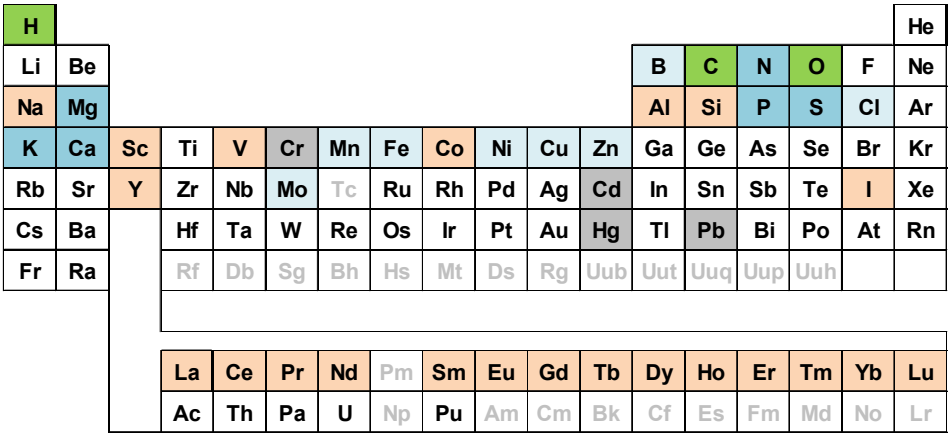


**Figure 2: Periodic table of elements considering essential and nonessential elements in higher plants**

**However not only macro- and micronutrients but another group of elements play a role in different mechanisms different mechanisms of a plant, too. Beneficial elements (peach in**

Figure 2) are not necessarily essential but can affect plant growth in a positive way. Especially regarding trace elements it is sometimes not definite whether an element is essential or not. Nevertheless sodium, silicium, cobalt, aluminium, selenium, iodine, vanadium and all rare earth elements are referred to be beneficial in some way.

**Moreover heavy metals (dark grey in**

Figure 2) like cadmium, chromium, lead and mercury have been located in higher plants as well. Though these accumulations are mainly due to environmental pollution but any beneficial effects have not been reported yet (Marschner, 1995).

Elements that were used for authentication purposes are highlighted in Figure 22 and Figure 27 (chapter 4) regarding wine and pumpkin seed (oil). These elements were selected upon availability in the respective matrices.

### 2.2.2 Rare earth elements

A homogenous group of elements are the so-called rare earth elements (REE) Scandium, Yttrium and the lanthanides (Lanthanum, Cerium, Praseodymium, Neodymium, Promethium, Samarium, Europium, Gadolinium, Terbium, Dysprosium, Holmium, Erbium, Thulium, Ytterbium

and Lutetium). They mistakenly got their name from being found as oxides formerly known as 'earths' in rare minerals. But the elements are not as rare in the earth curst as shown in Table 2 including also a ranking among elements of the periodic table of elements (Encyclopaedia Britannica 2009).

| Element | Symbol | Atomic number | rank* | Earth's crust abundance [μg $g^{-1}$] |
|---|---|---|---|---|
| Scandium | Sc | 21 | 46 | 5 |
| Yttrium | Y | 39 | 31 | 28 |
| Lanthanum | La | 57 | 35 | 18 |
| Cerium | Ce | 58 | 29 | 46 |
| Praseodymium | Pr | 59 | 45 | 5.5 |
| Neodymium | Nd | 60 | 32 | 24 |
| Samarium | Sm | 62 | 42 | 6.5 |
| Europium | Eu | 63 | 57 | 1.1 |
| Gadolinium | Gd | 64 | 43 | 6.4 |
| Terbium | Tb | 65 | 59 | 0.9 |
| Dysprosium | Dy | 66 | 50 | 4.5 |
| Holmium | Ho | 67 | 56 | 1.2 |
| Erbium | Er | 68 | 54 | 2.5 |
| Thulium | Tm | 69 | 65 | 0.2 |
| Ytterbium | Yb | 70 | 53 | 2.7 |
| Lutetium | Lu | 71 | 60 | 0.8 |

*Expressed in a range of 1 to 105.

**Table 2: Relative Abundance of REE in the earth crust (Encyclopaedia Britannica 2009)**

REE are considered to be similar due to their 4f-electrons while the 3d-shell determines their chemical properties. They can be divided into 2 groups: light rare earth elements (LREE) and heavy rare earth elements (HREE). Elements with an atomic number from 57 (La) to 64 (Gd) are referred to as LREE and elements with an atomic number from 65 (Tb) to 71 (Lu) are part of the HREE. Moreover the lanthanide contradiction paradox is very interesting: an increasing atomic number goes along with decreasing ionic radii due to the 4f-orbital. Additionally biochemical behavior can be explained by the similar ionic radius of lanthanides compared to $Ca^{2+}$(Brown et al., 1990). Their physical characteristics are of great importance as well, like electrical, thermal, magnetic, mechanical, optical or crystallographic properties but will not be discussed in more detail (Encyclopaedia Britannica, 2009). Due to the characteristic absorption spectra of lanthanides spectroscopy is useful for identification and quantification but also chromatographic techniques (HPLC) or X-ray fluorescence are used for various applications. However from an analytical point of view neutron activation analysis (NAA) and ICP-MS are analytical methods of choice especially for animal or human tissue and plants because concentrations are very low that is to say in the range of ng $g^{-1}$ (Liang et al., 2005; Tyler, 2004; Wyttenbach et al., 1994).

Bioavailability of REE in soil and their uptake by plants can have an impact on the distribution as well as element pattern in different parts of a plant. However transfer factors (soil plant ratio) are as low as 0.02 to 0.05 because soil properties like pH, organic matter or cationic exchange

capacity have an influence on the exchangeable fraction of rare earth elements. Therefore concentrations in soil are much higher compared to root > leaves > stem > fruit (Cao et al., 2000; D. L. Jones, 1997; Li et al., 2001; Liang et al., 2005; Markert and De Li, 1991; Wen et al., 2001; Xu et al., 2002). As for wheat seed its distribution pattern is related to the soil content but again concentrations are three to four times lower (Liang et al., 2005). Nevertheless uptake differs between plant species as well. In addition anthropogenic sources provide the environment with rare earths in a more reactive form and they have higher bioavailability (Zhang and Shan, 2001). Furthermore plant uptake also takes place through leaves (Chua, 1998). Since China has large REE sources farmers use REE fertilizer to improve crop growth and quality by applying REE directly to the plants (Brown et al., 1990; Maheswaran J and Buckingham, 2001).

REE in wine has been under investigation for element fingerprinting by various researchers. Distinguishing different winegrowing areas has worked satisfyingly according to Augagneur. However Jakubowski reported an influence on the element pattern due to the wine producing process. Especially bentonites can affect the element concentration of rare earths (Mihucz et al., 2006; Rossano et al., 2007). Nevertheless isotopic and other element information should always be considered as well (Augagneur et al., 1996; Jakubowski et al., 1999). Furthermore the element pattern of REE in pumpkin seed oil is of great interest since China has been using REE fertilizer for more than 20 years now (Pang et al., 2001; Xu et al., 2002).

### 2.2.3 **Strontium isotopic system**

The alkaline earth element Strontium has four naturally occurring isotopes with atomic mass units of 84, 86, 87 and 88 and an abundance of 0.56, 9.86, 7.00 and 82.58, respectively, according to the IUPAC (Table 3). All of them are stable isotopes though $^{87}Sr$ is correlated to $^{87}Rb$ due to radioactive $\beta^-$ decay of the latter ($\tau_{1/2}$ = 4.88 ± 0.05 x $10^{10}$ a) (Steiger and JÃ¤ger, 1977). As a consequence the isotopic composition of Sr varies within the geoecological system. $^{87}Sr/^{86}Sr$ ratio is higher in older rocks than in younger ones leading to a dependency of a rocks age but Rb/Sr concentration plays an important role as well. Since strontium is omnipresent in nature it is possible to use it for dating but also as an indicator of geochemical origin (Capo et al., 1998).

| Isotope | Mass (amu) | Abundance (%) | RSU (%) |
|---|---|---|---|
| $^{84}Sr$ | 83.913435 | 0.56 | 0.01 |
| $^{86}Sr$ | 85.909267 | 9.86 | 0.01 |
| $^{87}Sr$ | 86.908884 | 7.00 | 0.01 |
| $^{88}Sr$ | 87.905619 | 82.58 | 0.01 |

**Table 3: Mass, relative abundance and RSU in % of Sr according to IUPAC (de Laeter et al., 2003)**

Strontium undergoes a natural cycle (Figure 3). It is released from rocks via weathering process and transferred to vegetation and to animal and human tissues via the food chain. Therefore it can be used as an ecosystem tracer. Additional sources of Sr are wet and dry precipitation and have to be considered as contributors to Sr composition as well.

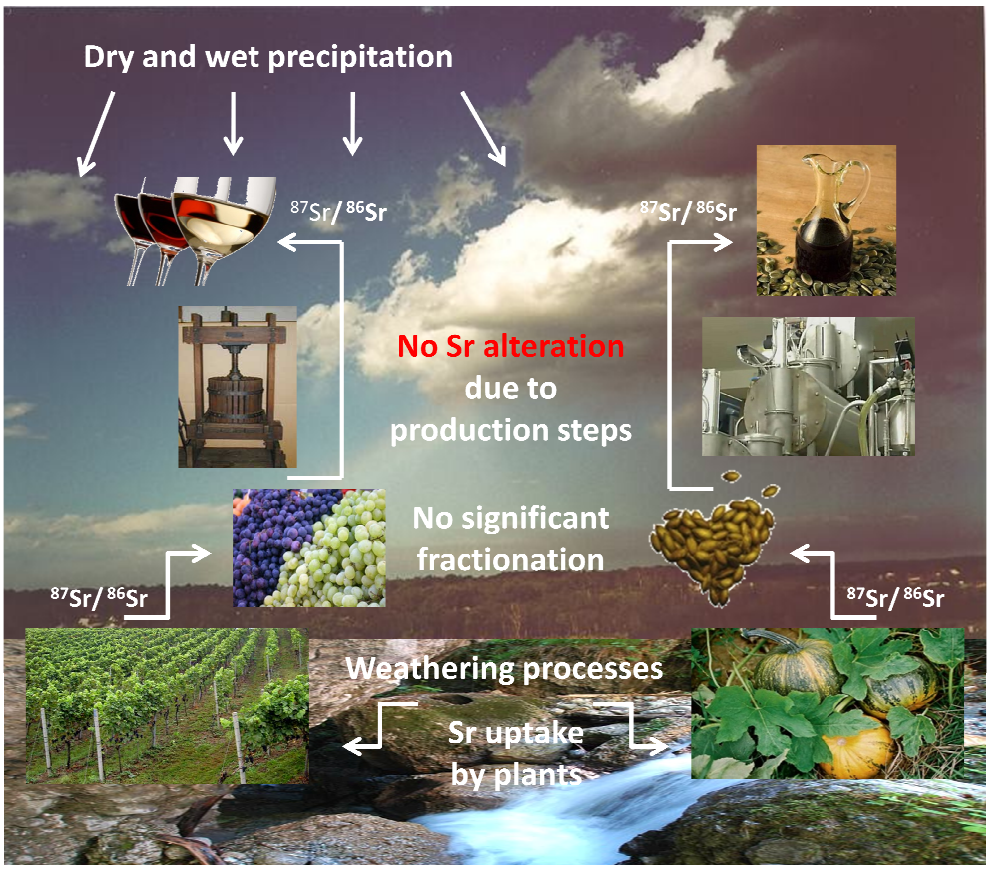


**Figure 3: Natural cycle of Sr**

No significant fractionation of Sr is known for biological processes which is the main advantage of using its isotopes for various authentication studies. It is based on the fact that Sr cations are 'exchangeable' in the ground which represents the main source for vegetation. Therefore the respective cations are leachable from the soil and are available for plants (Stewart et al., 1998). This process will be explained in more detail in chapter 3.3.2. Consequently strontium information of the soil goes directly into the plant through its water uptake and can be used for determination of geographic origin (McCulley et al., 2004). Nonetheless it has to be considered that only the bioavailable Sr contributes to the Sr isotopic composition in plants.

One project which has been funded by the EU is the 'TRACE' project dealing with food traceability. It maps strontium isotope ratios all over Europe. Main objective of the study has been the investigation whether an isotope ratio can be a predicting tool for food products

without the necessity of geographically linked reference material. Therefore a data map, deposited on a geological map, (Figure 4) of the isotopic composition of groundwater was elaborated since water reflects bioavailable strontium that can be significantly different to the total Sr in soil. Natural mineral waters from 19 different regions were sampled and their $^{87}Sr/^{86}Sr$ ratios were analyzed. The values range from 0.7035 up to 0.7777. About 90 % of the mean values of analyzed water samples lay within the predicted data range. In addition water results were compared to ammonium nitrate extracts from soil and digested honey and wheat samples and showed good correlation. However, sea spray might influence the $^{87}Sr/^{86}Sr$ value. Nevertheless in order to create a real 'prediction' map broader varieties of goods need to be analyzed regarding geological origin (Voerkelius et al.).

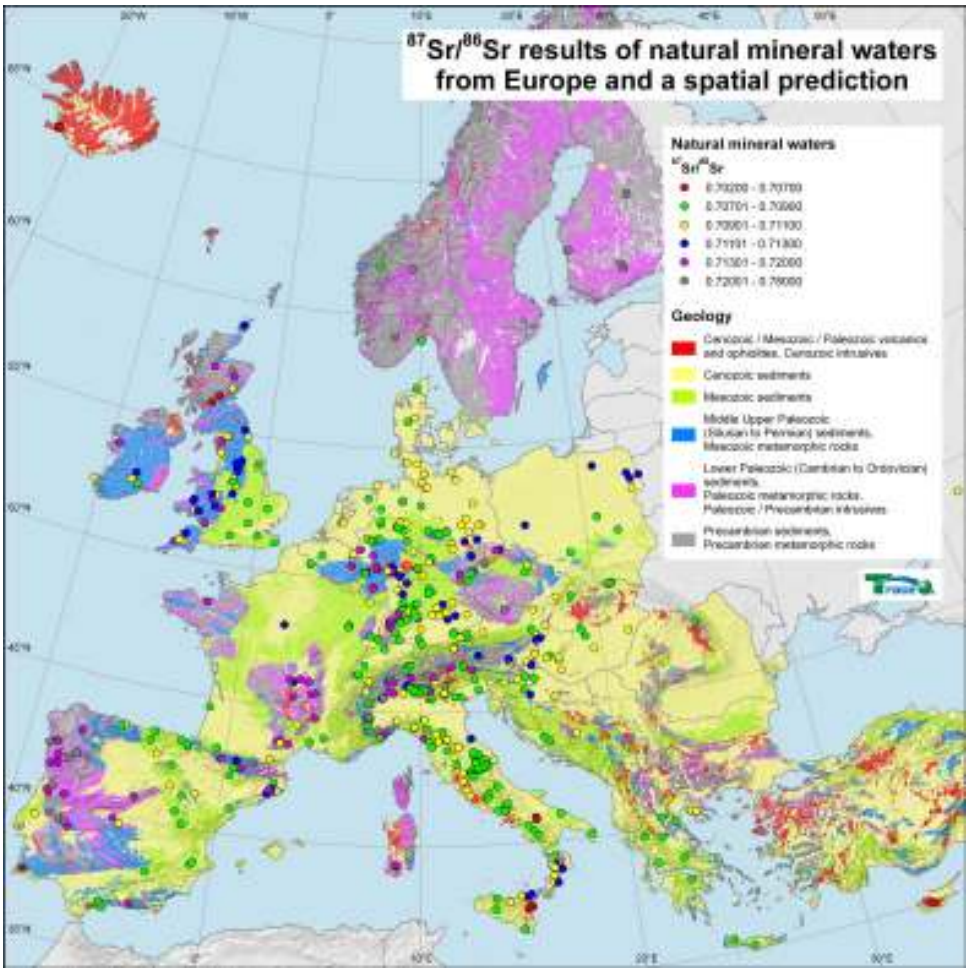


**Figure 4: $^{87}Sr/^{86}Sr$ results of natural water and prediction map (Voerkelius et al.)**

### 2.2.4 **Phosphorus**

Phosphorus has the atomic number of 15 and is located in the 3$^{rd}$ period and 5$^{th}$ main group of the periodic table of elements. Even though there are 23 P isotopes known only one is stable and therefore has an abundance of 100% in nature. As a result $^{31}P$ is a mono-isotopic element with a standard atomic mass unit of 30.97. Two other isotopes $^{32}P$ and $^{33}P$ are radioactive and

are used for scientific purposes as well (e.g. (Barquero et al., 2004; Daroub et al., 2000; Rousk et al., 2007)). They have a half life of 14.26 and 25.34 days respectively.

P is one of three main macronutrients for plants besides potassium and nitrogen. It is involved in many cell processes because it is part of molecules such as nucleic acids, ATP and phospholipids and acts mainly as energy carrier. Therefore the phosphorus cycle is closely linked to the cycles of carbon as well as oxygen, sulfur, nitrogen and iron (Föllmi, 1996). Nonetheless its availability in bulk soil is rather poor and does not meet a plants demand. Since P primarily moves through diffusion which is slow ($10^{-12}$ to $10^{-15}$ $m^{-2}s^{-1}$) the root area is becoming depleted. Thus root geometry and morphology have an influence on uptake of P which mainly occurs in form of inorganic phosphorous (Pi). This is the inorganic form of phosphorus, mostly $H_2PO^-_4$, taken up by plants that hardly exceeds 10 µM in soil solutions and depends on pH (Schachtman et al., 1998). As a consequence P is one of the main fertilizers used in agriculture because it is requested by plants for strong and fast growth.

Finally it can be stated that determination of phosphorus in biological samples can also be used as a potential tool for cancer research (Bandura et al., 2004). Nevertheless its detection is also of interest for oleochemicals (Wiedemann et al., 2004), steels (Yang and Jiang, 2004) and foodstuff (Wu et al., 2003).

## 2.3 Determination of elements and isotope ratios in groceries

As mentioned above element or isotopic fingerprints of groceries are under investigation regarding their provenance. Various analytical techniques can be used to obtain this information. The following table includes the latest research results in food authentication. Matrices, element pattern, isotopic systems and detecting devices are summarized in Table 4 (extension of Brunner, 2007 as shown in 6.5) but do not claim completeness.

| sample type/ matrices | isotopic system/ element pattern | analytical method | literature reference |
|---|---|---|---|
| **beverages** | | | |
| **milk** | | | |
| microwave digestion with nitric acid | P, S, K, Ca, V, Cr, Mn, Fe, Co, Zn, Ga, Rb, Sr, Mo, Cs and Ba | ICP-MS | (Benincasa et al., 2008) |
| skim milk | $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{18}O/^{16}O$, $^{34}S/^{32}S$, and $^{87}Sr/^{86}Sr$ | IRMS, TIMS | (Crittenden et al., 2007) |
| casein fraction | $^{13}C/^{12}C$, $^{15}N/^{14}N$, and $^{34}S/^{32}S$ | IRMS | |
| | $\delta^{18}O$ | GC-IRMS | (Engel et al., 2007) |

| | | | |
|---|---|---|---|
| ashed and dissolved in HCl | Li, Na, K, Mg, Ca | HPIC | (Sacco et al., 2009) |
| microwave digestion with nitric acid and hypochloric acid | Al, Cr, Cu, Fe, Mn, Ni, Zn, Pb, Se and Ba | ICP-AES | |
| | $^{13}C/^{12}C$ and $^{15}N/^{14}N$, | IRMS | |
| freeze-dried and dissolved in $D_2O$ | $^{1}H$ | NMR | |

| | | | |
|---|---|---|---|
| **lemon juice** | | | |
| ashed | As, Br, Co, Cr, Fe, La, Na, Rb, Sb, Sc, and Zn | INAA | (Pellerano et al., 2008) |
| **orange juice** | | | |
| extracted pulp, | $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$ | EA-IRMS | (Rummel et al.) |
| ashed and dissolved in nitric acid | $^{87}Sr/^{86}Sr$ | TIMS | |
| **sparkling drinks** | | | |
| head space gas | $^{13}C/^{12}C$ | GC-C-IRMS | (Calderone et al., 2007) |
| ethanol | $^{13}C/^{12}C$ | EA-IRMS | |
| **ginseng** | | | |
| microwave digestion with nitric acid | $^{87}Sr/^{86}Sr$ | ICP-MS | (Choi et al., 2008; You et al., 2009) |
| **tea (camellia sinensis)** | | | |
| digestion | Ti, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Tl, Pb, Bi, Th, and U | ICP-MS | (Pilgrim et al.) |
| dried tea leaves | $\delta D$, $\delta^{13}C$, $\delta^{15}N$ | IRMS | |
| **cider** | | | |
| digestion with nitric acid and hypochloric acid | $^{87}Sr/^{86}Sr$ | MC-ICP-MS | (García-Ruiz et al., 2007) |
| | Na, K, Ca and Mg | ICP-AES | |
| | Li, Be, B, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, Y, Mo, Cd, Sn, Sb, Cs, Ba, La, Ce, W, Tl, Pb, Bi, Th and U | ICP-MS | |
| **wine** | | | |
| dilution with nitric acid | Mg, Ca, Fe, Mn, Zn, Cu, Cr, Co, Ni, K and Na | FAAS | (Fabani et al.) |

| | | | |
|---|---|---|---|
| diluted | Ca, Fe, K, Mg, Mn, Na and Zn | AAS | (Galgano et al., 2008) |
| acidified with nitric acid | Al, B, Br, P, Rb, S, Si, Sr, Ag, As, Ba, Be, Bi, Cd, Co, Cr, Cs, Cu, Ga, Ge, I, In, Li, Mo, Nb, Ni, Pb, Sb, Sc, Se, Sn, Te, Th, Ti, Tl, U, V, W, Y, Z, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb | ICP-MS | |
| microwave digestion with nitric acid | Al, Ba, Be, Ca, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nd, Ni, Pb, Pr, Sc, Se, Sm, Sr, Tb, Ti, Tm, V, Y, Yb and Zn, | ICP-OES | (Gonzálvez et al., 2009) |
| dry ashing | Al, Ba, Cu, Fe, Mn, Sr, Zn, Ca, K, Na and Mg<br>Ni and Pb | ICP-OES<br>GF-AAS | (Moreno et al., 2007) |
| diluted | Li, Be, B, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Ba, Tl, U | ICP-MS | (Serapinas et al., 2008) |
| **food** | | | |
| **extra-virgin olive oil** | | | |
| | $^{13}C/^{12}C$ | IRMS | (Camin et al.) |
| | D/H, $^{18}O/^{16}O$ | GC-IRMS | |
| extraction with nitric acid/HCl | Li, B, Na, Mg, K, Ca, Mn, Co, Cu, Ga, Se, Rb, Sr, Mo, Cd, Cs, Ba, La, Ce, Nd, Sm, Eu, Yb, Tl, Pb, and U. | ICP-MS | |
| **olive oil** | | | |
| microwave digestion with nitric acid | Eu, Gd, Sm, Sc and Y, As, Be, Ca, Cd, Co, Cr, Fe, Mg, Mn, Ni, Sb, Se, Sr | ICP-MS | (Benincasa et al., 2007) |
| **onions** | | | |
| fresh, dried | Na, Mg, P, Mn, Zn, Rb, Sr, Mo, Cd, Cs, Ba | | (Ariyama et al., 2008) |
| **tomato paste** | | | |
| | $^{1}H$ | NMR | (Consonni et al., 2009) |
| **hazelnuts** | | | |

| | | | |
|---|---|---|---|
| dry ashing | La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu | ICP-MS | (Oddone et al., 2009) |
| **green coffe beans** | | | |
| grinded | $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$ | IRMS | (Rodrigues et al.) |
| **polished rice** | | | |
| powdered | C, N, $\delta^{13}C$, $\delta^{15}N$ | EA/IRMS | (Suzuki et al., 2008) |
| | $\delta^{18}O$ | TCEA/IRMS | |

| | | | |
|---|---|---|---|
| **asparagus** | | | |
| microwave digestion with nitric acid and hypochloric acid | $^{87}Sr/^{86}Sr$ | MC-ICP-MS | (Swoboda et al., 2008) |
| **honey** | | | |
| diluted and homogenized | $^{1}H$ | NMR | (Donarski et al., 2008) |
| diluted and homogenized | P, S, Cl, K, Ca, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Br, and Rb | X-RAY | (Necemer et al., 2009) |
| **vendace caviar** | | | |
| ashed caviar | $^{87}Sr/^{86}Sr$ | MC-ICP-MS | (Rodushkin et al., 2007) |
| | $^{187}Os/^{188}Os$ | | |
| microwave digestion with nitric acid | Cl, Na, P, S, K, Mg, Ca, Zn, Br, Fe, Mn, Si, Sr, Rb, Cu, I, Se, As, Ba, Al, B, Co, Pb, Ag, Mo, Li, Ti, Hg, Cs, Ni, Ge, Sn, Cd, V, Cr, Sb, Pd, Te, U, Tl, Zr, Nd, Ga, Rh, La, Y, Ce, W, Be, Ta, Bi, Gd, Ru, Pr, Sc, Sm, Th, Wu, Re, Dy | ICP-SFMS | |
| **farmed and wild turbot** | | | |
| freeze-dried tissue | $\delta^{13}C$, $\delta^{15}N$ | CF-EA-IRMS | (Busetto et al., 2008) |
| **salmon** | | | |
| lipid extract | $^{13}C$ | NMR | (Martinez et al., 2009) |
| **beef** | | | |
| defatted dry matter | $\delta^{13}C$, $\delta^{15}N$, $\delta^{18}O$ | EA/IRMS | (Nakashita et al., 2008) |
| defatted muscle | $^{13}C/^{12}C$, $^{15}N/^{14}N$, $^{34}S/^{32}S$ | EA-CF-IRMS | (Bahar et al., 2008) |
| defatted dry mass | $\delta^{13}C$, $\delta^{15}N$ | IRMS | |
| lipid | $\delta^{2}H$, $\delta^{18}O$ | GC-IRMS | |

| | | | |
|---|---|---|---|
| beef tissue UV-digestion with nitric acid and hypochloric acid | various elements | ICP-MS | (Heaton et al., 2008) |
| **cattle** | | | |
| tissue | $\delta^{13}C$ and $\delta^{15}N$ | IRMS | (Guo et al.) |
| **meat juice** | | | |
| | $\delta^{2}H$ and $\delta^{18}O$ | IRMS | (Horacek et al.) |
| **dried beef** | | | |
| | $^{1}H$ | NMR | (Shintu et al., 2007) |

| | | | |
|---|---|---|---|
| **poultry meat and dried beef** | | | |
| extracted water from meat | $\delta^{18}O$ | IRMS | (Franke et al., 2008) |
| microwave digeston with nitric acid | Ca, Cu, Ga, Ni, Pd, Rb, Tl, V, Zn, As, Se, Rb, Sr, Mo, Nd, Tl, Na, Gd | ICP-MS | |
| **lamb meat** | | | |
| fat-free dry mass and lipid fractions | $\delta^{2}H$, $\delta^{13}C$, $\delta^{15}N$, $\delta^{34}S$ | IRMS | (Camin et al., 2007) |

**Table 4: Element compounds detected in different foods using various analytical devices**

# 3 Experimental setup

The following chapters give a short overview of the used instruments as well as a listing of reagents, reference materials, different sample pretreatments and sample preparations for measuring procedures. Furthermore method validation is described in more detail.

## 3.1 Inductively Coupled Plasma Mass Spectrometry

During the early 1980s inductively coupled plasma mass spectrometry (ICP-MS) was introduced to the scientific world. It has become more and more a routine device since it combines very low detection limits (most elements have LoDs < 0.01 µg $l^{-1}$) with a high sample throughput and multi-element capabilities. Not only quantitative and qualitative information can be obtained but also isotope ratios can be measured simultaneously. Having the opportunity of coupling different devices e.g. a Laser-Ablation system, gas chromatography or different types of liquid chromatography to ICP-MS it is even more versatile than any other analytical instrument available. However it has its limitations as well. An experienced operator is required and running costs are higher compared to other methods. In addition spectral interferences, matrix effects as well as plasma instability might be a problem (Thomas 2001(a)).

### 3.1.1 General Overview

An ICP-MS can be divided into four different parts that will be described in more detail in the following chapters: sample introduction, ion source, mass analyzer and detector. A schematic set-up is shown below (Longerich and W., 2001). For an extensive examination it is recommended to read a book about that topic e.g. (Longerich and W., 2001; Nelms, 2005).

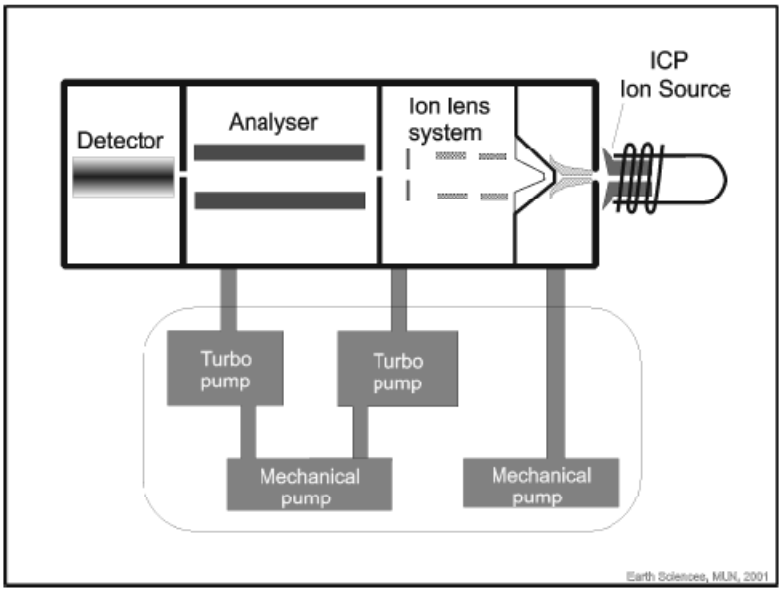


**Figure 5: Schematic set-up of an ICP-MS instrument (Longerich and W., 2001)**

#### *3.1.1.1 Sample introduction*

Nebulizer and spray chamber are part of the sample introduction considered to be the weakest part of the instrument. The sample is pumped into the nebulizer if the system is not operated in self aspirating mode. A peristaltic pump can be used because it provides a constant liquid flow and does not depend on the viscosity of different solutions. Once entered the nebulizer the liquid is sprayed into a fine aerosol by the nebulizer. Different nebulizer designs are used for ICP-MS: concentric, crossflow, microconcentric and microflow are among the mostly used. While the nebulizer forms tiny droplets different spray chambers are used to reject the larger aerosol droplets and also to reduce pump produced pulses before entering the plasma (Thomas 2001(a)).

#### *3.1.1.2 Ion source*

The ion source is generated by a plasma torch, a radio frequency (RF) coil and a RF power supply. Three concentric tubes usually made from quartz are the torch compounds which contain either plasma gas, auxiliary gas or nebulizer gas. Argon is the plasma gas of choice. The plasma consists of different temperature zones heating up to 7500 to 10 000 K. Therefore the sample aerosol goes through different steps of conversion. Starting as a droplet the solution desolvates and becomes solid to further vaporize followed by an atomization to finally become a positively charged ion.

An interface is needed in order to transport the ions from the plasma to the analyzer with pressure of 760 torr and $10^{-8}$ torr respectively. It consists of a sample cone and a skimmer cone made of nickel or aluminum. After passing the skimmer cone and the following ion optics the ions are directed into the mass analyzer (Thomas, 2001(b)).

#### *3.1.1.3 Mass analyzer*

Different kinds of mass analyzer are available. Nonetheless the ions are always separated according to their mass to charge ratio (m/z). Double focusing magnetic sector fields, quadrupole mass filter and time-of-flight mass separators have all different strengths and weak points that are discussed elsewhere (Thomas, 2001(c)).

A quadrupole filter is by far the most common analyzer of ICP-MS instruments. It is constructed of four parallel conductive binary gold metalized rods combined with ceramic mounting collars. A radio frequency field (RF) is applied at one pair of rods and a direct current field (DC) on the other pair. As a result only ions with a selected mass to charge ratio can pass through and arrive at the detector. All other ions are discarded from the quadrupole. It covers a mass range from 5 to 270 atomic mass unit (amu) in just a few milliseconds. However the resolving power (Equ. 1) is not as high as for other mass analyzers but improving the resolution always comes along with loss of sensitivity (Brenner, 2007).

**Equ. 1**

$$R = \frac{m}{\Delta m}$$

#### *3.1.1.4 Detector*

After mass separation ions are detected. Most common detectors are channel electron multipliers, secondary electron multipliers (SEM) and a Faraday cups. The first two are used for low ion count rates while the Faraday cup is useful for high ion count rates. A dual-stage discrete dynode detector is used to determine high and low concentrations switching between pulse and analog mode (Thomas, 2002).

### 3.1.2 **ICP- QMS**

The inductively coupled plasma quadrupole mass spectrometer used in this work is ELAN DRC-e (PerkinElmer, Ontario, Canada) which was used for multi-element analysis including REE, Sr/matrix separation screening and phosphorus measurements.

A PerkinElmer AS 93 Plus (PerkinElmer, Ontario, Canada) autosampler is attached to a MicroMist nebulizer (PerkinElmer, Ontario, Canada) via a tube. Due to a lower sample uptake necessary for Sr/Rb screening (3.3.4) a PFA nebulizer (PFA ST nebulizer, Amsterdam, Netherlands) was used instead for that procedure. Furthermore it is equipped with a cyclonic spray chamber (CPI International, Amsterdam, Netherlands).

A dual stage discrete dynode detector is located at the end of the ELAN DRC-e. It was operated in dual mode during all measurements.

The instrument was tuned on a daily basis prior to analysis for optimum indium intensity (> 500 000), oxide rate (< 5%), doubly charged ions rate (< 4%) and lens voltage (DAC value (In) should not be above 12 V). Multi-element analysis, phosphorus measurements and rare earth element analysis were carried out using the instrumental setup shown in Table 5 column three whereas Sr/Rb screening parameters are listed in column four. Additionally DRC cell parameters are summarized in Table 6.

The following isotopes have been measured during multi-element analysis: $^{7}$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, $^{85}$Se, $^{88}$Sr, $^{98}$Mo, $^{107}$Ag, $^{109}$Ag, $^{111}$Cd, $^{114}$Cd, $^{128}$Te, $^{130}$Te, $^{137}$Ba, $^{138}$Ba, $^{203}$Tl, $^{205}$Tl, $^{207}$Pb, $^{208}$Pb, $^{209}$Bi and $^{238}$U. Regarding measurements of rare earth elements these isotopes have been chosen: $^{45}$Sc, $^{89}$Y, $^{139}$La, $^{140}$Ce, $^{141}$Pr, $^{142}$Nd, $^{152}$Sm, $^{153}$Eu, $^{158}$Gd, $^{159}$Tb, $^{164}$Dy, $^{165}$Ho, $^{166}$Er, $^{169}$Tm, $^{174}$Yb, $^{175}$Lu.

| Parameter | Unit | multi-element, P, REE | Sr/Rb screening |
|---|---|---|---|
| Rf Power | [W] | 1250 | 1250 |
| plasma gas flow rate | [L*min$^{-1}$] | 15 | 15 |
| auxilliary gas flow rate | [L*min$^{-1}$] | 0.6 | 0.6 |
| nebulizer gas flow rate | [L*min$^{-1}$] | 0.98-1.02 | 0.98-1.02 |
| lens settings (DAC value) | [V] | < 12 (In) | < 12 (In) |
| signal intensity | [cps] | 650 000-900 000 | 400 000-650 000 |
| sample uptake rate | [µl*min$^{-1}$] | 100 | 40 |
| sample cone | | nickel | nickel |
| skimmer cone | | nickel | nickel |
| nebulizer | | glass | PFA |
| number of sweeps | | 10 | 8 |
| number of readings | | 1 | 1 |
| number of replicates | | 5 | 5 |
| flush delay | [sec] | 80 | 80 |
| pump velocity | [rpm] | 20 | 10 |

**Table 5: ELAN DRC-e operation parameters**

The dynamic reaction cell (DRC) was used for analyzing P. The DRC is positioned after the auto lens and before the analyzing quadrupole. It is generally used to remove major spectral interferences.

It is possible to operate the DRC with a number of different gases e.g.: He, Ar, $O_2$, $N_2$, $CH_4$ or $NH_3$.

Phosphorus has a rather poor ionization yield in the plasma (~33%) (Houk, 2008). Further its mass is not interference free. $^{15}N^{16}O^+$, $^{14}N^{16}O^1H^+$ and $^{12}C^1H^{316}O^+$ are the main polyatomic interferences for $^{31}P^+$. Therefore $O_2$ is used as reaction gas to shift $^{31}P^+$ to $^{31}P^{16}O^+$. Reaction with $O_2$ is thermodynamically not allowed for the interfering species while $^{12}C^{35}Cl^+$ and $^{48}Ti^+$ can potentially interfere with $PO^+$ (Bandura et al., 2002).

Cell parameters (Table 6) were optimized ahead of the first measurements series and used throughout all experiments.

| | | |
|---|---|---|
| cell gas | | $O_2$ |
| cell gas flow | [L*min$^{-1}$] | 0.4 |
| Rpa value | | 0 |
| Rpq value | | 0.45 |

**Table 6: DRC parameters for phosphorus measurements**

### 3.1.3 **HR-ICP-SFMS**

ELEMENT2 (Thermo Scientific, Bremen, Germany) is a high-resolution double focusing sector-field ICP-MS in reverse Nier-Johnson geometry. It was used for measurements of rare earth elements and related method validation.

A magnetic field acts as mass separator while the electrostatic analyzer focuses the energy as can be seen in Figure 6. As a result a resolution up to 10 000 can be achieved. Nevertheless the

ELEMENT2 can be operated in three different modes; low resolution (R<300), medium resolution (R=3000-3500) and high resolution (R>8500) depending on the preselected entrance and exit slit width.

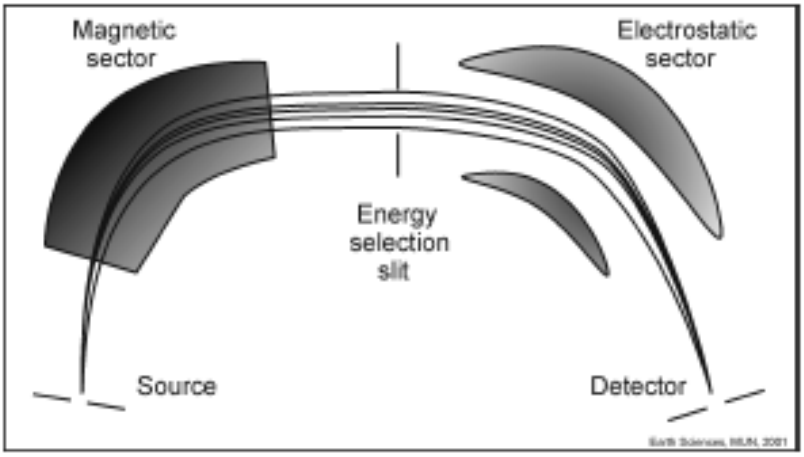


**Figure 6: reverse Nier-Johnson geometry (Longerich and W., 2001)**

The instrument is equipped with an ESI SC 4 (Elemental Scientific, Inc., Omaha, USA) autosampler, a Micromist nebulizer and a peltier cooled cinnabar spray chamber PC³ (Elemental Scientific Inc., Omaha, USA). The separated ions are detected by a SEM.

The instrument was tuned for maximum indium intensity and low oxide rate (5-9 % $UO_2$) which could not be achieved at all times.

The operation parameters for rare earth element measurements are summarized in Table 7.

| Parameter | Unit | REE |
|---|---|---|
| Rf Power | [W] | 1300 |
| cool gas flow rate | $L*min^{-1}$ | 16 |
| auxilliary gas flow rate | $L*min^{-1}$ | 1.15 |
| sample gas flow rate | $L*min^{-1}$ | 0.97 |
| DAC cool gas flow rate | $L*min^{-1}$ | 0.47 |
| signal intensity In (LR) | cps | ~ 1 200 000 |
| signal intensity In (MR) | cps | ~ 60 000 |
| signal intensity In (HR) | cps | ~ 10 000 |
| sample uptake rate | $\mu l*min^{-1}$ | 100 |
| sample cone | | aluminum |
| skimmer cone | | aluminum |
| nebulizer | | glass |
| spray chamber | | $PC^3$ |
| runs | | 3 |
| passes | | 3 |
| flush delay | [sec] | 80 |
| pump velocity | [rpm] | 6.35 |

**Table 7: ELEMENT2 operation parameters**

Different isotopes were measured in low resolution ($^{89}Y$, $^{139}La$, $^{140}Ce$, $^{141}Pr$, $^{147}Sm$, $^{149}Sm$, $^{143}Nd$, $^{145}Nd$, $^{146}Nd$, $^{151}Eu$, $^{153}Eu$, $^{165}Ho$, $^{166}Er$, $^{167}Er$, $^{169}Tm$, $^{171}Yb$, $^{172}Yb$, $^{173}Yb$, $^{155}Gd$, $^{175}Lu$, $^{159}Tb$, $^{161}Dy$,

$^{163}$Dy), medium resolution ($^{45}$Sc) and high resolution ($^{165}$Ho , $^{166}$Er, $^{167}$Er, $^{169}$Tm, $^{171}$Yb, $^{172}$Yb, $^{173}$Yb, $^{155}$Gd, $^{175}$Lu, $^{159}$Tb, $^{161}$Dy, $^{163}$Dy). Since count rates were rather low in high resolution the accordant isotopes were not taken into account for method validation or any evaluation with respect to rare earth elements.

### 3.1.4 **MC-HR-ICP-MS**

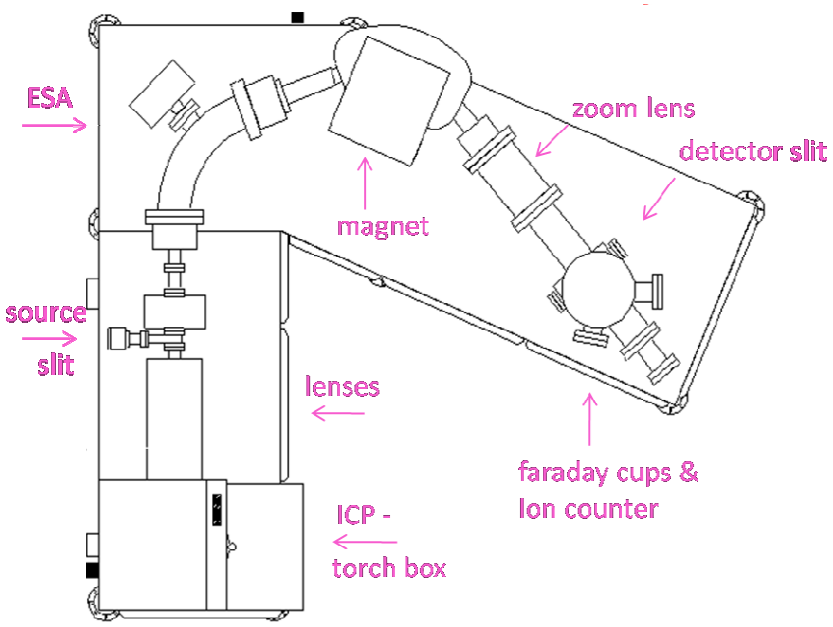


**Figure 7: Schematic set-up of the Nu Plasma (Nu Instruments, 2007 )**

Nu Plasma (Nu Instruments Ltd., Wrexham, UK) is an advanced double focusing high resolution multiple collector ICP-MS instrument. Its schematic set-up is shown above (Figure 7). The instrument is equipped with an ESI SC4 autosampler (Elemental Scientific, Inc., Omaha, USA) and a membrane desolvating system (DSN 100, Nu Instruments Ltd, North Wales, UK) for automatically sampling and producing a stable signal, respectively. A PTFE membrane, a PFA spray chamber and a self-aspirating PFA nebulizer are the main parts of the DSN. Membrane and spray chamber are heated up to about 110 ± 10 °C in order to dry the aspirated liquid sample that finally reaches the plasma. Due to low Sr concentration in some samples -especially oil digests- it was required to increase sensitivity. Therefore a high performing skimmer cone was used to enhance signal intensity. This has worked for e.g. neodymium but fractionation processes have not been fully understood so far (Newman et al., 2009).

Not only the complex lens system but also the electrostatic analyzer (ESA) as well as the magnet in Nier-Johnson geometry define the Nu Plasma. Extraction and deflection lenses are right behind the sample and skimmer cone. A zoom lens system is positioned before the faraday cup assembly (Nu Instruments, 2007 ).

Twelve Faraday cups and three ion counters (IC) represent the detection system (Nu Instruments, 2007 ). MC-ICP-MS was used for measuring strontium isotope ratios.

The faraday cup arrangement is shown in Table 8 together with masses as well as the natural abundance of each element.

| cup | L5 | L4 | L3 | L2 | L1 | Ax | H1 | H2 | H3 | H4 | H5 | H6 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| mass | 82 | 83 | 84 | 85 | | 86 | | 87 | | 88 | | 89 |
| Sr | | | 0.56 | | | 9.86 | | 7 | | 82.6 | | |
| Rb | | | | 72.2 | | | | 27.8 | | | | |
| Kr | 11.60 | 11.50 | 57 | | | 17.3 | | | | | | |

**Table 8: Faraday collector block arrangement**

$^{86}Sr$ was measured as axial mass. Mass separation for Sr is 0.5. Therefore mass 85 was measured on L2 and masses 87 and 88 on H2 and H4, respectively. In order to detect $^{87}Rb$ and $^{87}Sr$ individually a resolution of about 300 000 would be necessary but cannot be achieved. Consequently a separation step is required to get rid of possible interferences as explained in 3.3.3. Additionally a mathematical correction for residual Rb is obligatory with an appropriate mass bias correction as will be explained in the next sub-chapter.

#### *3.1.4.1 Measure zero method, mass bias correction and Rb correction*

A quite nice feature of the Nu Plasma software is its possibility to write so called NICE files. NICE is the abbreviation of 'Nu Instruments Calculation Editor'. A routine NICE file has been available for strontium ratio measurements and was used for that purpose (see 6.5). All equations that contribute to the final result can be stated and their outcome is shown on the output file if needed.

Evaluating the proper Sr isotope ratio a few calculation steps are required. First of all measure zero method is applied. These background signals will be subtracted from the beams measured. Additionally $^{87}Sr$ needs to be corrected for its isobar $^{87}Rb$ (Equ. 4). Even though a separation step takes place ahead of measurements (3.3.3) potentially residual Rb needs to be corrected for mathematically. Secondly the so called mass bias has to be corrected for appropriately. Exponential law is the most potential correction equation for that purpose (Equ.5). Therefore a fractionation factor is calculated (Equ. 2) (Albarède et al., 2004; Yang and Sturgeon, 2003). $^{86}Sr/^{88}Sr$ isotope ratio has an accepted value that is assumed to be stable having a value of 0.1194 and was used for that matter. However it has been stated that fractionation takes place in nature (Halicz et al., 2008) but was neglected throughout this thesis. Nevertheless the measured $^{86}Sr/^{88}Sr$ values and the accepted constant value are contributing to the fractionation

factor. This is in agreement with literature as long as the same correction factors are used which allows distinction of goods via their isotope ratios.

**Equ. 2**

$$f = \left( \log \left( \left( \frac{^{86}Sr}{^{88}Sr} \right)_{ref} \cdot \left( \frac{^{86}Sr}{^{88}Sr} \right)_{meas}^{-1} \right) \right) \cdot \left( \log \frac{m_{86}}{m_{88}} \right)^{-1}$$

**Equ. 3**

$$^{87}Rb_{corr} = {}^{85}Rb \cdot Rb_{factor} \cdot \left( \frac{m_{Rb87}}{m_{Rb85}} \right)^{-f}$$

**Equ. 4**

$$^{87}Sr_{corr} = {}^{87}Sr - {}^{87}Rb_{corr}$$

**Equ. 5**

$$\left( \frac{^{87}Sr}{^{86}Sr} \right)_{corr} = \left( \frac{^{87}Sr_{corr}}{^{86}Sr} \right)_{meas} \cdot \left( \frac{m_{87}}{m_{86}} \right)^{f}$$

NIST SRM 987 was used as reference material and measured every 5 samples past a $HNO_3$ (1% w/w) blank. Its certified isotope ratio range is 0.71034 ± 0.00026 and could be achieved throughout all measurements. However the commonly accepted value is 0.71026 (Balcaen et al., 2005).

Prior to starting the measurement series the instrument was tuned for optimum strontium intensities and isotope ratio precision on a daily basis. Hence torch position, gas flows and lens settings were adjusted as they affect sensitivity, peak shape and peak alignment. All essential parameters for strontium isotope ratio measurements are summarized in Table 9 Regular skimmer cone and high performing skimmer cone required 20 ng $g^{-1}$ or 5 ng $g^{-1}$ of NIST SRM 987 as tuning and reference solution, respectively. A voltage of 3-6 V could be achieved depending on the instrument's condition.

| Parameter | Unit | Sr IR |
|---|---|---|
| Rf power | [W] | 1300 |
| axial mass | [m/z] | 86 |
| mass resolution | [m/Δm] | 300 |
| plasma gas flow | [L*min$^{-1}$] | 13 |
| auxiliary gas flow | [L*min$^{-1}$] | 1.2 |
| nebulizer back pressure | [psi] | ~30 |
| DSN 100 hot gas flow | [L*min$^{-1}$] | ~0.3 |
| DSN 100 membrane gas flow | [L*min$^{-1}$] | ~3 |
| DSN 100 membrane temperature | [°C] | ~115 |
| spray chamber temperature | [°C] | ~115 |
| sample uptake rate | [µL*min$^{-1}$] | 40 |
| nebulizer | | PFA |
| sample cone | | nickel |
| skimmer cone | | nickel |
| instrumental sensitivity general | [V*ppm$^{-1}$] | ~200-500 |
| instrumental sensitivity high performing cone | [V*ppm$^{-1}$] | ~ 730 |
| measurements per block | | 10 |
| number of blocks | | 6 |

| | | |
|---|---|---|
| dwell time | [s] | 5 |

**Table 9: NuPlasma operation parameters**

As the detector must not be overloaded with immoderate amount of Sr matrix separated samples were screened as explained in 3.3.4 to obtain the Sr concentration for further dilution. Optimum voltage should be between 3-8 V and must not exceed 10 V at any time. The higher the voltage the better the precision, though. Since wine and oil samples had very low Sr content dilution was necessary for soil samples only.

## 3.2 Materials, reagents and samples

Laboratory work was performed in either a 10 000 or 100 000 cleanroom environment

### 3.2.1 Laboratory materials

New polyethylene (PE) disposable materials like tips, test tubes, setra-cups and bottles were cleaned prior to use. The first step contained acid purification in $HNO_3$ (10% w/w) overnight followed by soaking in $HNO_3$ (1% w/w). Afterwards all tools were rinsed with HQ water and air-dried. Sample and standard preparation took place in a class 100 000 cleanroom.

### 3.2.2 Reagents and reference material

Used reagents, standards and reference materials are listed below:

- *$HNO_3$ (65%) (p.a grade, MERCK KGaA, Darmstadt, Germany)*
- *deionised water (18MΩ) (SG,Wasseraufbereitung und Regenerierstation GmbH, Barsbüttel, Germany)*
- *$H_2O_2$ (31%) (p.a grade, MERCK KGaA, Darmstadt, Germany)*
- *Ammonium nitrate, (rectapure, VWR International GmbH, Vienna, Austria)*
- *ICP Multi Element Standard Solution VI (CertiPur, suprapure, MERCK KGaA, Darmstadt, Germany)*
- *NIST SRM 987 $SrCO_3$ (National Institute for Standards and Technology, Gaithersburg, USA)*
- *Phosphorus ICP Standard: 1010 mg $l^{-1}$ P (SIGMA, ARISTAR, VWR International GmbH, Vienna, Austria)*
- *Indium Standard: 1002 mg $l^{-1}$ (Merck KGaA, Darmstadt, Germany)*
- *REE Multi-element Solution 1 (Claritas PPT, SpexCertiPrep, Metuchen, NJ, USA)*
- *BCR-2 (United states Geological Survey, Certificate of Analysis, Denver, USA)*
- *BHVO-2 (United states Geological Survey, Certificate of Analysis ,Denver, USA)*

Deionised 18 MΩ water was purified by a laboratory grade water purification system (SG, Wasseraufbereitung und Regenerierstation GmbH, Barsbüttel, Germany', while sub-boiled water was generated by an ultrapure quartz apparatus (MLS DuoPur, MLS, Leutkirch im Allgäu, Germany). $HNO_3$ (p.a.) was sub-boiled twice in an ultrapure quartz apparatus (MLS DuoPur, MLS, Leutkirch im Allgäu, Germany). 1 % w/w $HNO_3$ or $H_2O$ (sub.) were used for further dilution. Standards and reference materials were prepared gravimetrically by using a laboratory balance (BP 210D, Sartorius AG, Göttingen, Germany) and stored in a refrigerator at 4 °C.

### 3.2.3 Sample material

Sampling of 99 authentic wines made of grapes from different areas in Austria (Figure 1) took place at 'HBLA und Bundesamt für Wein- und Obstbau, Klosterneuburg'. Each wine was filled in

a PE test tube and stored in the fridge (4°C) until digestion. Pumpkin seeds and oil used for method optimization were bought in local supermarkets (dm GmbH, Hofer KG) and used out of the packing. Traceable pumpkin seed oil (extracted with petroleum ether) and milled pumpkin seeds from various countries were provided by Micha Horacek (ARC Seibersdorf Research GmbH). In addition creek water, soil, seeds and oil (which was stored in an aluminum can) from a pumpkin seed oil mill in South-East-Styria were sampled locally. Creek water was acidified to approximately 2% w/w nitric acid content to avoid organic decomposition. Seeds were grinded in a ball mill and dried in the oven before digestion. All pumpkin related samples were stored at room temperature. Additionally digested coffee samples from Magdalena Lang (VIRIS Lab, Vienna) were used for method validation and phosphorus measurements.

All sample codes and evaluated concentrations are listed in chapter 6.

## 3.3 Sample preparation

Sample preparation is necessary in order to convert different matrices in appropriate and measurable solutions. Wine, pumpkin seed and pumpkin seed oil samples were digested using microwave assisted digestion (see 3.3.1). Soil samples underwent $NH_4NO_3$ extraction to retrieve bioavailable Sr fraction. Creek water was acidified after sampling and used that way. The subsequent separation step required for strontium isotope ratio measurements will be explained in more detail. Finally samples were diluted to reduce nitric acid content as well as obtain optimum element concentrations for ICP-MS analysis.

### 3.3.1 Microwave digestion (MW)

Microwave digestion is an important step in sample preparation since ICP-MS is not suitable for huge amounts of organic input of any kind because matrix effects occur and cones and tubes get clogged more easily. Therefore it is necessary to digest food and beverages before introducing them to the instrument. A suitable procedure for wine already exists and was applied on all wine samples (Katona et al., 2008). Regarding the pumpkin batch two digestion techniques were investigated.

#### *3.3.1.1 Pumpkin seed and Pumpkin seed oil MW digestion optimization*

Digestion procedure was optimized using pumpkin seeds and pumpkin seed oil from local supermarkets. Before digestion pumpkin seeds were grinded with a ball mill (Retsch, MM 2000, Haan, Germany) for 10 min at 20 rpm. Afterwards they were dried in the oven for 24 h at 90°C.

Different digestion programs were used for sunflower seed oil, olive oil, pumpkin seed oil and pumpkin seeds by various researchers. An amount of 0.1 g to 0.5 g of oil as well as seeds was digested with different mixtures of either nitric acid only or nitric acid and hydrogen peroxide.

The latter has a better digestion rate even though $H_2O_2$ can contain metal contamination. Consequently digestion with nitric acid only is preferred (Angioni et al., 2006; Ansari et al., 2009; Benincasa et al., 2007; Juranovic et al., 2003).

The optimization procedure was started with a quantity of 0.1 g seeds or oil adding 3 ml of nitric acid (65% w/w) in 'Teflon' digestion bombs. An established microwave program was used (microwave: MLS 1200mega, MLS, Leutkirch im Allgäu, Germany) and is summarized in Table 10. The solution was cooled in the bomb, emptied in a PE bottle and filled up to a quantity of 15 g with $H_2O$ (sub.). In order to get higher concentrated solutions the amount of seeds and oil was increased stepwise. 0.5 g of seed and 1 g of oil turned out be the quantity of choice using 5 ml and 10 ml nitric acid (65% w/w) respectively. The solution was filled up to an amount of 10 g with sub-boiled water after digestion.

| time [min] | power [W] |
|---|---|
| 5 | 250 |
| 5 | 400 |
| 10 | 600 |
| 5 | 250 |
| 10 | 0 |

**Table 10: Microwave program used for digestion**

In addition oil and seeds were digested using nitric acid and hydrogen peroxide. For a quantity of 0.5 g material 4 ml of $HNO_3$ and 2 ml of $H_2O_2$ were used and digested satisfyingly. Nevertheless the digestion procedure worked well even with nitric acid only for both oil and seed. Therefore $HNO_3/H_2O_2$ digestion was not further investigated.

| | initial weight (g) | $HNO_3$ (ml) | total weight (g) |
|---|---|---|---|
| pumpkin seed | 0.5 | 5 | 10 |
| pumpkin seed oil | 1 | 10 | 10 |
| wine | 0.2 | 4 | 15 |

**Table 11: Microwave assisted digestion procedure of pumpkin seed, pumpkin seed oil and wine**

Optimized digestion procedure for pumpkin seeds and pumpkin seed oil are summarized in Table 11.

### *3.3.1.2 Red and white wine MW digestion*

2 ml of wine were weighed into a 'Teflon' digestion bomb and 4 ml of nitric acid (65% w/w) were added (Table 11). The same program used in 3.3.1.1 was applied (Table 10). Cooled solutions were filled up with $H_2O$ (sub.) to a quantity of 15 g and stored at room temperature until further proceedings and measurements.

### 3.3.2 Soil extraction with ammonium nitrate

Leachable cations in soil are of interest because they are available for plant uptake. It is assumed that heavy metal mobility is influenced by different factors: dissolved organic matter (DOM), pH and dissolved organic carbon (DOC) (Hoffmann et al., 1998).

1 M ammonium-nitrate seems to be an appropriate way to extract soluble cations (Gryschko et al., 2005). Still some elements may be excluded due to low soluble contents in soil. Therefore misleading predictions may be possible. Of course, different chemical processes influence the extraction procedure. Due to dissociation of ammonium lower pH is achieved which is responsible for desorption of heavy metals in soil. Furthermore forming metal ammine complexes plays an important role depending on the energy gained from the new binding compared to soil-metal strength. In addition 1 M $NH_4NO_3$ suppresses colloid formation as well as soluble metal-organic complex formation because of high ionic strength. Since uptake by plants is hardly possible for these matters this is also an important aspect (Gryschko et al., 2005).

The extraction procedure was carried out as follows (DIN 19730 and 1996):

1. 25 ml 1 M $NH_4NO_3$ were added to 10 g oven dried (40°C for 48 h) and sieved (<2 mm) soil (solid solution ratio of 1:2.5)
2. 2 h rotation in an overhead shaker at 20 rpm and room temperature
3. Munktell folded filter grade 14/N were used in order to filtrate the soil solution though first 3 ml were discarded
4. Acidification with 0.3 ml nitric acid (65% w/w) to stabilize the solution for further analysis

An analytical blank was prepared just as the soil samples. Afterwards the solutions were stored at room temperature for further analysis.

### 3.3.3 Sr/matrix separation

Measuring Sr isotope ratios requires an indispensable preparation procedure because the isobaric interference on mass 87 cannot be overcome even by high resolution. Since $^{87}Sr$ has a mass of 86.90889 and $^{87}Rb$ of 86.90918 with an abundance of 7% and 27.8%, respectively, it is important to remove this interference as good as possible. Moreover any other matrix components can raise problems as well (e.g. Ca or P interferences). Therefore a separation procedure was developed (Prohaska et al., 2002) and further optimized (Swoboda et al., 2008). The following procedure was based on Swoboda et al., 2008.

In order to get an efficient Sr/matrix separation a resin, containing 4,4'(5')-di-t-butyl-cyclohexano 18-crown-6 (crown ether) on an inert substrate, supplied by Eichrome (ElChroM Industries, Inc., Darien, IL, USA) was used. A particle size of 100 µm to 150 µm was chosen. Functionality of the resin is based on the principle of a solid phase extraction. Strontium is retained on the stationary phase. All other ions and impurities can be washed off while Sr sticks to the crown ether. After removal of the unwanted matrix Sr can be eluted. It should be kept in mind that retention and elution are based on different pH values generated (EIChroM, 2009).

The resin was available in powdered form and therefore had to be soaked in $HNO_3$ (1 % w/w) overnight. Due to colloidal formation the supernatant needed to be removed and the elutriated resin was refilled with $HNO_3$ (1 % w/w). The slurry resin was ready for use. Small separation tubes were equipped with 10 µm filters (Separtis GmbH, Grenzach-Wyhlen, Germany) and about one ml of Sr resin was applied. A washing (4 x 0.5 ml $H_2O$ sub.) and equilibration (6 x 0.5 ml $HNO_3$ (6M)) step was carried out prior to drop by drop adding of the sample (2 x 1 ml). Unwanted elements were washed off with 8 M $HNO_3$ (10 x 0.5 ml). Finally Sr was eluted into a test tube with $H_2O$ sub-boiled (5 x 0.5 ml). Analytical blanks were treated the same way. They were used in order to monitor any contamination. About 24 samples were separated simultaneously to facilitate a high sample throughput. Additionally it could be assured that a flow rate of 0.5 ml*min$^{-1}$ was not exceeded.

Once the separation procedure was finished the resin was washed with $H_2O$ (sub.) and nitric acid (1 % w/w) and kept in the fridge at 4°C until the next procedure was carried out. Filters were stored in nitric acid (5 % w/w) and any residue was removed using an ultrasonic bath (Transsonic T80, Elma Hans Schmidbauer GmbH & Co. KG, Singen, Germany). Tubes were cleaned using nitric acid (5 % w/w) as well.

### 3.3.4 **Sr/Rb screening**

After separation a screening of all samples was necessary on the ELAN DRC-e in order to get approximate Sr and Rb concentrations. Since there was not much solution available for later measurement on the MC-ICP-MS only a small amount was taken for diluting the samples to get that information. Therefore a special setup was applied. A PFA nebulizer in addition to a slower sample flow rate was used. All parameters are summarized in Table 5.

For all measurement series separated samples were diluted 1:10 with nitric acid (1% w/w) and spiked with indium as internal standard. Measurement range was 0.01 ng g$^{-1}$ to 70 ng g$^{-1}$ concentration of Sr and Rb.

This measurement shows successful separation and gives the Sr concentration for possible further dilution of the samples for MC-ICP-MS.

Some separations failed due to low Sr concentrations in digests, or samples contained too much rubidium residue after separation. These samples had to be redone or separated repetitively.

### 3.3.5 Sample preparation for measurement

Measurement preparation, i.e. dilution of samples and adding an internal standard to blanks, standards and samples was carried out on the day of measurement or one day ahead. Depending on the instrument used as well as the sample matrix different dilution steps were necessary in order to meet instrument demands. Indium was used as internal standard with a final concentration of either 10 ng $g^{-1}$ or 1 ng $g^{-1}$ for internal normalization in quantitative analysis using ICP-QMS or ICP-SFMS respectively. Therefore a 1:11 dilution from a gravimetrically prepared batch solution with a concentration of either 110 ng $g^{-1}$ or 11 ng $g^{-1}$ was required.

Reference material TM 25.3 and TM 28.3 were used out of the bottle, while BCR-2 and BHVO-2 were diluted 1:100. Of course, indium was used as internal standard as mentioned above.

Regarding multi-element and rare earth element analysis all digested samples were diluted 1:5 with $H_2O$ sub-boiled. Soil extracts required a dilution step of 10 with $HNO_3$ (1% w/w for REE) and a 1:50 dilution for multi-element analysis due to its high element concentration and matrix effects occurring from ammonium nitrate.

#### *3.3.5.1 Determination of Phosphorus*

Various test arrangements were under investigation. That is to say different internal standards (In, Rh, Re, Sc, Ga and Ge) with a final concentration of 10 ng $g^{-1}$ were used for measurements and its behavior documented. Sample dilution varied and therefore is reported right at the result section. No reference material was available for quality control but a standard of a defined concentration was measured in between samples.

## 3.4 Method validation

This chapter gives an overview of the applied method validation for the detection of rare earth elements on two different instruments. Method validation gives an answer on the question whether a method is fit for the intended use. Method validation and its definitions were implemented according to the EURACHEM Guides: 'The Fitness for purpose on Analytical Methods' and 'Guide to Quality in Analytical Chemistry' (CITAC/EUROCHEM Guide, 2002; EUROCHEM Guide, 1998).

To produce reliable data a method that is so called fit-for-purpose should be used (IUPAC 'orange book' 1997). Therefore analytical methods need to be validated. The definition of

validation in general is as follows: 'Confirmation by examination and provision of objective evidence that the particular requirements for a specified intended use are fulfilled' while method validation is based on characteristic parameters describing potential as well as limitations (ISO 8402, 1994). Furthermore the suitability for a specific task needs to be verified as well.

### 3.4.1 **Method validation for REE analysis using ICP-QMS and ICP-SFMS**

The concentration of REE (2.2.2) in various matrices was measured with an ICP-QMS (3.1.2) and a HR-ICP-SFMS (3.1.3) using external calibration after internal normalization to $^{115}$In. Thus 8 calibration standards in the range of 0.01 ng $g^{-1}$ to 10 ng $g^{-1}$ or 0.001 ng $g^{-1}$ to 1 ng $g^{-1}$ were used for the instruments above, respectively. A 10 µg $g^{-1}$ rare earth elements stock solution from Claritas (3.2.2) was used for further standard preparation.

A selection of different samples was measured. Microwave digested coffee beans, pumpkin seed, pumpkin seed oil, wine as well as extracted soil samples together with 3 method blanks each were used to determine the validation parameters below. Reference materials Basalt, Columbia River, BCR-2 and Basalt, Hawaiian Volcanic Observatory, BHVO-2 were used for quality control and recovery purposes, respectively.

### 3.4.2 **Parameter**

The following parameters were used to validate the analytical method. They are summarized in chapter 4.1. Its definitions are as follows:

#### *3.4.2.1 Traceability*

Every single contributor needs to be traceable to its SI unit. Masses for instance are traceable to the balance which is traceable to the so called 'Ur-kilo' in Paris because it is calibrated according to that weight. Therefore traceability can be stated as 'Property of the result of a measurement or the value of a standard whereby it can be related with a stated uncertainty, to stated references, usually national or international standards (i.e. through an unbroken chain of comparisons).' The standards referred to here are measurement standards rather than written standards (ISO/IEC Guide 30, 1992).

#### *3.4.2.2 Measurement range*

ICP-MS has an extended dynamic range of about 9 orders of magnitude. Therefore it is not surprising that calibration curves are linear throughout the whole working range for all elements measured. Measurement range is referred to as the first and last calibration standard which ideally is linear all the way through. Depending on the instrument a start concentration of about 0.001 ng $g^{-1}$ and 0.01 ng $g^{-1}$ was used up to an end concentration of 1 ng $g^{-1}$ and 10 ng $g^{-1}$, respectively. Correlation factors as high as 0.999963 could be achieved.

### *3.4.2.3 Quality control*

In general quality control stands for the operational techniques and activities that are used to fulfill requirements of quality (ISO 8402, 1994). Moreover an internal quality control requires procedures that are used for monitoring purposes of operations and results of measurements. Therefore decision about reliability of methods can be stated (IUPAC 'orange book' 1997).

BCR-2 was used for quality control. Mean values of measured reference material were compared to certified values. Standard deviation of each element as stated on the certificate as well as measurement uncertainties were considered in order to verify the calibration curve of each element.

### *3.4.2.4 Limit of Detection and Limit of Quantification*

Limit of detection (LoD) is defined as the smallest amount measured with a statistically justifiable uncertainty. However that does not necessarily mean that the analyte can be quantified but it is only a statement of detectability. It strongly depends on the matrix of the blank. Therefore method limits of detection need to be considered. In order to find a threshold that is sufficient for quantifying a sample a so called limit of quantification (LoQ) is used. It is referred to as ten times the standard deviation (SD) of the blank for instrument and method $LoQ_{2,4}$. If the samples are not either instrument or method blank corrected $LoQ_{1,3}$ should be used instead. This can be implemented on LoD as well (Currie, 1999; ISO 11843-1, 1997).

Different approaches for the calculation of LoD as well as LoQ are common. On the one hand mean values of the blank concentration and the resulting standard deviations are considered in order to state limit of detection and limit of quantification (Thomsen et al., 2003). Equations are as follows:

**Equ. 6**
$$LoD_{1,3} = c_{blk} + 3 \cdot SD$$

**Equ. 7**
$$LoD_{2,4} = 3 \cdot SD$$

**Equ. 8**
$$LoQ_{1,3} = c_{blk} + 10 \cdot SD$$

**Equ. 9**
$$LoQ_{2,4} = 10 \cdot SD$$

On the other hand relative standard deviations of the intensity calculated by the instrument are used to determine LoD and LoQ. Therefore both limits are calculated using the following equations before blank correction:

**Equ. 10**
$$LoD_{1,3} = 3 \cdot \left( \frac{Int_{blk} \cdot RSD}{100} \right) \cdot Int_{In}^{-1} \cdot k^{-1} + \frac{Int_{blk}}{Int_{In}} \cdot k^{-1}$$

**Equ. 11**

$$LoQ_{1,3} = 10 \cdot \left( \frac{Int_{blk} \cdot RSD}{100} \right) \cdot Int_{In}^{-1} \cdot k^{-1} + \frac{Int_{blk}}{Int_{In}} \cdot k^{-1}$$

After blank correction:

**Equ. 12**

$$LoD_{2,4} = 3 \cdot \left( \frac{Int_{blk} \cdot RSD}{100} \right) \cdot Int_{In}^{-1} \cdot k^{-1}$$

**Equ. 13**

$$LoQ_{2,4} = 10 \cdot \left( \frac{Int_{blk} \cdot RSD}{100} \right) \cdot Int_{In}^{-1} \cdot k^{-1}$$

Again, due to several measured blanks a mean value of LoD or LoQ was indicated. In addition all limits were evaluated with respect to a solid matrix.

However either approach is more a statement about repeatability of a blank concentration than of accuracy (Bonnefoy et al., 2002).

The results of the latter approach (Equ. 10 to Equ. 13) are summarized in 4.1.7 and were used for method validation of rare earth elements. Subscribe numbers are used for instrument (1, 2) and method (3, 4) values. However due to a larger number of method blanks evaluation according to Thomsen was applied for multi-element data.

#### *3.4.2.5 Sensitivity*

Sensitivity is referred to as the slope of the calibration curve. It indicates the difference of small concentration changes in correlation to the response of the instrument (IUPAC 'orange book' 1997). Regarding the method validation sensitivity is specified either as $cps \cdot ng^{-1} \cdot g \cdot int(In)^{-1}$ or $cps \cdot ng^{-1} \cdot g$ (Currie, 1999).

#### *3.4.2.6 Recovery*

Interferences, contamination or loss of analytes can happen during digestion and extraction procedures. As a matter of fact every measuring system has a systematic error. Therefore a bias also called recovery must be calculated for compensating that matter. It is calculated using Equ. 15.

If the result is significantly different from the certified value it has to be considered that the correction for recovery contributes to the total combined uncertainty. Nevertheless it needs to be matrix matched as well. The reference material of choice was Basalt, Hawaiian Volcanic Observatory, BHVO-2 certified through United States Geological Survey. Since no reference

material was available for plant material recovery could only be calculated for the geological material but was not applied on the samples of interest.

BHVO-2 was measured about every 10 samples throughout the measurement series.

**Equ. 14**

$$\mathrm{Rec} = \frac{c_{obs}}{c_{ref}} \cdot 100$$

Recovery and its uncertainty are listed in 4.1.5.

#### *3.4.2.7 Repeatability (of results of measurements)*

'Closeness of the agreement between the results of successive measurement of the same measurand carried out in the same conditions of measurement.' (IUPAC 'orange book' 1997) Consequently each sample was measured three times.

It is calculated as follows:

**Equ. 15**

$$\mathrm{Rep} = 100 - \left( \frac{\mathrm{SD}}{\mathrm{mean}} \right) \cdot 100$$

### 3.4.3 **Results**

A result of a measurement is the value attributed to a measurand, obtained by a measurement. It is has to be stated though whether the result is corrected, uncorrected or if an average value is used. In any case a unit as well as the uncertainty of the measurement is obligatory for a complete statement (ISO VIM, 1993).

#### *3.4.3.1 Uncertainty budget*

As mentioned above an uncertainty budget is necessary for good analytical practice. For that reason ISO GUM method has been used. GUM is the abbreviation of 'Guide to Express of Uncertainty in Measurement'. It combines all quantified uncertainties that have an influence on the measurement.

In order to obtain a reasonable uncertainty a few steps need to be considered. First of all a measurand needs to be defined (e.g. the concentration of rare earth elements in pumpkin seed oil). It is also required to shape a model equation and find all sources of uncertainty. Furthermore each input needs to be quantified and its standard deviation calculated. By using the model equation the value of the measurand is calculated and additionally the combined standard uncertainty of the result and its expanded uncertainty are evaluated by error propagation. After analyzing and rethinking of the uncertainty contributions the result and its expanded uncertainty can be reported (Prohaska, 2009).

## 3.5 PASW statistical evaluation

In order to evaluate the enormous amount of data a software called PASW Statistics 18 (**P**redictive **A**nalytical **S**oft**w**are, SPSS Inc., Chicago, Illinois, USA) was used. It is a common tool for statistical data treatment. Moreover it helps to create graphical plots since visual representations can be understood more easily and can give a better understanding of data interactions.

A short overview of the applied statistical evaluation is given in the next subchapters.

### 3.5.1 Discriminant analysis

Discriminant analysis (DA) is used for classification purposes. Hence different classes are determined in advance. Its purposes can be summarized as follows (Statistik, 2009):

- Dependent variables can be explained through on or more independent variables
- Not only correlations between variables but also unknown values of dependent variables can be classified due to values of explaining variables
- DA relates cases to one or more alternative groups. Values of dependent variables show group belonging and therefore are scaled either nominal or ordinal

Affiliation of different regions to a group is illustrated in the result section.

### 3.5.2 Principal component analysis

Principal component analysis (PCA) is mainly used for data reduction. Therefore correlated variables are converted into uncorrelated principal components which contribute the highest amount of variability in the data set. Procedural method was as follows (Jolliffe, 2002):

- Eigenvalues were defined greater than one. However that overestimates significant factors
- Scree-test was performed to determine significant factors. However only factor one and two were considered
- Factors were transferred to a factor coordinate system and interpreted

PCA was used for pumpkin seed oil only due to a rather small sample pool.

# 4 Results and Discussion

## 4.1 REE method validation

As already discussed in chapter 3.4 method validation is essential in order to proof a method is fit for purpose. The evaluated parameters regarding that topic are listed and discussed below. Unfortunately different isotopes of five elements (Dy, Gd, Nd, Sm, Yb) were measured on each instrument but are identified as such with either mass added in the respective table. However regarding limit of detection and limit of quantification the measured mass was stated as far as only one instrument was concerned. In case of multiple measured isotopes only one was chosen as their values of different isotopes were almost identical.

### 4.1.1 Model equation

The following model equations were used for calculating the uncertainty of ICP-QMS and ICP-SFMS respectively.

Concentration of each sample was calculated by the instrument software. Method blank correction, consideration of a dilution factor and calculation back to its solid matrix was performed in addition.

#### *4.1.1.1 ICP-QMS*

Model equation of ICP-QMS is as follows:

**Equ. 16** $$c_{REE} = \left( \left( \frac{int_{sample}}{int_{In\,sample}} - \frac{int_{blk}}{int_{In\,blk}} \right) \cdot k^{-1} \cdot df - \left( \frac{int_{mblk}}{int_{In\,mblk}} - \frac{int_{blk}}{int_{In\,blk}} \right) \cdot k^{-1} \cdot df \right) \cdot m_{total} \cdot m_{sample}^{-1}$$

The slope k and its uncertainty as calculated and used by the instrument were considered. In addition k was calculated using masses and net intensities of each standard. The mass of each standard was traceable to the written standard. Consequently all dilution steps were taken into consideration. Net intensities of standards and calculated standard deviations were used resulting from intensities of standards and indium with the respective uncertainty of the given element for calculating the slope. Furthermore these two approaches were investigated concerning the contribution of the slope to the uncertainty budget (Equ. 18 to Equ. 20). Uncertainty was calculated according to Kragten. Results are summarized in 4.1.9.

#### *4.1.1.2 ICP-SFMS*

The mode equation of ICP-SFMS is slightly different to ICP-QMS. The first blank measured ahead of the calibration standards is considered to be standard zero with a concentration of zero. Therefore it is not subtracted from each sample but is part of the calibration curve.

**Equ. 17**
$$c_{REE} = \left( \left( \frac{int_{sample}}{int_{In\,sample}} - d \right) \cdot k^{-1} \cdot df - \left( \frac{int_{mblk}}{int_{In\,mblk}} - d \right) \cdot k^{-1} \cdot df \right) \cdot m_{total} \cdot m_{sample}^{-1}$$

The slope k was calculated using Equ. 18 to Equ. 20.

**Equ. 18**
$$Q_{xx} = \sum_{i=1}^{N} x_i^2 - \left( \sum_{i=1}^{N} x_i \right)^2 \cdot N^{-1}$$

**Equ. 19**
$$Q_{xy} = \sum_{i=1}^{N} (x_i \cdot y_i) - \sum_{i=1}^{N} x_i \cdot \sum_{i=1}^{N} y_i \cdot N^{-1}$$

**Equ. 20**
$$k = \frac{Q_{xy}}{Q_{xx}}$$

Intercept was calculated as follows:

**Equ. 21**
$$\bar{x} = \sum_{i=1}^{N} x_i \cdot N^{-1}$$

**Equ. 22**
$$\bar{y} = \sum_{i=1}^{N} y_i \cdot N^{-1}$$

**Equ. 23**
$$d = \bar{y} - k \cdot \bar{x}$$

Calculations of all concentrations ($x_i$) were based on the stock solution and its further dilutions. Net intensities ($y_i$) of each standard and their standard uncertainties were calculated with respect to the internal standard indium.

The ELEMENT software did not provide an uncertainty of the slope. Thus an uncertainty budget was calculated according to the previous equations.

Uncertainties of each element used for pumpkin evaluation are summarized in the appendix section.

### 4.1.2 **Traceability**

All components that are part of the model equations are traceable to its origin. The organigram of traceability is shown below (Figure 8).

Intensities of bank, method blank and sample but also slope and intercept are traceable to the calibration as they are based on direct comparisons. The calibration curve is based on certified standard stock solutions (each element is referred to a different NIST SRM* (National Institute of Standards and Technology, Standard Reference Material) – see Table 12) which are further

diluted gravimetrically. Gravimetrical dilution refers to the “Urkilo” in Paris since the balance is calibrated accordingly.

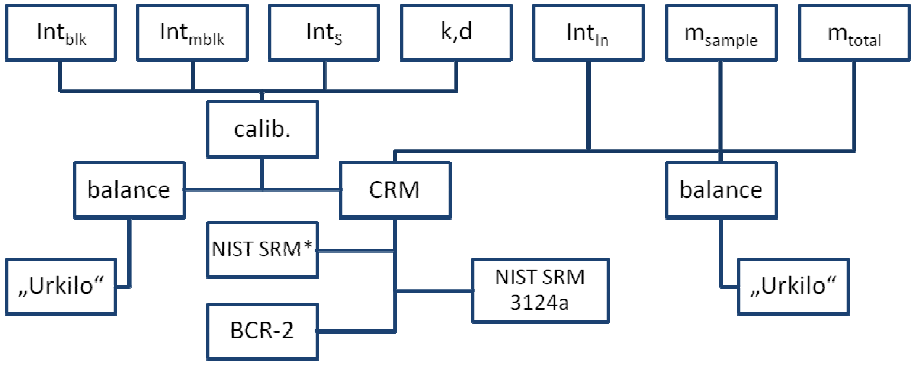


**Figure 8: Traceability organization chart**

In order to verify the calibration curve another CRM (BCR-2) was used which is traceable to its certificate. Intensity of indium is referred to its certificate (further NIST SRM 3124a) of the stock solution as well as to the balance where it was gravimetrically prepared. Samples were weighed into a Teflon bomb and filled up with $H_2O$ (sub.) after digestion into a bottle on a balance and therefore their masses are traceable.

| Analyte | NIST SRM | Analyte | NIST SRM |
|---|---|---|---|
| Ce | 3110 | Nd | 3135a |
| Dy | 3115a | Pr | 3142a |
| Er | 3116a | Sc | 3148a |
| Eu | 3117a | Sm | 3147a |
| Gd | 3118a | Tb | 3157a |
| Ho | 3123a | Tm | 3160a |
| La | 3127a | y | 3167 |
| Lu | 3130a | Yb | 3166a |

**Table 12: NIST SRM* referring to REEs**

### 4.1.3 **Working range**

Element concentrations of REE standard solutions for each instrument are listed in Table 13. Elements have about the same concentration but were calculated according to their measured mass on the certificate.

| c [ng $g^{-1}$] | Std1 | Std2 | Std3 | Std4 | Std5 | Std6 | Std7 | Std8 | Std9 |
|---|---|---|---|---|---|---|---|---|---|
| ELAN | 0.010 | 0.026 | 0.050 | 0.103 | 0.253 | 0.513 | 1.03 | 10.2 | |
| ELEMENT2 | 0.001 | 0.005 | 0.010 | 0.026 | 0.050 | 0.103 | 0.253 | 0.513 | 1.03 |

**Table 13: REE standard solutions**

Even though elements were measured in low, medium (Sc), and high (selected isotopes) resolution only low and medium resolution was considered for validation for ICP-SFMS measurements.

### 4.1.4 **Quality control**

Reference material BCR-2 was used in order to verify each calibration curve. Recommended values as well as information values with standard uncertainties (1SD) can be found in the appendix section (6.3). Values of all rare earth elements except of dysprosium and erbium are listed on the certificate. No uncertainty was stated for thulium though.

#### *4.1.4.1 ICP-QMS (ELAN DRC-e)*

Cerium, lanthanum, neodymium and ytterbium lay within their recommended values and stated uncertainties (olive in Figure 9). Recommended values were also given for europium, gadolinium, yttrium and scandium but could not be achieved (red in Figure 9). Scandium was way out of calibration that is to say concentration was about 50% higher than expected. Spectral interferences cannot be excluded.

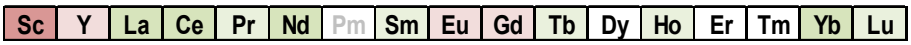


**Figure 9: Quality control ICP-QMS**

Even though concentrations were only stated as information all values lay within the given uncertainty with respect to holmium, lutetium, praseodymium and samarium (bright olive in Figure 9). Terbium was above information value at the beginning and end but also in the range during measurement series. Nonetheless concentration of some detected elements was slightly above 0.005 ng $g^{-1}$ in solution which was out of measurement range. No information was given for erbium, thulium and dysprosium (white in Figure 9). Considering calculated measurement uncertainties for each element all except of scandium passed quality control. Nonetheless elements achieving the stated value on the certificate (olive in Figure 9) or failing (red in Figure 9) are shown

However the internal standard indium did rise with pumpkin seed oil samples which affected the reference material measured last. Consequently concentration of some elements dropped with the exception of yttrium and gadolinium which achieved the recommended value after all. Concentration of Y rose continuously while concentration of Gd dropped all of a sudden. As a consequence reference material measured at the very end was not used for evaluation. Nonetheless matrix effects due to pumpkin seed oil should be monitored.

#### *4.1.4.2 ICP-SFMS (ELEMENT2)*

Indium was rather instable regarding measurement using ELEMENT2. Nevertheless the following isotopes lay within the given range of the certificate: $^{139}$La, $^{140}$Ce, $^{141}$Pr, $^{146}$Sm, $^{147}$Sm, $^{143}$Nd, $^{145}$Nd, $^{146}$Nd and $^{45}$Sc.

Concentration of yttrium and ytterbium was lower than stated on the certificate. Terbium was below the certified value during measurement series of coffee samples but above the given value during pumpkin samples. Europium was within the range during coffee measurements but almost double as stated on the certificate during pumpkin evaluation. It was the other way round regarding holmium. However certificate values for these elements were just for information. $^{155}$Gd was way out of range whereas lutetium could not be detected at all. Considering measurement uncertainty of these elements only terbium and holmium were not significantly different from the certificate and passed.

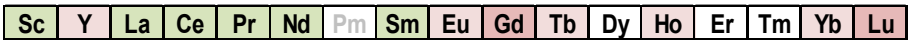


**Figure 10: Quality control ICP-SFMS**

Concerning stability issues some troubles could be observed regarding tuning of the instrument as well as during measurement. Oxide rate was sometimes higher than usually tolerated and signal intensity of indium was more than just fluctuating. Nonetheless validation procedure was carried out as far as data was available but due to the given circumstances the produced results should be observed critically.

Only elements that passed quality control were used for evaluation of pumpkin samples – from soil to seed to oil.

### 4.1.5 **Recovery**

Recovery of a geological material was calculated using reference material BHVO-2. Unfortunately no reference material was available for rare earth elements in plants. Recommended values were available for Ce, La, Nd, Sc and Y whereas information values were given for Gd, Ho, Lu, Sm, Tb and Yb. Uncertainty on the certificate was states as one time the standard deviation of the respective element. No uncertainty was stated for terbium (see 6.3). Therefore recovery of that element was not evaluated.

Since only a small sample batch of soil, seed and oil was measured on ICP-QMS only one series, with the respective matrices measured, was chosen for ICP-SFMS as well.

Recovery using ICP-QMS was between 97.5% and 105% with expanded uncertainty (U, k=2) between 6.3% and 9.3%. Ytterbium had a recovery of 107% but was not significantly different than the stated value due to a rather high expanded uncertainty of 12%. Only scandium and gadolinium were overestimated but with a decent uncertainty. Nonetheless its recovery would be considered regarding its contribution to the uncertainty budget of geological samples. However these two elements did not pass quality control either.

Results for ICP-QMS and ICP-SFMS are listed below:

| Recovery BHVO-2 | | ICP-QMS | | ICP-SFMS | |
|---|---|---|---|---|---|
| Analyte | Mass | % | (U, k=2) % | % | (U, k=2) % |
| Ce | 140 | 102 | 6.1 | 94 | 11 |
| Gd | 158/155 | 113 | 4.1 | 210 | 40 |
| Ho | 165 | 97.9 | 6.3 | 90.4 | 7.1 |
| La | 139 | 105 | 7.7 | 97 | 11 |
| Lu | 175 | 105 | 9.1 | < $LoD_1$ | < $LoD_1$ |
| Nd | 142/145 | 98.9 | 8.5 | 94.4 | 10 |
| Sc | 45 | 195 | 8.0 | 93.6 | 6.4 |
| Sm | 152/149 | 99.4 | 8.2 | 97.9 | 9.5 |
| Y | 89 | 98.3 | 9.3 | 87 | 13 |
| Yb | 174/171 | 107 | 12 | 83 | 20 |

**Table 14: Recovery of BHVO-2 using ICP-QMS and ICP-SFMS**

Main contributor to the expanded uncertainty was the certified reference material, especially regarding higher concentrated elements (>80%) but not so much for elements near limit of detection (~20%). Measured and certified value did contribute equally to the uncertainty regarding holmium whereas measured values did matter with respect to scandium and lutetium.

There were some differences though considering ICP-SFMS. All elements except of gadolinium had a recovery below 100%. Ytterbium and yttrium were even below 90% but expanded uncertainty was rather high and therefore uncertainties were overlapping within 100%. Only holmium would be used for calculating the concentration of a geological sample. Not only that recovery of gadolinium was 210% but also expanded uncertainty was as high as 40%. Maybe using another isotope would overcome the interference problem. Lutetium was below instrument limit of detection just like for quality control.

Taking a closer look at contribution to the uncertainty a rather different picture of the main influence was shown. Ratio of measured and certified value was about 65:30 for Ho, Sc and Yb whereas it was the other way round for Ce, Sm and Nd. Contribution of either certified or measured value was equal considering La and Y. As expected highest contribution to uncertainty of Gd was the measured value.

### 4.1.6 **Repeatability of measurements**

In order to evaluate repeatability of ICP-QMS each matrix was measured three times and calculated using Equ. 15. Wine was excluded because all elements, except of dysprosium, were below method limit of detection. Repeatability in % is summarized in Table 15.

Pumpkin seeds valued the best repeatability most probably due to the highest concentration of each element in solution which led to a higher precision. All elements were above 96%, except

of Sc which did not pass quality control anyhow; whereas Yb was below that value showing a repeatability of 93.7%.

Considering the soil sample, which was also enriched of rare earth elements, repeatability between 90.2% and 99.7% was achieved and was even better than for some elements compared to pumpkin seed.

Repeatability of coffee digests was evaluated as well. With respect to lutetium it was only 27%. Tm and Eu were below 90% while all other elements were above.

| Rep [%] | Mass | Coffee | Soil | Seed | Oil |
|---|---|---|---|---|---|
| **Ce** | 140 | 99.5 | 99.4 | 99.7 | 98.8 |
| **Dy** | 164 | 95.8 | 97.6 | 96.3 | 93.6 |
| **Er** | 166 | 89.1 | 95.9 | 98.6 | 89.1 |
| **Eu** | 153 | 99.2 | 97.3 | 98.5 | 95.7 |
| **Gd** | 158 | 93.0 | 97.9 | 98.7 | 92.9 |
| **Ho** | 165 | 88.3 | 98.7 | 97.2 | 93.0 |
| **La** | 139 | 98.1 | 99.8 | 99.8 | 98.3 |
| **Lu** | 175 | 26.7 | 97.5 | 96.4 | n. e. |
| **Nd** | 142 | 95.6 | 99.4 | 99.3 | 97.2 |
| **Pr** | 141 | 96.5 | 99.7 | 99.3 | 99.1 |
| **Sc** | 45 | 91.7 | 98.8 | 89.1 | 95.4 |
| **Sm** | 152 | 94.2 | 97.6 | 96.5 | 95.8 |
| **Tb** | 159 | 94.4 | 93.8 | 97.4 | 75.4 |
| **Tm** | 169 | 86.5 | 96.4 | 96.0 | 93.0 |
| **Y** | 89 | 96.2 | 90.2 | 99.2 | 98.9 |
| **Yb** | 174 | 97.0 | 99.0 | 93.7 | 92.1 |

**Table 15: Repeatability of measurements using ICP-QMS**

Ho and Tb were between method limit of detection and method limit of quantification for pumpkin seed oil. Repeatability of Tb was only 75%. Concentration of Lu could not be determined due to low ion counts. Therefore repeatability of that element could not be evaluated. All other elements lay within 92% and 99%.

Repeatability of measurements using ICP-SFMS was not evaluated as not enough data was available.

### 4.1.7 Limit of Detection and Limit of Quantification

Limit of detection and limit of quantification were evaluated using four different equations that are explained in more detail in 3.4.2.4. Two approaches were considered but Equ. 10 to Equ. 13 were used for validation. Subscribe numbers one and two are referred to LoD and LoQ of the respective instrument. Limits regarding a method blank are labeled with three and four. Number one and three are applied before blank correction and number two and four after a sample was blank corrected. In addition all limits were calculated in correlation to digested pumpkin seeds (10 g/1 g) and coffee beans (15 g/0.5 g) as well as extracted soil (25 g/10 g) with

dilution weight and initial weight in brackets. Digestion procedure was carried out using nitric acid only for pumpkin seeds and pumpkinseed oil while nitric acid and hydrogen peroxide was used for coffee samples. Ammonium nitrate was used for extraction of soil samples (see 3.3.2).

Regarding instrument limits only pumpkin seeds were considered for solid LoDs and LoQs because they were the matrix of major interest. The data is representative for pumpkin seed oil as well because the digestion procedure was the same.

#### *4.1.7.1 LoDs*

Instrument limits of detection ($LoD_{1,2}$) are summarized in Table 16.

| LoD [ng $g^{-1}$] | | ICP-QMS | | | | ICP-SFMS | | | |
|---|---|---|---|---|---|---|---|---|---|
| Analyte | Mass | $LoD_1$ $HNO_3$ | $LoD_1$ p.seed | $LoD_2$ $HNO_3$ | $LoD_2$ p.seed | $LoD_1$ $HNO_3$ | $LoD_1$ p.seed | $LoD_2$ $HNO_3$ | $LoD_2$ p.seed |
| Ce | 140 | 1.42E-03 | 1.42E-02 | 4.54E-04 | 4.54E-03 | 8.74E-02 | 8.74E-01 | 3.20E-04 | 3.20E-03 |
| Dy | 164/161 | 8.53E-04 | 8.53E-03 | 4.82E-04 | 4.82E-03 | 1.28E-02 | 1.28E-01 | 2.06E-04 | 2.06E-03 |
| Er | 166 | 6.58E-04 | 6.58E-03 | 4.15E-04 | 4.15E-03 | 7.15E-03 | 7.15E-02 | 7.80E-05 | 7.80E-04 |
| Eu | 153 | 6.51E-04 | 6.51E-03 | 3.26E-04 | 3.26E-03 | 5.81E-03 | 5.81E-02 | 1.44E-04 | 1.44E-03 |
| Gd | 158/155 | 1.30E-03 | 1.30E-02 | 7.73E-04 | 7.73E-03 | 4.71E-02 | 4.71E-01 | 9.85E-04 | 9.85E-03 |
| Ho | 165 | 3.87E-04 | 3.87E-03 | 2.10E-04 | 2.10E-03 | 2.34E-03 | 2.34E-02 | 3.05E-05 | 3.05E-04 |
| La | 139 | 7.66E-04 | 7.66E-03 | 2.71E-04 | 2.71E-03 | 4.41E-02 | 4.41E-01 | 4.38E-04 | 4.38E-03 |
| Lu | 175 | 3.56E-04 | 3.56E-03 | 2.15E-04 | 2.15E-03 | 1.11E-03 | 1.11E-02 | 2.85E-05 | 2.85E-04 |
| Nd | 142/145 | 1.34E-03 | 1.34E-02 | 8.35E-04 | 8.35E-03 | 4.79E-02 | 4.79E-01 | 6.00E-04 | 6.00E-03 |
| Pr | 141 | 5.02E-04 | 5.02E-03 | 2.16E-04 | 2.16E-03 | 1.12E-02 | 1.12E-01 | 8.37E-05 | 8.37E-04 |
| Sc | 45 | 4.39E-01 | 4.39E+00 | 4.03E-02 | 4.03E-01 | 5.11E-02 | 5.11E-01 | 1.46E-04 | 1.46E-03 |
| Sm | 152/149 | 7.92E-04 | 7.92E-03 | 4.25E-04 | 4.25E-03 | 1.13E-02 | 1.13E-01 | 1.78E-04 | 1.78E-03 |
| Tb | 159 | 4.50E-04 | 4.50E-03 | 2.31E-04 | 2.31E-03 | 2.25E-03 | 2.25E-02 | 4.21E-05 | 4.21E-04 |
| Tm | 169 | 3.40E-04 | 3.40E-03 | 1.83E-04 | 1.83E-03 | 9.95E-04 | 9.95E-03 | 2.53E-05 | 2.53E-04 |
| Y | 89 | 1.03E-03 | 1.03E-02 | 4.05E-04 | 4.05E-03 | 5.08E-02 | 5.08E-01 | 7.86E-05 | 7.86E-04 |
| Yb | 174/171 | 7.29E-04 | 7.29E-03 | 4.66E-04 | 4.66E-03 | 7.34E-03 | 7.34E-02 | 1.87E-04 | 1.87E-03 |

**Table 16: Instrument limits of detection**

$LoD_1$ was up to two orders of magnitude higher in ICP-SFMS compared to ICP-QMS. This is the major result of the low precision resulting from an instrument which is not performing at its optimum. Only scandium had a higher $LoD_1$ of two orders of magnitude using ELAN-DRC-e. It had not only a high background level but scandium cannot be analyzed interference free using the quadrupole instrument. Comparing $LoD_2$ of the instruments with each other ICP-SFMS had lower thresholds. Due to lower RSDs of the measured signal intensity it is up to one order of magnitude lower compared to ICP-QMS. Nonetheless thresholds below 1 pg $g^{-1}$ seem rather low and might be questioned. However hardly any background was present and therefore limits seem adequate. Still samples that were near these limits had a rather high relative standard uncertainty. Therefore concentration of measured samples should always be somewhere in the middle of a calibration curve in order to reduce uncertainty to a reasonable level (see 4.1.9).

Method limits of detection ($LoD_{3,4}$) are listed in Table 17.

| ICP-QMS LoDs of solutions [ng $g^{-1}$] | | | | | | | |
|---|---|---|---|---|---|---|---|
| Analyte | Mass | $LoD_3$ $HNO_3$ | $LoD_3$ $HNO_3+H_2O_2$ | $LoD_3$ $NH_4NO_3$ | $LoD_4$ $HNO_3$ | $LoD_4$ $HNO_3+H_2O_2$ | $LoD_4$ $NH_4NO_3$ |
| Ce | 140 | 2.23E-02 | 1.64E-02 | 4.87E-02 | 4.71E-03 | 3.06E-03 | 1.02E-02 |
| Dy | 164 | 3.43E-03 | 3.51E-03 | 1.82E-02 | 2.04E-03 | 2.40E-03 | 1.02E-02 |
| Er | 166 | 2.64E-03 | 2.85E-03 | 9.41E-03 | 1.67E-03 | 1.84E-03 | 5.04E-03 |
| Eu | 153 | 2.10E-03 | 1.68E-03 | 6.43E-02 | 1.12E-03 | 7.86E-04 | 1.01E-02 |
| Gd | 158 | 5.76E-03 | 4.73E-03 | 2.31E-02 | 3.09E-03 | 2.20E-03 | 1.08E-02 |
| Ho | 165 | 1.33E-03 | 1.03E-03 | 3.74E-03 | 8.70E-04 | 6.89E-04 | 2.14E-03 |
| La | 139 | 1.21E-02 | 8.96E-03 | 4.91E-02 | 3.21E-03 | 2.32E-03 | 8.97E-03 |
| Lu | 175 | 8.51E-04 | 1.10E-03 | 2.33E-03 | 5.14E-04 | 6.80E-04 | 1.39E-03 |
| Nd | 142 | 1.47E-02 | 1.27E-02 | 4.29E-02 | 9.03E-03 | 7.48E-03 | 1.39E-02 |
| Pr | 141 | 3.35E-03 | 2.48E-03 | 1.39E-02 | 1.43E-03 | 1.18E-03 | 5.55E-03 |
| Sc | 45 | 1.89E+00 | 1.82E+00 | 3.55E+00 | 1.35E-01 | 1.36E-01 | 4.63E-01 |
| Sm | 152 | 5.02E-03 | 4.66E-03 | 1.05E-01 | 2.55E-03 | 2.69E-03 | 2.31E-02 |
| Tb | 159 | 1.23E-03 | 1.11E-03 | 4.62E-03 | 6.69E-04 | 5.83E-04 | 2.73E-03 |
| Tm | 169 | 8.77E-04 | 1.15E-03 | 1.83E-03 | 4.65E-04 | 7.46E-04 | 8.57E-04 |
| Y | 89 | 8.17E-03 | 7.41E-03 | 4.52E-02 | 3.18E-03 | 1.98E-03 | 9.07E-03 |
| Yb | 174 | 2.69E-03 | 2.21E-03 | 8.41E-03 | 1.68E-03 | 1.19E-03 | 5.05E-03 |

**Table 17: Method limits of detection regarding ICP-QMS**

Method limits of detection are about 2 to 10 times higher compared to instrument values due to various procedures ahead of measurement and different reagents used. Ammonium nitrate produced the highest blank level for all elements. Especially samarium had a much higher limit of detection comparing extracts and digests.

Method limits of detection (respectively quantification) were mainly used as a threshold for evaluation of samples. Consequently every procedure should always produce method blanks in order to monitor any contamination or alteration in element composition from reagents or materials used throughout the procedure. In the end one should be more interested in these values rather than instrument limits because samples can get contaminated during these steps.

Table 18 lists all $LoD_{3,4}$ with respect to solid material using ICP-QMS.

| ICP-QMS LoDs of solids [ng $g^{-1}$] | | | | | | | |
|---|---|---|---|---|---|---|---|
| Analyte | Mass | $LoD_3$ p.seed | $LoD_3$ coffee | $LoD_3$ soil | $LoD_4$ p.seed | $LoD_4$ coffee | $LoD_4$ soil |
| Ce | 140 | 2.23E-01 | 6.55E-01 | 1.22E-01 | 4.71E-02 | 1.22E-01 | 2.56E-02 |
| Dy | 164 | 3.43E-02 | 1.40E-01 | 4.55E-02 | 2.04E-02 | 9.61E-02 | 2.54E-02 |
| Er | 166 | 2.64E-02 | 1.14E-01 | 2.35E-02 | 1.67E-02 | 7.35E-02 | 1.26E-02 |
| Eu | 153 | 2.10E-02 | 6.70E-02 | 1.61E-01 | 1.12E-02 | 3.14E-02 | 2.52E-02 |
| Gd | 158 | 5.76E-02 | 1.89E-01 | 5.78E-02 | 3.09E-02 | 8.80E-02 | 2.71E-02 |
| Ho | 165 | 1.33E-02 | 4.14E-02 | 9.35E-03 | 8.70E-03 | 2.75E-02 | 5.36E-03 |
| La | 139 | 1.21E-01 | 3.58E-01 | 1.23E-01 | 3.21E-02 | 9.26E-02 | 2.24E-02 |
| Lu | 175 | 8.51E-03 | 4.41E-02 | 5.84E-03 | 5.14E-03 | 2.72E-02 | 3.47E-03 |
| Nd | 142 | 1.47E-01 | 5.08E-01 | 1.07E-01 | 9.03E-02 | 2.99E-01 | 3.47E-02 |
| Pr | 141 | 3.35E-02 | 9.90E-02 | 3.47E-02 | 1.43E-02 | 4.73E-02 | 1.39E-02 |
| Sc | 45 | 1.89E+01 | 7.28E+01 | 8.87E+00 | 1.35E+00 | 5.42E+00 | 1.16E+00 |
| Sm | 152 | 5.02E-02 | 1.86E-01 | 2.62E-01 | 2.55E-02 | 1.08E-01 | 5.77E-02 |
| Tb | 159 | 1.23E-02 | 4.44E-02 | 1.15E-02 | 6.69E-03 | 2.33E-02 | 6.82E-03 |
| Tm | 169 | 8.77E-03 | 4.59E-02 | 4.58E-03 | 4.65E-03 | 2.98E-02 | 2.14E-03 |
| Y | 89 | 8.17E-02 | 2.97E-01 | 1.13E-01 | 3.18E-02 | 7.92E-02 | 2.27E-02 |
| Yb | 174 | 2.69E-02 | 8.86E-02 | 2.10E-02 | 1.68E-02 | 4.77E-02 | 1.26E-02 |

**Table 18: Method limits of detection in solids regarding ICP-QMS**

The following tables present limits of detection with respect to ICP-SFMS. Table 19 represents $LoD_{3,4}$ in solutions while Table 20 lists limits regarding solids.

| ICP-SFMS LoDs of solutions [ng $g^{-1}$] | | | | | | | |
|---|---|---|---|---|---|---|---|
| Analyte | Mass | $LoD_3$ $HNO_3$ | $LoD_3$ $HNO_3+H_2O_2$ | $LoD_3$ $NH_4NO_3$ | $LoD_4$ $HNO_3$ | $LoD_4$ $HNO_3+H_2O_2$ | $LoD_4$ $NH_4NO_3$ |
| Ce | 140 | 2.66E-02 | 3.20E-02 | 4.09E-02 | 2.80E-03 | 1.28E-02 | 8.22E-03 |
| Dy | 161 | 5.62E-03 | 4.29E-03 | 1.47E-02 | 2.77E-03 | 2.31E-03 | 8.42E-03 |
| Er | 166 | 2.18E-03 | 1.52E-03 | 7.40E-03 | 1.28E-03 | 1.44E-03 | 4.57E-03 |
| Eu | 153 | 2.19E-03 | 4.90E-03 | 1.87E-01 | 1.09E-03 | 2.40E-03 | 1.11E-02 |
| Gd | 155 | 1.59E-02 | 1.20E-02 | 1.44E+00 | 3.38E-03 | 7.73E-03 | 8.28E-02 |
| Ho | 165 | 4.83E-04 | 3.12E-04 | 2.15E-03 | 2.28E-04 | 3.23E-04 | 1.22E-03 |
| La | 139 | 1.44E-02 | 1.62E-02 | 3.88E-02 | 2.00E-03 | 9.58E-03 | 5.37E-03 |
| Lu | 175 | 3.38E-04 | 2.18E-04 | 8.64E-04 | 1.83E-04 | 2.43E-04 | 4.01E-04 |
| Nd | 145 | 2.12E-02 | 1.16E-02 | 4.42E-02 | 8.03E-03 | 7.19E-03 | 1.97E-02 |
| Pr | 141 | 3.54E-03 | 3.62E-03 | 6.28E-03 | 1.07E-03 | 1.85E-03 | 1.33E-03 |
| Sc | 45 | 7.96E-03 | 2.72E-03 | 6.69E-03 | 3.27E-03 | 1.31E-04 | 3.26E-03 |
| Sm | 149 | 6.16E-03 | 2.36E-02 | 1.52E-02 | 3.60E-03 | 5.67E-03 | 7.72E-03 |
| Tb | 159 | 6.15E-04 | 3.54E-04 | 2.04E-03 | 2.52E-04 | 4.03E-04 | 1.03E-03 |
| Tm | 169 | 4.15E-04 | 4.22E-04 | 1.29E-03 | 2.94E-04 | 4.89E-04 | 9.01E-04 |
| Y | 89 | 8.09E-03 | 5.80E-03 | 2.61E-02 | 1.57E-03 | 2.94E-03 | 3.25E-03 |
| Yb | 171 | 3.59E-03 | 1.35E-03 | 6.45E-03 | 2.31E-03 | 2.05E-03 | 4.61E-03 |

**Table 19: Method limits of detection regarding ICP-SFMS**

$LoD_3$ are similar for all elements except of Sc, Sm, Tb and Y comparing nitric acid and hydrogen peroxide. As already mentioned blank level of ammonium nitrate was much higher compared to digestion procedure. LoDs before blank correction were between two and ten times higher compared to values after blank correction.

| ICP-SFMS LoDs of solids [ng $g^{-1}$] | | | | | | | |
|---|---|---|---|---|---|---|---|
| Analyte | Mass | $LoD_3$ p.seed | $LoD_3$ coffee | $LoD_3$ soil | $LoD_4$ p.seed | $LoD_4$ coffee | $LoD_4$ soil |
| Ce | 140 | 2.66E-01 | 1.28E+00 | 1.02E-01 | 2.80E-02 | 5.12E-01 | 2.05E-02 |
| Dy | 161 | 5.62E-02 | 1.71E-01 | 3.68E-02 | 2.77E-02 | 9.24E-02 | 2.11E-02 |
| Er | 166 | 2.18E-02 | 6.06E-02 | 1.85E-02 | 1.28E-02 | 5.77E-02 | 1.14E-02 |
| Eu | 153 | 2.19E-02 | 1.96E-01 | 4.67E-01 | 1.09E-02 | 9.59E-02 | 2.77E-02 |
| Gd | 155 | 1.59E-01 | 4.78E-01 | 3.59E+00 | 3.38E-02 | 3.09E-01 | 2.07E-01 |
| Ho | 165 | 4.83E-03 | 1.25E-02 | 5.36E-03 | 2.28E-03 | 1.29E-02 | 3.04E-03 |
| La | 139 | 1.44E-01 | 6.48E-01 | 9.70E-02 | 2.00E-02 | 3.83E-01 | 1.34E-02 |
| Lu | 175 | 3.38E-03 | 8.74E-03 | 2.16E-03 | 1.83E-03 | 9.72E-03 | 1.00E-03 |
| Nd | 145 | 2.12E-01 | 4.65E-01 | 1.10E-01 | 8.03E-02 | 2.87E-01 | 4.91E-02 |
| Pr | 141 | 3.54E-02 | 1.45E-01 | 1.57E-02 | 1.07E-02 | 7.38E-02 | 3.34E-03 |
| Sc | 45 | 7.96E-02 | 1.09E-01 | 1.67E-02 | 3.27E-02 | 5.25E-03 | 8.14E-03 |
| Sm | 149 | 6.16E-02 | 9.43E-01 | 3.80E-02 | 3.60E-02 | 2.27E-01 | 1.93E-02 |
| Tb | 159 | 6.15E-03 | 1.42E-02 | 5.09E-03 | 2.52E-03 | 1.61E-02 | 2.57E-03 |
| Tm | 169 | 4.15E-03 | 1.69E-02 | 3.24E-03 | 2.94E-03 | 1.96E-02 | 2.25E-03 |
| Y | 89 | 8.09E-02 | 2.32E-01 | 6.52E-02 | 1.57E-02 | 1.17E-01 | 8.11E-03 |
| Yb | 171 | 3.59E-02 | 5.41E-02 | 1.61E-02 | 2.31E-02 | 8.21E-02 | 1.15E-02 |

**Table 20: Method limits of detection of solids regarding ICP-SFMS**

### *4.1.7.2 LoQs*

No further explanations will be given with respect to limit of quantification since only a constant factor has changed compared to limits of detection.

Instrument limits of quantification are shown below:

| LoQ [ng $g^{-1}$] | | ICP-QMS | | | | ICP-SFMS | | | |
|---|---|---|---|---|---|---|---|---|---|
| Analyte | Mass | $LoQ_1$ $HNO_3$ | $LoQ_1$ p.seed | $LoQ_2$ $HNO_3$ | $LoQ_2$ p.seed | $LoQ_1$ $HNO_3$ | $LoQ_1$ p.seed | $LoQ_2$ $HNO_3$ | $LoQ_2$ p.seed |
| Ce | 140 | 2.48E-03 | 2.48E-02 | 1.51E-03 | 1.51E-02 | 8.96E-02 | 8.96E-01 | 2.49E-03 | 2.49E-02 |
| Dy | 164/161 | 1.98E-03 | 1.98E-02 | 1.61E-03 | 1.61E-02 | 1.40E-02 | 1.40E-01 | 1.36E-03 | 1.36E-02 |
| Er | 166 | 1.63E-03 | 1.63E-02 | 1.38E-03 | 1.38E-02 | 8.28E-03 | 8.28E-02 | 1.21E-03 | 1.21E-02 |
| Eu | 153 | 1.41E-03 | 1.41E-02 | 1.09E-03 | 1.09E-02 | 7.32E-03 | 7.32E-02 | 1.65E-03 | 1.65E-02 |
| Gd | 158/155 | 3.11E-03 | 3.11E-02 | 2.58E-03 | 2.58E-02 | 6.68E-02 | 6.68E-01 | 2.07E-02 | 2.07E-01 |
| Ho | 165 | 8.77E-04 | 8.77E-03 | 6.99E-04 | 6.99E-03 | 2.70E-03 | 2.70E-02 | 3.91E-04 | 3.91E-03 |
| La | 139 | 1.40E-03 | 1.40E-02 | 9.04E-04 | 9.04E-03 | 5.23E-02 | 5.23E-01 | 8.65E-03 | 8.65E-02 |
| Lu | 175 | 8.59E-04 | 8.59E-03 | 7.18E-04 | 7.18E-03 | 1.39E-03 | 1.39E-02 | 3.03E-04 | 3.03E-03 |
| Nd | 142/145 | 3.29E-03 | 3.29E-02 | 2.78E-03 | 2.78E-02 | 5.40E-02 | 5.40E-01 | 6.69E-03 | 6.69E-02 |
| Pr | 141 | 1.01E-03 | 1.01E-02 | 7.20E-04 | 7.20E-03 | 1.16E-02 | 1.16E-01 | 4.16E-04 | 4.16E-03 |
| Sc | 45 | 5.33E-01 | 5.33E+00 | 1.34E-01 | 1.34E+00 | 5.24E-02 | 5.24E-01 | 1.41E-03 | 1.41E-02 |
| Sm | 152/149 | 1.78E-03 | 1.78E-02 | 1.42E-03 | 1.42E-02 | 1.27E-02 | 1.27E-01 | 1.58E-03 | 1.58E-02 |
| Tb | 159 | 9.88E-04 | 9.88E-03 | 7.69E-04 | 7.69E-03 | 2.60E-03 | 2.60E-02 | 3.98E-04 | 3.98E-03 |
| Tm | 169 | 7.67E-04 | 7.67E-03 | 6.10E-04 | 6.10E-03 | 1.46E-03 | 1.46E-02 | 4.94E-04 | 4.94E-03 |
| Y | 89 | 1.98E-03 | 1.98E-02 | 1.35E-03 | 1.35E-02 | 5.16E-02 | 5.16E-01 | 8.38E-04 | 8.38E-03 |
| Yb | 174/171 | 1.82E-03 | 1.82E-02 | 1.55E-03 | 1.55E-02 | 1.04E-02 | 1.04E-01 | 3.21E-03 | 3.21E-02 |

**Table 21: Instrument limits of quantification**

Method limits of quantification of ICP-QMS are listed as follows:

| ICP-QMS | LoQs of solutions [ng $g^{-1}$] | | | | | | |
|---|---|---|---|---|---|---|---|
| Analyte | Mass | $LoQ_3$ $HNO_3$ | $LoQ_3$ $HNO_3+H_2O_2$ | $LoQ_3$ $NH_4NO_3$ | $LoQ_4$ $HNO_3$ | $LoQ_4$ $HNO_3+H_2O_2$ | $LoQ_4$ $NH_4NO_3$ |
| Ce | 140 | 3.33E-02 | 1.43E-02 | 7.26E-02 | 1.57E-02 | 1.02E-03 | 3.41E-02 |
| Dy | 164 | 8.20E-03 | 1.91E-03 | 4.19E-02 | 6.81E-03 | 8.01E-04 | 3.39E-02 |
| Er | 166 | 6.53E-03 | 1.63E-03 | 2.12E-02 | 5.55E-03 | 6.12E-04 | 1.68E-02 |
| Eu | 153 | 4.73E-03 | 1.15E-03 | 8.78E-02 | 3.75E-03 | 2.62E-04 | 3.36E-02 |
| Gd | 158 | 1.30E-02 | 3.26E-03 | 4.84E-02 | 1.03E-02 | 7.34E-04 | 3.61E-02 |
| Ho | 165 | 3.36E-03 | 5.76E-04 | 8.74E-03 | 2.90E-03 | 2.30E-04 | 7.14E-03 |
| La | 139 | 1.96E-02 | 7.42E-03 | 7.00E-02 | 1.07E-02 | 7.72E-04 | 2.99E-02 |
| Lu | 175 | 2.05E-03 | 6.48E-04 | 5.57E-03 | 1.71E-03 | 2.27E-04 | 4.63E-03 |
| Nd | 142 | 3.58E-02 | 7.70E-03 | 7.53E-02 | 3.01E-02 | 2.49E-03 | 4.62E-02 |
| Pr | 141 | 6.68E-03 | 1.69E-03 | 2.69E-02 | 4.75E-03 | 3.94E-04 | 1.85E-02 |
| Sc | 45 | 2.20E+00 | 1.73E+00 | 4.63E+00 | 4.49E-01 | 4.52E-02 | 1.54E+00 |
| Sm | 152 | 1.10E-02 | 2.86E-03 | 1.59E-01 | 8.51E-03 | 8.97E-04 | 7.69E-02 |
| Tb | 159 | 2.79E-03 | 7.22E-04 | 1.10E-02 | 2.23E-03 | 1.94E-04 | 9.09E-03 |
| Tm | 169 | 1.96E-03 | 6.51E-04 | 3.83E-03 | 1.55E-03 | 2.49E-04 | 2.86E-03 |
| Y | 89 | 1.56E-02 | 6.09E-03 | 6.64E-02 | 1.06E-02 | 6.60E-04 | 3.02E-02 |
| Yb | 174 | 6.62E-03 | 1.42E-03 | 2.02E-02 | 5.61E-03 | 3.98E-04 | 1.68E-02 |

**Table 22: Method limits of quantification regarding ICP-QMS**

Method limits of quantification of solid material with respect to ICP-QMS are summarized in Table 23.

| ICP-QMS | LoQs of solids [ng $g^{-1}$] | | | | | | |
|---|---|---|---|---|---|---|---|
| Analyte | Mass | $LoQ_3$ p.seed | $LoQ_3$ coffee | $LoQ_3$ soil | $LoQ_4$ p.seed | $LoQ_4$ coffee | $LoQ_4$ soil |
| Ce | 140 | 3.33E-01 | 5.74E-01 | 1.81E-01 | 1.57E-01 | 4.08E-02 | 8.52E-02 |
| Dy | 164 | 8.20E-02 | 7.62E-02 | 1.05E-01 | 6.81E-02 | 3.20E-02 | 8.47E-02 |
| Er | 166 | 6.53E-02 | 6.50E-02 | 5.29E-02 | 5.55E-02 | 2.45E-02 | 4.20E-02 |
| Eu | 153 | 4.73E-02 | 4.61E-02 | 2.20E-01 | 3.75E-02 | 1.05E-02 | 8.41E-02 |
| Gd | 158 | 1.30E-01 | 1.30E-01 | 1.21E-01 | 1.03E-01 | 2.93E-02 | 9.02E-02 |
| Ho | 165 | 3.36E-02 | 2.30E-02 | 2.18E-02 | 2.90E-02 | 9.18E-03 | 1.79E-02 |
| La | 139 | 1.96E-01 | 2.97E-01 | 1.75E-01 | 1.07E-01 | 3.09E-02 | 7.47E-02 |
| Lu | 175 | 2.05E-02 | 2.59E-02 | 1.39E-02 | 1.71E-02 | 9.07E-03 | 1.16E-02 |
| Nd | 142 | 3.58E-01 | 3.08E-01 | 1.88E-01 | 3.01E-01 | 9.97E-02 | 1.16E-01 |
| Pr | 141 | 6.68E-02 | 6.75E-02 | 6.71E-02 | 4.75E-02 | 1.58E-02 | 4.63E-02 |
| Sc | 45 | 2.20E+01 | 6.92E+01 | 1.16E+01 | 4.49E+00 | 1.81E+00 | 3.86E+00 |
| Sm | 152 | 1.10E-01 | 1.14E-01 | 3.96E-01 | 8.51E-02 | 3.59E-02 | 1.92E-01 |
| Tb | 159 | 2.79E-02 | 2.89E-02 | 2.75E-02 | 2.23E-02 | 7.77E-03 | 2.27E-02 |
| Tm | 169 | 1.96E-02 | 2.60E-02 | 9.57E-03 | 1.55E-02 | 9.94E-03 | 7.14E-03 |
| Y | 89 | 1.56E-01 | 2.44E-01 | 1.66E-01 | 1.06E-01 | 2.64E-02 | 7.56E-02 |
| Yb | 174 | 6.62E-02 | 5.68E-02 | 5.05E-02 | 5.61E-02 | 1.59E-02 | 4.21E-02 |

**Table 23: Method limits of quantification of solids regarding ICP-QMS**

LoQ for ICP-SFMS are listed in Table 24 and in Table 25 regarding solutions and solid matter respectively.

| ICP-SFMS LoQs of solutions [ng $g^{-1}$] | | | | | | | |
|---|---|---|---|---|---|---|---|
| Analyte | Mass | $LoQ_3$ $HNO_3$ | $LoQ_3$ $HNO_3+H_2O_2$ | $LoQ_3$ $NH_4NO_3$ | $LoQ_4$ $HNO_3$ | $LoQ_4$ $HNO_3+H_2O_2$ | $LoQ_4$ $NH_4NO_3$ |
| Ce | 140 | 3.32E-02 | 3.80E-02 | 6.01E-02 | 9.35E-03 | 5.69E-02 | 2.74E-02 |
| Dy | 161 | 1.21E-02 | 5.36E-03 | 3.44E-02 | 9.24E-03 | 1.03E-02 | 2.81E-02 |
| Er | 166 | 5.18E-03 | 2.19E-03 | 1.81E-02 | 4.28E-03 | 6.41E-03 | 1.52E-02 |
| Eu | 153 | 4.73E-03 | 6.02E-03 | 2.13E-01 | 3.63E-03 | 1.07E-02 | 3.69E-02 |
| Gd | 155 | 2.38E-02 | 1.56E-02 | 1.63E+00 | 1.13E-02 | 3.44E-02 | 2.76E-01 |
| Ho | 165 | 1.01E-03 | 4.63E-04 | 4.98E-03 | 7.59E-04 | 1.43E-03 | 4.06E-03 |
| La | 139 | 1.91E-02 | 2.07E-02 | 5.14E-02 | 6.68E-03 | 4.26E-02 | 1.79E-02 |
| Lu | 175 | 7.64E-04 | 3.32E-04 | 1.80E-03 | 6.09E-04 | 1.08E-03 | 1.34E-03 |
| Nd | 145 | 3.99E-02 | 1.50E-02 | 9.00E-02 | 2.68E-02 | 3.19E-02 | 6.55E-02 |
| Pr | 141 | 6.02E-03 | 4.48E-03 | 9.40E-03 | 3.55E-03 | 8.20E-03 | 4.45E-03 |
| Sc | 45 | 1.56E-02 | 2.78E-03 | 1.43E-02 | 1.09E-02 | 5.83E-04 | 1.09E-02 |
| Sm | 149 | 1.45E-02 | 2.62E-02 | 3.32E-02 | 1.20E-02 | 2.52E-02 | 2.57E-02 |
| Tb | 159 | 1.20E-03 | 5.43E-04 | 4.44E-03 | 8.39E-04 | 1.79E-03 | 3.43E-03 |
| Tm | 169 | 1.10E-03 | 6.50E-04 | 3.40E-03 | 9.81E-04 | 2.17E-03 | 3.00E-03 |
| Y | 89 | 1.17E-02 | 7.17E-03 | 3.37E-02 | 5.22E-03 | 1.30E-02 | 1.08E-02 |
| Yb | 171 | 8.98E-03 | 2.31E-03 | 1.72E-02 | 7.69E-03 | 9.12E-03 | 1.54E-02 |

**Table 24: Method limits of quantification regarding ICP-SFMS**

| ICP-SFMS LoQs of solids [ng $g^{-1}$] | | | | | | | |
|---|---|---|---|---|---|---|---|
| Analyte | Mass | $LoQ_3$ p.seed | $LoQ_3$ coffee | $LoQ_3$ soil | $LoQ_4$ p.seed | $LoQ_4$ coffee | $LoQ_4$ soil |
| Ce | 140 | 3.32E-01 | 1.52E+00 | 1.50E-01 | 9.35E-02 | 2.28E+00 | 6.85E-02 |
| Dy | 161 | 1.21E-01 | 2.15E-01 | 8.59E-02 | 9.24E-02 | 4.11E-01 | 7.02E-02 |
| Er | 166 | 5.18E-02 | 8.76E-02 | 4.52E-02 | 4.28E-02 | 2.57E-01 | 3.81E-02 |
| Eu | 153 | 4.73E-02 | 2.41E-01 | 5.32E-01 | 3.63E-02 | 4.26E-01 | 9.22E-02 |
| Gd | 155 | 2.38E-01 | 6.22E-01 | 4.07E+00 | 1.13E-01 | 1.38E+00 | 6.90E-01 |
| Ho | 165 | 1.01E-02 | 1.85E-02 | 1.25E-02 | 7.59E-03 | 5.74E-02 | 1.01E-02 |
| La | 139 | 1.91E-01 | 8.26E-01 | 1.28E-01 | 6.68E-02 | 1.70E+00 | 4.48E-02 |
| Lu | 175 | 7.64E-03 | 1.33E-02 | 4.50E-03 | 6.09E-03 | 4.32E-02 | 3.34E-03 |
| Nd | 145 | 3.99E-01 | 5.99E-01 | 2.25E-01 | 2.68E-01 | 1.28E+00 | 1.64E-01 |
| Pr | 141 | 6.02E-02 | 1.79E-01 | 2.35E-02 | 3.55E-02 | 3.28E-01 | 1.11E-02 |
| Sc | 45 | 1.56E-01 | 1.11E-01 | 3.57E-02 | 1.09E-01 | 2.33E-02 | 2.71E-02 |
| Sm | 149 | 1.45E-01 | 1.05E+00 | 8.30E-02 | 1.20E-01 | 1.01E+00 | 6.44E-02 |
| Tb | 159 | 1.20E-02 | 2.17E-02 | 1.11E-02 | 8.39E-03 | 7.17E-02 | 8.56E-03 |
| Tm | 169 | 1.10E-02 | 2.60E-02 | 8.49E-03 | 9.81E-03 | 8.70E-02 | 7.51E-03 |
| Y | 89 | 1.17E-01 | 2.87E-01 | 8.42E-02 | 5.22E-02 | 5.22E-01 | 2.70E-02 |
| Yb | 171 | 8.98E-02 | 9.24E-02 | 4.30E-02 | 7.69E-02 | 3.65E-01 | 3.84E-02 |

**Table 25: Method limits of quantification of solids regarding ICP-SFMS**

### 4.1.8 **Sensitivity**

Table 26 lists relative sensitivities in relation to the internal standard indium as well as sensitivities in absolute intensities for REE measured on ICP-QMS (10 ng $g^{-1}$ In) and ICP-SFMS (1 ng $g^{-1}$ In).

| Sensitivity | | ICP-QMS (10 ng $g^{-1}$ In) | | ICP-SFMS (1 ng $g^{-1}$ In) | |
|---|---|---|---|---|---|
| Analyte | Mass | cps·$ng^{-1}$·g·int(In)$^{-1}$ | cps·$ng^{-1}$·g | cps·$ng^{-1}$·g·int(In)$^{-1}$ | cps·$ng^{-1}$·g |
| Ce | 140 | 1.06E-01 | 7.22E+04 | 1.01E+00 | 1.31E+06 |
| Dy | 164/161 | 3.57E-02 | 2.42E+04 | 2.15E-01 | 2.78E+05 |
| Er | 166 | 4.08E-02 | 2.77E+04 | 3.43E-01 | 4.44E+05 |
| Eu | 153 | 6.99E-02 | 4.75E+04 | 4.93E-01 | 6.40E+05 |
| Gd | 158/155 | 3.03E-02 | 2.06E+04 | 1.73E-01 | 2.24E+05 |
| Ho | 165 | 1.21E-01 | 8.22E+04 | 1.02E+00 | 1.33E+06 |
| La | 139 | 1.13E-01 | 7.66E+04 | 1.12E+00 | 1.46E+06 |
| Lu | 175 | 1.22E-01 | 8.27E+04 | 8.37E-01 | 1.08E+06 |
| Nd | 142/145 | 3.70E-02 | 2.51E+04 | 9.30E-02 | 1.21E+05 |
| Pr | 141 | 1.33E-01 | 9.06E+04 | 1.14E+00 | 1.48E+06 |
| Sc | 45 | 2.95E-02 | 2.00E+04 | 8.98E-01 | 6.12E+04 |
| Sm | 152/149 | 3.61E-02 | 2.45E+04 | 1.43E-01 | 1.86E+05 |
| Tb | 159 | 1.25E-01 | 8.48E+04 | 1.13E+00 | 1.47E+06 |
| Tm | 169 | 1.26E-01 | 8.56E+04 | 9.85E-01 | 1.28E+06 |
| Y | 89 | 7.33E-02 | 4.98E+04 | 1.07E+00 | 1.38E+06 |
| Yb | 174/171 | 4.03E-02 | 2.74E+04 | 1.38E-01 | 1.79E+05 |

**Table 26: Sensitivity of ICP-QMS and ICP-SFMS regarding REEs**

Absolute and relative sensitivity of the sector-field instrument was about one order of magnitude higher compared to the quadrupole instrument except of scandium which was higher about three times due to spectral interferences. Praseodymium had the highest sensitivity ($1.48 \cdot 10^6$; $9.06 \cdot 10^4$ cps·$ng^{-1}$·g) and scandium the lowest ($6.12 \cdot 10^4$; $2.00 \cdot 10^4$ cps·$ng^{-1}$·g) as shown in brackets for ELEMENT2 and ELAN-DRC-e respectively.

### 4.1.9 **Uncertainty budget: contribution of the slope**

Four elements have been chosen in order to evaluate the contribution of the slope to the uncertainty budget. Therefore results of rare earth elements in three different matrices were under investigation with a close look on the relative standard uncertainty (RSU) with a coverage factor of 2 (k=2). After evaluation it will be decided whether the standard uncertainty of the slope, as calculated by the instrument, can be used or whether each input of the slope needs to be considered in order to state a reasonable uncertainty.

Relative standard deviation of the slope as calculated by the ELAN software and relative standard uncertainty of the slope using the Kragten approach were compared (Equ. 20Equ. 18 to Equ. 20). RSD, RSU (k=1) as well as mean values of both approaches are listed in Table 27. Even though each input is supposed to be used for calculating an uncertainty budget this was not quite the case with respect to the slope. Instead of using intensities of each standard and the respective intensity of indium only net intensity of each standard and calculated standard uncertainty was used as part of the slope. This reduced its standard uncertainty. However the other way seemed way too overestimating because only intensities of the last standard as well as its internal standard were main contributors.

| Slope | RSD ELAN | RSU (k=1) Kragten | Slope | RSD ELAN | RSU (k=1) Kragten |
|---|---|---|---|---|---|
| Ce | 0.56% | 0.87% | Nd | 0.38% | 0.98% |
| Dy | 0.67% | 0.97% | Pr | 0.50% | 0.79% |
| Er | 0.32% | 0.76% | Sc | 0.12% | 0.56% |
| Eu | 0.63% | 1.04% | Sm | 0.54% | 1.36% |
| Gd | 0.82% | 0.76% | Tb | 0.29% | 0.96% |
| Ho | 0.16% | 0.53% | Tm | 0.30% | 0.58% |
| La | 0.23% | 0.91% | Y | 0.37% | 0.75% |
| Lu | 0.30% | 0.81% | Yb | 0.47% | 0.62% |
| **mean** | 0.42% | 0.83% | | | |

**Table 27: RSD and RSU (k=1) of the slope using different calculation approaches**

RSU is about double compared to RSD. Additionally to weighted linear calculation of the slope regression by the ELAN software supposes that x-axis values, that is to say concentrations, are free of error. However main error is stated on net intensity of the last standard using the Kragten approach since it has the highest count rate and therefore highest standard deviation. Consequently standard deviation of intensity is not distributed equally but rises with each standard. As a result relative standard uncertainty is much higher because net intensity of the highest is the main contributor.

Nevertheless each contributor as well as the influence of the slope on the expanded total combined uncertainty is given on the example of cerium, neodymium, praseodymium, ytterbium and lanthanum. These elements are of high, medium and low concentration present in soil, seed and oil samples. However concentrations of the measured solutions are highest in soil, closely followed by seed while the concentration in oil is rather low. Results are listed for each element separately and a conclusion is given afterwards.

#### *4.1.9.1 Cerium*

Concentration was significantly different with respect to oil seed and soil and so was their relative standard uncertainty. However the final result did not really make a difference using either RSD of the slope as provided by the ELAN software or the Kragten approach (Table 28).

| Cerium | c [ng $g^{-1}$] | RSU (k=2) Kragten | RSU (k=2) ELAN |
|---|---|---|---|
| oil | 2.01 | 8.2% | 8.1% |
| seed | 15.4 | 4.2% | 4.0% |
| soil | 10.6 | 7.1% | 7.0% |

**Table 28: Concentration, RSU (k=2) of cerium of oil, seed and soil**

The following figures show main contributors to the expanded total combined uncertainty calculating the final concentration. On the one hand (Figure 11) all variables were used for calculating the RSU (k=1) of the slope while on the other hand (Figure 12) the slope k and its uncertainty calculated either way were used to get a final result. Differences are shown for soil, seed and oil.

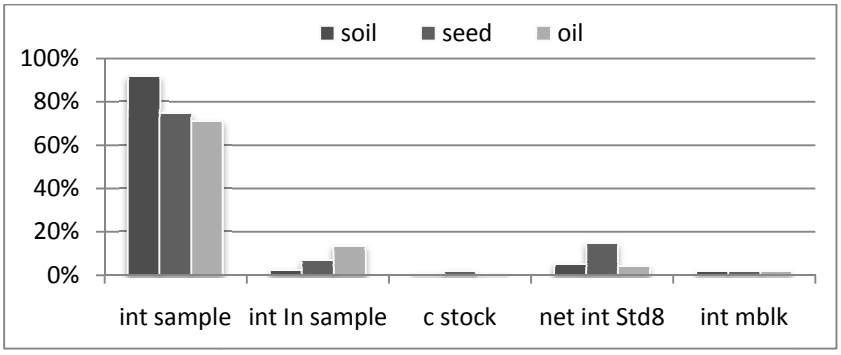


**Figure 11: Main contributors to total combined uncertainty using Kragten (Ce)**

Intensity of the sample was the main contributor to the relative standard uncertainty. Intensity of indium of the sample played an important role considering pumpkin seed oil as well whereas influence of the intensity of the last calibration standard (Std8) was not that big than for pumpkin seeds where even concentration of the stock solution had a minor influence on RSU (k=1). Consequently contribution of the slope was highest for pumpkin seeds especially using the Kragten approach.

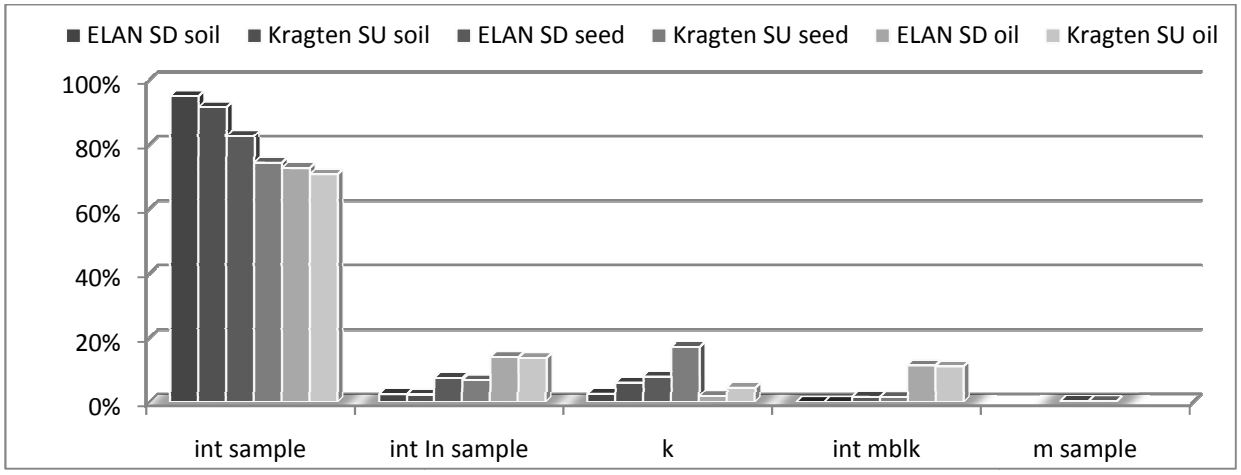


**Figure 12: Main contributors to total combined uncertainty (Ce)**

Relative standard uncertainty was double for soil compared to oil whereas seed samples had a slightly lower RSU (k=2). Even though contribution of the slope was quite different for these samples, the influence on the end result was not significant, that is to say only 0.1% for low and medium concentration and 0.2% for higher concentrated samples. The higher the concentration of the measured solution the lower the total combined uncertainty because influence is more concentrated on one factor than summing up of many.

#### *4.1.9.2 Neodymium*

Neodymium was chosen because sensitivity was amongst lowest of all elements. Even though count rate of Nd in oil was almost as much as standard three a very high relative standard uncertainty was calculated, that is to say 19%. Soil and pumpkin seed intensities, between

standard four and five, had a much lower RSU (k=2) (Table 29). Differences using either approach for calculating the slope were slightly higher compared to Ce with 0.3%.

| Neodymium | c [ng $g^{-1}$] | RSU (k=2) Kragten | RSU (k=2) ELAN |
|---|---|---|---|
| oil | 1.37 | 19% | 19% |
| seed | 10.3 | 5.0% | 4.7% |
| soil | 5.22 | 5.6% | 5.3% |

**Table 29: Concentration, RSU (k=2) of neodymium of oil, seed and soil**

Intensity of the sample did matter especially for lower count rates whereas intensity of indium had hardly any influence (Figure 13). Contribution of the net intensity of the internal standard eight rose with higher concentration while it was the other way around with respect to the intensity of the method blank.

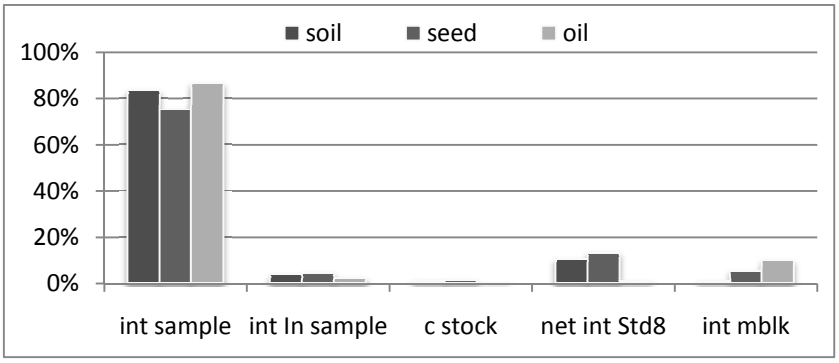


**Figure 13: Main contributors to total combined uncertainty using Kragten (Nd)**

Concentration of the stock solution did not show any contribution to the total combined uncertainty of the slope at all.

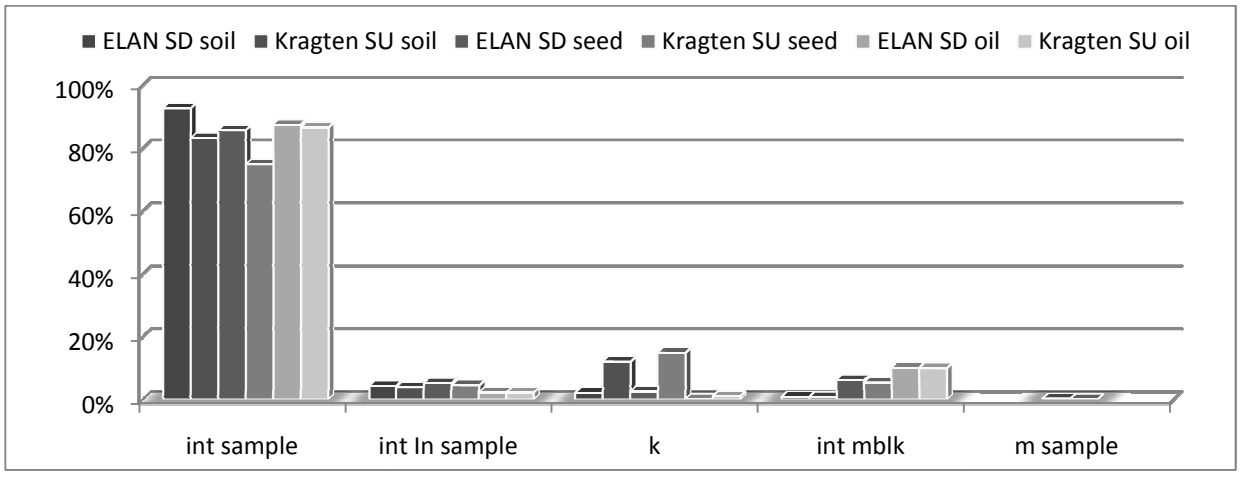


**Figure 14: Main contributors to total combined uncertainty (Nd)**

Since intensity of the method blank was much lower for neodymium compared to cerium its relative standard uncertainty was much higher. Therefore contribution was much higher but

not different using either calculation approach of the slope. However concerning seed and soil samples the slope as calculated by Kragten did contribute much more to the uncertainty budget compared to standard deviation of ELAN but with minor change of the final result.

#### *4.1.9.3 Praseodymium*

Even though concentrations were much lower compared to neodymium relative standard uncertainties (k=2) were about the same for seed and soil samples (Table 30). However RSU of oil samples were as low as of cerium even though relative signal intensity was more in the range of neodymium.

| Praseodymium | c [ng $g^{-1}$] | RSU (k=2) Kragten | RSU (k=2) ELAN |
|---|---|---|---|
| oil | 0.34 | 7.8% | 7.7% |
| seed | 2.71 | 5.5% | 5.4% |
| soil | 1.40 | 5.4% | 5.3% |

**Table 30: Concentration, RSU (k=2) of praseodymium of oil, seed and soil**

Intensities of oil samples were just as high as the first standard. Pumpkin seed and pumpkin seed oil were as high as standard three. On the one hand praseodymium had the highest sensitivity of all elements which could explain the rather low uncertainty even for low ion counts on the example of oil samples. On the other hand intensity of the method blank did contribute most to RSU of oil (Figure 15 and Figure 16).

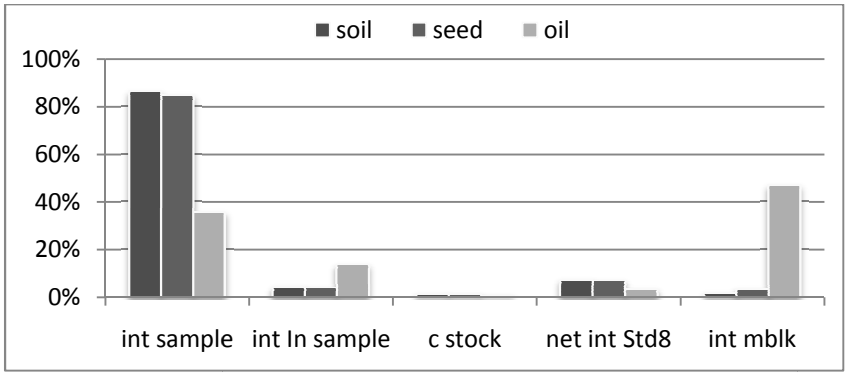


**Figure 15: Main contributors to total combined uncertainty using Kragten (Pr)**

Influence of intensity of indium was also much higher compared to the net intensity of standard eight respectively the slope in general. Concentration of the stock solution did only matter for soil and seed samples (Figure 15) whereas mass of the sample was once again only contributing to the total uncertainty of seed samples (Figure 16).

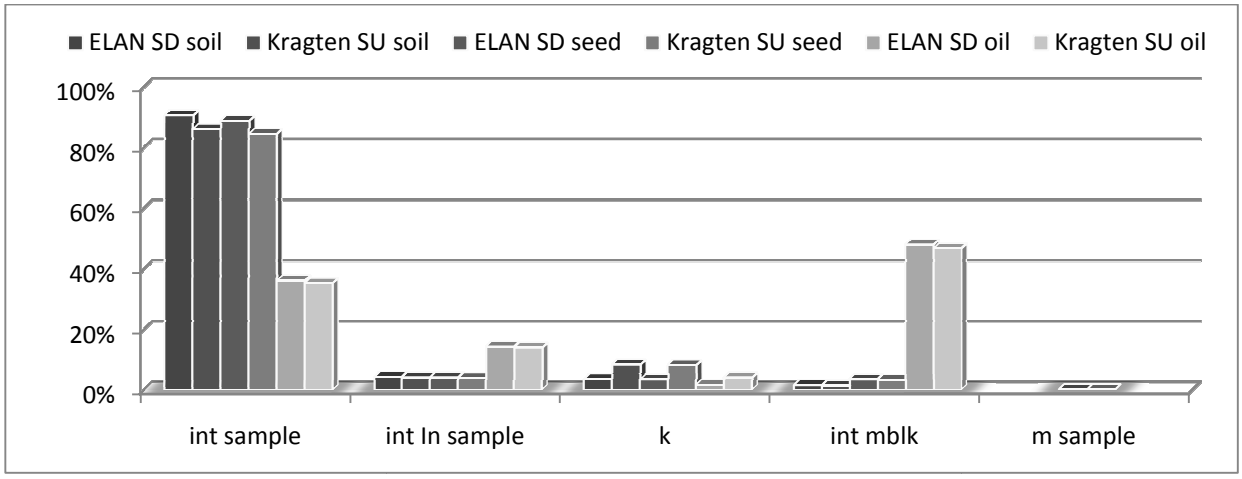


**Figure 16: Main contributors to total combined uncertainty (Pr)**

### *4.1.9.4 Ytterbium*

Sensitivity of ytterbium was rather low as well. In addition no sample could be detected within the working range. However all samples were above limit of quantification.

| Ytterbium | c [ng $g^{-1}$] | RSU (k=2) Kragten | RSU (k=2) ELAN |
|---|---|---|---|
| oil | 0.124 | 24% | 24% |
| seed | 0.529 | 19% | 19% |
| soil | 0.181 | 29% | 29% |

**Table 31: Concentration, RSU (k=2) of ytterbium of oil, seed and soil**

Consequently the highest relative standard uncertainty of all elements was calculated. Since intensity of the sample was very low it was the main contributor. Only intensity of the method blank as well as intensity of indium of the sample did play a minor role as well. Consequently no influence according to the calculation of the slope was present. However considering that ytterbium was not measured within the working range and relative high total combined uncertainty of this element it should not be used for interpretation.

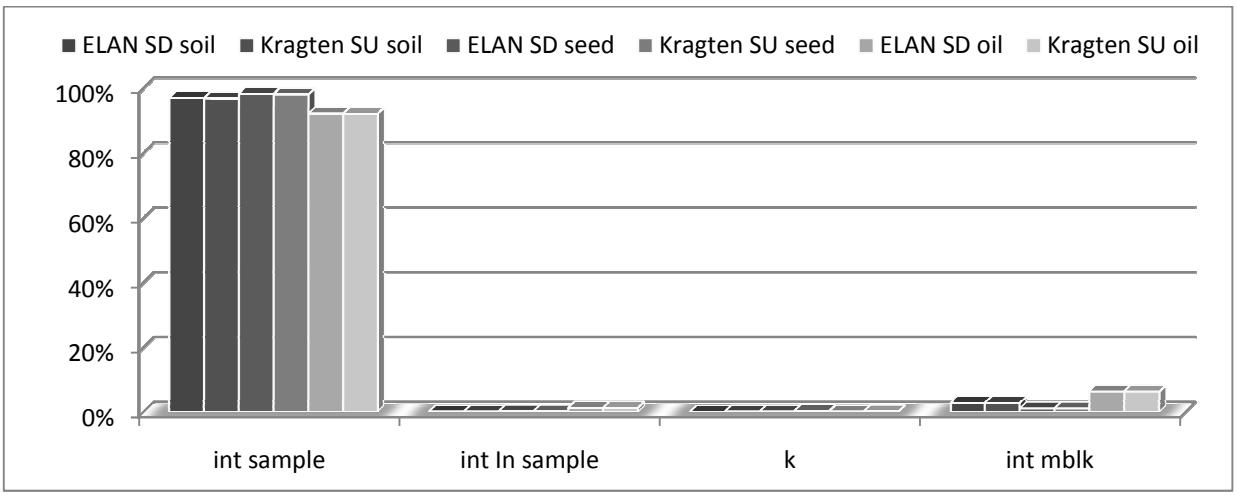


**Figure 17: Main contributors to total combined uncertainty (Yb)**

### *4.1.9.5 Lanthanum*

A totally different picture was shown by lanthanum. Since relative intensity of the soil and seed samples and sensitivity of the element were similar to cerium one would expect a similar behavior with respect to the relative uncertainty as well. Even though RSD and signal intensity of each standard were about the same compared to Ce RSU of the slope was only half. These differences were evident but could not be explained. Only the blank signal of La was much lower but RSD was double compared to Ce. Nonetheless contributions to the uncertainty of the slope were similar to Figure 11. Overall the slope (RSU, k=1) was main contributor to the total combined uncertainty of the final result (Table 32) which was still rather low compared to other elements.

| Lanthanum | c [ng $g^{-1}$] | RSU (k=2) Kragten | RSU (k=2) ELAN |
|---|---|---|---|
| oil | 1.9 | 8.1% | 7.9% |
| seed | 15.6 | 2.8% | 2.2% |
| soil | 14.7 | 2.7% | 2.1% |

**Table 32: Concentration, RSU (k=2) of lanthanum of oil, seed and soil**

Using RSD of the slope, according to ELAN, contribution of the intensity of indium of the sample was much higher compared to the slope as well as to calculations mentioned above. In the end differences using either ELAN RSD or Kragten RSU (k=1) were as much as 0.6% which is quite high when RSU (k=2) is 2.1% and 2.7% respectively.

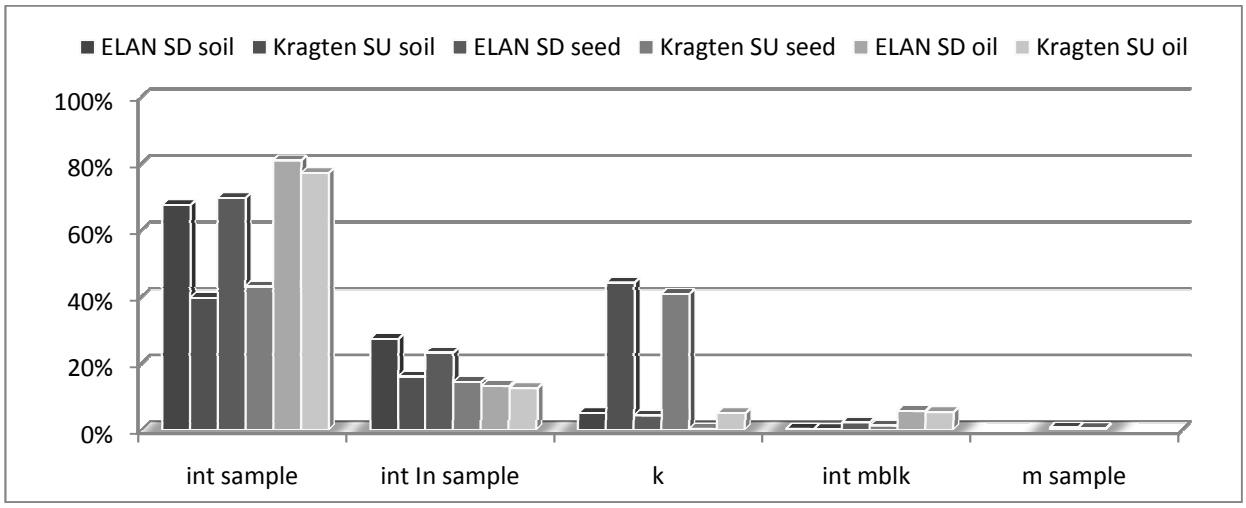


**Figure 18: Main contributors to total combined uncertainty (La)**

Samarium did show similar behavior with respect to the higher concentrated soil sample as well. RSD of the slope was about the same compared to Ce even though RSD of each calibration standard of samarium was much higher. In addition sensitivity was very low.

#### *4.1.9.6 Conclusion*

As expected the relative standard uncertainty of the slope was strongly dependent on the net intensity of the highest calibration standard. SD of the concentration of the stock solution played only a minor role.

Contribution of the slope to the total combined uncertainty was positively related to the intensity of the sample. Even though its influence was up to 15% any changes to the final result were not above 0.3%. As a matter of fact only results of neodymium did vary that much as for other elements difference was only 0.1%. Small changes could be reported using either approach for calculating the uncertainty of the slope. Since a coverage factor of two was used relative standard uncertainty of the final result was expanded already. Therefore it is justifiable to use the given standard deviation of the slope as given by the instrument in order to calculate RSU (k=2) of a sample. Calculation is much easier that way without any significant differences. However this could be examined for low concentrations only. It is evident that the calculated way by ELAN gives the uncertainty of the slope using a confidence interval whereas the Kragten approach focuses more on each contributor.

Much bigger differences could be observed concerning lanthanum and samarium but lowest total combined uncertainties were calculated of these elements. However calculated RSUs (k=2) were significantly different with respect to the applied calibration approach. Weighted linear calculation of the slope as calculated via the ELAN software seems to have an influence on the expected uncertainty as well.

Correlation coefficients ($r^2$) of all elements were above 0.9998 which could explain the rather low uncertainty, below 1%, of the slope. It may rise however with lower $r^2$ and therefore contribution to the total combined uncertainty of the concentration of an element probably increases as well.

### 4.1.10 **ELAN vs. ELEMENT2**

Different parameters have been under investigation so far and were discussed in previous chapters above. Last but not least a short summary should explain advantages and disadvantages of each instrument. Additionally concentrations of measured samples are compared with each other.

All elements except of scandium passed quality control using ICP-QMS. Sc was measured correctly using ICP-SFMS however problems were observed with gadolinium, yttrium, europium, ytterbium and lutetium. No certified value was available for dysprosium, erbium and thulium. Recovery of elements was slightly better using ICP-QMS even though overestimation, probably due to interferences, was the problem compared to underestimation using ICP-SFMS.

Limit of detection and quantification before blank correction were lower using ELAN while ELEMENT2 had a much better precision, consequently LoD/Q after blank correction decreased. The sensitivity of ICP-SFMS it was one order of magnitude higher than in ICP-QMS. Repeatability of measurements was only calculated for the quadrupole instrument.

Finally total concentration of the measured samples and their expanded standard uncertainty were examined. Unfortunately results did not turn out as expected, probably due to the instability of the sector field instrument. Concentration and RSU (k=2) of each element measured with either instrument are listed in Table 33 . They are illustrated as well in Figure 19, Figure 20 and Figure 21 for pumpkin seed oil, pumpkin seed and soil respectively.

Ce, Er, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm and Yb showed no obvious differences regarding pumpkin seed oil. However relative standard uncertainty of most elements was rather high.

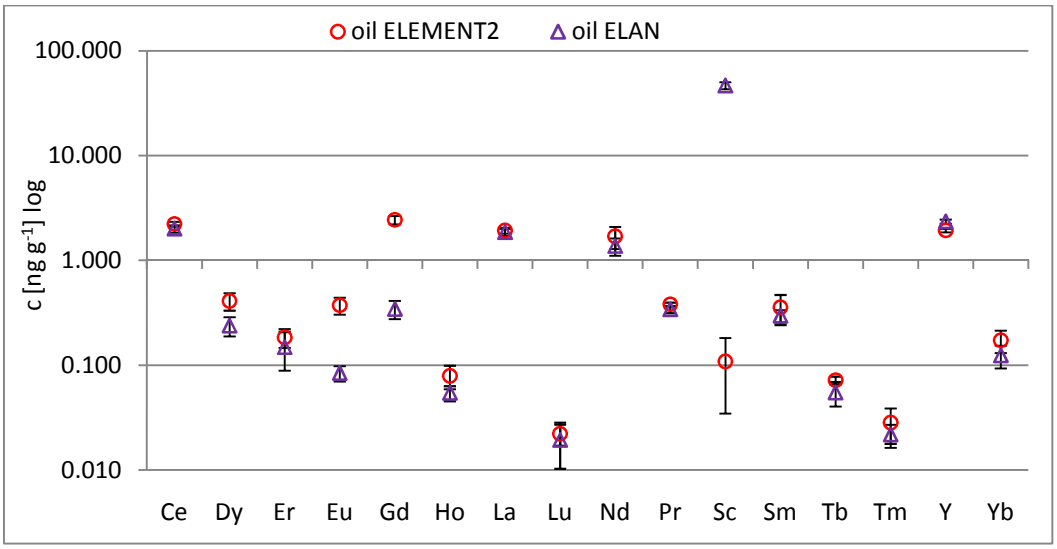


**Figure 19: Concentration and RSU (k=2) of pumpkin seed oil measured with either ELAN or ELEMENT2**

Concentration of Dy and Y was significantly different even though relative standard uncertainty of Dy was about 20%. However it was only 5% considering Y. Since $^{155}Gd$ was interfered by $^{139}La^{16}O^{+}$using ICP-SFMS and problems occurred for measurement of Sc using ICP-QMS these elements did not overlap within any matrix, neither did Eu.

All elements in pumpkin seeds, except of yttrium, were significantly different using the two instruments (Figure 20). Due to the poor instrumental performance during the measurements of these samples no further conclusion can be drawn from these results.

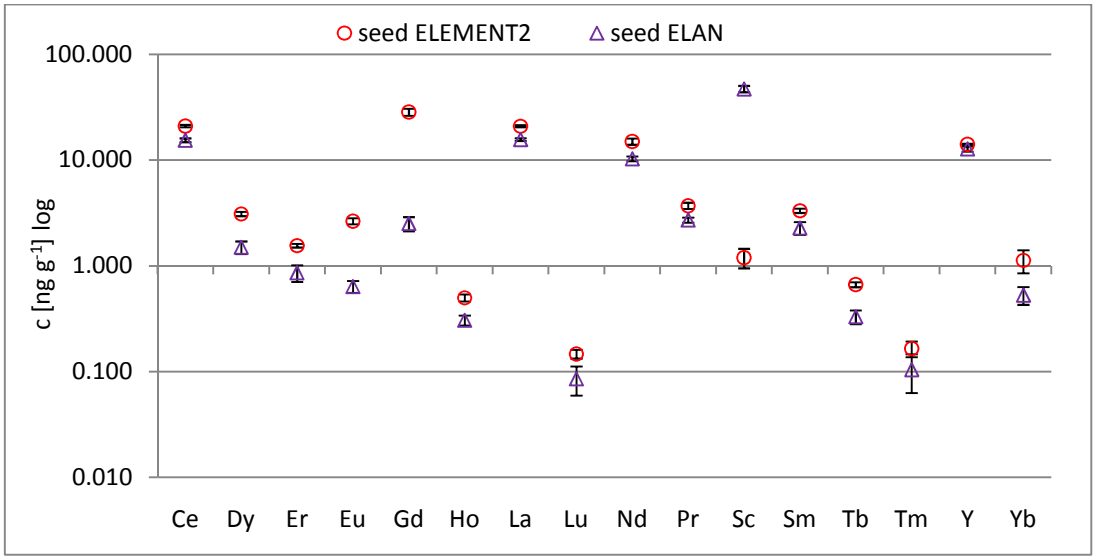


**Figure 20: Concentration and RSU (k=2) of pumpkin seed measured with either ELAN or ELEMENT2**

Significant differences observed in soil samples were similar the result of the oil data. In addition to elements mentioned earlier Lu and Sm did not overlap either even though Y concentrations did match in soil samples. RSU of elements in soil was in between seed and oil samples for most elements.

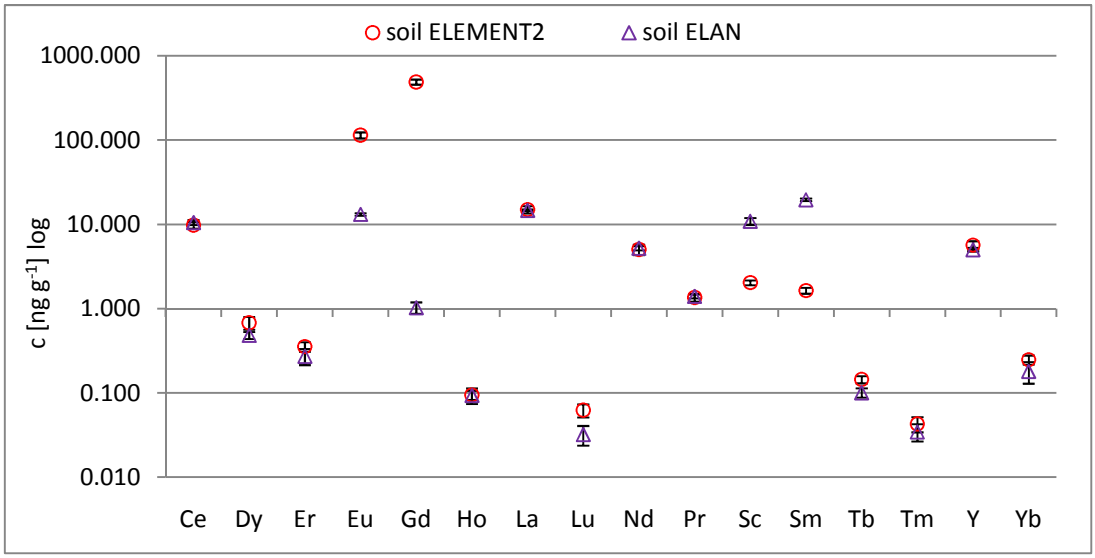


**Figure 21: Concentration and RSU (k=2) of soil measured with either ELAN or ELEMENT2**

In general it can be said that element concentration was highest in pumpkin seed and lowest in pumpkin seed oil. Consequently inverse total combined uncertainty was observed. Considering oil samples, results were acceptable for Ce, La, Pr and Y for either instrument as well as for Tb using ICP-SFMS and Sm and Eu using ICP-QMS. RSU for all other elements was above 20%. It was below 10% for elements detected in pumpkin seeds using ELEMENT2 except of Sc, Tm and Yb which were out of measurement range. RSU of the ELAN measurements was between 2.8%

and 5.6% for Ce, La, Nd, Pr and Y and between 11% and 19% for Dy, Er, Eu, Gd, ho, Sm, Tb and Yb. Probably due to severe matrix effects using ICP-SFMS total combined uncertainty of soil samples was much higher compared to ICP-QMS which seemed more robust.

| Matrix | | oil | | seed | | soil | | oil | | seed | | soil | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Analyte | Mass | c [ng $g^{-1}$] | | c [ng $g^{-1}$] | | c [ng $g^{-1}$] | | RSU, k=2[%] | | RSU, k=2[%] | | RSU, k=2[%] | |
| Ce | 140 | 2.23 | 2.01 | 20.9 | 15.4 | 9.81 | 10.6 | 5.1 | 8.2 | 2.7 | 4.2 | 9.0 | 7.1 |
| Dy | 164/161 | 0.41 | 0.24 | 3.09 | 1.50 | 0.68 | 0.48 | 19 | 21 | 4.6 | 14 | 17 | 9.4 |
| Er | 166 | 0.18 | 0.15 | 1.55 | 0.86 | 0.35 | 0.27 | 20 | 40 | 4.1 | 18 | 13 | 22 |
| Eu | 153 | 0.37 | 0.08 | 2.64 | 0.64 | 115 | 13.2 | 19 | 16 | 6.6 | 13 | 8.1 | 3.5 |
| Gd | 158/155 | 2.44 | 0.34 | 28.4 | 2.51 | 490 | 1.03 | 9.3 | 20 | 7.7 | 15 | 6.9 | 16 |
| Ho | 165 | 0.08 | 0.05 | 0.50 | 0.31 | 0.09 | 0.09 | 25 | 16 | 7.7 | 11 | 12 | 21 |
| La | 139 | 1.93 | 1.86 | 20.9 | 15.6 | 15.0 | 14.7 | 6.3 | 8.1 | 2.3 | 2.8 | 10 | 2.7 |
| Lu | 175 | 0.02 | 0.02 | 0.15 | 0.09 | 0.06 | 0.03 | 23 | 47 | 9.5 | 31 | 18 | 26 |
| Nd | 142/145 | 1.70 | 1.37 | 15.0 | 10.3 | 5.04 | 5.22 | 24 | 19 | 6.9 | 5.0 | 14 | 5.6 |
| Pr | 141 | 0.38 | 0.34 | 3.70 | 2.71 | 1.36 | 1.40 | 4.2 | 7.8 | 6.8 | 5.5 | 11 | 5.5 |
| Sc | 45 | 0.11 | 46.7 | 1.20 | 47.0 | 2.03 | 10.9 | 68 | 7.9 | 21 | 6.9 | 6.8 | 9.5 |
| Sm | 152/149 | 0.36 | 0.30 | 3.32 | 2.28 | 1.63 | 19.6 | 32 | 14 | 4.6 | 14 | 8.0 | 3.5 |
| Tb | 159 | 0.07 | 0.05 | 0.66 | 0.33 | 0.14 | 0.10 | 8.4 | 26 | 5.5 | 15 | 10 | 12 |
| Tm | 169 | 0.03 | 0.02 | 0.16 | 0.10 | 0.04 | 0.03 | 37 | 25 | 17 | 40 | 20 | 23 |
| Y | 89 | 1.93 | 2.35 | 14.1 | 12.7 | 5.66 | 5.02 | 3.8 | 4.8 | 1.3 | 5.6 | 12 | 5.5 |
| Yb | 174/171 | 0.17 | 0.12 | 1.13 | 0.53 | 0.25 | 0.18 | 24 | 24 | 25 | 19 | 13 | 29 |

**Table 33: Concentration and RSU (k=2) of oil, seed and soil samples: highlighted columns refer to ICP-SFMS whereas plain columns refer to ICP-QMS**

Precision of ICP-SFMS is significantly higher for analysis of REE of to pumpkin seeds and slightly better for pumpkin seed oil. However problems that occurred during ICP-SFMS measurements of soil and seed samples had an influence on the accuracy respectively. Dilution of these samples might overcome that problem however lower concentrations go along with higher relative standard uncertainties. Nonetheless further tests with respect to interferences, especially gadolinium and europium, as well as matrix problems have to be carried out. Since concentrations in oil samples were really low it is questionable whether either method is fit for purpose at all. Only a few elements out of 16 rare earth elements can be used considering all validation parameters which were evaluated. Nevertheless sometimes precision should be sacrificed in order to gain a bigger pool of data for statistical treatment because only relations are taken a look at.

## 4.2 Evaluation of the wine data

Multi-element analysis and strontium isotope ratio measurements were performed on 99 wine samples (3.2.3). They were of different vintage, kind and region that are summarized in Table 41.

The ‘original code’ defines samples out of the same vineyard. However samples from 2003 are excluded due to a new labeling system starting from 2004. Sample preparation is explained in chapter 3.3

### 4.2.1 Multi-element analysis

All wine samples were method blank corrected for multi-element analysis. Furthermore limits of detection as well as limits of quantification regarding the used method were evaluated that decided about whether an element was an appropriate candidate for statistical evaluation or not. Chosen elements had to exceed at least three times the standard deviation of the method blank in order to be used for discriminate analysis. However a few elements were chosen even though some samples were below LoD and set to zero in that case. All involved elements are highlighted in the periodic table of elements in Figure 22.

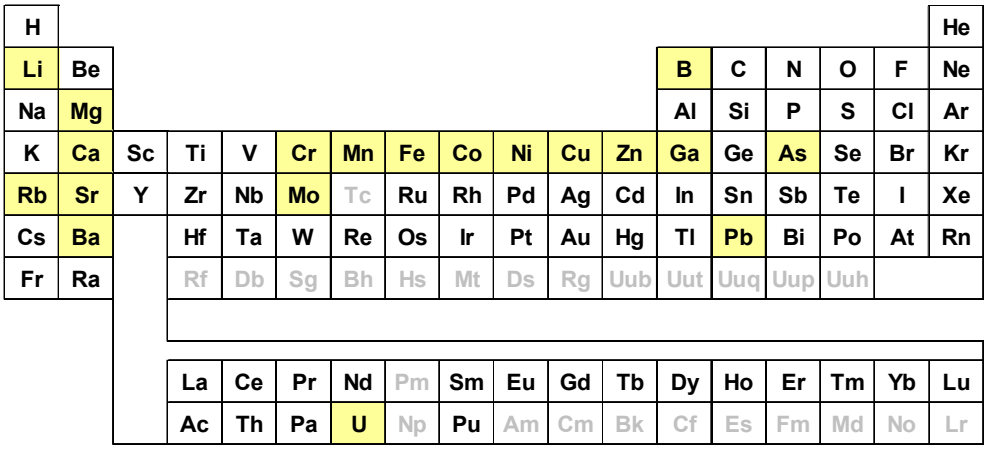


**Figure 22: Elements used for multi-element analysis regarding wine provenance**

Even though aluminum was above LoD for most samples it was not taken into account. First of all it did not contribute in any way to statistical evaluation. Secondly Al could not be detected in wine samples cultured in 2008. These were stored in glass bottles like the other samples but did not have metal lids but plastic ones. Additionally no filtering process had been taken place so far. Furthermore concentration in some samples was rather higher. It was questionable whether it was just from the grape itself or not. Thus it seemed that Al detected in other samples resulted from possible contamination.

Even though vintage does not matter regarding provenance studies it should be worth mentioned that concentration of uranium was below LoQ but even below LoD in wine from 2008 only. This has to be investigated more closely whether U is influenced by the filtering process or storage in general. Another peculiarity is the relatively low strontium concentration and very high rubidium concentration in white wine from South-East Styria. It has been reported though that uptake of trace elements can be different with respect to skin and flesh of a grape. In addition due to different wine making processes, with respect to white and red

wine, it is possible that these elements might leach out due to longer contact of skin and grape juice (Coetzee, 2005).

Screening of rare earth elements of a few samples showed no detectability and was not further investigated.

Element concentration of all samples, the corresponding LoD and LoQ as well as relative standard uncertainty of each element is listed in Table 42.

#### *4.2.1.1 Provenance of white wine*

A number of 26 white wines were available; one from the region of Central-Burgenland (CB), one from Lake Neusiedl (LN) and another one from Lake Neusiedl-Hills (LN-H) that were grouped together representing the federal state of Burgenland (1). Eight wine samples were pressed of grapes from either South-East-Styria (SE-ST) (5 samples) and one of each from West-Styria (W-ST), South-Styria (S-ST) and Styria (ST) (that was not further specified) that build group number two. The third pool included samples from all over Lower Austria (3); eight from Weinviertel, four from Kamptal, one of each from Donauland and Traisental and one from Vienna that was included as well. Quantity of each region regarding white wines is listed in Table 34.

| Region | CB | NS | NS/HL | SE-ST | W-ST | S-ST | ST | WV | KaT | DL | TT | V |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Burgenland | 1 | 1 | 1 | | | | | | | | | |
| Styria | | | | 5 | 1 | 1 | 1 | | | | | |
| Lower Austria | | | | | | | | 8 | 4 | 1 | 1 | 1 |

**Table 34: Sample distribution of white wine**

Discriminate analysis was carried out using three different regions as mentioned above. The visual outcome is shown below (Figure 23).

Concentration of elements which were above LoDs was used in the left figure while only concentrations that could be quantified were used in the right one. Consequently Ga, As and Pb were not included using limits of quantification as a benchmark. In addition sample concentration of an element that was below the chosen threshold was set zero. Furthermore Cu and Zn were below LoQ for a few samples only and were used as well. Purple diamonds represent Burgenland, green triangles symbolize Styrian samples and blue circles embody Lower Austria. Each group has a center which is shown as a red filled square.

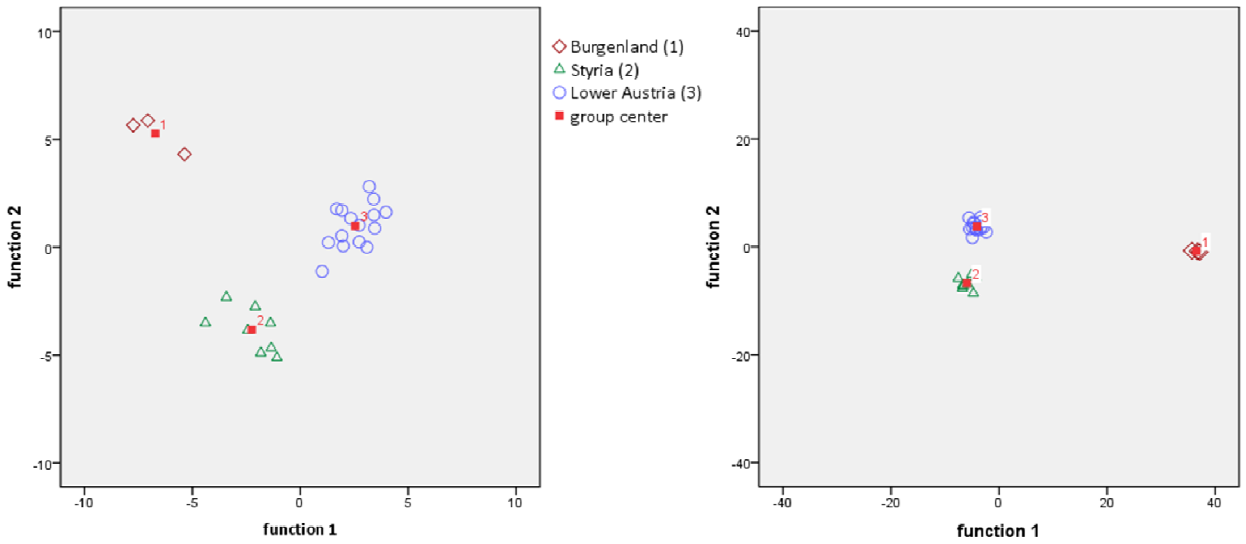


**Figure 23: Discriminant function of white wine only using either LoQ (left figure) or LoD (right figure) as a threshold of element concentration**

All wine samples could be classified according to their origin no matter what procedure was applied. However some elements were mostly in between LoD and LoQ. Therefore a much clearer discrimination could be achieved using these concentrations as well and not set zero (Figure 23 right). Even though there is only a small gap between these two thresholds reliability of the concentration of an analyte is only given by LoQ.

Discrimination of white wine of different provenance, pooled according to their federal state, seems to work satisfyingly. However it should be kept in mind, that the sample pool of 26 and its distribution among the federal states is probably not significant in order to get a 100% classification rate at any time. In addition the sample pool was somewhat homogeneous, some wine samples from different vintage but originating of the same vineyard, which might influence the result in a desirable way.

### *4.2.1.2 Provenance of red wine*

Red wine samples originated from Central-Burgenland (16), Lake Neusiedl (7), LN-Hills (4), Carnuntum (5) form one group, South-East-Styria (5), West-Styria (6), South-Styria (1) outlines group number two and Weinviertel (17), Kamptal (2), Thermenregion (6), Kremstal (1), Donauland (2) and Traisental (1) are considered to form group Lower Austria.

The wine region Carnuntum shares climate and soil properties with the federal state of Burgenland. Therefore this region was grouped with wine from Burgenland even though it is located in Lower Austria.

Discriminate analysis was performed on red wines only. Combined regions and distribution among them are listed below.

| Region | CB | NS | NS/HL | C | SE-ST | W-ST | S-ST | WV | KaT | TR | KrT | DL | TT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Burgenland | 16 | 7 | 4 | 5 | | | | | | | | | |
| Styria | | | | | 5 | 6 | 1 | | | | | | |
| Lower Austria | | | | | | | | 17 | 2 | 6 | 1 | 2 | 1 |

**Table 35: Sample distribution of red wine**

In order to gain a scatter plot as shown below (Figure 24) two different limits, as mentioned in the previous chapter, were used as well. LoD considered being threshold made it possible to use all elements for statistical evaluate (Figure 24 left). On the other hand a threshold of LoQ (Figure 24 right) excluded lead and arsenic even though Zn and Cu were rather low as well but were used, too. In addition red wine seems to have a higher concentration of gallium compared to white wine. Therefore this element could be used for both statistical treatments as well. Due to the high RSU of As it should be excluded though.

Symbolic association used in the scatter plot is equal to Figure 23. However Burgenland was expanded in terms of the region of Carnuntum.

Nonetheless differentiation of red wine samples is not as obvious as categorizing white wine.

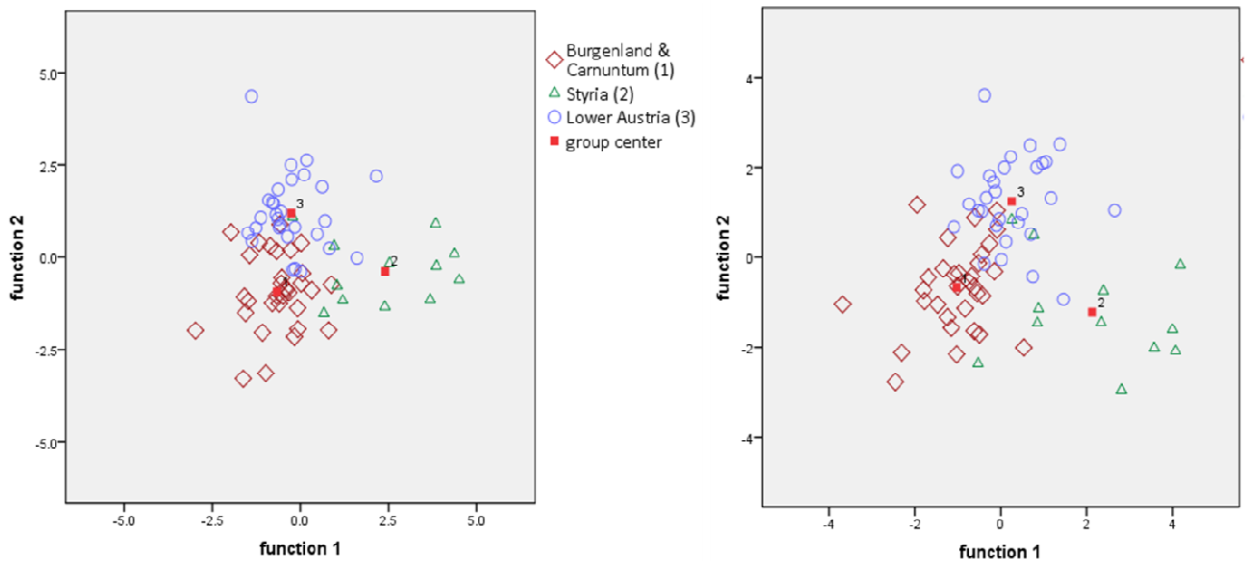


**Figure 24: Discriminant function of red wine only using either LoQ (left figure) or LoD (right figure) as a threshold of element concentration**

Nevertheless classification results of 80.8% using LoD or LoQ for evaluation is quite satisfying regarding a sample pool of 73 wine samples. The results are summarized in Table 36 and Table 37. 14 wine samples could not be assigned correctly regarding each examination. However eleven did not fit in the predicted group using either threshold. All in all a number of 17 samples were classified incorrectly. That is about one out of five.

| | | predicted group | | | total | Incorrectly classified wine samples | | |
|---|---|---|---|---|---|---|---|---|
| | | 1.0 | 2.0 | 3.0 | | 1.0 | 2.0 | 3.0 |
| quantity | 1.0 | 27 | 1 | 4 | 32 | | W2 | W39, W46,W26, W44 |
| | 2.0 | 1 | 9 | 2 | 12 | W37 | | W51, W92 |
| | 3.0 | 3 | 3 | 23 | 29 | W16,W30,W53 | W9,W47, W15 | |
| % | 1.0 | 84.4 | 3.1 | 12.5 | 100 | 80.8% of original grouped cases could be classified correctly | | |
| | 2.0 | 8.3 | 75.0 | 16.7 | 100 | | | |
| | 3.0 | 10.3 | 10.3 | 79.3 | 100 | | | |

**Table 36: Classification result regarding LoD values of red wine**

Two samples, W44 and W26, are from the same vineyard, different vintage though, originating of Lake Neusiedl-Hills and were predicted in group three. The same applies on W37 and W51 grown on South-East Styrian soil but being classified either within the region of Burgenland or Lower Austria. Vintage of W47 and W53 is the same as well as place of origin (vineyard in WV). Nonetheless these wine samples were categorized in different groups as well. Therefore it seems more a random prediction error rather than any influence of different kind, vintage or vineyard.

Considering LoQ being used as a benchmark about 81 % of the samples from Burgenland & Carnuntum and Lower Austria were classified correctly. Every fifth sample was identified incorrectly regarding wine from Styria. Due to a much smaller sample pool this rather low categorization could be explained. Nevertheless the result might be significantly influenced by the production process of red wine as well.

| | | predicted group | | | total | Incorrectly classified wine samples | | |
|---|---|---|---|---|---|---|---|---|
| | | 1.0 | 2.0 | 3.0 | | 1.0 | 2.0 | 3.0 |
| quantity | 1.0 | 26 | 0 | 6 | 32 | | | W39,W46,W12,W27,W26,W44 |
| | 2.0 | 1 | 9 | 2 | 12 | W37 | | W51, W92 |
| | 3.0 | 3 | 2 | 24 | 29 | W16, W30,W93 | W9, W47 | |
| % | 1.0 | 81.3 | .0 | 18.8 | 100 | 80.8% of original grouped cases could be classified correctly | | |
| | 2.0 | 8.3 | 75.0 | 16.7 | 100 | | | |
| | 3.0 | 10.3 | 6.9 | 82.8 | 100 | | | |

**Table 37: Classification result regarding LoQ values of red wine**

Regarding red wine and further a bigger sample pool it does not make much of a difference using either LoD or LoQ values as a threshold.

Considering the rather wide geographical distribution of the regions within a group as well as sample distribution therein, comparing Central-Burgenland and Weinviertel only reached a

better distinction. These two regions contained by far the most samples compared to the other regions. Additionally West-Styria and/or South-East Styria were taken into account in order to expand the sample pool a little further.

The LoQ was set as threshold. The results are as follows:

Comparing only Central-Burgenland and Weinviertel with each other 97% of original grouped cases could be classified correctly. That is to say only one sample, W46, was considered to be from WV. It was not predicted correctly within the other approaches as well.

Results were not as good building a third group of W-ST and SE-ST or W-ST only. Three samples were predicted falsely. However considering only the region of SE-ST, two samples did not fit into the assigned group. Overall it can be said that considering a third group, representing Styria, as well 92% to 94% of the samples could be classified correctly.

#### *4.2.1.3 Determination of origin considering all wine samples*

Red and white wine, pooled, was investigated according to their origin. Evaluation was performed just as mentioned above in 4.2.1.1. Carnuntum was considered to be part of Burgenland again. Classifications were even lower than considering either red or white wine only. 79.8% could be classified correctly regarding values above LoD while 76.8% could be achieved using LoQ's threshold. To put it in another way 20 out of 99 samples in the first case and 23 out of 99 samples in the second case were predicted falsely. In any case samples were widely scattered around each group center. Thus red and white wines do seem to have different pattern with respect to element concentration because classification is worse than using either red or white wine separately.

### 4.2.2 **Strontium isotope ratios**

$^{87}Sr/^{86}Sr$ ratio was under investigation regarding the determination of origin. Each wine region was examined as such but not grouped. Measurements were performed on different days but with similar instrument performance. Strontium signal for all samples hardly ever dropped below 1V and did not exceed 6V. The limit of relative rubidium content was set to 0.2%. However samples with a higher proportion were separated (3.3.3) and measured again but did not show any significant difference and fit within the range of its region. Especially for wine samples with low strontium concentration it was hard to achieve the limits.

In order to even measure some samples a high performing skimmer cone was required as sensitivity had to be improved. However the signal was about 1 V all the time. Consequently relative rubidium content was higher than 0.2% throughout the samples and was corrected mathematically.

Resulting isotope ratios for all wine samples are listed in Table 42. Sample ratios that did not fulfill the requirements are highlighted. Mean values (c Sr [ng $g^{-1}$], IR) and their standard deviations regarding each region are summarized in Table 38. Isotope ratios only and the representing homogeneity of each region are illustrated in Figure 25 and concerning the element concentration pictured in Figure 26. Only regions that had at least five representatives were compared with each other, besides Lake Neusiedl and Lake Neusiedl-Hills were pooled.

| | mean c Sr [ng $g^{-1}$] | mean IR | SD (c Sr [ng $g^{-1}$]) | SD (IR) |
|---|---|---|---|---|
| SE-ST | 224 | 0.708870 | 197 | 1.25E-03 |
| TR | 253 | 0.708872 | 75.3 | 2.31E-04 |
| LN/LN-H | 353 | 0.709537 | 163 | 6.50E-04 |
| C | 171 | 0.710197 | 50.6 | 5.79E-04 |
| WV | 311 | 0.710555 | 127 | 8.20E-04 |
| KaT | 232 | 0.710979 | 135 | 8.38E-04 |
| CB | 257 | 0.711203 | 103 | 9.41E-04 |
| W-ST | 314 | 0.711749 | 70.4 | 9.48E-04 |

**Table 38: Mean concentration and isotope ratio of different wine regions**

Smallest mean strontium isotope ratios belonged to the region of South-East Styria and Thermenregion. Standard deviation with respect to homogeneity of the isotope ratios was highest for SE-ST and lowest for TR. Their mean concentration was around average with highest standard deviation for SE-ST and very small SD for TR. Only six wine samples were from Thermeregion, five of them originating from the same vineyard. The small standard deviations can be explained by the homogeneity of the sample pool. Lake Neusiedl-Hills was grouped with Lake Neusiedl. However Carnuntum also consisted of a sample pool of five wines originating from 2 different vineyards but had an average SD concerning IR but the lowest SD in terms of Sr concentration.

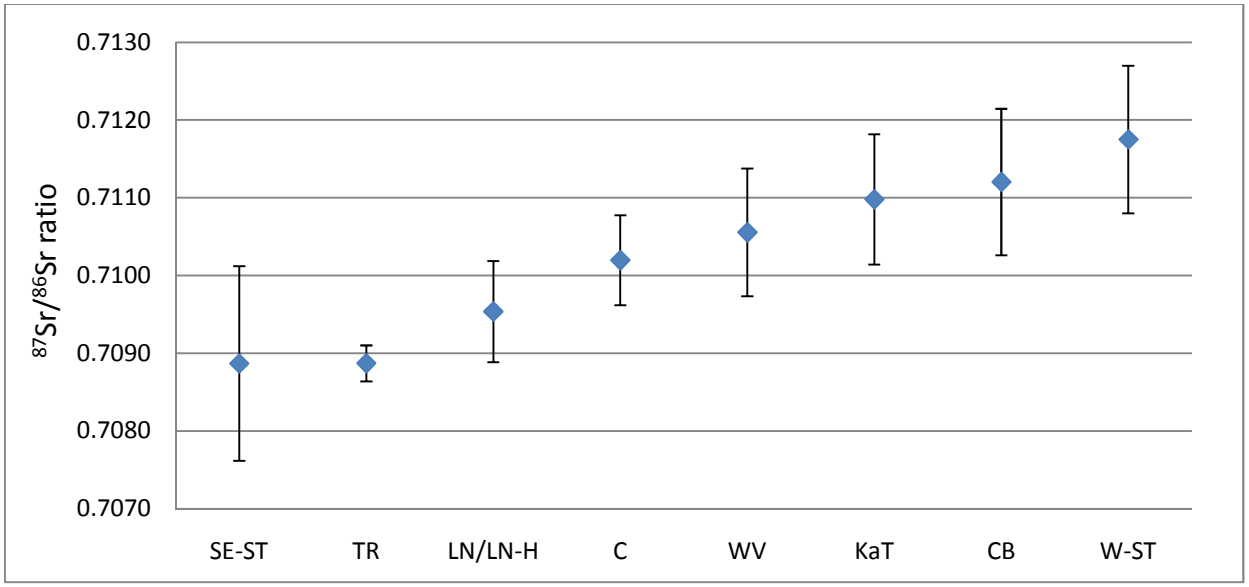


**Figure 25: Mean values of $^{87}Sr/^{86}Sr$ with SD representing the homogeneity of each region**

Highest mean isotope ratio and second highest mean Sr concentration was found in West-Styria.

Wine from Burgenland (LN/LN-H and CB) could be distinguished within the federal state, as could be wine from Styria (SE-ST and W-ST). Wine samples from LN/LN-H were also different from West-Styria regarding the $^{87}Sr/^{86}Sr$ but could not be distinguished from SE-ST and TR. However both regions from Burgenland did overlap with Carnuntum, Weinviertel as well as Kamptal. Thermenregion is different from all regions except of South-East-Styria and LN/LN-H. However a bigger sample pool might alter the result and it could overlap with Carnuntum too. West-Styria is clearly different from South-East-Styria and Thermenregion. Volcanic bedrock in South-East-Styria could explain the significant difference as well as its high standard deviation. Yet South-East-Styria (0.708870) borders the lower end of $^{87}Sr/^{86}Sr$ and West-Styria (0.71175) the upper end.

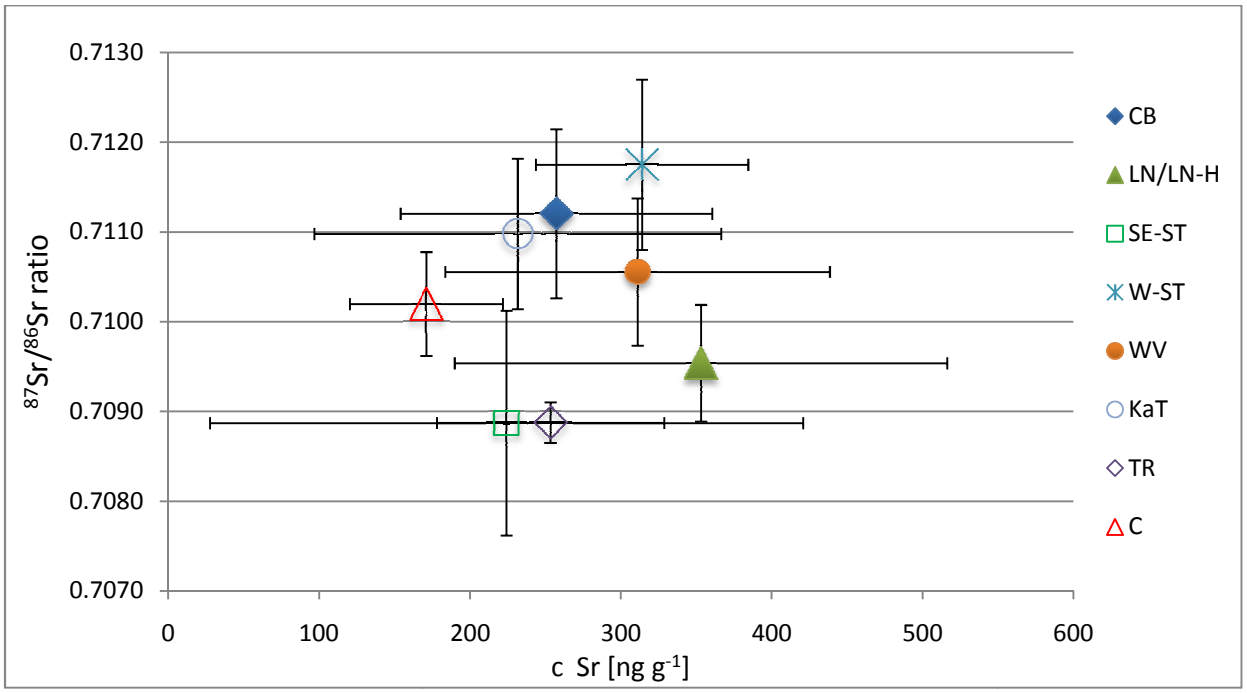


**Figure 26: Mean Sr isotope ratio vs. mean Sr concentration [ng $g^{-1}$]**

Wine samples from Carnuntum overlapped with samples from LN/LN-H as well as with samples from Central-Burgenland. This leads to the assumption that Carnuntum could be considered to be part of Burgenland, as it was shown using multi-element analysis. However Weinviertel and Kamptal are not different either but belong to Lower Austria.

Relative standard deviation within a region was about 40% to 50% regarding strontium concentrations and was around 0.10% concerning isotope ratios. Even though the resulting range was very high within one region single samples did not match the range.

Strontium isotope ratios and Sr concentrations did not seem to be an appropriate way in order to distinguish all Austrian authentic wine samples according to their provenance. However compared to the geological map (Voerkelius et al.) mean values of each region were within the predicted range. Not all areas might be different from each other regarding their isotopic composition yet the ones who are could be successfully differentiated.

## 4.3 Pumpkin evaluation: from soil to seed to oil

After an optimized digestion procedure (3.3.1.1) seeds and oil were analyzed concerning their concentration of elements and their $^{87}Sr/^{86}Sr$ ratio. Furthermore any characteristic pattern regarding provenance were under investigation as well as element transfer and contamination from soil to seed to oil. For the latter pumpkin seeds and related pressed oil was provided by a pumpkin seed oil mill in Styria. Additionally soil from that area which these seeds grew on and creek water from the area was available, too.

Oil originating from various regions (Hungary, Styria, Lower Austria and Croatia) was hardly enough for digestion procedure and only a few elements could be detected. However two simultaneous digestions of oil from four different regions (Lower Austria, Slovenia, Serbia and China) were carried out because a higher quantity was available.

Roasted and grinded seeds but also their residue after extraction was available. These samples originated from Hungary. All other seeds (bought in a local supermarket and the ones from Styria) were simply grinded and dried prior digestion but no extraction took place. The outcome was rather oily indeed. Nonetheless grinded seeds were handled just like the extracted seed samples.

Element concentration of all samples, respectively mean values regarding several digestions of the same sample, limits of detection and quantification, relative standard uncertainty and strontium isotope ratios are listed in Table 43.

### 4.3.1 Multi-element analysis

In order to get reliable multi-element data, all samples were method blank corrected. LoD and LoQ were calculated according to the validation approach.

Figure 27 gives an overview of the elements that were measured and could actually be detected in either seed or oil.

Elements that are highlighted green could be detected in pumpkin seeds whereas elements detected in pumpkin seed oil are shaded yellow. Rare earth elements (highlighted brown) are included as well but will be further discussed during the next chapter. U, Tb, Ho and Tm could not be detected in oil samples except of China and therefore were not shaded yellow.

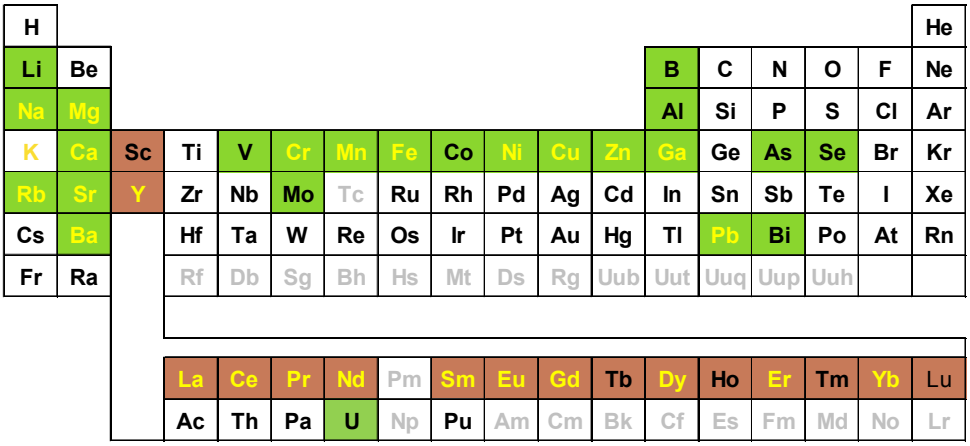


**Figure 27: Detectable elements regarding pumpkin seeds (multi-element (green), REE (brown)) and pumpkin seed oil (yellow)**

Due to a rather small sample pool discriminate analysis could not be performed. Instead principal component analysis was used for evaluation.

First of all results of all samples that provided enough digestion material will be summarized.

Multi-element pattern of oil of different provenance is shown in Figure 28. Oil bought in a local supermarket was pressed from seeds originating from Russia, China, Romania and Slovenia.

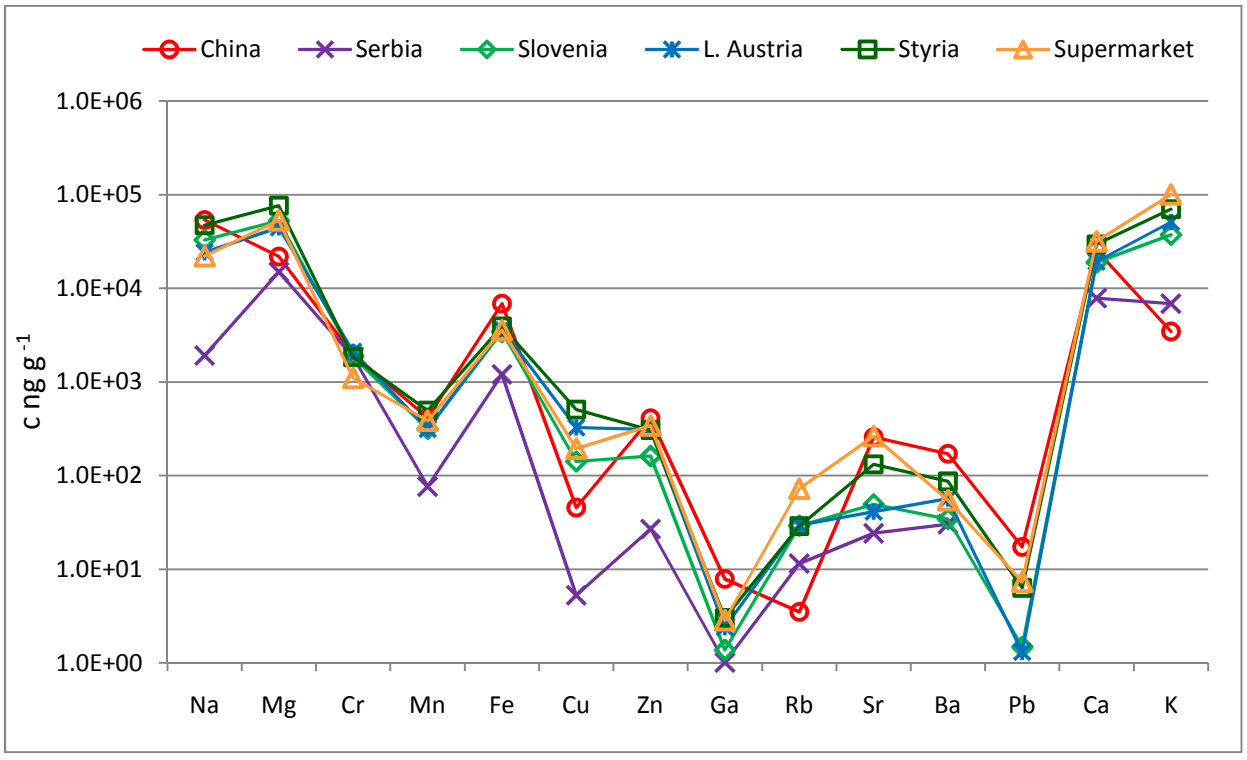


**Figure 28: Multi-element pattern of different pumpkin seed oil**

Oil extracted from seeds originating in Serbia had the lowest concentration of elements, even below limit of detection, compared to other oil. It was the other way round with oil from China

except of Mn, Cu, Rb, and K. In addition patterns were different considering oil from Serbia, China, Supermarket oil and the rest. Oil from Slovenia, Lower Austria and Styria did have similar pattern but varied within some elements.

Positive correlation of magnesium to potassium as reported in literature could be found (Figure 29). It was even linear, excluding oil from the supermarket (orange triangle) which was way off the trend-line ($r^2$=0.89). Due to mixing of different seeds correlation of these two elements might get lost.

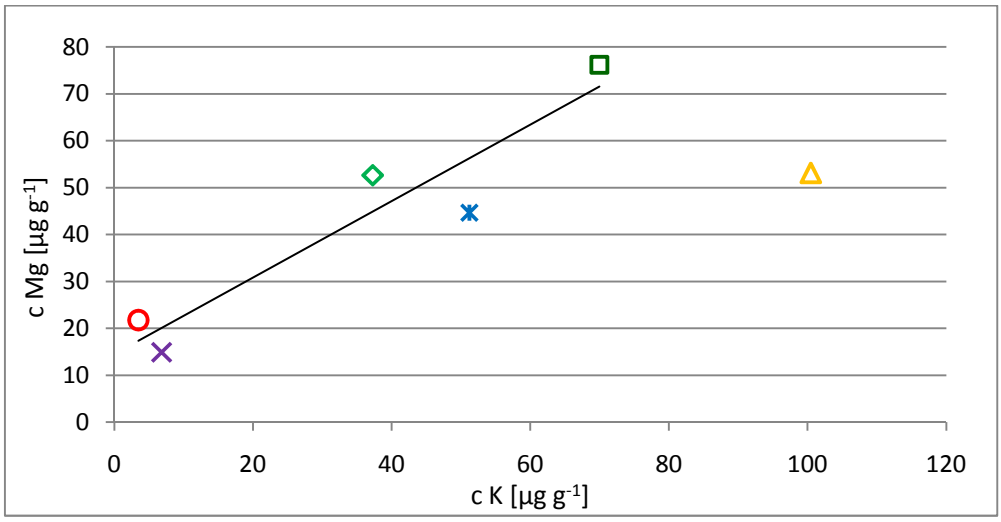


**Figure 29: Linear correlation of Mg and K in pumpkin seed oil**

Mg/K ratios of measured oil samples were between 0.52 and 2.2. However oil from China had a much higher ratio (6.3) compared to other samples (Figure 30). Potassium varies with variety and culture location of pumpkin seeds which could explain the difference. Phosphorus correlates in a positive way with these elements as well and should be kept in mind for further authentication studies (Fruhwirth and Albin Hermetter, 2007).

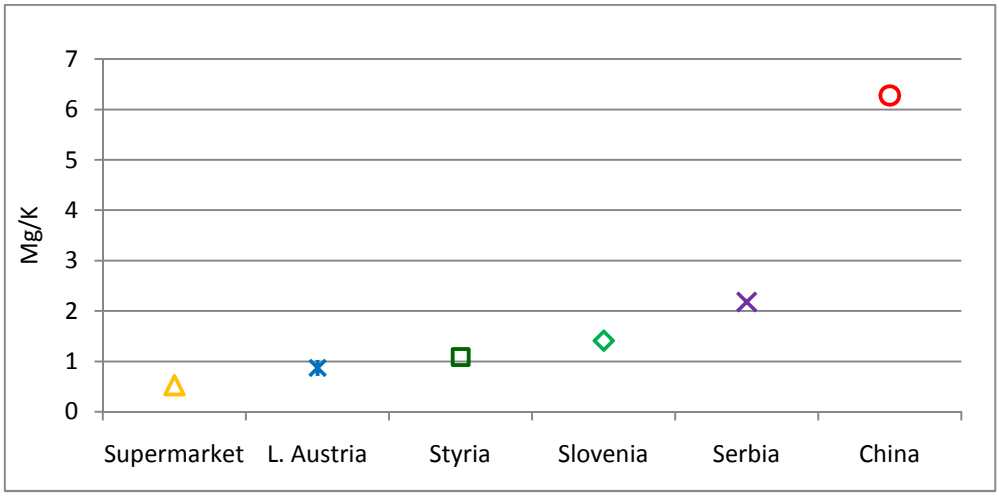


**Figure 30: Ratio of magnesium to potassium in pumpkin seed oil**

Principal component analysis was carried out for these six samples as well. Considering all elements as shown in Figure 28 the following diagram was generated.

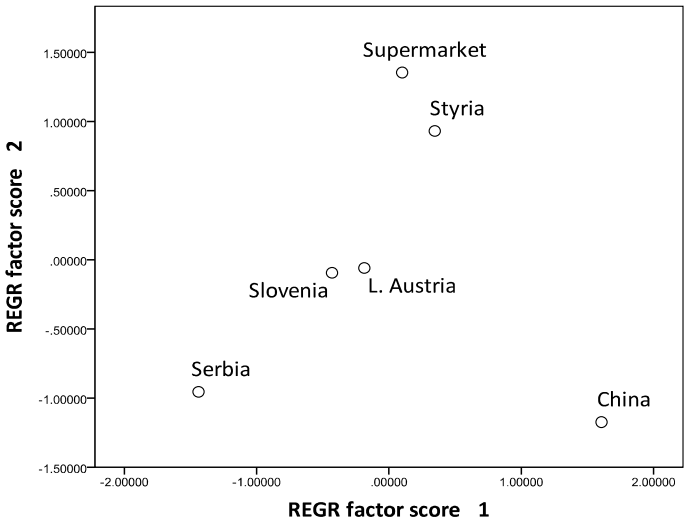


**Figure 31: Multi-element PCA of pumpkin seed oil**

Extracted pumpkin seed oil samples from China and Serbia were clearly different from each other and the other samples. Slovenia and Lower Austria were neighbors though. Commercially available oil from the supermarket and pressed oil from Styria was not that far away from each other either.

However considering only elements that might not be altered in any way (see 4.3.4) a much clearer differentiation could be achieved (Figure 32). Only Rb, Sr, Ba and Mn were used for that matter. 90% of the data could be explained compared to 79% using all elements.

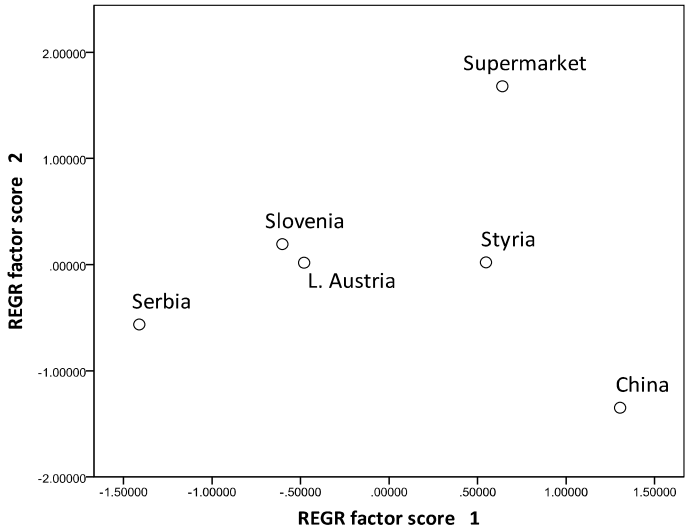


**Figure 32: PCA of pumpkin seed oil using Rb, Sr, Ba and Mn**

Distribution of extracted samples is not much different using either all detected elements or only so called non contaminant ones. However it does make a difference with respect to

pressed oil. Only the chosen elements could distinguish between the pressed oil sample from Styria and the one bought in the supermarket. However one should keep in mind that mixing different seeds with each other influences the composition of elements and place of origin itself cannot be identified anymore. Nonetheless mixed oil was clearly different from Austrian oil as well as pure oil from other countries as well.

PCA was performed on extracted pumpkin seed oil from Hungary, Croatia, Lower Austria and Styria combined with samples mentioned above as well. However concentration of some elements was below limit of detection while others were hardly above due to low initial weight for digestion. Values below LoD were set zero. The PCA plot looked similar to Figure 31. However samples with elements close to limit of detection did cluster in the area of Serbia (which had a rather low concentration of elements as well even though 1 g was used for digestion). These were mainly all samples from the first batch with initial weight below 0.4 g. Only one sample (China (low)) is farther away from the other samples probably due to higher concentrated elements in oil from that region. The other oil sample from China (from the second batch) and an unknown sample were located close to each other. The unknown sample was labeled as oil from Styria in a supermarket but was stated to be from China due to taste and color from an expert (additional information: Dr. Micha Horacek). This assumption could be verified (see Figure 33).

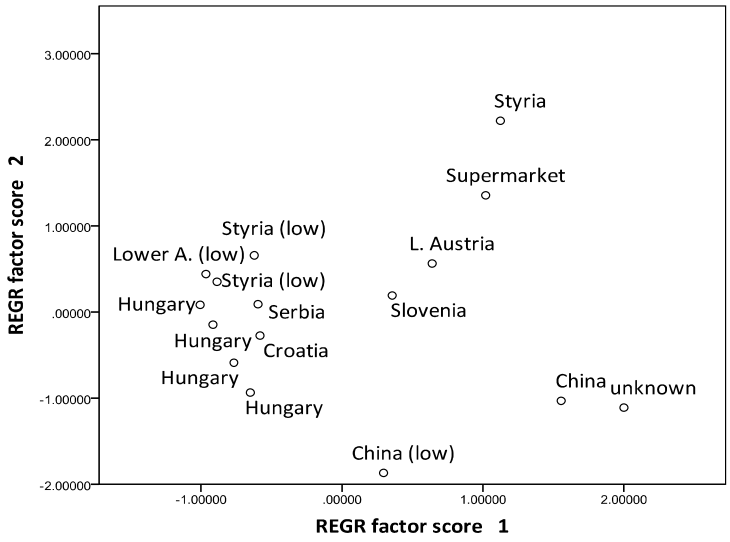


**Figure 33: Multi-element PCA of all pumpkin seed oil samples**

It seems that most minerals in pumpkin seeds are embedded in cellulose compounds and protein bound. Therefore not much information of the composition of elements is pressed into pumpkin seed oil. Still there is certain information available of the original seed. Even though a rather small sample pool was evaluated there have been promising differences between oil samples of several places of origin. However oil extracted with petrol ether might be different

from pressed oil due to a difference in solubility of elements or contamination of production steps.

### 4.3.2 Rare earth element analysis

Rare earth elements are highly present in pumpkin seeds. All elements could be quantified with ICP-MS. Even in pumpkin seed oil all REE except of scandium and lutetium could be quantified. However terbium, holmium and thulium could only be detected in oil from China. Nonetheless an appropriate quantity of digestion material was obligatory as well. Therefore only extracted oil from China, Serbia, Slovenia and Lower Austria as well as pressed oil from Styria, the supermarket and the unknown sample were examined. In addition not all elements did pass quality control. Therefore only selected isotopes were used for evaluation regarding chondrite pattern (according to (McDonough and Sun, 1995)) as well as principal component analysis. In order to obtain chondrite pattern samples were standardized according to C1 carbonaceous chondrite values as investigated by McDonough and Sun. These C1 carbonaceous chondrites are the most primitive ones among chondritic meteorites and are used, in addition to other meteorites, for constructing and constraining models of planetary compositions.

Concentration of REE in oil from China was highest but lowest in oil from Serbia. Consequently chondrite pattern of these oil samples were shifted almost two orders of magnitude. Main differences lay within the elements cerium and praseodymium. Differences in pattern of the other oil samples were hardly visible in Figure 34. Therefore a close up was shown as well in order to distinguish between samples that were really close to each other (Figure 35).

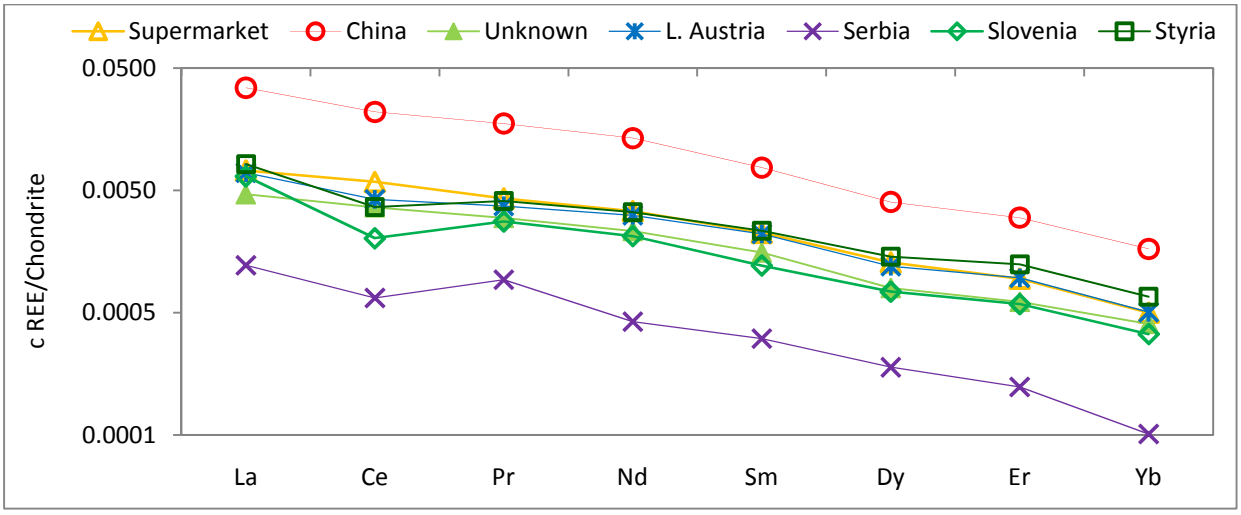


**Figure 34: Chondrite pattern of oil samples**

Pattern of supermarket oil and unknown oil was exactly the same but shifted because former oil was higher concentrated. Oil from Styria and Lower Austria was almost similar and showed

comparable behavior with oil from Slovenia. Except of major differences in concentrations only small differences could be observed with respect to their pattern.

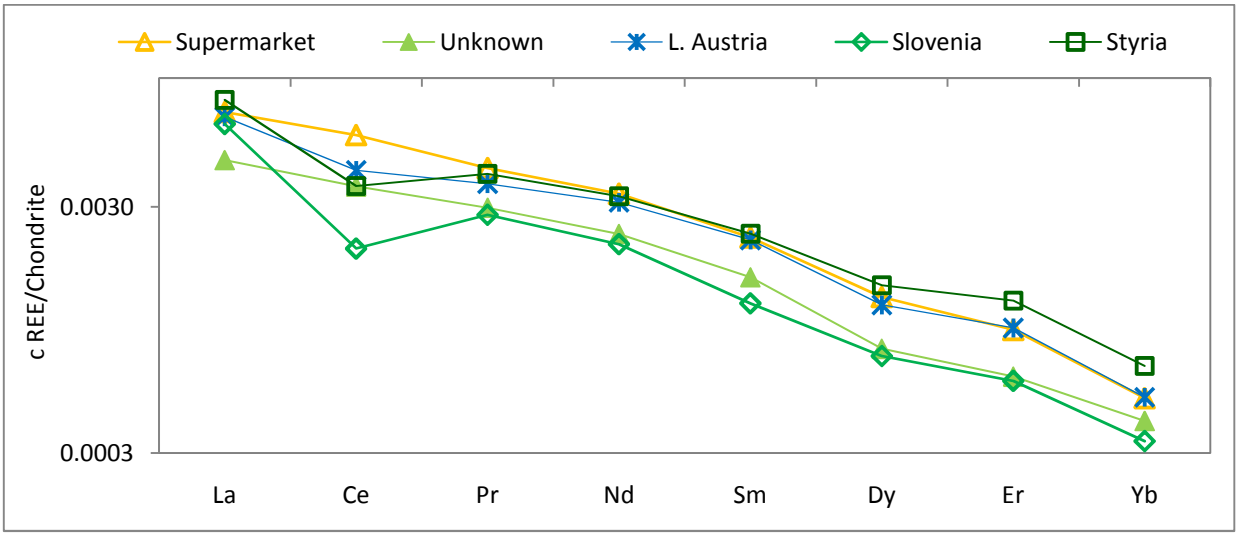


**Figure 35: Close up of Figure 34 in order to compare various CI pattern of pumpkin seed oil**

Same samples and elements were used as well for principal component analysis (Figure 36). Oil from China was clearly different from other samples and so was oil from Serbia which could be observed using chondrite pattern above. Even though C1 pattern and element concentration of Styrian pumpkin seed oil was similar to Lower Austria it is located far away regarding the PCA plot. Slovenian oil was different from the unknown samples with respect to chondrite pattern but not significantly different using PCA. Classification by means of rare earth elements did not verify that the unknown sample originates from China.

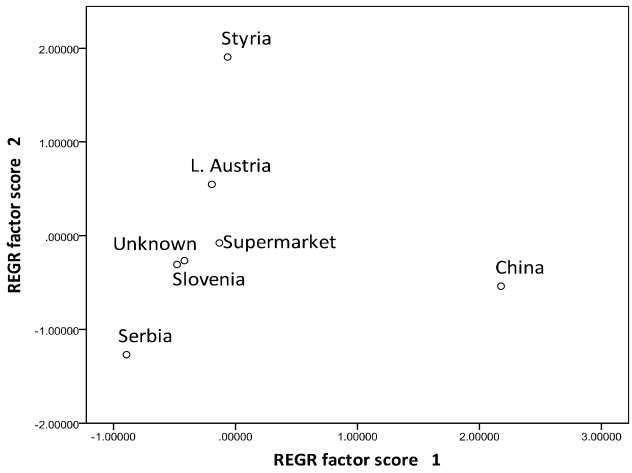


**Figure 36: Rare earth element PCA of various pumpkin oil samples**

Even though concentrations of rare earth elements were pretty low statistical differences concerning place of origin of the extracted pumpkin seeds were similar using multi-element

data. Only the unknown sample as well as the sample from the supermarket could not be determined to being different from the other samples.

Unfortunately yttrium could not be used for evaluation of pumpkin seed oil even though this element was present in high concentration. It did not pass quality control but should be considered for further investigations with respect to provenance studies of pumpkin seed oil using rare earth elements. Due to rather low concentrations of Dy, Er and Yb their contribution is probably not significant enough also considering their total combined uncertainty.

In addition to REE elements another approach was tried as well. Concentration of multi-elements, that is to say Rb, Sr, Ba and Mn, as well as REE, that is to say La, Ce, Pr, Nd and Sm were used for principal component analysis (Figure 37). On the one hand only pressed samples were investigated while on the other hand only extracted samples were examined. Even though it was not the case using both oil gaining procedures Lower Austria could again not be distinguished from Slovenia, just like using multi-elements only. Chondrite pattern of unknown and supermarket samples were parallel. However considering PCA the unknown sample was clearly different from the supermarket sample, and so was Styrian oil.

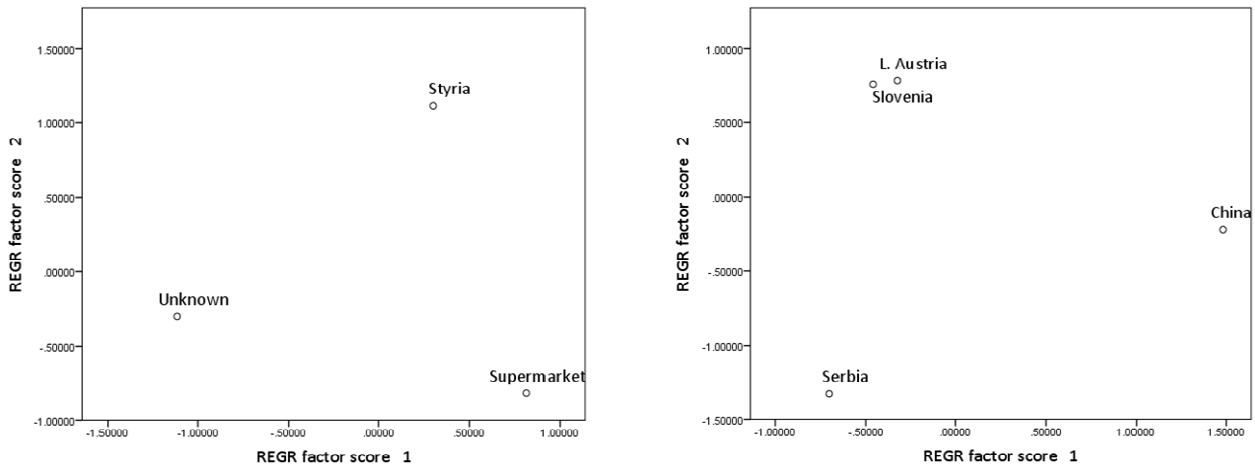


**Figure 37: PCA of pressed (left) and extracted (right) samples using REE and multi-element concentration**

A similar picture was given using REE only. Regarding pressed oil it looked alike only Supermarket and Styria switching places. However concerning extracted oil Slovenia was clearly different from Lower Austria being located more closely to Serbia though. Therefore concentration of REE only is expected to distinguish between oil from Lower Austria and Slovenia but neither using multi-element data nor strontium isotope ratios as explained in the next chapter.

Two different digestion procedures with respect to pumpkin seed oil bought in the supermarket were carried out. They were both measured, but not within the same run. Total concentration of each element was significantly different from one another. It was even only half sometimes.

Regarding pumpkin seeds it was interesting to observe significantly different concentration of Styrian pumpkin seeds and pumpkin seeds bought in the supermarket. Not only that purchased seeds originated from different regions that is to say Lower Austria, Styria and Hungary but they were of different species as well. Differences were up to one order of magnitude. Their chondrite pattern was almost similar, except of the shift due to concentration, but totally different with respect to cerium and samarium.

### 4.3.3 Strontium isotope ratios

Strontium concentration was high enough in digested solutions of pumpkin seeds. Produced data will be discussed in the next chapter. Sr concentration in oil was pretty low and separation was not easy to achieve. Anyhow, samples that provided a measurable quantity were analyzed with MC-ICP-MS. Extracted oil from Lower Austria, Serbia and Slovenia had a signal intensity of 1 V or lower and additionally relative rubidium content was between 0.25 and 1.3%. Only oil from China had enough strontium concentration to overcome that problem.

Only a limited number of samples were available for evaluation since enough strontium was present in seven samples only. Figure 38 shows isotope ratios of strontium (error bar: measurement RSU, k=2) versus strontium concentration.

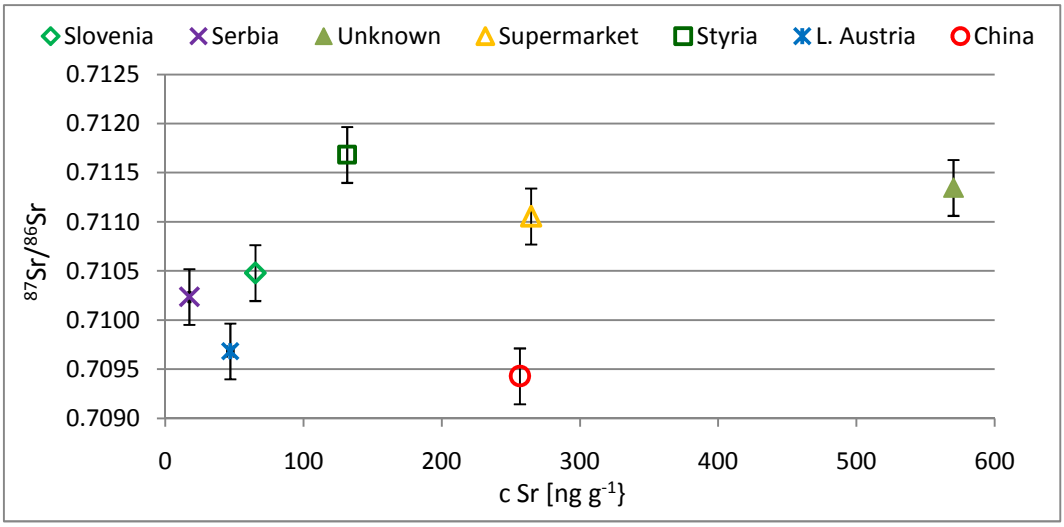


**Figure 38: Strontium isotope ratio vs. strontium concentration of pumpkin seed oil**

The unknown sample contained highest strontium concentration while pumpkin seed oil from Serbia was lowest concentrated. Oil from China and the supermarket were similar with respect to their Sr concentration but were significantly different regarding their isotope ratios. Styrian pumpkin seed oil had the highest ratio but was not significantly different from the unknown oil and oil bought in the supermarket. However their concentrations were significantly different.

Comparing homogeneity distribution of isotope ratios and concentration in wine samples it is hard to tell whether a clear distinction of oil is possible or not. However since areas, on which original Styrian pumpkin seed oil are allowed to grow, are strictly defined total information could be gained due to stepwise investigation. Anyhow concentrations in oil from Lower Austria, Serbia and Slovenia were probably too low and relative rubidium content too high in order to take these values for granted. On the other hand pressed oil seemed to have higher strontium concentration and therefore should be used for further isotope ratio studies. Oil can contain small residues of seed after the milling process which can explain the higher concentration in these oil samples. Nonetheless only extracted oil from Chinese seeds had a high Sr concentration as well.

Any changes of isotope ratios were under investigation because that would cause problems as well. However no alteration took place due to pressing of pumpkin seed oil (4.3.4.3). $^{87}Sr/^{86}Sr$ of pumpkin seed residue after extraction did not change either which is probably the case for extracted oil as well (4.3.4.4).

### 4.3.4 **Conclusions from soil to seed to oil**

Transfer from soil to seed to oil regarding elements that could be detected in oil was taken a closer look at. Potassium was excluded because it could neither be detected in soil nor in seed since concentration was too high in order to be detected<<mp. In addition ratios regarding creek water were examined. Comparison was possible since soil, seed, oil and creek water was available from a mill in Styria. Moreover the oil was pressed only from seeds originating from that area.

First of all multi-element pattern were under investigation. Secondly rare earth elements were compared in order to find any similarities and finally strontium isotope ratios were examined. Furthermore the extraction process was examined as well. Therefore considerations concerning from soil to seed to oil were applied on seed and extracted seed.

#### *4.3.4.1 Multi-element data*

Element concentrations of oil and seeds were compared to soil and creek. Respective ratios are shown in Figure 39. Regarding the oil to seed ratio elements are listed from smallest ratio starting with nickel (0.22%) on the left hand side to sodium (563%) on the right hand side. All ratios are listed in Table 39.

Pumpkin seeds and pumpkin seed oil had a similar pattern with respect to soil and creek water. However there were rather big differences regarding the element concentration and consequently the respective ratio. That is to say, ratio of seed to creek was about two orders of magnitude higher than seed to soil. The same applied to pumpkinseed oil but with a lower

ratio. Since only bio-available elements were extracted from the soil sample the similar pattern to creek water could be explained. Nevertheless a much lower concentration was found in creek water. Usually the order of the ratio was as follows: oil to soil < seed to soil < oil to creek < seed to creek. Ratios in between were almost alike for calcium and strontium. Since strontium can substitute calcium in an organism their similar behavior was not surprising. Moreover seed to soil ratios switched places with oil to creek ratios concerning barium and gallium. These two elements had a rather low concentration in seeds compared to soil. Sodium was the only element with ratios of reverse order.

| Analyte | oil to seed | oil to soil | oil to creek | seed to soil | seed to creek |
|---|---|---|---|---|---|
| Ni | 0.22% | 4% | 118% | 1828% | 53539% |
| Zn | 0.39% | 64% | 5581% | 16338% | 1421527% |
| Rb | 0.62% | 13% | 645% | 2107% | 103639% |
| Mn | 0.89% | 8% | 544% | 868% | 60824% |
| Mg | 1.48% | 19% | 584% | 1283% | 39522% |
| Cu | 3.10% | 964% | 19162% | 31044% | 617363% |
| Fe | 3.26% | 30% | 247% | 915% | 7563% |
| Ca | 3.49% | 0.81% | 40% | 23.3% | 1151% |
| Sr | 5.63% | 1.50% | 51% | 26.7% | 909% |
| Ba | 10.1% | 0.23% | 196% | 2.28% | 1930% |
| Ga | 10.3% | 0.19% | 97% | 1.86% | 937% |
| Pb | 50.4% | < LoD | 955% | < LoD | 1895% |
| Cr | 137% | < LoD | 103301% | < LoD | 75217% |
| Na | 563% | 738% | 326% | 131% | 58% |

**Table 39: Element ratios of soil, oil, seed and creek in %**

Regarding the element concentration in oil pressed from respective seeds nickel, zinc, rubidium and manganese had a recovery below one percent. Magnesium, copper, iron, calcium, strontium, barium and gallium had a recovery between one and ten percent. On the other hand lead, chromium and sodium rose extremely in oil. Since oil is pressed mechanically increased Pb and Cr concentrations could be explained by contamination. Due to adding of salt a higher quantity of oil can be pressed. Consequently oil contains the highest amount of sodium. In addition magnesium, calcium and potassium might be influenced as well (Juranovic, 2003).

Lead and chromium could not be detected in extracted oil solution by ICP-MS. That is to say, these elements could not be extracted from the soil respectively concentration was too low in order to be detected. Therefore no ratios were shown for these elements

There have been troubles detecting aluminum throughout measurement series due to a high blank level regarding method blanks. Nonetheless contamination could occur easily due to the milling process or storage and using this element for provenance studies would give a hint on the manufacturing location itself rather than origin of the seeds used.

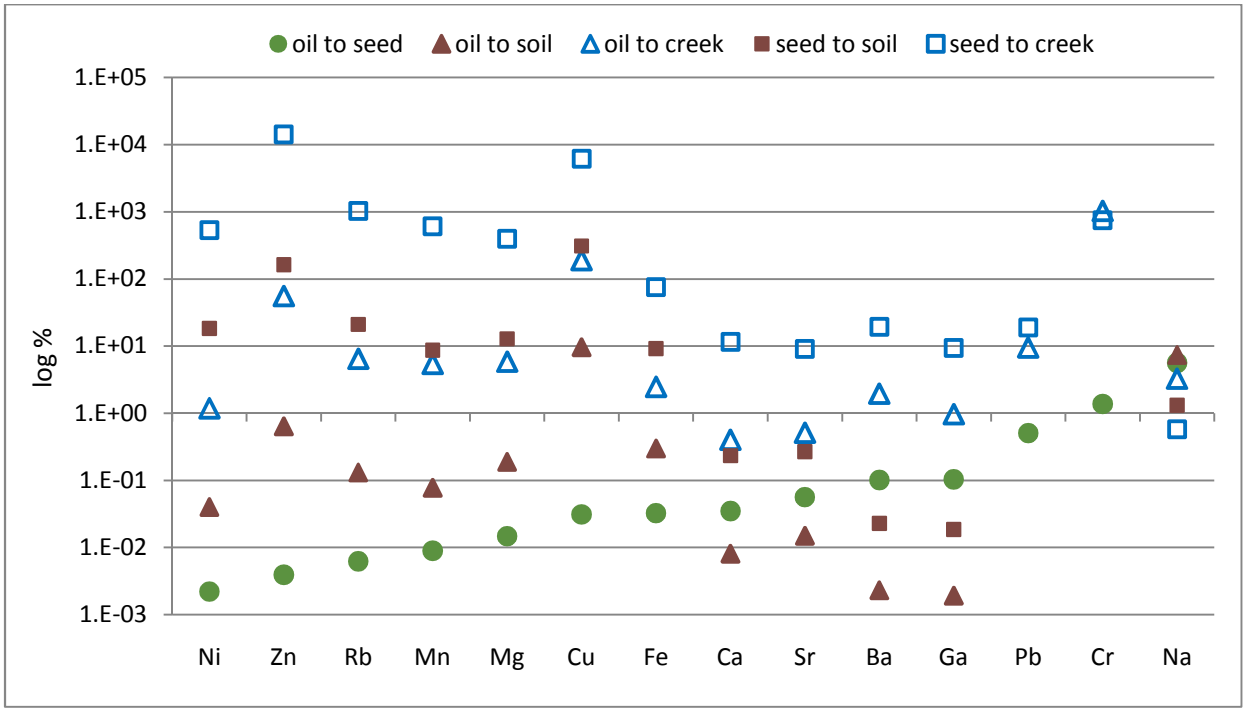


**Figure 39: Element ratios of soil, oil, seed and creek in %**

As shown above, only a small number of elements could be for authentication. Elements that were less abundant in pumpkin seeds did not find their way into the processed pumpkin seed oil either. That is to say elements that were above 750 ng $g^{-1}$ in seeds could be detected in oil with the exception of boron and aluminum. However concentration of gallium was only 29.0 ng $g^{-1}$ but relative abundance in oil was higher than most other elements. This led to the assumption that contamination influences this element as well. In addition concentration was similar to creek water. Yet abundance in the earth crust is rather low but it is a side product of aluminum production. On the other hand gallium might be bound to fatty acids more closely than other elements. Being more mobile it could be not as bound to cellulose than for instance magnesium. Nonetheless its properties are similar to zinc and aluminum which were rather low or not present at all. These assumptions could exclude gallium as well from being used for provenance studies.

Nonetheless rubidium, barium, manganese and strontium were most promising elements with respect to provenance studies using multi-element pattern.

### *4.3.4.2 Rare earth element data*

A totally different picture was given concerning ratio patterns of rare earth elements (Figure 40) compared to multi-element pattern. In addition chondrite pattern of rare earth elements were under investigation with respect to any changes from seed to oil and availability in soil and creek.

Concentration of REEs was lowest in creek water and highest in pumpkin seeds. Just like in chapter 4.3.4.1 different ratios were calculated and are summarized in Table 40.

| | oil to seed | oil to soil | seed to soil | oil to creek | seed to creek |
|---|---|---|---|---|---|
| La | 8% | 13% | 157% | 260% | 3156% |
| Ce | 9% | 23% | 248% | 139% | 1482% |
| Pr | 9% | 29% | 316% | 194% | 2141% |
| Nd | 9% | 31% | 339% | 194% | 2117% |
| Sm | 10% | 20% | 199% | 198% | 1992% |
| Dy | 10% | 55% | 529% | 221% | 2142% |
| Er | 12% | 58% | 498% | 231% | 1986% |
| Yb | 13% | 70% | 528% | 226% | 1698% |

**Table 40: REE ratios of soil, oil, seed and creek in %**

REE are similar in their behavior which led to oil to seed ratio between 8% and 15% for all elements.

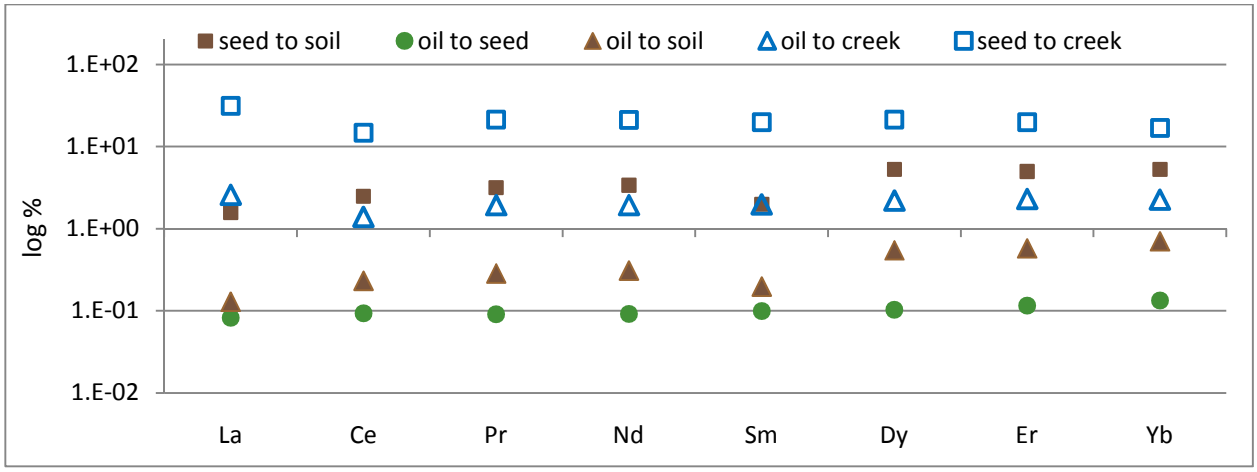


**Figure 40: REE ratios of soil, seed, oil and creek in %**

Soil and creek ratio pattern were similar as well with the exception of lanthanum and samarium. With respect to soil ratio an increase could be examined but with a small break-in of samarium. Ratio of REE in creek decreased evenly with increasing atomic number compared to oil. However relative concentration of lanthanum was much lower compared to other elements. Since concentration of REE in seed was between two and five times as high as in soil total extractability of these elements with ammonium nitrate could not be observed but bio-availability could be shown due to pattern recognition compared to creek water.

Chondrite pattern of seed and oil were alike except of a shift due to different concentrations (Figure 41). As a matter of fact they were almost parallel. Additionally pattern of soil and creek were similar with the exception of La and Sm as mentioned above considering different ratios.

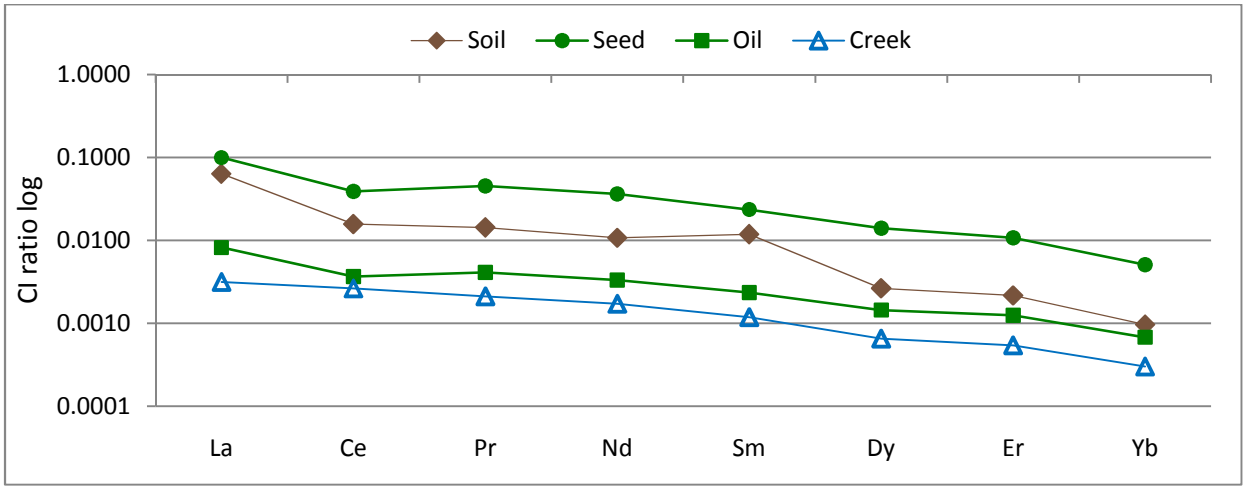


**Figure 41: Chondrite pattern of REE in soil, seed, oil and creek**

Pattern of rare earth elements in oil were not altered by any production step. Even though concentration was only one tenth compared to pumpkin seeds abundance among these elements remained the same and was not changed. It is impressive though that such a high recovery of REEs in oil is given since concentration was not above 30 ng $g^{-1}$. In fact it had the same ratio considering the low total concentration in seeds as gallium. However constant contamination of REEs seems rather unlikely and was ruled out.

Nevertheless uptake of REE by plants is very low and distribution depends on its species. Comparing soil, the respective pumpkin seeds and furthermore pumpkin seed oil small differences in rare earth element pattern could not be denied. Total digestion of soil would give more information on whether REEs in seeds were distributed in the same way or fractionation in pumpkin seeds took place.

### *4.3.4.3 Strontium isotope ratios*

In addition to multi-element and rare earth element measurements strontium isotope ratios of all four matrices were determined as well. Ratios and error bars (RSU=0.04%, k=2) are given in Figure 42.

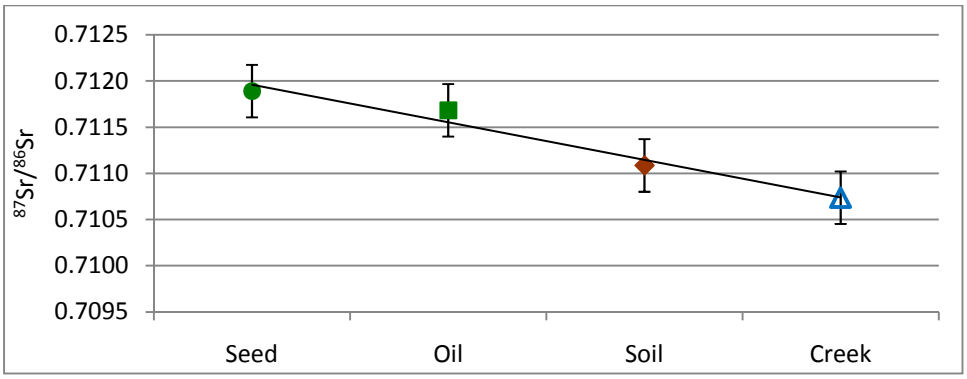


**Figure 42: $^{87}Sr/^{86}Sr$ of seed, oil, soil and creek**

On the one hand no alteration of strontium isotope ratios took place from pumpkin seed to the pressed pumpkin seed oil. On the other hand isotope ratio of bioavailable strontium in soil and creek was not significantly different either. Since precipitation and ground water play a role in uptake of strontium in plants as well the ratio in seed was different from soil and creek. However a linear correlation could be established.

Since soil was only extracted but not digested there is no information available on total strontium content and the respective isotope ratio.

#### *4.3.4.4 Extraction process*

Concentration of three seed samples and their residue after extraction were compared with each other. In addition the extracted oil was measured as well. Unfortunately it was not enough sample material available in order to draw conclusions considering all elements measured. All pumpkin seed samples were from Hungary.

Residue of extracted seeds had between 180% and 220% relative metal content as seeds before extraction (stmkp1-p3 compared to stmk1-3 → Seed ratio1-3, p is for pressed). It seems that elements are accumulated in cellulose and proteins of seed and hardly any metal content is bound to the fatty acids. Since pumpkin seeds contain about 50% of oil it is obvious that elements are concentrated in the residue and are double as high compared to the original seed.

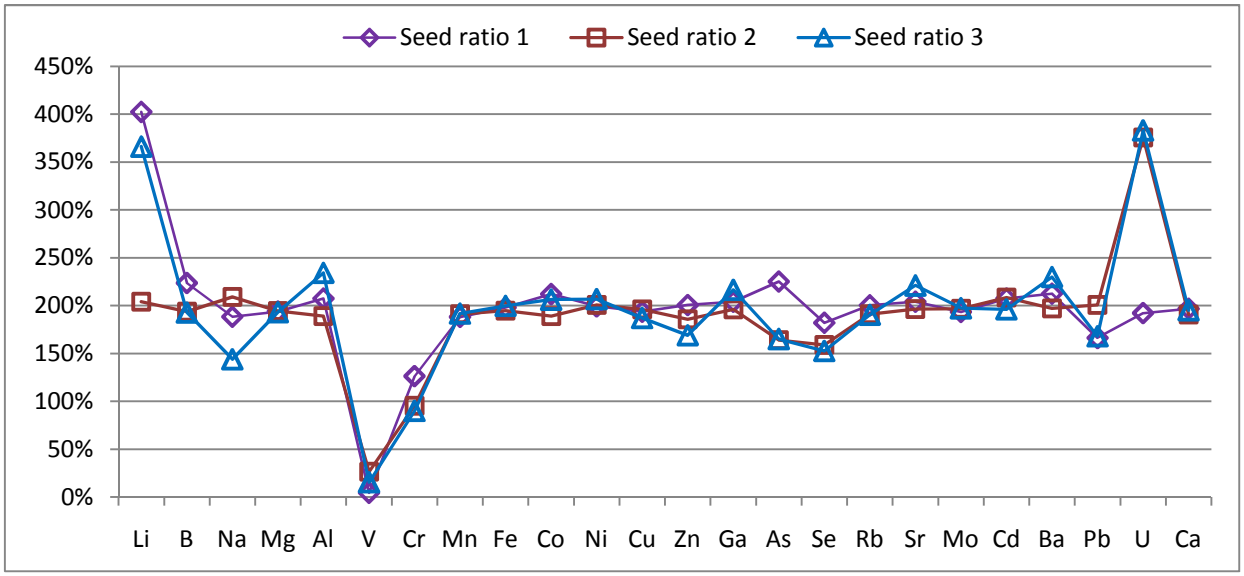


**Figure 43: Multi-element ratios of seed residue to seed using extraction**

Ratios of lithium, vanadium, chromium, and uranium were completely different and not within the range mentioned above. Differences were evident but not as big with respect to arsenic, selenium and lead. Concentration of chromium was almost the same in seed and its residue after extraction. Consequently Cr content in residue was only half compared to the original

seed considering about 50% of loss due to oil extraction. Due to the milling process of roasted seeds chromium contamination could be possible. Consequently concentration in seed was higher and in addition chromium would not be bound to organic matter but could easily be extracted which could explain lower concentration in residue. Two ratios out of three were between 350% and 400% for Li and U whereas ratios between 4% and 27% were given for V.

Considering the rather high concentration of boron in pumpkin seeds, it would lead to the assumption that it should be found in pumpkin seed oil as well. However that was not the case for sample digests of pressed oil. Neither could it be detected in extracted samples with an initial weight for digestion of 1 g. On the other hand B was present in extracted oil samples with a sample weight of way below 0.5 g. Even though most of the other elements were at blank level considering these samples it was not the case with respect to boron. Its extraction efficiency was between 15 and 25%. Regarding sodium extraction efficiency was between 5 and 15% whereas concentration of chromium was much higher in either seed or residue. Only 0.05% of magnesium was extracted and about 1% of strontium. Other elements were also below 1 % or extraction efficiency could not be calculated at all because elements were at blank level due to the low initial weight as pointed out above.

Extraction of REE does not seem to work as evenly as with other elements. Even though they should behave in a similar way it was not the case comparing seeds and their residue after extraction. Concentration in residue was either equal, two times or three times as high for different samples but the same element. The third sample pair had a ratio of 300% to 200% whereas the first sample pair was different from 100% to 200% starting from La to Yb. The second sample pair was somewhere in the middle between 200% and 150%. It is illustrated in Figure 44.

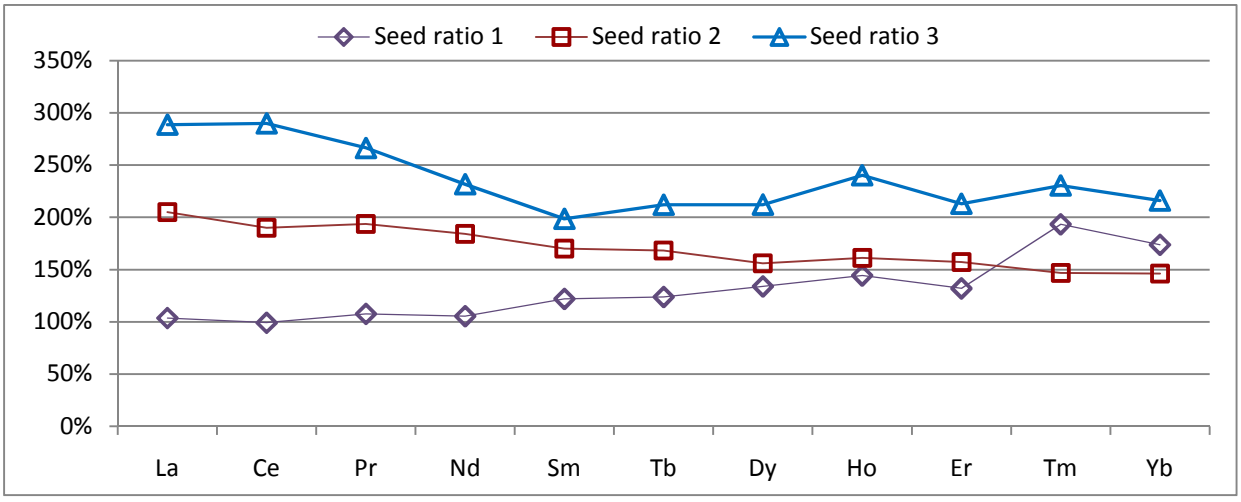


**Figure 44: Ratio of seed residue to original seed of REE**

Even though total concentration in seed one and seed three were not significantly different for almost all elements their residues did not show any correlation. Therefore it is questionable whether extracted oil samples do reflect composition of rare earth elements in seed. Unfortunately not enough sample material was available of the respective oil extracts in order to verify this assumption. Measurements did take place but should be handled with caution since sample weight was very low. Considering seed one and seed three concentration in the extracts was about 3% and 4%, respectively. This was much lower compared to pressed oil. Recovery in oil was 0% for seed number two even though it contained twice as much rare earth elements compared to seed one and three.

Strontium isotope ratios were not significantly different comparing pumpkin seeds and their residue. Relative standard uncertainty (k=2) was 0.05%. Isotope ratios and error bars are given in Figure 45. As already mentioned above total concentration of strontium was two times as high for seed residue number one and two whereas concentration of seed residue number three was even 220% of concentration in total seed. Since no alteration took place in pumpkin seed residues it is more likely that extracted oil reflects the isotope ratio of their seeds as well.

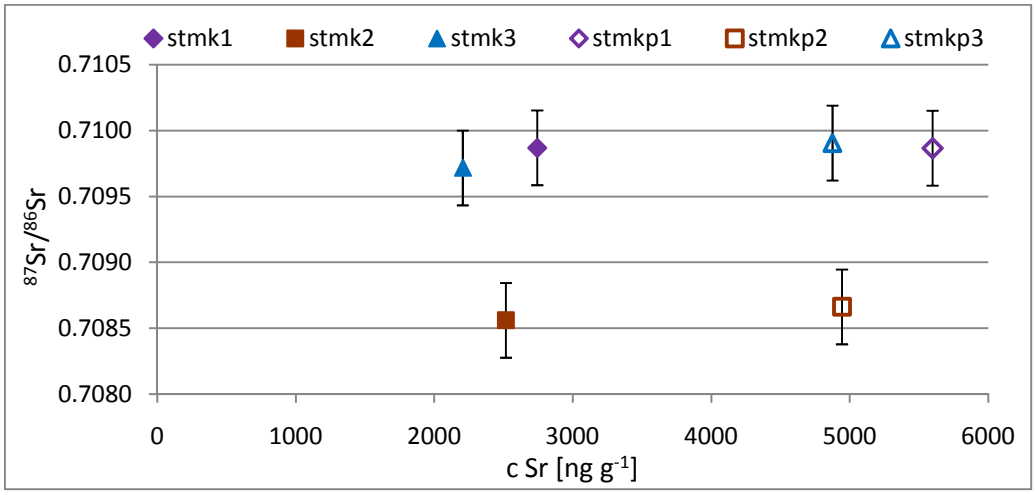


**Figure 45: $^{87}Sr/^{86}Sr$ of pumpkin seed (filled) and pumpkin seed residue (not filled) after extraction**

Even though all three samples were from Hungary isotope ratio of seed number two was significantly different from the other samples. However regarding the strontium prediction map (Voerkelius et al.) and heterogeneity of big areas these seeds did fit in perfectly within the predicted range.

## 4.4 Determination of Phosphorus using DRC

The dynamic reaction cell has a rejection mechanism of unwanted interferences as explained in 3.1.2. Either the mass of interest or the overlapping elements are shifted to another mass. Due to collision with the reaction gas phosphorus is measured as its oxide. However the internal

normalization standard (IS) should stay constant at all time in order to monitor the instrument fluctuations. Indium is an established IS as far as measurements using standard mode are concerned. However there have been difficulties operating in DRC mode. Indium does not remain stable but rises and drops with respect to sample matrix. As a consequence concentration outcome of a sample varies depending on the intensity of In. Therefore several approaches have been investigated in order to overcome that problem. First of all different internal standards were under investigation regarding its steadiness throughout different samples. Secondly In was measured in standard mode while phosphorus still was detected as PO using DRC.

An external calibration of 6 standards, between 50 ng $g^{-1}$ and 2500 ng $g^{-1}$, was used for quantification. Different samples as well as standard solutions were measured and behavior of the internal standard was examined. It will be explained in more detail throughout the next subchapters.

### 4.4.1 **Internal standards**

Since indium did not seem to be an appropriate internal standard being used in DRC mode other elements were under investigation. Behavior of scandium, rhenium and rhodium was compared to indium. Their final concentration was 10 ng $g^{-1}$ and added to each measured solution if not stated differently. In addition a different rpq value (0.25) was tested as well but did not work differently than using the optimized value (0.45) for determination of PO. Rhenium and Rhodium acted exactly like indium as can be seen in Figure 46 (rpq=0.45). Its intensities were lower though. Scandium however was even worse with its intensity rising throughout the calibration measurement and dropping afterwards. However rpq value of 0.25 showed a different behavior but not as desired either. Additionally Sc is present in geological and biological samples and is therefore an inadequate internal normalization standard.

After the calibration a blank and standard five were measured again. The standard solution five, with a concentration of 1000 ng $g^{-1}$, was measured in between in order to monitor any changes due to memory effect or loss of intensity. Intensity did drop indeed but of the internal standard and not as much of the measured PO. Another Std5 solution was spiked with double amount of the internal standard mix (2*IS). Intensities were about two times higher. Then Std5 was diluted 1:1 and intensities dropped accordingly so did Std5 with 2*IS also diluted 1:1. However intensities of In and Rh were lower than expected. A geological sample was diluted either 1:5 or 1:100 and also additionally spiked with double amount of IS. Matrix effects are evident and intensities did rise enormously by a factor of 1.5. However even a sample that was diluted 1:100 did show higher intensities regarding In and Rh. Even though the sample spiked with IS

was diluted 1:1 its intensities were higher than expected but in the range of the standard solutions except of Rh which was higher after all.

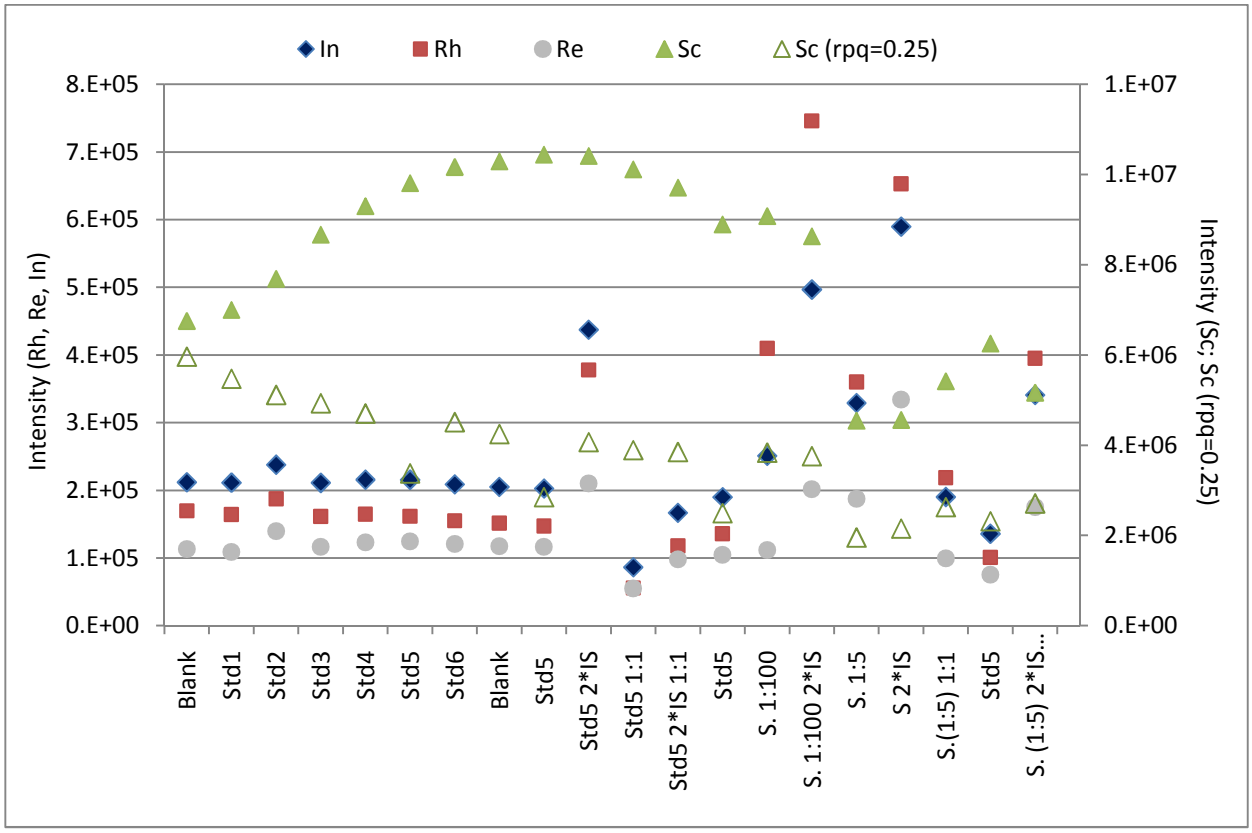


**Figure 46: Intensity of different internal standards using DRC**

Consequently the investigated internal standards did not seem to help solving the problem. Another two internal standards were under investigation: germanium and gallium. Not only matrix problems seemed to be a problem but also higher acid concentration. Therefore solutions with different $HNO_3$ concentration but constant or none phosphorus concentration were prepared. External quantification was performed as mentioned above and the internal standards had a final concentration of 10 ng $g^{-1}$ as well. Intensities using Ga as IS are shown in Figure 47. Gallium dropped constantly all through the measurement but rose when sample one (coffee 1:10) and three (pumpkinseed 1:10) were measured due to matrix effect. Pumpkinseed oil (sample number two, diluted 1:10) does not affect Ga intensity. However it is significantly low as it happened to fall during the measurement.

As expected PO intensity went down rapidly with higher acid concentration. Besides all acid solution did have the same concentration as Std5 but intensities were different even concerning the same acid concentration.

Germanium had a much lower intensity (about 20 000) but acted exactly the way as Ga. However acid concentration had a greater impact on the IS. PO intensity was equal to St5 but

dropped even worse towards higher acid concentrations of the solution. Sample concentrations did not match by means of Ge or Ga as IS as well as neglecting the internal standard and just using intensities.

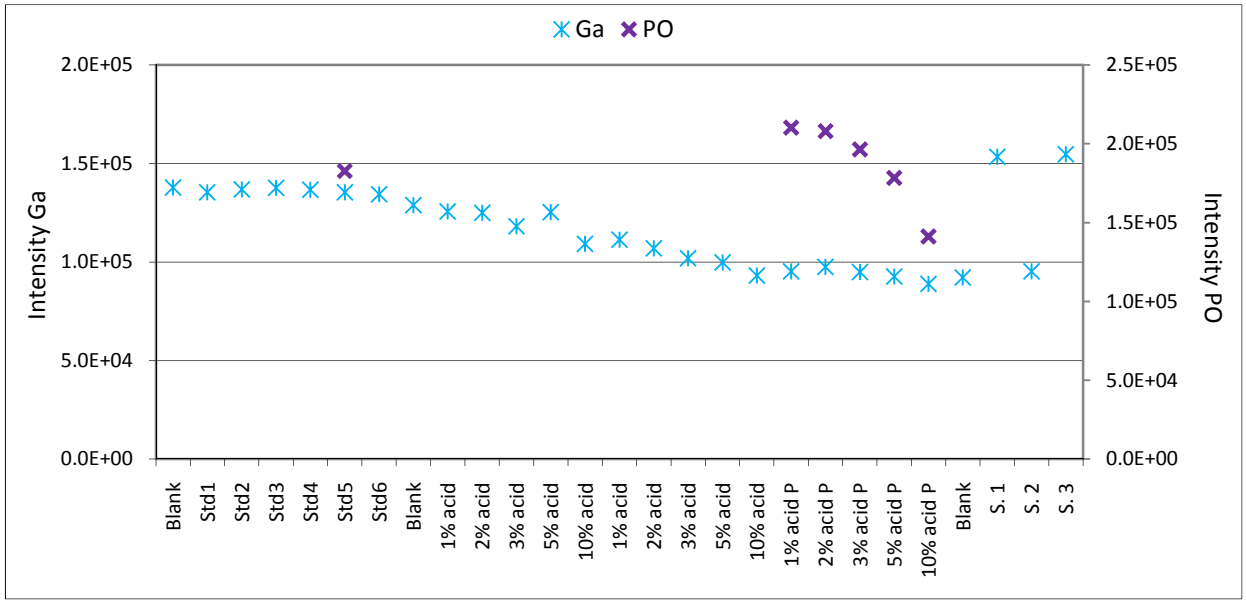


**Figure 47: Ga and PO intensity measured in DRC mode**

Different internal standards are not able to overcome the problem being used in DRC-mode. Therefore another attempt was investigated.

### 4.4.2 Standard mode and DRC mode used at once

Previous investigations led to the assumption that difficulties using internal standards in DRC mode might not be solved by using a different element solely. On the other hand indium does work well in standard mode. Therefore In was measured in standard mode while phosphorus was still detected as PO using DRC. However the instrument needs one minute in order to switch between both modes. This prolongs measurement time. Nevertheless that could be sacrificed for a reliable result.

Indium measured in standard mode slightly increased throughout the measurement as shown in Figure 48.

Three different dilution steps of 10, 50 and 100 were used for coffee, seed and oil samples. Pumpkin seeds contained way too much phosphorus that all three steps were out of the calibration range. Ten times dilution is not enough regarding coffee samples. Since oil is pressed which decreases concentration of elements the working range did fit perfectly. Repeatability of oil and coffee number two was 98.8% and 98.5% respectively. Even though pumpkin seed samples were out of calibration repeatability of dilution step 50 and 100 was 94.1%. However relative standard deviation of mean concentration of coffee sample number one was 13%

which is quite high. It seems, however, that maybe an inaccuracy happened during measurement preparation. Consequently, neglecting dilution step 50 a repeatability of 93.6% could be achieved. Nevertheless a 50 fold dilution seems to work with oil and coffee matrices tested and should be used for further samples with respect to the applied working range as well as total combined uncertainty. Even though it is lowest for pumpkin seed oil using a 10 fold dilution it seems more reasonable to increase dilution in order to avoid matrix effects. However since coffee samples are higher concentrated a 1:100 dilution would work just as good and additionally decreased expanded uncertainty. RSU of pumpkin seeds decreased with dilution as well and should probably be diluted 1:150.

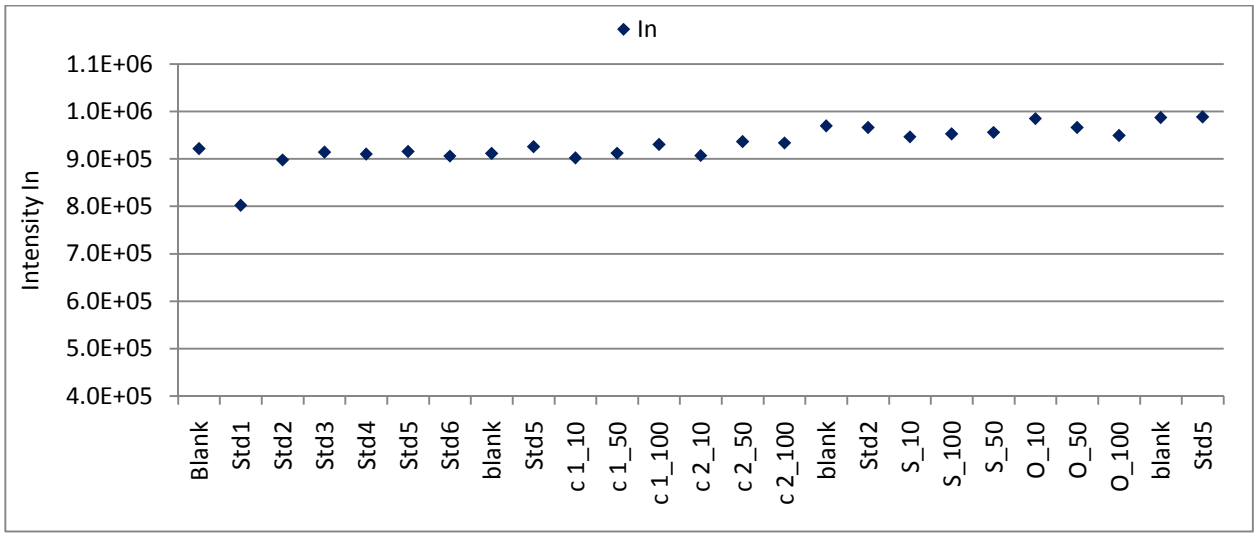


**Figure 48: Indium intensity measured in standard mode**

Concentrations of pumpkin seed oil were not significantly different neither were concentrations of coffee samples with respect to their 50 and 100 times dilution. All measured pumpkin seed concentrations did not show any correspondence however 50 and 100 fold dilution was close to each other.

Additionally standard two or standard five were measured every six samples subsequent to a blank. Std5 measured right after the calibration curve was not significantly different. However the signal did not remain stable. Both standards measured afterwards were significantly different and sample concentration did rise with measurement time even though intensity of indium did slightly rise as well. Due to the small sample batch it was not possible to tell whether higher concentration was determined due to interferences of PO or suppression of indium. Since high concentrated samples were measured in advance any memory effects could have occurred as well or respective wash time might not have been enough.

First steps have been undertaken in order to determine phosphorus in DRC mode while using indium as internal standard operated in standard mode. Nonetheless further investigations are

necessary in order to get more information on the process of using dynamic reaction cell and standard mode at once.

# 5 Summary & Outlook

In this work, a full method validation was performed successfully for the determination of trace elements (especially REE elements) for multi-element pattern analysis by ICP-QMS as well as ICP-SFMS for further application in food provenance studies. The latter instrument led to results with higher quality even though both instruments proved to be suitable for this type of analysis especially since detection limits of both instruments were similar. The used ICP-SFMS showed poor performance within this study and thus there is room for significant improvement of the results. Nonetheless, the final data were in agreement with the results of the quality control samples and thus multi-element data measured by ICP-SFMS could be used for further provenance studies.

Besides improvement of ICP-SFMS performance, repeatability of measurements will have to be investigated in the future in order to have a full validated method and to prove stability and robustness of the derived data. This is a prerequisite since the data have to be used in steadily growing data base for food authentication research in the future.

The results on wine and pumpkin seeds and oil proved that even a small number of elements can be used successfully for provenance studies. It has only to be made clear that the elements are from the original source and are not prone to contamination by processing steps. Even though, contaminants by the processing can be used as unique fingerprint if they are specific for a certain company using a particular process.

The limited number of samples led to excellent results. However extending the sample pool could give a different picture e.g. for white wine since distribution among vineyards was narrow. The results obtained for red wine samples showed a significant difference and a larger spread of the elemental pattern within one geographic origin. Every fifth red wine sample could not be allocated to its place of origin. Different production procedures compared to white wine could influence element pattern gained from grapes and hide background information. Even though 73 red wine samples from various vineyards were investigated Central-Burgenland and Weinviertel were the major representatives. These winegrowing areas could be distinguished from each other with a classification rate of 97%. Besides multi element pattern proved already very successful, strontium concentration and isotope ratios did give additional information on the provenance of wine. Consequently, in order to get an overall picture of composition of elements as well as isotope ratios in wine samples from Austria more vineyards have to be analyzed to get a statistically representative picture. Within the sample pool we could use the unique opportunity to analyze authentic wine samples only. As a consequence, no results concerning contamination by additives during the manufacturing processes as used by local wine farms were revealed.

Both multi-element and isotopic pattern proved to be successful for provenancing pumpkin seed and pumpkin seed oil, as well. Investigations from soil to seed to oil showed promising results of using REE and multi-element pattern for determination of origin. Especially Rb, Sr, Ba and Mn do not seem to be contaminated due to production steps and have high potential being used for authentication studies. Considering REE only Y, Ce, La and Pr were high enough in concentration. RSU of Sm, Nd, Dy, Er and Yb were up to 30% for these elements. Reduction of the uncertainty of the latter elements could make these elements suitable for food authentication as well. It was obvious that oil from China showed much higher concentration of REE whereas concentration of rare earth elements in Serbian oil was lowest. In addition using REE pattern of extracted oil samples a clear distinction between oil from China, Serbia, Slovenia and Lower Austria could be observed.

Differences with respect to either oil gaining process and secondly contaminations need to be fully understood in order to distinguish oil pressed from seed of different provenance. These contaminations must not necessarily disturb pattern recognition but could be useful with respect to different mills as well. Any influences on element concentration due to mixing of different seeds or pressed oil have to be taken into account as well. Therefore ratios of different elements will have to be observed more closely.

The investigation of the use of DRC to analyze P in plant matrices led to the first applicable analytical strategy to provide accurate data. Yet further steps need to be taken in order to verify the given results and the experience with P is currently extended to S measurements, where the same problem can be observed. This leads to the possibility of using P for authenticity studies different regions as well. Nonetheless, this potential needs to be investigated.

The development of appropriate reference materials is finally a prerequisite but future challenge for quality control in provenance studies.

# 6 Appendix

## 6.1 Sample identification, element concentration and Sr IR of wine

| code | region | kind | year | original code | code | region | kind | year | original code |
|---|---|---|---|---|---|---|---|---|---|
| W1 | CB | BF | 2003 | 131 | W9 | WV | BP | 2003 | 133 |
| W2 | CB | BF | 2003 | 130 | W11 | WV | BZ | 2004 | 27 |
| W6 | CB | BZ | 2003 | 129 | W14 | WV | BZ | 2004 | 35 |
| W7 | CB | BZ | 2003 | 86 | W15 | WV | BP | 2004 | 133 |
| W20 | CB | BZ | 2005 | 86 | W16 | WV | BZ | 2004 | 26 |
| W22 | CB | BF | 2005 | 85 | W19 | WV | BP | 2004 | 21 |
| W23 | CB | BZ | 2005 | 129 | W30 | WV | BZ | 2005 | 174 |
| W32 | CB | BF | 2005 | 130 | W34 | WV | BZ | 2005 | 179 |
| W39 | CB | BF | 2005 | 79 | W35 | WV | BP | 2005 | 21 |
| W41 | CB | BF | 2006 | 79 | W36 | WV | BZ | 2005 | 177 |
| W43 | CB | BZ | 2006 | 86 | W42 | WV | BB | 2006 | 181 |
| W45 | CB | BZ | 2006 | 86 | W47 | WV | BZ | 2006 | 174 |
| W46 | CB | BF | 2006 | 65 | W49 | WV | BZ | 2006 | 179 |
| W78 | CB | BZ | 2007 | 129 | W50 | WV | BP | 2006 | 21 |
| W82 | CB | BZ | 2007 | 129 | W53 | WV | BZ | 2006 | 174 |
| W95 | CB | BF | 2008 | 85 | W77 | WV | BZ | 2007 | 197 |
| W96 | CB | Ch | 2008 | 253 | W94 | WV | BZ | 2008 | 197 |
| W10 | LN | BZ | 2003 | 136 | W60 | WV | R | 2006 | 39 |
| W12 | LN | BZ | 2004 | 136 | W61 | WV | GV | 2006 | 198 |
| W27 | LN | SL | 2005 | 173 | W63 | WV | WB | 2007 | 191 |
| W29 | LN | BZ | 2005 | 136 | W65 | WV | GV | 2007 | 198 |
| W48 | LN | BZ | 2006 | 136 | W70 | WV | GV | 2007 | 176 |
| W52 | LN | SL | 2006 | 173 | W91 | WV | GV | 2008 | 180 |
| W75 | LN | BZ | 2007 | 136 | W97 | WV | WR | 2008 | 126 |
| W72 | LN | GV | 2007 | 128 | W98 | WV | WB | 2008 | 191 |
| W26 | LN/H | BF | 2005 | 77 | W24 | KaT | BZ | 2005 | 161 |
| W38 | LN/H | BZ | 2005 | 175 | W85 | KaT | BZ | 2008 | 161 |
| W44 | LN/H | BF | 2006 | 77 | W59 | KaT | R | 2006 | 199 |
| W83 | LN/H | BF | 2007 | 77 | W62 | KaT | WB | 2006 | 201 |
| W87 | LN/H | WR | 2008 | 135 | W69 | KaT | GV | 2007 | 158 |
| W3 | SE-ST | BZ | 2003 | 170 | W71 | KaT | GV | 2007 | 158 |
| W4 | SE-ST | BZ | 2003 | 103 | W25 | TR | SL | 2005 | 162 |
| W13 | SE-ST | BZ | 2004 | 103 | W54 | TR | SL | 2006 | 162 |
| W18 | SE-ST | BZ | 2004 | 107 | W55 | TR | BZ | 2006 | 197 |
| W51 | SE-ST | BZ | 2006 | 103 | W76 | TR | SL | 2007 | 162 |
| W64 | SE-ST | T | 2007 | 105 | W80 | TR | SL | 2004 | 162 |
| W73 | SE-ST | T | 2007 | 105 | W81 | TR | SL | 2007 | 162 |
| W74 | SE-ST | WR | 2007 | 101 | W31 | C | BF | 2005 | 163 |
| W86 | SE-ST | T | 2008 | 105 | W33 | C | BZ | 2005 | 56 |
| W99 | SE-ST | WR | 2008 | 101 | W56 | C | BZ | 2006 | 56 |
| W5 | W-ST | BW | 2003 | 106 | W79 | C | BF | 2007 | 163 |
| W8 | W-ST | BW | 2003 | 95 | W84 | C | BZ | 2007 | 56 |
| W17 | W-ST | BW | 2004 | 97 | W57 | KrT | BZ | 2006 | 197 |
| W21 | W-ST | BW | 2005 | 97 | W68 | V | Ch | 2007 | 160 |
| W40 | W-ST | BW | 2006 | 97 | W28 | DL | BZ | 2005 | 178 |
| W92 | W-ST | BW | 2008 | 97 | W93 | DL | BZ | 2008 | 178 |
| W66 | W-ST | SB | 2007 | 106 | W67 | DL | Ch | 2007 | 185 |
| W90 | ST | Ch | 2008 | 255 | W58 | TT | BZ | 2006 | 187 |
| W37 | SE-ST | BZ | 2005 | 103 | W88 | TT | GV | 2008 | 121 |
| W89(2) | S-ST | WB | 2008 | 104 | | | | | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Blauburgunder | BB | Riesling | R | Central-Burgenland | CB | Thermenregion | TR |
| Blauer Portugieser | BP | Sankt Laurent | SL | Lake Neusiedl | LN | Carnuntum | C |
| Blauer Wildbacher | BW | Sauvignon blanc | SB | LN/Hills | LN/H | Kremstal | KrT |
| Blauer Zweigelt | BZ | Traminer | T | South-East-Styria | SE-ST | Vienna | V |
| Blaufränkisch | BF | Weißburgunder | WB | West-Styria | W-ST | Donauland | DL |
| Chardonnay | Ch | Welschriesling | WR | Weinviertel | WV | Traisental | TT |
| Grüner Veltliner | GV | | | Kamptal | KaT | | |

**Table 41: Labeling of 99 wine samples**

| Analyte | Mass | $LoD_4$ | $LoQ_4$ | RSU (%) | W1 | W2 | W6 | W7 | W20 | W22 | W23 | W32 | W39 | W41 | W43 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | 7 | 0.216 | 0.719 | 20 | 2.05 | 2.23 | 2.34 | 0.910 | 0.894 | 2.30 | 1.24 | 3.60 | 1.66 | 1.85 | 9.62 |
| B | 11 | 126 | 419 | 3.6 | 4.80E+03 | 3.64E+03 | 2.51E+03 | 5.42E+03 | 3.56E+03 | 3.40E+03 | 3.05E+03 | 5.03E+03 | 6.35E+03 | 7.20E+03 | 2.86E+03 |
| Mg | 26 | 231 | 770 | 27 | 6.62E+04 | 5.53E+04 | 5.49E+04 | 5.79E+04 | 6.81E+04 | 7.26E+04 | 5.82E+04 | 7.12E+04 | 7.57E+04 | 8.72E+04 | 7.13E+04 |
| Cr | 52 | 9.60 | 32.0 | 12 | 2.75E+02 | 1.47E+02 | 1.51E+02 | 1.85E+02 | 1.13E+02 | 1.13E+02 | 1.59E+02 | 2.51E+02 | 2.78E+02 | 1.51E+02 | 1.51E+02 |
| Mn | 55 | 3.31 | 11.0 | 2.4 | 5.68E+02 | 5.35E+02 | 5.48E+02 | 5.08E+02 | 8.74E+02 | 4.44E+02 | 6.30E+02 | 7.63E+02 | 5.75E+02 | 8.94E+02 | 5.87E+02 |
| Fe | 57 | 102 | 340 | 7 | 1.92E+03 | 1.60E+03 | 9.65E+02 | 1.67E+03 | 1.24E+03 | 1.26E+03 | 1.24E+03 | 1.63E+03 | 1.17E+03 | 1.82E+03 | 1.43E+03 |
| Co | 59 | 0.137 | 0.456 | 13 | 1.20 | 0.855 | 1.03 | 0.516 | 1.68 | 0.895 | 1.06 | 1.06 | 0.401 | 1.50 | 5.03 |
| Ni | 60 | 1.63 | 5.42 | 5.7 | 41.1 | 42.4 | 40.7 | 73.3 | 39.6 | 36.2 | 23.6 | 41.8 | 16.4 | 18.4 | 81.0 |
| Cu | 65 | 6.98 | 23.3 | 10 | 10.3 | 11.1 | 12.6 | 12.1 | 8.26 | 24.4 | 10.0 | 11.2 | 7.01 | 74.9 | 275 |
| Zn | 68 | 96.6 | 322 | 8 | 2.79E+02 | 2.38E+02 | 2.14E+02 | 2.08E+02 | 4.56E+02 | 4.30E+02 | 3.62E+02 | 1.47E+02 | < LoD | 3.84E+02 | 7.09E+02 |
| Ga | 69 | 0.581 | 1.94 | 15 | 3.84 | 5.45 | 2.59 | 2.65 | 3.31 | 3.94 | 1.63 | 3.45 | 2.57 | 2.58 | 4.41 |
| As | 75 | 0.290 | 0.966 | 56 | 0.84 | 0.85 | 0.67 | 0.77 | 0.80 | 0.53 | 0.56 | 0.74 | 0.50 | 0.42 | 1.59 |
| Rb | 85 | 1.52 | 5.05 | 5.8 | 8.62E+02 | 5.03E+02 | 7.97E+02 | 1.01E+03 | 5.71E+02 | 1.75E+03 | 6.89E+02 | 9.51E+02 | 1.01E+03 | 7.76E+02 | 3.25E+03 |
| Sr | 88 | 6.42 | 21.4 | 6.1 | 1.65E+02 | 2.16E+02 | 1.48E+02 | 2.03E+02 | 2.29E+02 | 4.19E+02 | 1.46E+02 | 2.46E+02 | 1.92E+02 | 2.69E+02 | 4.46E+02 |
| Mo | 98 | 0.122 | 0.408 | 17 | 1.34 | 0.623 | 0.541 | 0.444 | 0.360 | 0.805 | 0.962 | 0.563 | 3.09 | 0.788 | 0.422 |
| Ba | 138 | 1.45 | 4.82 | 6.9 | 62.4 | 98.3 | 44.3 | 46.3 | 70.2 | 85.2 | 34.4 | 76.8 | 56.9 | 57.1 | 96.2 |
| Pb | 208 | 3.03 | 10.1 | 7.3 | 5.28 | 5.14 | 5.42 | 3.36 | 5.63 | 12.5 | 4.58 | 8.50 | 3.62 | 7.62 | 7.26 |
| U | 238 | 0.0131 | 0.0438 | 13 | 0.302 | 0.193 | 0.229 | 0.167 | 0.280 | 0.241 | 0.259 | 0.309 | 0.141 | 0.249 | 0.948 |
| Ca | 44 | 1.32E+04 | 4.40E+04 | 13 | 7.34E+04 | 8.14E+04 | 5.01E+04 | 5.41E+04 | 5.53E+04 | 6.52E+04 | 5.07E+04 | 6.48E+04 | 5.31E+04 | 6.91E+04 | 6.47E+04 |
| $^{87}Sr/^{86}Sr$ | | | | 0.04 | 0.71072 | 0.71159 | 0.71156 | 0.71257 | 0.71206 | 0.71110 | 0.71130 | 0.71115 | 0.71075 | 0.70989 | 0.71135 |

**Table 42: Concentration of elements, $LoD_4$ and $LoQ_4$ in ng $g^{-1}$ as well as RSU (k=2) and $^{87}Sr/^{86}Sr$ ratio of wine samples; highlighted concentrations were below limit of quantification while LoD is referred to $LoD_4$; highlighted ratios did not fulfill requirements but were used for evaluation as well; to be continued on the following pages**

| Analyte | W45 | W46 | W78 | W82 | W95 | W96 | W10 | W12 | W27 | W29 | W48 | W52 | W75 | W72 | W26 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | 9.10 | 1.35 | 2.37 | 2.20 | 1.04 | 1.19 | 3.60 | 1.36 | 19.44 | 1.52 | 1.69 | 24.4 | 2.05 | 1.64 | 0.92 |
| B | 2.80E+03 | 6.01E+03 | 3.77E+03 | 5.58E+03 | 4.88E+03 | 7.26E+03 | 5.61E+03 | 3.75E+03 | 7.09E+03 | 4.15E+03 | 4.89E+03 | 7.25E+03 | 5.35E+03 | 3.63E+03 | 4.79E+03 |
| Mg | 6.97E+04 | 7.48E+04 | 6.37E+04 | 7.05E+04 | 7.68E+04 | 1.08E+05 | 6.48E+04 | 5.83E+04 | 9.41E+04 | 6.41E+04 | 6.75E+04 | 9.36E+04 | 6.63E+04 | 6.93E+04 | 6.47E+04 |
| Cr | 1.41E+02 | 1.37E+02 | 2.11E+02 | 2.62E+02 | 1.74E+02 | 2.04E+02 | 2.86E+02 | 2.04E+02 | 2.47E+02 | 1.93E+02 | 2.94E+02 | 1.25E+02 | 1.52E+02 | 2.50E+02 | 9.73E+01 |
| Mn | 5.62E+02 | 8.75E+02 | 6.17E+02 | 9.05E+02 | 4.23E+02 | 6.29E+02 | 7.44E+02 | 7.83E+02 | 9.21E+02 | 8.26E+02 | 6.69E+02 | 8.89E+02 | 8.81E+02 | 7.04E+02 | 8.39E+02 |
| Fe | 1.40E+03 | 1.06E+03 | 1.24E+03 | 1.79E+03 | 1.75E+03 | 7.02E+02 | 2.15E+03 | 1.38E+03 | 1.04E+03 | 1.97E+03 | 1.70E+03 | 1.43E+03 | 1.69E+03 | 1.12E+03 | 1.08E+03 |
| Co | 4.37 | 1.02 | 2.60 | 1.47 | 1.19 | 2.80 | 1.19 | 0.779 | 1.05 | 2.10 | 1.64 | 2.19 | 1.39 | 3.27 | 0.74 |
| Ni | 77.3 | 13.1 | 28.0 | 23.3 | 27.0 | 9.06 | 12.8 | 8.18 | 18.5 | 24.7 | 17.6 | 16.0 | 19.1 | 168 | 14.1 |
| Cu | 262 | 35.7 | 96.3 | 104 | 38.7 | 29.3 | 14.8 | 25.9 | 7.20 | 14.8 | 47.0 | 30.2 | 101 | 41.0 | < LoD |
| Zn | 7.06E+02 | 3.96E+02 | 3.59E+02 | 5.88E+02 | 6.23E+02 | 6.39E+02 | 1.83E+02 | 2.57E+02 | 1.40E+02 | 4.01E+02 | 5.62E+02 | 3.91E+02 | 6.25E+02 | 6.24E+02 | < LoD |
| Ga | 3.83 | 1.98 | 1.84 | 4.58 | 3.29 | 2.10 | 3.32 | 2.64 | 3.69 | 3.27 | 3.00 | 3.96 | 4.26 | 1.92 | 1.97 |
| As | 0.96 | < LoD | 0.29 | 0.75 | 0.30 | 3.27 | 1.03 | 0.88 | 0.86 | 1.41 | 0.88 | 0.45 | 0.78 | 1.08 | 0.67 |
| Rb | 3.25E+03 | 7.65E+02 | 4.89E+02 | 1.25E+02 | 9.10E+02 | 1.13E+03 | 2.95E+02 | 9.95E+01 | 1.03E+03 | 8.82E+01 | 1.58E+02 | 1.29E+03 | 1.21E+02 | 2.49E+02 | 5.48E+02 |
| Sr | 4.36E+02 | 2.42E+02 | 1.50E+02 | 3.98E+02 | 2.63E+02 | 2.05E+02 | 3.48E+02 | 2.02E+02 | 5.98E+02 | 3.07E+02 | 2.87E+02 | 7.05E+02 | 3.89E+02 | 2.21E+02 | 2.61E+02 |
| Mo | 0.478 | 1.04 | 0.925 | 0.859 | 1.29 | 2.53 | 0.594 | 0.589 | 1.23 | 0.384 | 0.595 | 1.53 | 0.819 | 1.79 | 1.88 |
| Ba | 85.6 | 45.5 | 41.8 | 102.9 | 77.7 | 50.1 | 66.4 | 50.2 | 80.3 | 71.4 | 67.4 | 88.7 | 98.3 | 45.8 | 42.2 |
| Pb | 5.60 | 3.71 | 7.04 | 8.55 | 3.38 | 5.18 | 9.92 | 8.39 | 12.2 | 8.11 | 5.26 | 5.57 | 16.3 | 6.15 | 4.96 |
| U | 0.694 | 0.738 | 0.886 | 0.185 | < LoD | 0.024 | 0.077 | 0.109 | 0.146 | 0.387 | 0.143 | 0.391 | 0.120 | 0.204 | 0.334 |
| Ca | 6.19E+04 | 4.98E+04 | 6.41E+04 | 5.72E+04 | 7.42E+04 | 7.80E+04 | 5.19E+04 | 4.67E+04 | 5.57E+04 | 7.37E+04 | 5.46E+04 | 8.19E+04 | 5.45E+04 | 6.38E+04 | 4.87E+04 |
| $^{87}Sr/^{86}Sr$ | 0.71113 | 0.71219 | 0.71179 | 0.70859 | 0.71203 | 0.71068 | 0.71007 | 0.70828 | 0.70980 | 0.70855 | 0.70957 | 0.70993 | 0.70940 | 0.70861 | 0.70966 |

| Analyte | W38 | W44 | W83 | W87 | W3 | W4 | W13 | W18 | W51 | W64 | W73 | W74 | W86 | W99 | W5 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | 1.91 | 1.69 | 0.74 | 11.1 | 2.48 | 5.14 | 3.85 | 1.06 | 3.00 | 0.841 | 0.743 | 3.49 | 0.845 | 2.55 | 0.756 |
| B | 4.46E+03 | 5.74E+03 | 4.06E+03 | 8.51E+03 | 2.56E+03 | 3.56E+03 | 4.01E+03 | 3.61E+03 | 5.32E+03 | 3.92E+03 | 4.07E+03 | 2.58E+03 | 4.73E+03 | 2.70E+03 | 5.91E+03 |
| Mg | 6.97E+04 | 7.64E+04 | 6.79E+04 | 1.30E+05 | 6.50E+04 | 5.31E+04 | 5.40E+04 | 6.37E+04 | 7.07E+04 | 4.28E+04 | 4.55E+04 | 6.03E+04 | 5.34E+04 | 6.23E+04 | 5.47E+04 |
| Cr | 1.12E+02 | 1.45E+02 | 1.98E+02 | 2.43E+02 | 1.76E+02 | 1.91E+02 | 1.64E+02 | 1.92E+02 | 1.29E+02 | 1.74E+02 | 1.74E+02 | 1.47E+02 | 1.66E+02 | 1.83E+02 | 1.31E+02 |
| Mn | 5.31E+02 | 1.10E+03 | 6.96E+02 | 9.70E+02 | 6.30E+02 | 4.27E+02 | 6.06E+02 | 7.80E+02 | 6.24E+02 | 2.22E+02 | 2.28E+02 | 3.69E+02 | 2.41E+02 | 2.92E+02 | 1.09E+03 |
| Fe | 1.31E+03 | 1.36E+03 | 1.22E+03 | 6.50E+02 | 1.77E+03 | 1.57E+03 | 1.68E+03 | 2.07E+03 | 1.42E+03 | 3.65E+02 | 4.22E+02 | 4.38E+02 | 4.36E+02 | 3.08E+02 | 2.48E+03 |
| Co | 1.72 | 1.36 | 1.51 | 3.43 | 0.739 | 0.957 | 1.29 | 1.90 | 2.44 | 3.02 | 3.03 | 2.33 | 3.09 | 4.07 | 3.29 |
| Ni | 35.6 | 15.2 | 13.6 | 21.9 | 39.0 | 27.2 | 23.9 | 32.1 | 19.3 | 11.7 | 12.0 | 13.3 | 7.7 | 13.1 | 23.1 |
| Cu | 43.6 | 37.7 | 15.0 | 150 | 11.9 | 12.4 | 11.7 | 29.9 | 99.6 | 94.8 | 92.9 | 69.1 | 197 | 58.4 | 14.5 |
| Zn | 2.48E+02 | 2.78E+02 | 2.35E+02 | 2.43E+03 | 9.72E+01 | 1.22E+02 | 3.12E+02 | 7.78E+02 | 5.53E+02 | 1.04E+03 | 9.79E+02 | 2.75E+02 | 5.14E+02 | 2.14E+02 | 5.63E+02 |
| Ga | 2.41 | 1.73 | 1.78 | 7.18 | 8.13 | 3.85 | 3.19 | 4.95 | 1.88 | 0.89 | 0.88 | 0.84 | 1.23 | < LoD | 6.15 |
| As | 2.01 | 0.36 | 0.65 | 3.84 | 1.04 | 1.07 | 1.41 | 0.60 | 0.36 | 0.36 | 0.46 | 0.38 | < LoD | 0.44 | 0.78 |
| Rb | 1.45E+03 | 7.25E+02 | 4.39E+02 | 1.43E+03 | 1.30E+03 | 7.15E+02 | 6.67E+02 | 1.88E+03 | 1.61E+03 | 1.16E+03 | 1.19E+03 | 1.01E+03 | 1.02E+03 | 4.02E+02 | 9.35E+02 |
| Sr | 2.64E+02 | 2.61E+02 | 1.97E+02 | 5.50E+02 | 6.31E+02 | 3.18E+02 | 2.53E+02 | 4.55E+02 | 2.35E+02 | 6.88E+01 | 7.06E+01 | 8.08E+01 | 6.78E+01 | 6.15E+01 | 3.80E+02 |
| Mo | 0.412 | 1.81 | 0.377 | 3.29 | 0.847 | 0.896 | 0.741 | 0.486 | 2.15 | 0.207 | 0.252 | 0.458 | 0.683 | 0.410 | 1.76 |
| Ba | 50.7 | 38.5 | 41.1 | 168 | 157 | 69.7 | 53.9 | 105 | 43.0 | 21.9 | 20.8 | 21.5 | 30.6 | 15.0 | 127 |
| Pb | 8.72 | 3.59 | 8.96 | 6.22 | 6.00 | 6.70 | 4.12 | 4.68 | 7.58 | 6.45 | 3.82 | 3.76 | < LoD | < LoD | 4.56 |
| U | 1.10 | 0.201 | 4.00 | 0.037 | 0.576 | 1.42 | 0.582 | 0.210 | 0.747 | 0.322 | 0.279 | 0.414 | < LoD | 0.029 | 0.658 |
| Ca | 6.53E+04 | 7.12E+04 | 5.64E+04 | 6.33E+04 | 9.09E+04 | 6.55E+04 | 6.84E+04 | 5.33E+04 | 5.68E+04 | 4.75E+04 | 4.70E+04 | 5.26E+04 | 5.27E+04 | 4.85E+04 | 9.34E+04 |
| $^{87}Sr/^{86}Sr$ | 0.71027 | 0.70994 | 0.70976 | 0.71014 | 0.70737 | 0.70922 | 0.70941 | 0.70606 | 0.70978 | 0.70940 | 0.70891 | 0.71034 | 0.70939 | 0.70881 | 0.71203 |

| Analyte | W8 | W17 | W21 | W40 | W92 | W66 | W90 | W37 | W89(2) | W9 | W11 | W14 | W15 | W16 | W19 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | 1.92 | 1.62 | 1.33 | 1.80 | 2.14 | 0.846 | 1.31 | 3.65 | 0.383 | 5.23 | 5.32 | 1.68 | 5.74 | 3.51 | 12.8 |
| B | 6.00E+03 | 5.18E+03 | 5.28E+03 | 6.29E+03 | 6.50E+03 | 3.53E+03 | 4.13E+03 | 3.59E+03 | 2.63E+03 | 4.02E+03 | 3.76E+03 | 4.18E+03 | 3.41E+03 | 4.83E+03 | 7.73E+03 |
| Mg | 5.68E+04 | 5.91E+04 | 5.91E+04 | 7.20E+04 | 8.41E+04 | 5.71E+04 | 6.63E+04 | 5.49E+04 | 5.85E+04 | 4.95E+04 | 7.27E+04 | 8.31E+04 | 5.85E+04 | 8.57E+04 | 7.43E+04 |
| Cr | 1.58E+02 | 1.07E+02 | 1.92E+02 | 1.82E+02 | 1.98E+02 | 1.64E+02 | 1.46E+02 | 1.37E+02 | 1.37E+02 | 6.96E+01 | 2.28E+02 | 2.82E+02 | 1.46E+02 | 1.90E+02 | 2.92E+02 |
| Mn | 8.07E+02 | 8.59E+02 | 6.64E+02 | 8.95E+02 | 1.05E+03 | 4.32E+02 | 3.58E+02 | 3.87E+02 | 7.95E+02 | 7.50E+02 | 7.24E+02 | 1.02E+03 | 7.60E+02 | 1.11E+03 | 5.92E+02 |
| Fe | 2.89E+03 | 2.06E+03 | 1.31E+03 | 2.20E+03 | 1.59E+03 | 7.83E+02 | 3.94E+02 | 1.50E+03 | 4.02E+02 | 8.08E+02 | 2.32E+03 | 1.88E+03 | 1.55E+03 | 2.20E+03 | 2.10E+03 |
| Co | 1.10 | 1.92 | 1.50 | 1.70 | 1.32 | 1.91 | 5.02 | 0.792 | 5.46 | 0.618 | 1.37 | 2.35 | 2.05 | 2.16 | 1.74 |
| Ni | 20.9 | 20.1 | 23.1 | 26.7 | 10.5 | 16.2 | 9.0 | 18.2 | 11.0 | 10.5 | 45.2 | 26.3 | 18.5 | 33.8 | 7.9 |
| Cu | 43.2 | 38.2 | 9.7 | 37.6 | 30.8 | 26.5 | 47.7 | 10.8 | 41.3 | 20.8 | 592 | 21.5 | 111.4 | 30.5 | 60.8 |
| Zn | 3.94E+02 | 5.27E+02 | 6.85E+02 | 5.54E+02 | 6.35E+02 | 2.98E+02 | 8.98E+02 | 1.85E+02 | 6.19E+02 | 1.07E+02 | 7.35E+02 | 5.14E+02 | 2.33E+02 | 5.36E+02 | 6.13E+02 |
| Ga | 5.17 | 9.93 | 11.32 | 9.97 | 2.48 | 5.92 | < LoD | 2.09 | 1.48 | 3.01 | 2.69 | 4.09 | 2.11 | 4.50 | 2.87 |
| As | 0.89 | 0.55 | 1.54 | 0.39 | 0.49 | < LoD | < LoD | 0.40 | < LoD | 0.46 | 0.68 | 0.68 | 0.84 | 0.52 | 0.53 |
| Rb | 1.20E+03 | 6.12E+02 | 8.09E+02 | 5.54E+02 | 1.40E+03 | 3.24E+03 | 1.27E+03 | 5.11E+02 | 7.25E+02 | 1.15E+03 | 1.17E+03 | 9.31E+02 | 1.41E+03 | 9.79E+02 | 1.05E+03 |
| Sr | 2.82E+02 | 3.24E+02 | 4.00E+02 | 3.52E+02 | 2.55E+02 | 2.05E+02 | 1.05E+02 | 2.93E+02 | 1.17E+02 | 3.15E+02 | 2.56E+02 | 2.73E+02 | 3.87E+02 | 3.32E+02 | 4.43E+02 |
| Mo | 14.1 | 1.97 | 2.24 | 1.31 | 1.57 | 0.530 | 0.329 | 1.074 | 0.653 | 0.354 | 0.605 | 0.859 | 0.383 | 1.28 | 7.68 |
| Ba | 107 | 223 | 256 | 231 | 58.1 | 131.4 | 11.3 | 46.4 | 36.1 | 57.6 | 50.9 | 82.2 | 42.5 | 95.9 | 63.1 |
| Pb | < LoD | 4.39 | 6.12 | 4.20 | 3.35 | 12.2 | < LoD | 5.50 | < LoD | 4.85 | 25.1 | 6.26 | 9.53 | 7.02 | 6.18 |
| U | 0.212 | 0.329 | 0.319 | 0.197 | < LoD | 1.22 | < LoD | 0.175 | < LoD | 0.080 | 0.741 | 0.196 | 2.75 | 0.580 | 0.645 |
| Ca | 8.89E+04 | 8.23E+04 | 4.36E+04 | 1.03E+05 | 6.56E+04 | 6.57E+04 | 5.73E+04 | 6.12E+04 | 5.42E+04 | 6.69E+04 | 5.57E+04 | 6.71E+04 | 5.67E+04 | 7.05E+04 | 5.44E+04 |
| $^{87}Sr/^{86}$ Sr | 0.71296 | 0.71101 | 0.71135 | 0.71128 | 0.71060 | 0.71302 | 0.71074 | 0.70922 | 0.71085 | 0.71065 | 0.71168 | 0.70990 | 0.70990 | 0.71052 | 0.71080 |

| Analyte | W30 | W34 | W35 | W36 | W42 | W47 | W49 | W50 | W53 | W77 | W94 | W60 | W61 | W63 | W65 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | 3.34 | 1.82 | 11.3 | 1.39 | 2.97 | 6.28 | 2.94 | 13.1 | 1.34 | 0.898 | 1.96 | 8.16 | 5.00 | 17.8 | 3.32 |
| B | 6.86E+03 | 4.08E+03 | 6.56E+03 | 6.02E+03 | 5.14E+03 | 5.11E+03 | 4.31E+03 | 7.64E+03 | 6.27E+03 | 5.73E+03 | 5.80E+03 | 7.80E+03 | 3.05E+03 | 3.81E+03 | 2.63E+03 |
| Mg | 9.28E+04 | 7.44E+04 | 6.57E+04 | 7.06E+04 | 8.66E+04 | 8.86E+04 | 9.05E+04 | 8.21E+04 | 7.64E+04 | 7.99E+04 | 7.47E+04 | 8.46E+04 | 7.14E+04 | 7.27E+04 | 7.60E+04 |
| Cr | 2.14E+02 | 1.39E+02 | 2.11E+02 | 2.11E+02 | 2.66E+02 | 1.43E+02 | 1.65E+02 | 2.30E+02 | 1.68E+02 | 1.69E+02 | 2.01E+02 | 1.60E+02 | 1.96E+02 | 1.80E+02 | 2.22E+02 |
| Mn | 1.02E+03 | 1.07E+03 | 6.05E+02 | 1.09E+03 | 1.16E+03 | 5.61E+02 | 1.12E+03 | 7.28E+02 | 8.76E+02 | 6.64E+02 | 5.61E+02 | 7.10E+02 | 5.37E+02 | 4.22E+02 | 3.63E+02 |
| Fe | 1.51E+03 | 1.02E+03 | 1.55E+03 | 7.50E+02 | 1.43E+03 | 1.71E+03 | 1.48E+03 | 1.22E+03 | 1.12E+03 | 1.32E+03 | 1.14E+03 | 3.22E+02 | 9.42E+02 | 5.07E+02 | 6.86E+02 |
| Co | 2.13 | 1.23 | 2.27 | 1.26 | 2.73 | 2.74 | 2.13 | 1.71 | 1.06 | 1.06 | 0.833 | 2.37 | 2.96 | 1.15 | 3.48 |
| Ni | 26.0 | 11.6 | 43.8 | 11.9 | 16.3 | 31.2 | 16.2 | 7.8 | 13.7 | 6.5 | 14.6 | 25.5 | 9.9 | 11.8 | 8.1 |
| Cu | 21.8 | 13.1 | 172 | 11.3 | 177 | 65.8 | 45.1 | 48.8 | 84.4 | 159 | 57.9 | 27.9 | 46.0 | 14.8 | 137 |
| Zn | 1.38E+03 | 1.30E+02 | 2.80E+02 | < LoD | 5.08E+02 | 5.80E+02 | 4.14E+02 | 4.64E+02 | 4.54E+02 | 7.60E+02 | 3.19E+02 | 2.01E+03 | 6.07E+02 | 4.72E+02 | 5.52E+02 |
| Ga | 9.12 | 1.96 | 4.03 | 2.28 | 2.75 | 4.67 | 2.86 | 2.55 | 2.08 | 2.02 | 2.65 | 1.49 | 0.98 | 1.71 | 1.13 |
| As | 1.22 | 0.44 | 3.66 | 0.56 | 1.51 | 0.31 | 0.73 | 0.38 | < LoD | 0.33 | 0.77 | 1.01 | 0.74 | 0.59 | 0.80 |
| Rb | 7.36E+02 | 5.32E+02 | 1.23E+03 | 5.08E+02 | 6.50E+02 | 3.10E+03 | 6.19E+02 | 1.43E+03 | 7.82E+02 | 8.53E+02 | 1.18E+03 | 4.93E+02 | 3.50E+02 | 5.48E+02 | 3.99E+02 |
| Sr | 3.48E+02 | 3.94E+02 | 4.59E+02 | 2.14E+02 | 4.63E+02 | 4.79E+02 | 5.68E+02 | 5.12E+02 | 2.44E+02 | 2.69E+02 | 2.63E+02 | 1.95E+02 | 1.31E+02 | 3.89E+02 | 1.45E+02 |
| Mo | 0.924 | 0.516 | 3.735 | 0.698 | 0.745 | 1.09 | 0.890 | 5.34 | 1.14 | 1.97 | 1.59 | 2.47 | 0.375 | 1.33 | < LoD |
| Ba | 200 | 43.4 | 89.0 | 49.3 | 59.8 | 104.2 | 64.2 | 59.2 | 48.0 | 47.8 | 64.0 | 36.3 | 23.4 | 38.1 | 27.0 |
| Pb | 14.72 | 6.57 | 11.03 | 6.77 | 6.16 | 4.26 | 5.16 | 5.07 | 10.33 | < LoD | < LoD | < LoD | 6.77 | < LoD | 3.07 |
| U | 0.555 | 0.248 | 0.475 | 0.296 | 0.707 | 0.312 | 0.398 | 0.558 | 2.47 | 0.194 | < LoD | 0.099 | 0.237 | 0.201 | 0.466 |
| Ca | 6.55E+04 | 5.71E+04 | 5.41E+04 | 5.58E+04 | 9.31E+04 | 6.94E+04 | 5.42E+04 | 4.90E+04 | 5.09E+04 | 5.64E+04 | 5.39E+04 | 2.99E+04 | 5.41E+04 | 5.67E+04 | 5.33E+04 |
| $^{87}Sr/^{86}Sr$ | 0.71006 | 0.71049 | 0.71030 | 0.71011 | 0.70979 | 0.71020 | 0.71096 | 0.71051 | 0.71042 | 0.71047 | 0.71227 | 0.71319 | 0.70951 | 0.71043 | 0.70966 |

| Analyte | W70 | W91 | W97 | W98 | W24 | W85 | W59 | W62 | W69 | W71 | W25 | W54 | W55 | W76 | W80 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | 2.78 | 4.61 | 9.62 | 28.6 | 0.912 | 1.47 | 7.01 | 4.54 | 4.46 | 4.36 | 3.31 | 1.84 | 1.77 | 2.77 | 3.69 |
| B | 4.17E+03 | 4.66E+03 | 3.80E+03 | 3.22E+03 | 4.54E+03 | 8.12E+03 | 3.63E+03 | 3.96E+03 | 5.23E+03 | 5.13E+03 | 5.86E+03 | 5.56E+03 | 4.53E+03 | 6.99E+03 | 6.16E+03 |
| Mg | 8.22E+04 | 7.71E+04 | 5.70E+04 | 7.93E+04 | 6.74E+04 | 8.29E+04 | 6.22E+04 | 7.03E+04 | 8.26E+04 | 7.84E+04 | 7.09E+04 | 7.80E+04 | 8.09E+04 | 7.61E+04 | 7.57E+04 |
| Cr | 2.35E+02 | 1.64E+02 | 2.30E+02 | 1.40E+02 | 1.64E+02 | 1.19E+02 | 1.14E+02 | 2.88E+02 | 2.82E+02 | 1.50E+02 | 2.71E+02 | 1.20E+02 | 2.83E+02 | 1.19E+02 | 2.79E+02 |
| Mn | 6.63E+02 | 5.05E+02 | 2.21E+02 | 3.34E+02 | 1.07E+03 | 1.02E+03 | 2.97E+02 | 7.97E+02 | 4.94E+02 | 4.75E+02 | 6.18E+02 | 5.62E+02 | 8.58E+02 | 3.97E+02 | 7.84E+02 |
| Fe | 1.19E+03 | 6.42E+02 | 5.24E+02 | 5.27E+02 | 1.38E+03 | 1.05E+03 | 5.63E+02 | 6.01E+02 | 4.32E+02 | 3.76E+02 | 6.15E+02 | 9.70E+02 | 7.69E+02 | 1.10E+03 | 8.53E+02 |
| Co | 3.62 | 2.49 | 3.10 | 3.62 | 1.94 | 1.41 | 2.37 | 2.12 | 1.99 | 4.04 | 0.571 | 0.918 | 0.746 | 1.51 | 0.965 |
| Ni | 14.7 | 11.1 | 15.6 | 9.87 | 33.0 | 7.89 | 14.3 | 8.19 | 5.75 | 12.2 | 11.4 | 12.9 | 6.07 | 12.1 | 8.82 |
| Cu | 287 | 350 | 98 | 137 | 9.9 | 20.6 | 635 | 38.9 | 30.1 | 56.9 | < LoD | 47.6 | 23.3 | 36.9 | 17.6 |
| Zn | 7.18E+02 | 4.80E+02 | 3.82E+02 | 5.59E+02 | 9.72E+01 | 2.24E+02 | 6.46E+02 | 5.38E+02 | 5.50E+02 | 5.53E+02 | < LoD | 3.08E+02 | 2.06E+02 | 1.89E+02 | 1.89E+02 |
| Ga | 1.23 | 0.78 | < LoD | < LoD | 2.77 | 3.95 | 1.88 | 0.71 | 1.03 | 1.12 | 2.78 | 1.57 | 1.84 | 2.31 | 3.52 |
| As | 0.73 | 0.33 | < LoD | 0.73 | 0.50 | 0.50 | 0.92 | 0.68 | 0.63 | 0.64 | 0.62 | < LoD | 0.48 | < LoD | 0.32 |
| Rb | 7.25E+02 | 1.23E+03 | 1.33E+03 | 5.33E+02 | 7.64E+02 | 3.43E+02 | 6.26E+02 | 3.61E+02 | 8.44E+02 | 8.25E+02 | 2.80E+02 | 1.01E+03 | 2.83E+02 | 7.82E+02 | 2.19E+02 |
| Sr | 1.80E+02 | 1.65E+02 | 1.48E+02 | 2.05E+02 | 1.77E+02 | 4.69E+02 | 1.08E+02 | 1.12E+02 | 2.54E+02 | 2.70E+02 | 2.00E+02 | 2.28E+02 | 2.06E+02 | 3.40E+02 | 1.88E+02 |
| Mo | 0.812 | 0.589 | 0.520 | 1.182 | 0.959 | 0.892 | 0.383 | 1.42 | 0.658 | 1.18 | 1.35 | 0.733 | 1.64 | 2.64 | 2.48 |
| Ba | 28.7 | 21.2 | 12.0 | 11.6 | 58.9 | 89.7 | 43.4 | 17.5 | 25.1 | 27.4 | 61.0 | 37.2 | 43.5 | 54.5 | 79.6 |
| Pb | 50.30 | < LoD | 6.26 | < LoD | 5.28 | 3.52 | 5.86 | 7.59 | 7.32 | 5.18 | 4.34 | < LoD | 4.23 | 3.09 | 3.36 |
| U | 0.437 | 0.035 | < LoD | < LoD | 0.226 | 0.078 | 0.620 | 0.153 | 0.263 | 0.148 | 0.157 | 0.096 | 0.153 | 0.364 | 0.0819 |
| Ca | 5.90E+04 | 4.93E+04 | 6.04E+04 | 6.38E+04 | 5.32E+04 | 5.29E+04 | 5.49E+04 | 5.94E+04 | 5.47E+04 | 5.09E+04 | 4.85E+04 | 4.27E+04 | 5.58E+04 | 5.84E+04 | 5.42E+04 |
| $^{87}Sr/^{86}Sr$ | 0.71009 | 0.71029 | 0.71037 | 0.70994 | 0.71029 | 0.71090 | 0.71246 | 0.71141 | 0.71046 | 0.71036 | 0.70865 | 0.70901 | 0.70901 | 0.70884 | 0.70857 |

| Analyte | W81 | W31 | W33 | W56 | W79 | W84 | W57 | W68 | W28 | W93 | W67 | W58 | W88 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Li | 2.84 | 1.38 | 1.28 | 2.81 | 2.66 | 1.54 | 0.866 | 2.57 | 2.37 | 2.06 | 10.9 | 1.13 | 1.61 |
| B | 7.42E+03 | 5.81E+03 | 6.44E+03 | 6.62E+03 | 1.55E+03 | 7.73E+03 | 6.86E+03 | 5.74E+03 | 7.73E+03 | 8.03E+03 | 3.89E+03 | 5.97E+03 | 3.65E+03 |
| Mg | 8.00E+04 | 7.30E+04 | 5.90E+04 | 7.49E+04 | 7.59E+04 | 7.19E+04 | 7.89E+04 | 7.33E+04 | 6.83E+04 | 6.91E+04 | 6.63E+04 | 9.38E+04 | 5.80E+04 |
| Cr | 1.53E+02 | 1.91E+02 | 1.46E+02 | 1.62E+02 | 2.05E+02 | 1.90E+02 | 1.67E+02 | 1.46E+02 | 1.26E+02 | 2.47E+02 | 1.61E+02 | 2.59E+02 | 1.43E+02 |
| Mn | 4.14E+02 | 6.16E+02 | 5.04E+02 | 9.31E+02 | 7.79E+02 | 7.34E+02 | 1.08E+03 | 4.45E+02 | 1.12E+03 | 9.57E+02 | 3.85E+02 | 1.30E+03 | 5.30E+02 |
| Fe | 9.84E+02 | 1.36E+03 | 1.16E+03 | 1.31E+03 | 2.88E+03 | 2.40E+03 | 1.33E+03 | 1.07E+03 | 8.92E+02 | 1.38E+03 | 7.02E+02 | 1.19E+03 | 3.12E+02 |
| Co | 1.86 | 1.44 | 0.64 | 1.51 | 1.11 | 1.22 | 1.50 | 4.49 | 1.53 | 1.26 | 3.45 | 3.01 | 1.10 |
| Ni | 12.7 | 69.9 | 10.9 | 15.8 | 30.1 | 10.4 | 10.9 | 8.88 | 18.2 | 12.0 | 15.5 | 17.2 | 7.54 |
| Cu | 31.3 | 32.6 | 31.5 | 34.4 | 26.9 | 12.1 | 143 | 179 | 9.2 | 44.6 | 220 | 319 | 410 |
| Zn | 1.88E+02 | 1.74E+02 | < LoD | 5.72E+02 | 3.52E+02 | 2.69E+02 | 3.65E+02 | 1.52E+03 | 3.45E+02 | 4.31E+02 | 5.17E+02 | 6.17E+02 | 2.20E+02 |
| Ga | 2.43 | 2.11 | 1.07 | 2.10 | 1.94 | 1.30 | 2.54 | 0.99 | 3.48 | 1.73 | 1.14 | 2.44 | < LoD |
| As | < LoD | 0.79 | 0.56 | 0.41 | < LoD | < LoD | 0.66 | 0.81 | 2.54 | < LoD | 0.66 | 0.77 | 0.69 |
| Rb | 8.31E+02 | 4.56E+02 | 5.15E+02 | 1.23E+03 | 2.73E+03 | 5.14E+02 | 1.17E+03 | 3.94E+02 | 4.75E+02 | 5.22E+02 | 5.13E+02 | 5.51E+02 | 4.66E+02 |
| Sr | 3.58E+02 | 1.54E+02 | 1.41E+02 | 2.61E+02 | 1.42E+02 | 1.57E+02 | 2.74E+02 | 1.63E+02 | 2.71E+02 | 2.10E+02 | 1.34E+02 | 2.43E+02 | 7.97E+01 |
| Mo | 1.61 | 0.812 | 0.880 | 1.45 | 0.760 | 0.471 | 0.666 | 0.994 | 1.92 | 3.37 | 0.384 | 2.45 | 0.845 |
| Ba | 57.1 | 43.7 | 21.8 | 48.0 | 45.6 | 31.6 | 58.4 | 24.2 | 75.3 | 42.5 | 27.4 | 56.7 | 16.4 |
| Pb | 5.11 | 7.35 | 4.98 | 9.09 | 5.97 | 5.49 | 6.36 | 8.99 | 7.39 | < LoD | 10.2 | 17.9 | < LoD |
| U | 0.685 | 0.380 | 0.186 | 3.921 | 0.158 | 0.457 | 0.479 | 0.257 | 0.656 | < LoD | 0.911 | 0.423 | 0.030 |
| Ca | 5.68E+04 | 5.57E+04 | 4.98E+04 | 5.82E+04 | 5.22E+04 | 4.99E+04 | 5.56E+04 | 8.47E+04 | 4.79E+04 | 6.85E+04 | 5.63E+04 | 7.33E+04 | 6.11E+04 |
| $^{87}Sr/^{86}Sr$ | 0.70916 | 0.70932 | 0.71049 | 0.71019 | 0.71088 | 0.71010 | 0.71244 | 0.70986 | 0.70963 | 0.70987 | 0.71019 | 0.71022 | 0.71009 |

## 6.2 Sample code and element concentration of pumpkin seeds and pumpkin seed oil

| sample code | | | | | Poil (3-5) | Goil (1-3) | stmk1-oil | stmk2-oil | stmk3-oil | 152215 | 149875 | 149877 | 149872 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| initial weight (g) | | | | | 0.7 - 1 | ~ 1 | 0.212 | 0.149 | 0.184 | 0.161 | 0.357 | 0.223 | 0.196 |
| total weight (g) | | | | | 15 | ~ 10 | 10.392 | 9.870 | 10.208 | 10.720 | 10.245 | 10.134 | 10.260 |
| Analyte | Mass | $LoD_4$ | $LoQ_4$ | RSU (%) | Supermarket | Styria | Hungary | Hungary | Hungary | Hungary | Styria (low) | Lower A. (low) | Styria (low) |
| B | 10 | 1.53E+02 | 5.10E+02 | | < LoD | < LoD | 1.70E+03 | 2.59E+03 | 2.04E+03 | 2.91E+03 | 2.31E+03 | 2.95E+03 | 1.69E+03 |
| Na | 23 | 5.32E+02 | 1.77E+03 | 4.9 | 2.19E+04 | 4.70E+04 | 1.45E+03 | 1.98E+03 | 2.14E+03 | 7.02E+03 | 3.67E+03 | 1.89E+03 | 1.52E+03 |
| Mg | 26 | 1.80E+02 | 5.99E+02 | 4.5 | 5.91E+04 | 7.62E+04 | 2.34E+03 | 2.80E+03 | 1.16E+03 | 1.27E+04 | 8.05E+03 | 4.28E+03 | 3.52E+03 |
| Cr | 52 | 19.1 | 63.7 | 3.7 | 1.06E+03 | 1.84E+03 | 1.20E+03 | 1.30E+03 | 1.04E+03 | 7.07E+02 | 1.11E+03 | 1.78E+03 | 1.55E+03 |
| Mn | 55 | 19.4 | 64.8 | 5.4 | 387 | 496 | < LoD | < LoD | 3.60 | 10.5 | 25.7 | 7.90 | 13.5 |
| Fe | 57 | 3.09E+02 | 1.03E+03 | 8.6 | 3.69E+03 | 3.93E+03 | 1.63E+02 | 3.84E+02 | 3.50E+02 | 4.68E+02 | 8.98E+02 | 1.62E+02 | 3.10E+02 |
| Ni | 60 | 5.37 | 17.9 | | < LoD | 8.49 | < LoD | 24.1 | 5.17 | 21.1 | < LoD | < LoD | < LoD |
| Cu | 63 | 3.47 | 11.6 | 8 | 201 | 507 | < LoD | 16.3 | < LoD | 54.0 | 320 | 143 | 180 |
| Zn | 66 | 18.2 | 60.8 | 5.7 | 339 | 262 | 12.4 | 170 | 118.96 | 178 | 63.9 | 15.7 | 124 |
| Ga | 69 | 0.310 | 1.03 | 5.8 | 3.24 | 3.00 | 0.921 | < LoD | 1.102 | 0.367 | 1.26 | < LoD | < LoD |
| Rb | 85 | 0.208 | 0.695 | 4.6 | 72.3 | 28.7 | < LoD | < LoD | < LoD | 6.61 | 5.20 | < LoD | 1.08 |
| Sr | 88 | 9.08 | 30.3 | 6.4 | 263 | 132 | 36.9 | 19.3 | 23.3 | 37.3 | 3.89 | < LoD | < LoD |
| Mo | 98 | 0.616 | 2.05 | 29 | < LoD | 0.296 | < LoD | < LoD | < LoD | < LoD | < LoD | < LoD | < LoD |
| Ba | 138 | 0.329 | 1.10 | 3.4 | 56.4 | 86.7 | 4.32 | 5.93 | 17.2 | 13.1 | 33.4 | < LoD | 5.08 |
| Pb | 208 | 0.453 | 1.51 | 56 | < LoD | 7.16 | < LoD | 11.2 | 5.86 | 27.8 | 4.83 | 1.49 | 4.02 |
| U | 238 | 0.497 | 1.66 | 18 | < LoD | < LoD | 0.804 | < LoD | < LoD | 2.66 | < LoD | < LoD | 0.880 |
| Ca | 44 | 5.97E+03 | 1.99E+04 | 6.1 | 4.40E+04 | 4.54E+04 | 1.52E+04 | 4.49E+04 | 1.32E+04 | 3.36E+04 | 1.56E+04 | 1.36E+04 | 1.43E+04 |
| K | 39 | 2.84E+03 | 9.48E+03 | 6.3 | 9.99E+04 | 7.00E+04 | < LoD | < LoD | < LoD | 8.89E+03 | 1.49E+04 | < LoD | 2.32E+03 |
| La | 139 | 0.020 | 0.067 | 6.3 | 1.72 | 1.94 | 0.588 | < LoD | 0.822 | < LoD | 1.39 | < LoD | p.c. |
| Ce | 140 | 0.028 | 0.094 | 5.1 | 3.60 | 2.24 | 1.12 | < LoD | 1.38 | < LoD | 2.30 | < LoD | p.c. |
| Pr | 141 | 0.011 | 0.036 | 4.2 | 0.400 | 0.379 | 0.168 | < LoD | 0.203 | < LoD | 0.277 | < LoD | p.c. |
| Nd | 145 | 0.080 | 0.268 | 24 | 1.55 | 1.51 | 0.708 | < LoD | 0.835 | < LoD | 0.909 | < LoD | p.c. |
| Sm | 149 | 0.036 | 0.120 | 32 | 0.333 | 0.346 | 0.093 | < LoD | 0.177 | < LoD | 0.190 | < LoD | < LoD |
| Dy | 161 | 0.028 | 0.092 | 19 | 0.317 | 0.354 | < LoD | < LoD | < LoD | < LoD | < LoD | < LoD | < LoD |
| Er | 166 | 0.013 | 0.043 | 20 | 0.152 | 0.199 | < LoD | < LoD | < LoD | < LoD | < LoD | < LoD | < LoD |
| Yb | 171 | 0.023 | 0.077 | 24 | 0.081 | 0.109 | < LoD | < LoD | < LoD | < LoD | < LoD | < LoD | < LoD |
| $^{87}Sr/^{86}Sr$ | | | | 0.04 | 0.71106 | 0.71168 | n.e | n.e | n.e | n.e | n.e | n.e | n.e |

n.e. not evaluated due to low Sr concentration in solution; p.c. probably contaminated

**Table 43: Concentration of elements, $LoD_4$ and $LoQ_4$ in ng $g^{-1}$ as well as RSU (k=2) and $^{87}Sr/^{86}Sr$ ratio of pumpkin seed oil; highlighted concentrations were below limit of quantification while LoD is referred to $LoD_4$; highlighted ratios did not fulfill requirements but were used for evaluation as well; to be continued on the following pages**

| sample code | 152216 | 152217 | kk-oil-152218 | Noe | China | Serb | Slov |
|---|---|---|---|---|---|---|---|
| initial weight (g) | 0.224 | 0.181 | 0.645 | ~ 1 | ~ 1 | ~ 1 | ~ 1 |
| total weight (g) | 10.554 | 10.078 | 10.086 | ~ 10 | ~ 10 | ~ 10 | ~ 10 |
| Analyte | Croatia | China (low) | Unknown | L. Austria | China | Serbia | Slovenia |
| B | 6.23E+03 | 6.48E+03 | 2546.32714 | < LoD | 125 | < LoD | < LoD |
| Na | 8.17E+03 | 9.19E+03 | 5.00E+04 | 2.41E+04 | 5.34E+04 | 1.92E+03 | 3.28E+04 |
| Mg | 2.19E+04 | 3.45E+04 | 8.85E+04 | 4.23E+04 | 2.10E+04 | 1.45E+04 | 4.99E+04 |
| Cr | 9.26E+02 | 1.82E+03 | 1.25E+03 | 2.11E+03 | 1.94E+03 | 1.85E+03 | 1.88E+03 |
| Mn | 79.8 | 190 | 533 | 314 | 415 | 76.2 | 315.8 |
| Fe | 8.19E+02 | 5.66E+02 | 3.75E+03 | 3.46E+03 | 6.05E+03 | 8.13E+02 | 2.61E+03 |
| Ni | 13.1 | 4.59 | 9.37 | < LoD | < LoD | < LoD | 4.31 |
| Cu | 81.6 | 11.9 | 86.0 | 325 | 45.4 | 5.26 | 141 |
| Zn | 275 | 592 | 273 | 310 | 410 | 26.9 | 161 |
| Ga | 0.309 | 1.10 | 4.61 | 2.40 | 7.87 | 1.01 | 1.37 |
| Rb | 15.5 | 6.98 | 58.2 | 29.6 | 3.50 | 11.5 | 29 |
| Sr | < LoD | 201 | 570 | 41.0 | 257 | 24.2 | 49 |
| Mo | < LoD | < LoD | 6.22 | 0.653 | < LoD | < LoD | 1.03 |
| Ba | 4.14 | 38.4 | 85.2 | 56.5 | 170 | 30.3 | 34.3 |
| Pb | 10.8 | 27.7 | 6.35 | 1.31 | 17.3 | < LoD | 1.48 |
| U | 1.32 | 0.494 | 1.05 | < LoD | 2.11 | < LoD | < LoD |
| Ca | 2.11E+04 | 6.81E+04 | 9.49E+04 | 4.18E+04 | 4.64E+04 | 2.81E+04 | 3.92E+04 |
| K | 1.52E+04 | 1.43E+04 | 8.01E+04 | 5.12E+04 | 3.47E+03 | 6.84E+03 | 3.73E+04 |
| La | < LoD | 1.202 | 1.10 | 1.65 | 8.18 | 0.289 | 1.55 |
| Ce | < LoD | 2.427 | 2.23 | 2.59 | 13.44 | 0.405 | 1.24 |
| Pr | < LoD | 0.271 | 0.276 | 0.346 | 1.634 | 0.086 | 0.259 |
| Nd | < LoD | 0.817 | 1.06 | 1.43 | 6.11 | 0.193 | 0.967 |
| Sm | < LoD | 0.124 | 0.230 | 0.326 | 1.136 | 0.045 | 0.180 |
| Dy | < LoD | < LoD | 0.196 | 0.295 | 0.989 | 0.044 | 0.183 |
| Er | < LoD | < LoD | 0.098 | 0.154 | 0.479 | 0.020 | 0.094 |
| Yb | < LoD | < LoD | 0.065 | 0.081 | 0.267 | 0.008 | 0.054 |
| $^{87}Sr/^{86}Sr$ | n.e | n.e | 0.71135 | 0.70968 | 0.70943 | 0.71024 | 0.71048 |

| initial weight [g] | | | | | 0.5 | 1 | | 10 | 0.177 | 0.147 | 0.123 | 0.282 | 0.305 | 0.383 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| total weight [g] | | | | | 15 | 10 | | 25 | 10.525 | 10.627 | 10.280 | 10.108 | 10.286 | 10.101 |
| Analyte | Mass | $LoD_4$ | $LoQ_4$ | RSU (%) | Market seed | Styria seed | creek | soil | stmk1-p | stmk2-p | stmk3-p | stmk1 | stmk2 | stmk3 |
| Li | 7 | 0.637 | 2.12 | 7.8 | 6.35 | 8.05 | 3.02 | 69.2 | 67.0 | 93.7 | 84.5 | 16.6 | 45.9 | 23.1 |
| B | 10 | 7.78E+01 | 2.59E+02 | 5.4 | 1.21E+04 | 1.68E+04 | 4.22E+01 | 1.25E+02 | 2.42E+04 | 2.08E+04 | 2.08E+04 | 1.08E+04 | 1.07E+04 | 1.06E+04 |
| Na | 23 | 3.33E+01 | 1.11E+02 | 3.4 | 3.03E+04 | 8.35E+03 | 1.44E+04 | 6.37E+03 | 3.81E+04 | 2.60E+04 | 6.34E+04 | 2.02E+04 | 1.24E+04 | 4.40E+04 |
| Mg | 26 | 7.07E+01 | 2.36E+02 | 3.3 | 4.42E+06 | 5.16E+06 | 1.30E+04 | 4.02E+05 | 8.51E+06 | 9.06E+06 | 9.03E+06 | 4.39E+06 | 4.66E+06 | 4.68E+06 |
| Al | 27 | 25.5 | 85.0 | 12 | 3.37E+03 | 4.99E+03 | 3.78E+02 | 5.42E+02 | 2.83E+04 | 8.12E+04 | 6.22E+04 | 1.36E+04 | 4.29E+04 | 2.66E+04 |
| V | 51 | 0.70 | 2.32 | 8.1 | 7.16 | 13.5 | 2.25 | 3.45 | 74.6 | 205 | 128 | 1687 | 773 | 836 |
| Cr | 52 | 11.3 | 37.5 | 5.4 | 9.10E+02 | 1.34E+03 | 1.78E+00 | < LoD | 9.57E+02 | 1.29E+03 | 1.06E+03 | 7.58E+02 | 1.35E+03 | 1.17E+03 |
| Mn | 55 | 1.23 | 4.11 | 4.6 | 3.43E+04 | 5.54E+04 | 9.11E+01 | 6.39E+03 | 9.52E+04 | 8.56E+04 | 8.82E+04 | 5.06E+04 | 4.48E+04 | 4.60E+04 |
| Fe | 57 | 1.12E+02 | 3.74E+02 | 3.1 | 8.64E+04 | 1.21E+05 | 1.60E+03 | 1.32E+04 | 2.46E+05 | 2.68E+05 | 2.42E+05 | 1.24E+05 | 1.37E+05 | 1.21E+05 |
| Co | 59 | 0.17 | 0.58 | 3.1 | 47.9 | 100 | 0.897 | 10.3 | 122 | 182 | 137 | 57.4 | 96.3 | 66.5 |
| Ni | 60 | 1.93 | 6.43 | 6.6 | 7.76E+02 | 3.13E+03 | 5.85E+00 | 1.71E+02 | 5.13E+03 | 3.92E+03 | 6.45E+03 | 2.59E+03 | 1.92E+03 | 3.10E+03 |
| Cu | 63 | 1.07 | 3.57 | 7.0 | 1.44E+04 | 1.17E+04 | 2.45 | 4.10E+01 | 2.87E+04 | 2.77E+04 | 2.72E+04 | 1.48E+04 | 1.42E+04 | 1.45E+04 |
| Zn | 66 | 4.93 | 16.45 | 7.7 | 8.31E+04 | 6.68E+04 | 4.70 | 4.09E+02 | 1.58E+05 | 1.55E+05 | 1.41E+05 | 7.96E+04 | 6.68E+04 | 6.78E+04 |
| Ga | 69 | 0.308 | 1.03 | 4.6 | 14.1 | 29.0 | 3.10 | 1.56E+03 | 98.1 | 149 | 141 | 48.1 | 76.0 | 64.9 |
| As | 75 | 0.705 | 2.35 | 23 | 10.0 | 7.63 | 3.60 | 3.83 | 27.9 | 35.9 | 34.0 | 12.4 | 21.9 | 20.6 |
| Se | 77 | 19.7 | 65.7 | 86 | 79.7 | 24.5 | 0.62 | < LoD | 267 | 204 | 327 | 147 | 128 | 214 |
| Rb | 85 | 0.207 | 0.689 | 4.6 | 5.34E+03 | 4.62E+03 | 4.46E+00 | 2.19E+02 | 1.70E+04 | 1.59E+04 | 1.73E+04 | 8.50E+03 | 8.32E+03 | 9.11E+03 |
| Sr | 88 | 0.560 | 1.866 | 5.5 | 1.67E+03 | 2.35E+03 | 2.58E+02 | 8.79E+03 | 5.60E+03 | 4.94E+03 | 4.88E+03 | 2.74E+03 | 2.52E+03 | 2.21E+03 |
| Mo | 98 | 0.305 | 1.016 | 5.9 | 1.40E+03 | 3.52E+02 | 4.72E-01 | < LoD | 1.01E+03 | 2.08E+03 | 1.93E+03 | 5.23E+02 | 1.06E+03 | 9.79E+02 |
| Cd | 114 | 0.316 | 1.055 | 7.4 | 9.0204 | 7.5576 | 0.0178 | 6.3851 | 19.8105 | 31.0820 | 21.4878 | 9.5971 | 13.1895 | 10.9058 |
| Ba | 138 | 0.429 | 1.431 | 3.8 | 2.82E+02 | 8.56E+02 | 4.43E+01 | 3.76E+04 | 2.42E+03 | 3.21E+03 | 3.30E+03 | 1.14E+03 | 1.61E+03 | 1.43E+03 |
| Pb | 208 | 0.357 | 1.189 | 11 | 9.23 | 13.9 | 0.809 | < LoD | 50.6 | 394 | 58.8 | 30.5 | 196 | 35.0 |
| U | 238 | 0.042 | 0.141 | 25 | 2.15 | 1.16 | 2.36 | < LoD | 12.2 | 10.4 | 12.4 | 6.34 | 2.76 | 3.24 |
| Ca | 44 | 5.10E+02 | 1.70E+03 | 6.7 | 5.52E+05 | 7.63E+05 | 6.87E+04 | 3.85E+06 | 1.71E+06 | 1.78E+06 | 1.34E+06 | 8.68E+05 | 9.33E+05 | 6.87E+05 |
| K | 39 | 2.69E+02 | 8.97E+02 | 6.3 | a. l. | a.l. | 8.60E+03 | < LoD | a.l. | a.l. | a.l. | a.l. | a.l. | a.l. |
| Sr IR | | | | 0.04 | 0.71066 | 0.71189 | 0.71074 | 0.71109 | 0.70987 | 0.70866 | 0.70990 | 0.70987 | 0.70856 | 0.70972 |

**Table 44: Concentration of multi-elements, $LoD_4$ and $LoQ_4$ in ng $g^{-1}$ as well as RSU (k=2) and $^{87}Sr/^{86}Sr$ ratio of pumpkin seed; K was above linear range (a.l.) for seed and soil samples and concentration could not be determined**

| initial weight [g] | | | | | 0.5 | 1 | | 10 | 0.177 | 0.147 | 0.123 | 0.282 | 0.305 | 0.383 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| total weight [g] | | | | | 15 | 10 | | 25 | 10.525 | 10.627 | 10.280 | 10.108 | 10.286 | 10.101 |
| Analyte | Mass | $LoD_4$ | $LoQ_4$ | RSU (%) | Market seed | Styria seed | creek | soil | stmk1-p | stmk2-p | stmk3-p | stmk1 | stmk2 | stmk3 |
| La | 139 | 2.00E-02 | 6.68E-02 | 2.3 | 1.7 | 23.5 | 0.156 | 15.0 | 21.6 | 94.3 | 58.7 | 20.8 | 46.0 | 20.3 |
| Ce | 140 | 2.80E-02 | 9.35E-02 | 2.7 | 3.60 | 23.9 | 0.327 | 9.60 | 42.3 | 185 | 108 | 42.7 | 97.5 | 37.1 |
| Pr | 141 | 1.07E-02 | 3.55E-02 | 6.8 | 0.400 | 4.19 | 0.039 | 1.32 | 5.52 | 22.5 | 13.1 | 5.13 | 11.6 | 4.91 |
| Sm | 149 | 3.60E-02 | 1.20E-01 | 4.6 | 0.333 | 3.48 | 0.035 | 1.75 | 5.19 | 17.5 | 8.18 | 4.25 | 10.3 | 4.12 |
| Nd | 145 | 8.03E-02 | 2.68E-01 | 6.9 | 1.55 | 16.6 | 0.157 | 4.88 | 21.8 | 86.5 | 44.2 | 20.6 | 46.9 | 19.1 |
| Ho | 165 | 2.28E-03 | 7.59E-03 | 7.7 | 0.048 | 0.549 | 0.004 | 0.093 | 0.654 | 2.00 | 1.30 | 0.453 | 1.24 | 0.543 |
| Er | 166 | 1.28E-02 | 4.28E-02 | 4.1 | 0.152 | 1.716 | 0.017 | 0.345 | 2.07 | 6.36 | 4.05 | 1.57 | 4.04 | 1.90 |
| Tm | 169 | 2.94E-03 | 3.81E-03 | 17 | 0.020 | 0.180 | 0.001 | 0.043 | 0.261 | 0.680 | 0.433 | 0.135 | 0.463 | 0.188 |
| Yb | 171 | 2.31E-02 | 7.69E-02 | 25 | 0.081 | 0.818 | 0.010 | 0.155 | 1.13 | 3.20 | 2.12 | 0.650 | 2.19 | 0.982 |
| Tb | 159 | 2.52E-02 | 8.39E-03 | 5.5 | 0.064 | 0.737 | 0.006 | 0.148 | 0.877 | 2.89 | 1.65 | 0.708 | 1.717 | 0.776 |
| Dy | 161 | 2.77E-02 | 9.24E-02 | 4.6 | 0.317 | 3.43 | 0.032 | 0.648 | 4.32 | 13.006 | 7.66 | 3.23 | 8.33 | 3.61 |
| Sc | 45 | 3.27E-02 | 1.09E-01 | 21 | 0.133 | 1.35 | 0.009 | 2.43 | 5.44 | 18.042 | 12.589 | 3.11 | 10.333 | 5.43 |

**Table 45: Concentration of REE, $LoD_4$ and $LoQ_4$ in ng $g^{-1}$ as well as RSU (k=2) of pumpkin seed**

## 6.3 Phosphorus data

| Internal Standard | Ga (DRC) | Ge (DRC) |
|---|---|---|
| Sample code | c P [ng g-1] | c P [ng g-1] |
| 1% acid P | 1.69E+03 | 1.16E+03 |
| 2% acid P | 1.63E+03 | 1.10E+03 |
| 3% acid P | 1.58E+03 | 1.03E+03 |
| 5% acid P | 1.47E+03 | 9.29E+02 |
| 10% acid P | 1.21E+03 | 7.93E+02 |
| S.1 | 5.11E+05 | 3.12E+05 |
| S.2 | 2.15E+05 | 1.25E+05 |
| S.3 | 1.48E+07 | 8.14E+06 |

**Table 46: Concentration of measured samples using Ga and Ge as internal normalization standard in DRC mode**

| Internal Standard | In (Std) | |
|---|---|---|
| Sample | c P [ng g-1] | RSU [%] |
| Std5 | 1.03E+03 | 2.6 |
| c 1_10 | 2.41E+06 | 4.6 |
| c 1_50 | 2.83E+06 | 4.4 |
| c 1_100 | 2.20E+06 | 2.1 |
| c 2_10 | 2.37E+06 | 4.6 |
| c 2_50 | 2.62E+06 | 4.4 |
| c 2_100 | 2.68E+06 | 2.1 |
| Std2 | 1.08E+02 | 2.6 |
| S_10 | 1.44E+07 | 4.2 |
| S_100 | 1.89E+07 | 3.5 |
| S_50 | 2.05E+07 | 2.8 |
| O_10 | 3.65E+05 | 2.5 |
| O_50 | 3.70E+05 | 6.5 |
| O_100 | 3.62E+05 | 10 |
| Std5 | 1.30E+03 | 2.6 |

**Table 47: Concentration of measured samples using In as internal standard in standard mode**

## 6.4 Reference Material

CLARITAS PPT™

CERTIFICATE OF ANALYSIS

**Catalog Number:** CLMS-1

**Description:** Multi-element Solution 1

**Matrix:** 5% HNO3

**Lot Number:** 12-143AS

**Instrument Analysis by ICP Spectrometer:**

| Analyte | Labeled (ug/mL) | Measured (ug/mL) | NIST SRM |
|---|---|---|---|
| Ce | 10.00 | 10.09 | 3110 |
| Dy | 10.00 | 10.02 | 3115a |
| Er | 10.00 | 10.06 | 3116a |
| Eu | 10.00 | 10.03 | 3117a |
| Gd | 10.00 | 10.05 | 3118a |
| Ho | 10.00 | 10.20 | 3123a |
| La | 10.00 | 10.05 | 3127a |
| Lu | 10.00 | 10.17 | 3130a |
| Nd | 10.00 | 10.04 | 3135a |
| Pr | 10.00 | 10.03 | 3142a |
| Sc | 10.00 | 10.08 | 3148a |
| Sm | 10.00 | 10.11 | 3147a |
| Tb | 10.00 | 10.09 | 3157a |
| Th | 10.00 | 10.04 | 3159 |
| Tm | 10.00 | 10.03 | 3160a |
| Y | 10.00 | 10.03 | 3167 |
| Yb | 10.00 | 10.05 | 3166a |

**SPEX Chemical Reference Multi Lot Number:** 2-247BOREF, 10-108AS, 9.96AS

**Trace Metallic Impurities in the Actual Solution, in PPB, via ICP-MS Analysis:**

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Ag | 0.30 | Cd | 0.06 | Hg | <0.01 | Nb | 0.02 | Ru | <0.01 | Tl | 0.2 |
| Al | 4.00 | Co | 0.02 | In | 0.20 | Ni | <0.05 | Sb | 0.05 | U | 0.03 |
| As | <30.00 | Cr | <0.20 | Ir | <0.30 | P | <5.00 | Se | <2000 | V | <0.02 |
| Au | <0.02 | Cs | <0.01 | K | <10.00 | Pb | 3.00 | Si | <20.00 | W | <40.00 |
| B | <0.10 | Cu | 0.20 | Li | <0.04 | Pd | 0.20 | Sn | 0.10 | Zn | <0.50 |
| Ba | 0.30 | Fe | <5.00 | Mg | 10.00 | Pt | 0.04 | Sr | 1.00 | Zr | 0.70 |
| Be | <0.01 | Ga | <0.20 | Mn | <0.20 | Rb | <2.00 | Ta | <60.00 | | |
| Bi | <0.20 | Ge | <30.00 | Mo | 0.30 | Re | <0.70 | Te | 0.05 | | |
| Ca | 25.00 | Hf | <50.00 | Na | 5.00 | Rh | <0.01 | Ti | 0.30 | | |

Balances are calibrated with NIST weight sets NJ #92589 and #92550, according to NIST circular 547 3.4.3

CLARITAS PPT reference standards are guaranteed stable and accurate to ± 0.5%, averaged certified analyte concentrations, for a period of one year from date of shipment. For these solutions we use the highest purity acids applicable, 18 megohm double-deionized water and acid-leached, triple-rinsed bottles. All glassware used is Class A.

Manufacturing Manager

OCT 15 1998
Date

SPEX CertiPrep
203 NORCROSS AVENUE
METUCHEN, NJ 08840
908-549-7144
1-800-LAB-SPEX
FAX: 908-603-9647
E-mail: CRMSales@spexcsp.com

ISO 9001 CERTIFIED

PRELIMINARY

# United States Geological Survey
# Certificate of Analysis

## Basalt, Hawaiian Volcanic Observatory, BHVO-2

Material used in the preparation of BHVO-2 was taken from the surface layer of the pahoehoe lava that overflowed from the Halemaumau crater in the fall of 1919. This is the same location used to provide material for BHVO-1. Collection of BHVO-2 was accomplished in 1995 under the direction of Carl Thornberg, USGS. Details of the collection, preparation, and testing are available (Wilson, S.A., 1998).

Element concentrations were determined in a round robin study involving 20 international laboratories. Recommended values are listed when analytical results provided by three independent laboratories using a minimum of three independent analytical procedures are in statistical agreement. Information values with standard deviations are listed when at least two independent laboratories using two independent analytical procedures have provided information. Information values without standard deviations represent information from a single laboratory or analytical procedure.

**Recommended values**

| Element | Wt % | ± | Oxide | Wt % | ± |
|---|---|---|---|---|---|
| Al | 7.16 | 0.08 | $Al_2O_3$ | 13.5 | 0.2 |
| Ca | 8.17 | 0.12 | CaO | 11.4 | 0.2 |
| $Fe_{TOT}$ | 8.63 | 0.14 | $Fe_2O_{3\ TOT}$ | 12.3 | 0.2 |
| K | 0.43 | 0.01 | $K_2O$ | 0.52 | 0.01 |
| Mg | 4.36 | 0.07 | MgO | 7.23 | 0.12 |
| Na | 1.64 | 0.06 | $Na_2O$ | 2.22 | 0.08 |
| P | 0.12 | 0.01 | $P_2O_5$ | 0.27 | 0.02 |
| Si | 23.3 | 0.3 | $SiO_2$ | 49.9 | 0.6 |
| Ti | 1.63 | 0.02 | $TiO_2$ | 2.73 | 0.04 |

| Element | µg/g | ± | Element | µg/g | ± |
|---|---|---|---|---|---|
| Ba | 130 | 13 | Nd | 25.0 | 1.8 |
| Ce | 38 | 2 | Ni | 119 | 7 |
| Co | 45 | 3 | Rb | 9.8 | 1.0 |
| Cr | 280 | 19 | Sc | 32 | 1 |
| Cu | 127 | 7 | Sr | 389 | 23 |
| Ga | 21.7 | 0.9 | V | 317 | 11 |
| Hf | 4.1 | 0.3 | Y | 26 | 2 |
| La | 15 | 1 | Zn | 103 | 6 |
| Mn | 1290 | 40 | Zr | 172 | 11 |

## Information values

| Element | µg/g | ± | Element | µg/g | ± |
|---|---|---|---|---|---|
| F | 370 | | Sm | 6.2 | 0.4 |
| Gd | 6.3 | 0.2 | Sn | 1.9 | |
| Ho | 1.04 | 0.04 | Ta | 1.4 | |
| Li | 5 | | Tb | 0.9 | |
| Lu | 0.28 | 0.01 | Th | 1.2 | 0.3 |
| Nb | 18 | 2 | Yb | 2.0 | 0.2 |

## Bibliography

Wilson, S.A., 1997, Data compilation for USGS reference material BHVO-2, Hawaiian Basalt, U.S. Geological Survey Open-File Report xxxxx.

## Glossary

| | |
|---|---|
| Wt % | Percent of total element concentration |
| µg/g | Total element concentration expressed as micrograms of element per gram of solid sample |
| ± | One standard deviation |

Issued 4-30-98
Denver, Colorado

Dr. Geoff Plumlee
U.S. Geological Survey
Central Region Mineral Team

## Ordering Information

USGS reference materials (RMs) may be obtained directly from Dr. Stephen A. Wilson at the address or numbers listed below. The price for each bottle of RM is $80.00 (U.S.) **except** DGPM-1 which is $175.00 (U.S.). This cost includes all shipping and handling charges using normal mail delivery. Urgent requests for RMs should be initiated by FAX or e-mail. If required, overnight delivery is available with these charges added to the final bill.

Dr. Stephen A. Wilson
U.S. Geological Survey
Box 25046, MS 964
Denver, CO 80225

Tel: 303-236-2454
FAX: 303-236-3200 or 303-236-1425
e-mail: swilson@usgs.gov

## Payment Options

**Domestic customers:** Payment options include purchase order, check, money order, or credit card (Visa, Mastercard).

**International customers:** Payment on foreign orders may be made by any of the following:

a. Banker's draft against an international bank,
b. International money order,
c. Credit card (Visa, Mastercard)

Payments for domestic or international orders using a credit card receive a 10% discount on the per bottle price.

PRELIMINARY

# United States Geological Survey
# Certificate of Analysis

## Basalt, Columbia River, BCR-2

Material used in the preparation of BCR-2 was collected in 1996, from the Bridal Veil Flow Quarry under the direction of Stephen A. Wilson, U.S. Geological Survey. The quarry, located approximately 29 miles east of Portland, Oregon is the same collection site used to provide material for BCR-1.

Element concentrations were determined in a round-robin study involving 20 international laboratories. Recommended total element concentrations are reported when analytical results provided by three independent laboratories using a minimum of three independent analytical procedures are in statistical agreement. Information values with standard deviations, are provided when two or more independent laboratories using at least two independent analytical procedures have provided information. Information values without standard deviations represent information from a single laboratory or analytical procedure.

### Recommended values

| Element | Wt % | ± | Oxide | Wt % | ± |
|---|---|---|---|---|---|
| Al | 7.14 | 0.10 | $Al_2O_3$ | 13.5 | 0.2 |
| Ca | 5.09 | 0.08 | CaO | 7.12 | 0.11 |
| $Fe_{tot}$ | 9.65 | 0.15 | $Fe_2O_{3\ tot}$ | 13.8 | 0.2 |
| K | 1.49 | 0.04 | $K_2O$ | 1.79 | 0.05 |
| Mg | 2.16 | 0.03 | MgO | 3.59 | 0.05 |
| Na | 2.34 | 0.08 | $Na_2O$ | 3.16 | 0.11 |
| P | 0.15 | 0.01 | $P_2O_5$ | 0.35 | 0.02 |
| Si | 25.3 | 0.4 | $SiO_2$ | 54.1 | 0.8 |
| Ti | 1.35 | 0.03 | $TiO_2$ | 2.26 | 0.05 |

| Element | µg/g | ± | Element | µg/g | ± |
|---|---|---|---|---|---|
| Ba | 683 | 28 | Rb | 48 | 2 |
| Ce | 53 | 2 | Sc | 33 | 2 |
| Co | 37 | 3 | Sr | 346 | 14 |
| Cr | 18 | 2 | Th | 6.2 | 0.7 |
| Eu | 2.0 | 0.1 | U | 1.69 | 0.19 |
| Ga | 23 | 2 | V | 416 | 14 |
| Gd | 6.8 | 0.3 | Y | 37 | 2 |
| La | 25 | 1 | Yb | 3.5 | 0.2 |
| Mn | 1520 | 60 | Zn | 127 | 9 |
| Mo | 248 | 17 | Zr | 188 | 16 |
| Nd | 28 | 2 | | | |

## Information values

| Element | µg/g | ± | Element | µg/g | ± |
|---|---|---|---|---|---|
| Cs | 1.1 | 0.1 | Lu | 0.51 | 0.02 |
| Cu | 19 | 2 | Pb | 11 | 2 |
| F | 440 | | Pr | 6.8 | 0.3 |
| Hf | 4.8 | 0.2 | Sm | 6.7 | 0.3 |
| Ho | 1.33 | 0.06 | Tb | 1.07 | 0.04 |
| Li | 9 | 2 | Tm | 0.54 | |

| Element | Isotopic Ratios | ± | N |
|---|---|---|---|
| Pb $^{206}/_{204}$ | 18.750 | 0.011 | 1 |
| Pb $^{207}/_{204}$ | 15.615 | 0.003 | 1 |
| Pb $^{208}/_{204}$ | 38.691 | 0.021 | 1 |

## Bibliography

Wilson, S.A., 1997, The collection, preparation and testing of USGS reference material BCR-2, Columbia River, Basalt, U.S. Geological Survey Open-File Report 98-00x.

## Glossary

| | |
|---|---|
| Wt % | Percent of total element concentration |
| µg/g | Total element concentration expressed as micrograms of element per gram of solid sample |
| ±- | One standard deviation |
| N | Number of labs reporting |

Issued 4-30-98
Denver, Colorado

Dr. Geoff Plumlee
U.S. Geological Survey
Central Region Mineral Team

## Ordering Information

USGS reference materials (RMs) may be obtained directly from Dr. Stephen A. Wilson at the address or numbers listed below. The price for each bottle of RM is $80.00 (U.S.) **except** DGPM-1 which is $175.00 (U.S.). This cost includes all shipping and handling charges using normal mail delivery. Urgent requests for RMs should be initiated by FAX or e-mail. If required, overnight delivery is available with these charges added to the final bill.

Dr. Stephen A. Wilson
U.S. Geological Survey
Box 25046, MS 964
Denver, CO 80225

Tel: 303-236-2454
FAX: 303-236-3200 or 303-236-1425
e-mail: swilson@usgs.gov

## 6.5 NICE File

```
Dim Obs_R, Fract, Sr88, Sr86, Sr87, Sr84, Rb85, Rb87, Kr83, Kr82

       Const M86 = 85.909267, M88 = 87.905619, M87 = 86.908884

       Const M84 = 83.91343, MRb87 = 86.90918, MRb85 = 84.91180

       Const True_R = 0.1194, Rb_Factor = 0.38506


' First subtract zero from all beams

    Sr88 = Mass(1, 3) - Zero(1, 3)

    Sr87 = Mass(1, 5) - Zero(1, 5)

    Sr86 = Mass(1, 7) - Zero(1, 7)

    Rb85 = Mass(1, 9) - Zero(1, 9)

' Calculate Fractionation factor

    Obs_R = Sr86 / Sr88

      Fract = (Log(True_R / Obs_R)) / (Log(M86 / M88))

      Rb87 = Rb85 * Rb_Factor / ((MRb87 / MRb85) ^ Fract)

    Result(0) = Fract

' Calculate 87/86 Ratio

    Result(1) = (Sr87 / Sr86) * (M87 / M86) ^ Fract

' Calculate measured 86/88

    Result(2) = Sr86 / Sr88

' Calculate Rb 85

    Result(3) = Rb85

' Calculate 87/86

     Sr87 = Sr87 - Rb87

    Result(4) = (Sr87 / Sr86) * (M87 / M86) ^ Fract

 ' Calculate Sr Beam

    Result(5) = Sr88 + Sr87 + Sr86
```

## 6.6 Foodtable Brunner, 2007

| sample type/ matrices | isotopic system/ elemental pattern | analytical method | literature reference |
|---|---|---|---|
| **beef** | | | |
| triglycerides | D/H<br>$^{13}C/^{12}C$<br>$^{18}O/^{16}O$ | NMR<br>GS-IRMS | (Renou et al., 2004) |
| defatted muscle tissue<br><br><br><br>meat water | $^{13}C/^{12}C$<br>$^{15}N/^{14}N$<br>$^{34}S/^{32}S$<br>$^{18}O/^{16}O$<br>D/H | CF-IRMS<br><br><br>GS-IRMS | (Schmidt et al., 2005) |
| raw protein | $^{15}N/^{14}N$<br>$^{13}C/^{12}C$<br>$^{34}S/^{32}S$ | GS-IRMS | (Boner and rstel, 2004) |
| **mutton** | | | |
| raw fat and protein<br>raw protein | $^{13}C/^{12}C$<br>$^{15}N/^{14}N$ | GS-IRMS | (Piasentier et al., 2003) |
| **pork** | | | |
| muscle tissue<br>liver tissue<br>adipose tissue | $^{13}C/^{12}C$ | GS-IRMS | (Gonzalez-Martin et al., 1999) |
| microwave digested<br>hepatic tissue | $^{13}C/^{12}C$<br>$^{34}S/^{32}S$ | GS-IRMS | (Gonzalez-Martn et al., 2001) |
| **milk** | | | |
| freeze-dried skim milk casein | $^{18}O/^{16}O$<br>$^{34}S/^{32}S$<br>$^{13}C/^{12}C$<br>$^{15}N/^{14}N$<br>$^{87}Sr/^{86}Sr$ | IRMS<br><br><br><br>TIMS | (Crittenden et al., 2007) |
| lyophilized milk<br>casein<br>whey<br>milk fat | $^{18}O/^{16}O$<br>$^{13}C/^{12}C$<br>$^{15}N/^{14}N$ | IRMS<br>CF-IRMS | (Kornexl et al., 1997) |
| microwave digested | Al, Sc, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, As, Ag, Pt, Au, Pb | ICP-SFMS | (Prohaska et al., 2000) |
| microwave digested milk skimmed milk and whey | Na, Ca, Mg, Al, Cr, Mn, Fe, Ni, Cu, Zn, Se, Sr, Cd, Hg, Pb | DF-ICP-MS | (Martino et al., 2001) |
| ultracentrifugated milk (whey) | Fe, Cu, Zn, Mn, Sr, I, Br, Ca, Mg | HPLC-ICP-MS | (Martino et al., 2002) |
| **buffalo milk/mozzarella** | | | |
| freeze-dried cheese | $^{1}H$<br>$^{13}C/^{12}C$<br>$^{15}N/^{14}N$ | NMR<br>CF-IRMS | (Brescia et al., 2005) |

| | | | |
|---|---|---|---|
| microwave digested | Li, Na, K, Mg, Ca, Al, Cr, Cu, Fe, Mn, Ni, Zn, Pb, Se, Ba | ICP-OES, ICP-AES | |
| **Emmental cheese** | | | |
| microwave digested | $^{90}Sr$<br>$^{238}U$ | AAS<br>α-spectrometry | (Froidevaux et al., 2004) |
| directly analysed | $^{1}H$ | HRMAS-NMR | (Shintu and Caldarelli, 2005) |
| glycerol<br>cheese water<br>defatted and lyophilised | $^{13}C/^{12}C$,<br>$^{18}O/^{16}O$<br>$^{15}N/^{14}N$,<br>D/H<br>$^{87}Sr/^{86}Sr$ | IRMS | (Pillonel et al., 2003) |
| acid digested<br>microwave digested<br>ashed | Ca, Mg, Na, K, Cu, Mn, Mo, I<br>$^{90}Sr$, $^{234}U$, $^{238}U$ | AAS<br>ICP-MS<br>α-spectrometry | |
| **cheese** | | | |
| casein and glycerol<br>casein<br>glycerol<br>casein | $^{13}C/^{12}C$<br>$^{18}O/^{16}O$<br>$^{15}N/^{14}N$<br>$^{34}S/^{32}S$ | IRMS | (Camin et al., 2004) |
| casein | $^{13}C/^{12}C$<br>$^{15}N/^{14}N$ | IRMS | (Manca et al., 2001) |
| **butter** | | | |
| bulk butter/proteins<br>melted butter<br>proteins | $^{13}C/^{12}C$<br>$^{18}O/^{16}O$<br>$^{15}N/^{14}N$<br>$^{34}S/32S$ | GS-IRMS<br>IRMS<br>GS-IRMS | (Rossmann et al., 2000) |
| ashed bulk butter | $^{87}Sr/^{86}Sr$ | TIMS | |
| butter, margarine (solubilized)<br>vegetable oils (used directly) | Cd, Co, Cr, Cu, Ni, Mn | ICP-OES | (De Souza et al., 2005) |
| **rice** | | | |
| microwave digested<br>powder | Al, Ca, Mg, P, Na, K, Mn, Fe, Co, Ni, Cu, Zn, Sr, Mb, Cd, Pb, REE<br>$^{13}C/^{12}C$<br>$^{18}O/^{16}O$ | ICP-MS<br>CF-IRMS | (Kelly et al., 2002) |
| brown rice | $^{87}Sr/^{86}Sr$ | ICP-MS | (Kawasaki et al., 2002) |
| **fresh fruits** | | | |
| homogenised, freeze-dried | Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, V, Zn<br>$^{15}N/^{14}N$<br>$^{13}C/^{12}C$ | ICP-AES | (Perez et al., 2006) |
| diluted and filtered | Ca, Mg | AAS | (Pohl and Prusisz, 2006) |

| | | | |
|---|---|---|---|
| **fruit juice** | | | |
| dilution | $^{13}C/^{12}C$<br>$^{18}O/^{16}O$<br>D/H | IRMS<br><br>GS-IRMS | (Koziet et al., 1995)<br>(Guillou et al., 1999) |
| extracted citric acid | D/H<br>$^{13}C/^{12}C$ | IRMS | (Jamin et al., 2005) |
| filtered<br><br>fermented and distilled | $^{13}C/^{12}C$<br>$^{18}O/^{16}O$<br>D/H | IRMS<br><br>SNIF-NMR | (Pupin et al., 1998) |
| citric acid, L-malic acid and sugars of lemon juice | $^{13}C/^{12}C$<br>D/H | IRMS<br>SNIF-NMR | (Gonzalez et al., 1998) |
| orange juice: concentrated juice, peel extracts, pulpwashes | $^{13}C/^{12}C$ | IRMS | (Simpkins et al., 2000) |
| **wine** | | | |
| UV-irradiated | $^{87}Sr/^{86}Sr$ | ICP Q MS | (Almeida and Vasconcelos, 2001) |
| vineyard soil<br>grape juices<br><br>finished wine | Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cs, Cu, Fe, Ga, Hf, Li, Mn, Mo, Nb, Ni, Pb, Rb, Sb, Sc, Sr, Ti, Th, Tl, U, V, W, Y, Zn, Zr, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, L | ICP Q MS and AAS | (Almeida and Vasconcelos, 2003) |
| vineyard soil<br>grape juices<br>wine leaves<br>finished wine | $^{204}Pb/^{206}Pb$<br>$^{207}Pb/^{206}Pb$<br>$^{208}Pb/^{20}6Pb$<br>total Pb | ICP-MS and AAS | (Almeida and Vasconcelos, 2003) |
| vineyard soil<br>seeds<br>grape juices<br>finished wine | $^{87}Sr/^{86}Sr$ | ICP-MS | (Almeida and Vasconcelos, 2004) |
| acid addition | Na, K, Ca, Mg, Mn, Fe, Ag, Al, As, Ba, Be, Pb, Cr, Cu, Li, Ni, Sb, Tl, U, V, Rb, Sr, Zn, Cd, Co | AAS and ICP Q MS | (Kment et al., 2005) |
| microwave digested | REE | ICP-HR-MS | (Jakubowski et al., 1999) |
| microwave digested | $^{208}Pb/^{206}Pb$<br>$^{207}Pb/^{206}Pb$<br>$^{204}Pb/^{206}Pb$ | ICP Q MS<br>ICP TOF MS<br>ICP-SF-MC-MS | (Barbaste et al., 2001)<br><br>(Augagneur et al., 1997) |
| directly analyzed | Cu, Pb, Zn, Cd | SV-TFMGE | (Brainina et al., 2004) |
| directly analyzed | REE<br>$^{208}Pb/^{206}Pb$<br>$^{208}Pb/^{204}Pb$<br>$^{207}Pb/^{204}Pb$<br>$^{206}Pb/^{207}Pb$<br>$^{206}Pb/^{204}Pb$ $^{208}Pb/^{207}Pb$. | ICP-MS | (Barbaste et al., 2002) |

| | | | |
|---|---|---|---|
| | Te, Re, Pt, Au, Tl, Be, Pd, Cd, Sn,<br>Sb, Cs, Co, Ga, As, Zr, W, Li, V, Ni, Pb, Ti, Cu, Zn, Rb, Sr, Ba. | | |
| directly analysed | Li, Be, Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rh, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, U, P | ICP-MS | (Baxter et al., 1997) |
| diluted and microwave digested | Li, B, Mg, Al, Si, Cl, Sc, Mn, Ni, Ga, Se, Rb, Sr, Nb, Cs, Ba, La, W, Tl, U | ICP Q MS | (Coetzee et al., 2005) |
| diluted and microwave digested | $^{11}B/^{10}B$ | ICP Q MS | (Coetzee and Vanhaecke, 2005) |
| diluted | Li, B, Mg, Ca, V, Mn, Co, Fe, Zn, Rb, Sr, Cs, Pb | ICP-SFMS | (Castineira Gomez et al., 2004) |
| directly analysed | As, Ca, Cu, Fe, K, Mg, Mn, Na, Zn | AAS | (Guerrero et al., 1997) |
| directly analysed | $^{206}Pb/^{207}Pb$, $^{208}Pb/^{206}Pb$<br>$^{208}Pb/^{207}Pb$, $^{206}Pb/^{204}Pb$<br>$^{207}Pb/^{204}Pb$, $^{208}Pb/^{204}Pb$<br>$^{207}Pb/^{206}Pb$, $^{204}Pb/^{206}Pb$ | ICP-MS | (Larcher et al., 2003) |
| vineyard soil (extraction)<br>wine (acid digested) | $^{208}Pb/^{206}Pb$<br>$^{206}Pb/^{207}Pb$<br>total Pb | ICP-MS | (Mihaljevic et al., 2006) |
| diluted wine | Li, Be, Mg, Al, P, Cl, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Ag, Cd, Sb, I, Cs, Ba, La, Ce, Tl, Pb, Bi, Th, U | ICP Q MS | (Taylor et al., 2003) |
| white wine | Cu, Fe, K, Na, Mg, Ca | AAS | (Sauvage et al., 2002) |
| **vinegar** | | | |
| extracted acetic acid | D/H | NMR | (Hermann, 2001) |
| **port wine** | | | |
| UV-irradiated | $^{207}Pb/^{206}Pb$<br>$^{208}Pb/^{206}Pb$<br>$^{204}Pb/^{206}Pb$<br>total Pb | ICP-MS<br><br><br>ET-AAS | (Almeida and Vasconcelos, 1999) |
| **alcoholic beverages** | | | |
| dilution<br>acidification | Al, Sb, As, Ba, Be, B, Cd, Cr, Co, Cu, Fe, Pb, Ag, Mn, Au, La, Li, Ir, … | ICP-SMS | (Rodushkin et al., 1999) |
| **Tequila** | | | |
| diluted | $^{13}C/^{12}C$<br>D/H | GC-IRMS<br>SNIF-NMR | (Bauer-Christoph et al., 2003) |
| **Zivania** | | | |
| freeze-dried | Fe, Cu, Al, Mn, Mg, Zn, Sb, As. | ICP-MS | (Kokkinofta et al., 2003) |

| | | | |
|---|---|---|---|
| | Se, Cr, Cd, Pb, Ca, Na, K, Ba | | |
| **potatoes** | | | |
| digestion with nitric acid | K, Mg, Ca, Sr, Ba, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, S, Cd, Pb, P | ICP-AES | (Anderson et al., 1999) |
| ashed and dissolved in HCl | K, Na, Rb, Li, Zn, Fe, Mn, Cu, Mg, Ca | fAES<br>fAAS | (Peña et al., 2002) |
| **coffee** | | | |
| digestion with nitric acid | K, Mg, Ca, Na, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, S, Cd, Pb, P | ICP-AES | (Anderson and Smith, 2002) |
| dried and digested with nitric and sulphuric acid | Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P, Sr, Zn | ICP-AES | (Martín et al., 1999) |
| **raw pistachios** | | | |
| digestion with nitric acid | Ba, Be, Ca, Cu, Cr, K, Mg, Mn, Na, V, Fe, Co, Ni, Cu, Zn, Sr, Ti, Cd, P | ICP-AES | (Anderson and Smith, 2004) |
| powdered | $^{13}C/^{12}C$<br>$^{15}N/^{14}N$ | TIMS | (Anderson and Smith, 2006) |
| **olive oil** | | | |
| directly analysed | $^{13}C/^{12}C$,<br>$^{18}O/^{16}O$ | TIMS | (Angerosa et al., 1999) |
| | Cu, Cd, Pb, Zn | ICP-OES | (Angioni et al., 2006) |
| microwave digested | Be, Mg, Ca, Sc, Cr, Mn, Fe, Co, Ni, As, Se, Sr, Y, Cd, Sb, Sm, Eu, Gd | ICP-MS | (Benincasa et al., 2007) |
| **mustard oil** | | | |
| distilled and extracted allyl isothiocyanates | D/H<br>$^{13}C/^{12}C$<br>$^{15}N/^{14}N$<br>$^{34}S/^{32}S$ | SNIF-NMR<br>IRMS | (Remaud et al., 1997) |
| **diverse plant oils** | | | |
| fatty acids<br>bulk | $^{13}C/^{12}C$ | GC-MS<br>EA-IRMS | (Spangenberg and Ogrinc, 2001) |
| **fennel and anise oil** | | | |
| hydrodistilled seeds | $^{13}C/^{12}C$<br>D/H | GC-IRMS | (Bilke and Mosandl, 2002) |
| **lavender oil** | | | |
| extracted linalool and linalyl acetate | D/H | GC-IRMS | (Bilke and Mosandl, 2002) |
| **cinnamon oil** | | | |
| distilled | $^{13}C/^{12}C$<br>D/H | GC-IRMS<br>IRMS | (Sewenig et al., 2003) |
| **Welsh onion** | | | |
| digested with nitric and perchloric acid | Na, P, K, Ca, Mg, Mn, Fe, Cu, Zn, Sr, Ba, Co, Ni, Rb, Mo, Cd, Cs, La, Ce, Tl | AAS<br>ICP-OES<br>ICP-MS | (Ariyama et al., 2004) |

| | | | |
|---|---|---|---|
| **water** | | | |
| filtered natural water | $^{207}Pb/^{206}Pb$<br>$^{208}Pb/^{206}Pb$<br>$^{204}Pb/^{206}Pb$<br>total Pb | ICP-TOF-MS | (Benkhedda et al., 2004) |
| tap water | $^{18}O/^{16}O$<br>2H/1H | IRMS | (Förstel et al., 1997) |
| water | $^{18}O/^{16}O$<br>$^{17}O/^{16}O$<br>D/H | diode laser spectroscopy | (Kerstel et al., 2002) |
| **honey** | | | |
| extracted proteins<br>fermented | $^{13}C/^{12}C$<br>D/H | GC-IRMS<br>SNIF-NMR | (Cotte et al., 2007) |
| ashed and digested with nitric acid | Fe, Cu, Zn, Mg, Ca, Sr, K, Na, Li, Rb | AAS<br>AES | (Hernández et al., 2005) |
| sonicated and diluted | Pb, Cd, Cu, Cr, Co, Ni, Mn and Zn | ICP-AES | (Ioannidou et al., 2005) |
| stored at -3°C in glass bottle | Li, Rb, Na, K, Mg, Zn, Cu, Fe, Mn, Li, Rb, Na, K | AAS<br>AES | (Latorre et al., 2000) |
| bulk honey and proteins | $^{13}C/^{12}C$ | IRMS | (Marini et al., 2004) |
| ashed honey | K, Na, Ca, Mg, S | ICP-OES | (Terrab et al., 2004) |
| ashed honey | Al, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, S, Se, Si, Zn, Ca, K, Mg, Na, P, S, Si, Al, Cu, Fe, Li, Zn, As, Cd, Mo, Sr, V | ICP-OES | (Terrab et al., 2005) |
| digested with nitric acid | Al, Ba, Ca, Cu, Fe, La, Mg, Mn, Sr, Ti, Zn, Cd, Co, Cr, Cs, Hg, La, Li, Nd, Ni, Pb, Pr, Rb, Se, Sn, Ti, V, Zr | ICP-AES<br>ICP-MS | (Marcos et al., 1998) |
| digested<br>with nitric and sulphuric acid | Na, K, Fe, Ca, Zn, Cu | AAS | (Nanda et al., 2003) |
| diluted and digested with<br>nitric and perchloric acid | Ba, Cu, Pb, Zn<br>$^{135}Ba/^{138}Ba$<br>$^{65}Cu/^{63}Cu$<br>$^{206}Pb/^{208}Pb$<br>$^{66}Zn/^{68}Zn$ | ID-ICP-MS | (Packer and Giné, 2001) |
| proteins and whole honey | $^{13}C/^{12}C$ | IRMS | (Pang et al., 2006) |
| directly analysed | pyrolysate | IRMS | (Radovic et al., 2001) |
| **diverse food stuff** | | | |

| | | | |
|---|---|---|---|
| rice, cereals, potatoes sugars, confectioneries, oils and fats, pulses, fruits, green and yellow vegetables, other vegetables, fungi, algae, seasonings and beverages, fishes and shellfishes, meats, eggs, milk and milk products, prepared foods<br><br>freeze-dried, ashed and acid digested | Li, Sc, V, Cr, Mn, Co, Ni, Cu, Rb, Sr, Mo, Cd, Cs, Ba, Th, U, Sr, Cs, Th, U | ICP-MS | (Shiraishi, 1998) |

**Figure 49: (Brunner, 2007)**

# Abbreviations

| | |
|---|---|
| SD | Standard Deviation |
| RSD | Relative Standard Deviation |
| IUPAC | International Unity of Pure and Applied Chemistry |
| DRC | Dynamic Reaction Cell |
| m | Mass |
| obs | Observed |
| ref | Reference |
| Rec | Recovery |
| Rep | Repetability |
| U | Uncertainty |
| EU | European Union |
| RSU | Relative standard uncertainty |
| U, k=2 | Expanded uncertainty, coverage factor |
| int | Intensity |
| blk | Blank |
| mblk | Method blank |
| iblk | Instrument blank |
| REE | Rare Earth Elements |
| c | Concentration |
| cps | Counts per Second |
| °C | Degree Centigrade |
| LoD | Limit of Detection |
| LoQ | Limit of Quantification |
| W | Watt |
| V | Volt |
| rpm | Rounds per Minute |
| min | Minute |
| l | Liter |
| µl | Micro liter |
| DAC | Districtus Austriae Controllatus |
| R | Resolution |
| LR | Low resolution |
| HR | High resolution |
| K | Kelvin |
| z | Charge |
| PFA | Perfluoroalkoxylalkane |
| PE | Polyethylene |
| s | Seconds |
| psi | pound-force per square inch |
| IR | Isotope ratio |
| ppm | Parts per million |

# List of tables

# List of figures

# List of equations

Equ. 18 $$Q_{xx} = \sum_{i=1}^{N} x_i^2 - \left( \sum_{i=1}^{N} x_i \right)^2 \cdot N^{-1}$$ ..... 46

Equ. 19 $$Q_{xy} = \sum_{i=1}^{N} (x_i \cdot y_i) - \sum_{i=1}^{N} x_i \cdot \sum_{i=1}^{N} y_i \cdot N^{-1}$$ ..... 46

Equ. 20 $$k = \frac{Q_{xy}}{Q_{xx}}$$ ..... 46

Equ. 21 $$\bar{x} = \sum_{i=1}^{N} x_i \cdot N^{-1}$$ ..... 46

Equ. 22 $$\bar{y} = \sum_{i=1}^{N} y_i \cdot N^{-1}$$ ..... 46

Equ. 23 $$d = \bar{y} - k \cdot \bar{x}$$ ..... 46

# Bibliography


Albarède, F., P. Telouk, J. Blichert-Toft, et al. (2004). "Precise and accurate isotopic measurements using multiple-collector ICPMS." *Geochimica Et Cosmochimica Acta* **68**(12): 2725-2744.

Almeida, C. M. and M. Vasconcelos (2001). "ICP-MS determination of strontium isotope ratio in wine in order to be used as a fingerprint of its regional origin." *Journal of Analytical Atomic Spectrometry* **16**(6): 607-611.

Almeida, C. M. R. and M. Vasconcelos (1999). "UV-irradiation and MW-digestion pre-treatment of Port wine suitable for the determination of lead isotope ratios by inductively coupled plasma mass spectrometry." *Journal of Analytical Atomic Spectrometry* **14**(12): 1815-1821.

Almeida, C. M. R. and M. Vasconcelos (2003). "Lead contamination in Portuguese red wines from the Douro region: from the vineyard to the final product." *Journal of Agricultural and Food Chemistry* **51**(10): 3012-3023.

Almeida, C. M. R. and M. Vasconcelos (2003). "Multielement composition of wines and their precursors including provenance soil and their potentialities as fingerprints of wine origin." *Journal of Agricultural and Food Chemistry* **51**(16): 4788-4798.

Almeida, C. M. R. and M. T. S. D. Vasconcelos (2004). "Does the winemaking process influence the wine 87Sr/86Sr? A case study." *Food Chemistry* **85**(1): 7-12.

Anderson, K. A., B. A. Magnuson, M. L. Tschirgi, et al. (1999). "Determining the Geographic Origin of Potatoes with Trace Metal Analysis Using Statistical and Neural Network Classifiers." *Journal of Agricultural and Food Chemistry* **47**(4): 1568-1575.

Anderson, K. A. and B. W. Smith (2002). "Chemical Profiling To Differentiate Geographic Growing Origins of Coffee." *Journal of Agricultural and Food Chemistry* **50**(7): 2068-2075.

Anderson, K. A. and B. W. Smith (2004). "Use of Chemical Profiling to Differentiate Geographic Growing Origin of Raw Pistachios." *Journal of Agricultural and Food Chemistry* **53**(2): 410-418.

Anderson, K. A. and B. W. Smith (2006). "Effect of Season and Variety on the Differentiation of Geographic Growing Origin of Pistachios by Stable Isotope Profiling." *Journal of Agricultural and Food Chemistry* **54**(5): 1747-1752.

Angerosa, F., O. Breas, S. Contento, et al. (1999). "Application of Stable Isotope Ratio Analysis to the Characterization of the Geographical Origin of Olive Oils." *Journal of Agricultural and Food Chemistry* **47**(3): 1013-1017.

Angioni, A., M. Cabitza, M. T. Russo, et al. (2006). "Influence of olive cultivars and period of harvest on the contents of Cu, Cd, Pb, and Zn in virgin olive oils." *Food Chemistry* **99**(3): 525-529.

Angus, N. S., T. J. O' Keeffe, K. R. Stuart, et al. (2006). "Regional classification of New Zealand red wines using inductively-coupled plasma-mass spectrometry (ICP-MS)." *Australian Journal of Grape and Wine Research* **12**(2): 170-176.

Ansari, R., T. G. Kazi, M. K. Jamali, et al. (2009). "Variation in accumulation of heavy metals in different verities of sunflower seed oil with the aid of multivariate technique." *Food Chemistry* **115**(1): 318-323.

Ariyama, K., H. Horita and A. Yasui (2004). "Application of Inorganic Element Ratios to Chemometrics for Determination of the Geographic Origin of Welsh Onions." *Journal of Agricultural and Food Chemistry* **52**(19): 5803-5809.

Ariyama, K., M. Kadokura and T. Suzuki (2008). "Estimation of discrimination errors in the technique for determining the geographic origin of onions by mineral composition: Interlaboratory study." *Journal of Aoac International* **91**(2): 445-460.

Augagneur, S., B. Medina and F. Grousset (1997). "Measurement of lead isotope ratios in wine by ICP-MS and its applications to the determination of lead concentration by isotope dilution." *Fresenius' Journal of Analytical Chemistry* **357**(8): 1149-1152.

Augagneur, S., B. Medina, J. Szpunar, et al. (1996). "Determination of rare earth elements in wine by inductively coupled plasma mass spectrometry using a microconcentric nebulizer." *Journal of Analytical Atomic Spectrometry* **11**(9): 713-721.

Bahar, B., O. Schmidt, A. P. Moloney, et al. (2008). "Seasonal variation in the C, N and S stable isotope composition of retail organic and conventional Irish beef." *Food Chemistry* **106**(3): 1299-1305.

Balcaen, L., I. D. Schrijver, L. Moens, et al. (2005). "Determination of the 87Sr/86Sr isotope ratio in USGS silicate reference materials by multi-collector ICP-mass spectrometry." *International Journal of Mass Spectrometry* **242**(2-3): 251-255.

Bandoniene, D. T. M., D. Jöbstl, (2007). "Patterns of rare earth elements in pumpkin seed oils based on ICP-MS determinations " *Oral and Poster Sessions on Tuesday 20 February 2007* **TuPo54**: 39.

Bandura, D. R., V. I. Baranov and S. D. Tanner (2002). "Detection of ultratrace phosphorus and sulfur by quadrupole ICPMS with dynamic reaction cell." *Analytical Chemistry* **74**(7): 1497-1502.

Bandura, D. R., O. Ornatsky and L. Liao (2004). "Characterization of phosphorus content of biological samples by ICP-DRC-MS: potential tool for cancer research." *Journal of Analytical Atomic Spectrometry* **19**(1): 96-100.

Barbaste, M., L. Halicz, A. Galy, et al. (2001). "Evaluation of the accuracy of the determination of lead isotope ratios in wine by ICP MS using quadrupole, multicollector magnetic sector and time-of-flight analyzers." *Talanta* **54**(2): 307-317.

Barbaste, M., B. Medina, L. Sarabia, et al. (2002). "Analysis and comparison of SIMCA models for denominations of origin of wines from de Canary Islands (Spain) builds by means of their trace and ultratrace metals content." *Analytica Chimica Acta* **472**(1-2): 161-174.

Barquero, L. R., E. García-Toraño and J. M. Los Arcos (2004). "Standardization of 32P/33P and 204Tl by liquid scintillation counting." *Applied Radiation and Isotopes* **60**(2-4): 615-618.

Bauer-Christoph, C., N. Christoph, B. O. Aguilar-Cisneros, et al. (2003). "Authentication of tequila by gas chromatography and stable isotope ratio analyses." *European Food Research and Technology* **217**(5): 438-443.

Baxter, M. J., H. M. Crews, M. J. Dennis, et al. (1997). "The determination of the authenticity of wine from its trace element composition." *Food Chemistry* **60**(3): 443-450.

Benincasa, C., J. Lewis, E. Perri, et al. (2007). "Determination of trace element in Italian virgin olive oils and their characterization according to geographical origin by statistical analysis." *Analytica Chimica Acta* **585**(2): 366-370.

Benincasa, C., J. Lewis, G. Sindona, et al. (2008). "The use of multi element profiling to differentiate between cowand buffalo milk." *Food Chemistry* **110**(1): 257-262.

Benkhedda, K., H. Goenaga Infante and F. C. Adams (2004). "Determination of total lead and lead isotope ratios in natural waters by inductively coupled plasma time-of-flight mass spectrometry after flow injection on-line preconcentration." *Analytica Chimica Acta* **506**(2): 137-144.

Bilke, S. and A. Mosandl (2002). "2H/1H and 13C/12C Isotope Ratios of trans-Anethole Using Gas Chromatographyâ^'Isotope Ratio Mass Spectrometry." *Journal of Agricultural and Food Chemistry* **50**(14): 3935-3937.

Boner, M. and H. Rstel (2004). "Stable isotope variation as a tool to trace the authenticity of beef." *Analytical and Bioanalytical Chemistry* **378**: 301-310.

Bonnefoy, C., A. Menudier, C. Moesch, et al. (2002). "Validation of the determination of lead in whole blood by ICP-MS." *Journal of Analytical Atomic Spectrometry* **17**(9): 1161-1165.

Brainina, K. Z., N. Y. Stozhko, G. M. Belysheva, et al. (2004). "Determination of heavy metals in wines by anodic stripping voltammetry with thick-film modified electrode." *Analytica Chimica Acta* **514**(2): 227-234.

Brenner, I. J. (2007). "An Overview of Magnetic Sector Inductively Coupled ICP and GD-MS." *Proceedings of 12th ISMAS Symposium cum Workshop on Mass Spectrometry in Goa*: IT-2.

Brescia, M. A., M. Monfreda, A. Buccolieri, et al. (2005). "Characterisation of the geographical origin of buffalo milk and mozzarella cheese by means of analytical and spectroscopic determinations." *Food Chemistry* **89**(1): 139-147.

Brown, P. H., A. H. Rathjen, R. D. Graham, et al. (1990). Chapter 92 Rare earth elements in biological systems. Handbook on the Physics and Chemistry of Rare Earths, Elsevier. **Volume 13:** 423-452.

Brunner, M. (2007). "Determination of geographical origin of agricultural products via isotopic and elemental analyses by Inductively coupled plasma mass spectrometry (ICP-MS) on the example of Asparagus officinalis." *Master Thesis*.

Busetto, M. L., V. M. Moretti, J. M. Moreno-Rojas, et al. (2008). "Authentication of farmed and wild turbot (Psetta maxima) by fatty acid and isotopic analyses combined with chemometrics." *Journal of Agricultural and Food Chemistry* **56**(8): 2742-2750.

Calderone, G., C. Guillou, F. Reniero, et al. (2007). "Helping to authenticate sparkling drinks with 13C/12C of CO2 by gas chromatography-isotope ratio mass spectrometry." *Food Research International* **40**(3): 324-331.

Camin, F., L. Bontempo, K. Heinrich, et al. (2007). "Multi-element (H,C,N,S) stable isotope characteristics of lamb meat from different European regions." *Analytical and Bioanalytical Chemistry* **389**(1): 309-320.

Camin, F., R. Larcher, M. Perini, et al. "Characterisation of authentic Italian extra-virgin olive oils by stable isotope ratios of C, O and H and mineral composition." *Food Chemistry* **In Press, Corrected Proof**.

Camin, F., K. Wietzerbin, A. B. Cortes, et al. (2004). "Application of Multielement Stable Isotope Ratio Analysis to the Characterization of French, Italian, and Spanish Cheeses." *Journal of Agricultural and Food Chemistry* **52**(21): 6592-6601.

Cao, X., Y. Chen, Z. Gu, et al. (2000). "Determination of Trace Rare Earth Elements in Plant and Soil Samples by Inductively Coupled Plasma-Mass Spectrometry." *International Journal of Environmental Analytical Chemistry* **76**(4): 295 - 309.

Capo, R. C., B. W. Stewart and O. A. Chadwick (1998). "Strontium isotopes as tracers of ecosystem processes: theory and methods." *Geoderma* **82**(1-3): 197-225.

Castineira Gomez, M. D. M., R. Brandt, N. Jakubowski, et al. (2004). "Changes of the metal composition in German white wines through the winemaking process. A study of 63 elements by inductively coupled plasma-mass spectrometry." *J Agric Food Chem* **52**(10): 2953-61.

Castineira Gomez, M. D. M., I. Feldmann, N. Jakubowski, et al. (2004). "Classification of German white wines with certified brand of origin by multielement quantitation and pattern recognition techniques." *J Agric Food Chem* **52**(10): 2962-74.

Catarino, S., A. S. Curvelo-Garcia and R. B. De Sousa (2008). "Contaminant elements in wines: A review." *Ciencia E Tecnica Vitivinicola* **23**(1): 3-19.

Choi, S.-M., H.-S. Lee, G.-H. Lee, et al. (2008). "Determination of the strontium isotope ratio by ICP-MS ginseng as a tracer of regional origin." *Food Chemistry* **108**(3): 1149-1154.

Chua, H. (1998). "Bio-accumulation of environmental residues of rare earth elements in aquatic flora Eichhornia crassipes (Mart.) Solms in Guangdong Province of China." *The Science of The Total Environment* **214**(1-3): 79-85.

Citac/Eurochem Guide (2002). "Guide to Quality in Analytical Chemistry." *http://www.eurachem.org/guides/CITAC%20EURACHEM%20GUIDE.pdf* **Edition 2002** (19.August.2008).

Coetzee, P. P., F. E. Steffens, R. J. Eiselen, et al. (2005). "Multi-element analysis of South African wines by ICP-MS and their classification according to geographical origin." *Journal of Agricultural and Food Chemistry* **53**(13): 5060-5066.

Coetzee, P. P. and F. Vanhaecke (2005). "Classifying wine according to geographical origin via quadrupole-based ICP-mass spectrometry measurements of boron isotope ratios." *Analytical and Bioanalytical Chemistry* **383**(6): 977-984.

Consonni, R., L. R. Cagliani, M. Stocchero, et al. (2009). "Triple Concentrated Tomato Paste: Discrimination between Italian and Chinese Products." *Journal of Agricultural and Food Chemistry* **57**(11): 4506-4513.

Cotte, J. F., H. Casabianca, J. Lhéritier, et al. (2007). "Study and validity of 13C stable carbon isotopic ratio analysis by mass spectrometry and 2H site-specific natural isotopic fractionation by nuclear magnetic resonance isotopic measurements to characterize and control the authenticity of honey." *Analytica Chimica Acta* **582**(1): 125-136.

Crittenden, R. G., A. S. Andrew, M. Lefournour, et al. (2007). "Determining the geographic origin of milk in Australasia using multi-element stable isotope ratio analysis." *International Dairy Journal* **17**(5): 421-428.

Currie, L. A. (1999). "Nomenclature in evaluation of analytical methods including detection and quantification capabilities: (IUPAC Recommendations 1995)." *Analytica Chimica Acta* **391**(2): 105-126.

D. L. Jones (1997). "Trivalent metal (Cr, Y, Rh, La, Pr, Gd) sorption in two acid soils and its consequences for bioremediation." *European Journal of Soil Science* **48**(4): 697-702.

Daroub, S. H., F. J. Pierce and B. G. Ellis (2000). "Phosphorus Fractions and Fate of Phosphorus-33 in Soils under Plowing and No-Tillage." *Soil Sci Soc Am J* **64**(1): 170-176.

De Laeter, J. R., J. K. Böhlke, P. De Bièvre, et al. (2003). "Atomic weights of the elements. Review 2000 (IUPAC Technical Report)." *Pure Applied Chemistry* **75**(6): 683-800.

De Souza, R. M., B. M. Mathias, C. L. P. Da Silveira, et al. (2005). "Inductively coupled plasma optical emission spectrometry for trace multi-element determination in vegetable oils, margarine and butter after stabilization with propan-1-ol and water." *Spectrochimica Acta Part B: Atomic Spectroscopy* **60**(5): 711-715.

Din 19730 and (1996). "Bodenbeschaffenheit - Extraktion von Spurenelementen mit Ammoniumnitratlösung.-Normenausschuß Wasserwesen (NAW) im DIN Deutsches Institut für Normung e.V."

Donarski, J. A., S. A. Jones and A. J. Charlton (2008). "Application of cryoprobe 1H nuclear magnetic resonance spectroscopy and multivariate analysis for the verification of corsican honey." *Journal of Agricultural and Food Chemistry* **56**(14): 5451-5456.

Eichrom (2009). "Product description of Sr spec Resin: " *http://www.eichrom.com/products/info/sr_resin.cfm* (30.August.2009).

Encyclopaedia Britannica (2009). "rare-earth element Encyclopaedia Britannica Online:." *http://www.britannica.com/EBchecked/topic/491579/rare-earth-element* (4. August. 2009).

Engel, E., A. Ferlay, A. Cornu, et al. (2007). "Relevance of isotopic and molecular biomarkers for the authentication of milk according to production zone and type of feeding of the cow." *Journal of Agricultural and Food Chemistry* **55**(22): 9099-9108.

Eurochem Guide (1998). "The Fitness for Purpose of Analytical Methods, First internet Version, December 1998." *http://www.eurachem.org/guides/valid.pdf* (19.August.2009).

European Commission (2009(a)). "European Quality Labels." *http://ec.europa.eu/agriculture/quality/schemes/index_en.htm* (14.August.2009).

European Commission (2009(b)) "DOOR database Austria." *http://ec.europa.eu/agriculture/quality/door/list.html;jsessionid=46L8KFcWzy0VrrGPK6rSr1CXhMChQQxTxyTkZ0nR0LnD1jMs5s3G!-192850994?&recordStart= 0&filter.dossierNumber=&filter.comboName=&filterMin.submitted__mask=&filterMin.submitted=&filterMax.submitted__mask=&filterMax.submitted=&filter.country=AT&filter.category=&filter.type=&filter.status=*

European Commission (2009(c)) "E-Bacchus database." *http://ec.europa.eu/agriculture/markets/wine/e-bacchus/index.cfm?event =pwelcome &language=EN*

Fabani, M. P., R. C. Arrúa, F. Vázquez, et al. "Evaluation of elemental profile coupled to chemometrics to assess the geographical origin of Argentinean wines." *Food Chemistry* **In Press, Corrected Proof**.

Föllmi, K. B. (1996). "The phosphorus cycle, phosphogenesis and marine phosphate-rich deposits." *Earth-Science Reviews* **40**(1-2): 55-124.

Förstel, H., J. Houbé and H. Hützen (1997). "Use of tap water samples for monitoring the geographical variation of stable isotopes used in authenticity studies." *Zeitschrift für Lebensmitteluntersuchung und -Forschung A* **204**(2): 103-108.

Franke, B. M., R. Hadorn, J. O. Bosset, et al. (2008). "Is authentication of the geographic origin of poultry meat and dried beef improved by combining multiple trace element and oxygen isotope analysis?" *Meat Science* **80**(3): 944-947.

Froidevaux, P., J. J. Geering, L. Pillonel, et al. (2004). "90Sr, 238U, 234U, 137Cs, 40K and 239/240Pu in Emmental type cheese produced in different regions of Western Europe." *Journal of Environmental Radioactivity* **72**(3): 287-298.

Fruhwirth, G. and Albin Hermetter (2007). "Seeds and oil of the Styrian oil pumpkin: Components and biological activities." *European Journal of Lipid Science and Technology* **109**(11): 1128-1140.

Galgano, F., F. Favati, M. Camso, et al. (2008). "Analysis of trace elements in southern Italian wines and their classification according to provenance." *Lwt-Food Science and Technology* **41**(10): 1808-1815.

Galgano, F., F. Favati, M. Caruso, et al. (2008). "Analysis of trace elements in southern Italian wines and their classification according to provenance." *LWT - Food Science and Technology* **41**(10): 1808-1815.

García-Ruiz, S., M. Moldovan, G. Fortunato, et al. (2007). "Evaluation of strontium isotope abundance ratios in combination with multi-elemental analysis as a possible tool to study the geographical origin of ciders." *Analytica Chimica Acta* **590**(1): 55-66.

Gomez, M. D. M., I. Feldmann, N. Jakubowski, et al. (2004). "Classification of German white wines with certified brand of origin by multielement quantitation and pattern recognition techniques." *Journal of Agricultural and Food Chemistry* **52**(10): 2962-2974.

Gonzalez-Martin, I., C. Gonzalez-Perez, J. Hernandez Mendez, et al. (1999). "Use of isotope analysis to characterize meat fromIberian-breed swine." *Meat Science* **52**: 437-441.

Gonzalez-Martn, I., C. Gonzalez Perez, J. Hernandez Mendez, et al. (2001). "Differentiation of dietary regimene of Iberian swine by means of isotopic analysis of carbon and sulphur in hepatic tissue." *Meat Science* **58**: 25-30.

Gonzalez, J., E. Jamin, G. Remaud, et al. (1998). "Authentication of Lemon Juices and Concentrates by a Combined Multi-isotope Approach Using SNIF-NMR and IRMS." *Journal of Agricultural and Food Chemistry* **46**(6): 2200-2205.

Gonzálvez, A., A. Llorens, M. L. Cervera, et al. (2009). "Elemental fingerprint of wines from the protected designation of origin Valencia." *Food Chemistry* **112**(1): 26-34.

Greenough, J. D., L. M. Mallory-Greenough and B. J. Fryer (2005). "Geology and wine 9: Regional trace element fingerprinting of Canadian wines." *Geoscience Canada* **32**(3): 129-137.

Gryschko, R., R. Kuhnle, K. Terytze, et al. (2005). "Soil Extraction of Readily Soluble Heavy Metals and As with 1 M NH4NO3-Solution - Evaluation of DIN 19730 (6 pp)." *Journal of Soils and Sediments* **5**(2): 101-106.

Guerrero, M. I., C. Herce-Pagliai, A. M. Cameán, et al. (1997). "Multivariate characterization of wine vinegars from the south of Spain according to their metallic content." *Talanta* **45**(2): 379-386.

Guillou, C., J. Koziet, A. Rossmann, et al. (1999). "Determination of the 13C contents of organic acids and sugars in fruit juices: an inter-comparison study." *Analytica Chimica Acta* **388**(1-2): 137-143.

Guo, B. L., Y. M. Wei, J. R. Pan, et al. "Stable C and N isotope ratio analysis for regional geographical traceability of cattle in China." *Food Chemistry* **In Press, Corrected Proof**.

Halicz, L., I. Segal, N. Fruchter, et al. (2008). "Strontium stable isotopes fractionate in the soil environments?" *Earth and Planetary Science Letters* **272**(1-2): 406-411.

Heaton, K., S. D. Kelly, J. Hoogewerff, et al. (2008). "Verifying the geographical origin of beef: The application of multi-element isotope and trace element analysis." *Food Chemistry* **107**(1): 506-515.

Hermann, A. (2001). "Determination of D/H isotope ratio in acetic acid from vinegars and pickled products by 2H-NMR-spectroscopy." *European Food Research and Technology* **212**(6): 683-686.

Hernández, O. M., J. M. G. Fraga, A. I. Jiménez, et al. (2005). "Characterization of honey from the Canary Islands: determination of the mineral content by atomic absorption spectrophotometry." *Food Chemistry* **93**(3): 449-458.

Hoffmann, C., B. Marschner and M. Renger (1998). "Influence of DOM-Quality, DOM-Quantity and Water Regime on the Transport of Selected Heavy Metals." *Physics and Chemistry of The Earth* **23**(2): 205-209.

Horacek, M., E. Eisinger and W. Papesch "Reliability of stable isotope values from meat juice for the determination of the meat origin." *Food Chemistry* **In Press, Corrected Proof**.

Houk, R. S. (2008). "Mass spectrometry of inductively coupled plasmas." *Analytical Chemistry* **58**(1): 97A-105A.

Ioannidou, M. D., G. A. Zachariadis, A. N. Anthemidis, et al. (2005). "Direct determination of toxic trace metals in honey and sugars using inductively coupled plasma atomic emission spectrometry." *Talanta* **65**(1): 92-97.

Iso 8402 (1994). "Quality - Vocabulary."
Iso 11843-1 (1997). "Capability of detection - Part 1 Terms and definitions."
Iso Vim (1993). "International vocabulary of basic and general terms in metrology." (2nd edition).
Iso/Iec Guide 30 (1992). "Terms and definitions used in conjunction with reference materials."
Itis (2009). "Integrated Taxonomic Information System." *http://www.itis.gov/servlet/SingleRpt/SingleRpt?search_topic=TSN&search_value=22373* (15.August.2009).
Iupac 'Orange Book' (1997). "Compendium of Analytical Nomenclatures."
Jakubowski, N., R. Brandt, D. Stuewer, et al. (1999). "Analysis of wines by ICP-MS: Is the pattern of the rare earth elements a reliable fingerprint for the provenance?" *Fresenius Journal of Analytical Chemistry* **364**(5): 424-428.
Jamin, E., F. Martin, R. Santamaria-Fernandez, et al. (2005). "Detection of Exogenous Citric Acid in Fruit Juices by Stable Isotope Ratio Analysis." *Journal of Agricultural and Food Chemistry* **53**(13): 5130-5133.
Jolliffe, I. T. (2002). Principal Component Analysis. NY.
Juranovic, I., P. Breinhoelder and I. Steffan (2003). "Determination of trace elements in pumpkin seed oils and pumpkin seeds by ICP-AES." *Journal of Analytical Atomic Spectrometry* **18**(1): 54-58.
Katona, R., M. Brunner, Z. Stefanka, et al. (2008). "Food authenticity studies via multi-elemental and isotopic pattern using inductively coupled plasma mass spectrometry." *Poster*.
Kawasaki, A., H. Oda and T. Hirata (2002). "Determination of Strontium Isotope Ratio of Brown Rice for Estimating Its Provenance." *Soil science and plant nutrition* **48**(5): 635-640.
Kelly, S., M. Baxter, S. Chapman, et al. (2002). "The application of isotopic and elemental analysis to determine the geographical origin of premium long grain rice." *European Food Research and Technology* **214**(1): 72-78.
Kerstel, E. R. T., G. Gagliardi, L. Gianfrani, et al. (2002). "Determination of the 2H/1H, 17O/16O, and 18O/16O isotope ratios in water by means of tunable diode laser spectroscopy at 1.39 [mu]m." *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **58**(11): 2389-2396.
Kment, P., M. Mihaljevic, V. Ettler, et al. (2005). "Differentiation of Czech wines using multielement composition - A comparison with vineyard soil." *Food Chemistry* **91**(1): 157-165.
Kokkinofta, R., P. V. Petrakis, T. Mavromoustakos, et al. (2003). "Authenticity of the Traditional Cypriot Spirit â€œZivaniaâ€ on the Basis of Metal Content Using a Combination of Coupled Plasma Spectroscopy and Statistical Analysis." *Journal of Agricultural and Food Chemistry* **51**(21): 6233-6239.
Kornexl, B. E., T. Werner, A. Roßmann, et al. (1997). "Measurement of stable isotope abundances in milk and milk ingredients — a possible tool for origin assignment and quality control." *Zeitschrift für Lebensmitteluntersuchung und -Forschung A* **205**(1): 19-24.
Koziet, J., A. Rossmann, G. J. Martin, et al. (1995). "Determination of the oxygen-18 and deuterium content of fruit and vegetable juice water. An European inter-laboratory comparison study." *Analytica Chimica Acta* **302**(1): 29-37.
Larcher, R., G. Nicolini and P. Pangrazzi (2003). "Isotope ratios of lead in Italian wines by inductively coupled plasma mass spectrometry." *Journal of Agricultural and Food Chemistry* **51**(20): 5956-5961.

Latorre, M. J., R. Peã±A, S. Garcã-A, et al. (2000). Authentication of Galician (NW Spain) honeys by multivariate techniques based on metal content data.

Li, D., S. Huang, W. Wang, et al. (2001). "Study on the kinetics of cerium(III) adsorption-desorption on different soils of China." *Chemosphere* **44**(4): 663-669.

Liang, T., S. Zhang, L. Wang, et al. (2005). "Environmental biogeochemical behaviors of rare earth elements in soil–plant systems." *Environmental Geochemistry and Health* **27**(4): 301-311.

Longerich, H. P. and D. W. (2001). "Introduction to Mass Spectrometry: principles and applications." *Laser Ablation-ICP-MS in the Earth Sciences* **29**: 1-19.

Maheswaran J, B. M., N Reddy, K and P. A. S. Buckingham (2001). " Impact of rare earth elements on plant physiology and productivity : a report for the Rural Industries Research and Development Corporatio." *RIRDC*( 01/145): 1-51.

Manca, G., F. Camin, G. C. Coloru, et al. (2001). "Characterization of the Geographical Origin of Pecorino Sardo Cheese by Casein Stable Isotope (13C/12C and 15N/14N) Ratios and Free Amino Acid Ratios." *Journal of Agricultural and Food Chemistry* **49**(3): 1404-1409.

Mandl, A., G. Reich and W. Lindner (1999). "Detection of adulteration of pumpkin seed oil by analysis of content and composition of specific Δ7-phytosterols." *European Food Research and Technology* **209**(6): 400-406.

Marcos, A., A. Fisher, G. Rea, et al. (1998). "Preliminary study using trace element concentrations and a chemometrics approach to determine the geographical origin of tea." *Journal of Analytical Atomic Spectrometry* **13**(6): 521-529.

Marini, F., A. L. Magrì, F. Balestrieri, et al. (2004). "Supervised pattern recognition applied to the discrimination of the floral origin of six types of Italian honey samples." *Analytica Chimica Acta* **515**(1): 117-125.

Markert, B. and Z. De Li (1991). "Natural background concentrations of rare-earth elements in a forest ecosystem." *The Science of The Total Environment* **103**(1): 27-35.

Marschner, H. (1995). Mineral Nutrition in Higher Plants, Academic Press Limited**:** 6-7.

Marschner, H. (1995). Mineral Nutrition in Higher Plants, Academic Press Limited**:** 229-435.

Martín, M. J., F. Pablos and A. G. González (1999). "Characterization of arabica and robusta roasted coffee varieties and mixture resolution according to their metal content." *Food Chemistry* **66**(3): 365-370.

Martinez, I., I. B. Standal, D. E. Axelson, et al. (2009). "Identification of the farm origin of salmon by fatty acid and HR 13C NMR profiling." *Food Chemistry* **116**(3): 766-773.

Martino, F. A. R., M. L. F. Sanchez and A. S. Medel (2002). "Multi-elemental fractionation in milk whey by size exclusion chromatography coupled on line to ICP-MS." *Journal of Analytical Atomic Spectrometry* **17**(10): 1271-1277.

Martino, F. A. R., M. L. F. Sanchez and A. Sanz-Medel (2001). "The potential of double focusing-ICP-MS for studying elemental distribution patterns in whole milk, skimmed milk and milk whey of different milks." *Analytica Chimica Acta* **442**: 191-200.

Mcculley, R., E. Jobbágy, W. Pockman, et al. (2004). "Nutrient uptake as a contributing explanation for deep rooting in arid and semi-arid ecosystems." *Oecologia* **141**(4): 620-628.

Mcdonough, W. F. and S. S. Sun (1995). "The composition of the Earth." *Chemical Geology* **120**(3-4): 223-253.

Mihaljevic, M., V. Ettler, O. Sebek, et al. (2006). "Lead isotopic signatures of wine and vineyard soils - tracers of lead origin." *Journal of Geochemical Exploration* **88**(1-3): 130-133.

Mihucz, V. G., C. J. Done, E. Tatár, et al. (2006). "Influence of different bentonites on the rare earth element concentrations of clarified Romanian wines." *Talanta* **70**(5): 984-990.

Moreno, I. M., D. González-Weller, V. Gutierrez, et al. (2007). "Differentiation of two Canary DO red wines according to their metal content from inductively coupled plasma optical emission spectrometry and graphite furnace atomic absorption spectrometry by using Probabilistic Neural Networks." *Talanta* **72**(1): 263-268.

N. N. (2009(a)). "Austrian Wine." *http://www.winesfromaustria.com/eindex.php* (23.August.2009).

N. N. (2009(b)). *http://www.trace.eu.org/fa/teim/index.php.* (14.August.2009).

N. N. (2009(c)). "Das kulinarische i-Tüpferl, Steirisches Kürbiskernöl g.g.A." *http://www.steirisches-kuerbiskernoel-gga.at/* (15.August.2009).

Nakashita, R., Y. Suzuki, F. Akamatsu, et al. (2008). "Stable carbon, nitrogen, and oxygen isotope analysis as a potential tool for verifying geographical origin of beef." *Analytica Chimica Acta* **617**(1-2): 148-152.

Nanda, V., B. C. Sarkar, H. K. Sharma, et al. (2003). "Physico-chemical properties and estimation of mineral content in honey produced from different plants in Northern India." *Journal of Food Composition and Analysis* **16**(5): 613-619.

Necemer, M., I. J. Kosir, P. Kump, et al. (2009). "Application of Total Reflection X-ray Spectrometry in Combination with Chemometric Methods for Determination of the Botanical Origin of Slovenian Honey." *Journal of Agricultural and Food Chemistry* **57**(10): 4409-4414.

Nelms, S. (2005). "Inductively coupled plasma mass spectrometry handbook." *Blackwell Publishing, Oxford (UK)*.

Newman, K., P. A. Freedman, J. Williams, et al. (2009). "High sensitivity skimmers and non-linear mass dependent fractionation in ICP-MS." *Journal of Analytical Atomic Spectrometry* **24**(6): 742-751.

Nu Instruments (2007 ). "NuPlasma Manual, Nu Instruments: NuPlasma Multiplier Operation, Nu Instruments: Zero measurements, Nu Instruments: NP Faraday detectors."

Oddone, M., M. Aceto, M. Baldizzone, et al. (2009). "Authentication and Traceability Study of Hazelnuts from Piedmont, Italy." *Journal of Agricultural and Food Chemistry* **57**(9): 3404-3408.

Ogrinc, N., I. J. Kosir, M. Kocjancìœicìœ, et al. (2001). "Determination of Authenticy, Regional Origin, and Vintage of Slovenian Wines Using a Combination of IRMS and SNIF-NMR Analyses." *Journal of Agricultural and Food Chemistry* **49**(3): 1432-1440.

Packer, A. P. and M. F. Giné (2001). "Analysis of undigested honey samples by isotope dilution inductively coupled plasma mass spectrometry with direct injection nebulization (ID-ICP-MS)." *Spectrochimica Acta Part B: Atomic Spectroscopy* **56**(1): 69-75.

Pang, G.-F., C.-L. Fan, Y.-Z. Cao, et al. (2006). "Study on distribution pattern of stable carbon isotope ratio of Chinese honeys by isotope ratio mass spectrometry." *Journal of the Science of Food and Agriculture* **86**(2): 315-319.

Pang, X., D. Li and A. Peng (2001). "Application of rare-earth elements in the agriculture of china and its environmental behavior in soil." *Journal of Soils and Sediments* **1**(2): 124-129.

Pellerano, R. G., S. S. Mazza, R. A. Marigliano, et al. (2008). "Multielement analysis of Argentinean lemon juices by instrumental neutronic activation analysis and their classification according to geographical origin." *Journal of Agricultural and Food Chemistry* **56**(13): 5222-5225.

Peña, F., S. Cárdenas, M. Gallego, et al. (2002). "Characterization of olive oil classes using a Chemsensor and pattern recognition techniques." *Journal of the American Oil Chemists' Society* **79**(11): 1103-1108.

Peres, B., N. Barlet, G. Loiseau, et al. (2007). "Review of the current methods of analytical traceability allowing determination of the origin of foodstuffs." *Food Control* **18**(3): 228-235.

Pérez-Magariño, S., M. Ortega-Heras and M. L. González-San José (2002). "Multivariate classification of rosé wines from different Spanish protected designations of origin." *Analytica Chimica Acta* **458**(1): 187-190.

Perez, A. L., B. W. Smith and K. A. Anderson (2006). "Stable Isotope and Trace Element Profiling Combined with Classification Models To Differentiate Geographic Growing Origin for Three Fruits: Effects of Subregion and Variety." *Journal of Agricultural and Food Chemistry* **54**(13): 4506-4516.

Piasentier, E., R. Valusso, F. Camin, et al. (2003). "Stable isotope ratio analysis for authentication of lamb meat." *Meat Science* **64**: 239-247.

Pilgrim, T. S., R. J. Watling and K. Grice "Application of trace element and stable isotope signatures to determine the provenance of tea (Camellia sinensis) samples." *Food Chemistry* **In Press, Corrected Proof**.

Pillonel, L., R. Badertscher, P. Froidevaux, et al. (2003). "Stable isotope ratios, major, trace and radioactive elements in emmental cheeses of different origins." *Lebensmittel-Wissenschaft und -Technologie* **36**: 615-623.

Piperno, D. R. and K. E. Stothert (2003). "Phytolith evidence for early Holocene Cucurbita domestication in Southwest Ecuador." *Science* **299**(5609): 1054-1057.

Pohl, P. and B. Prusisz (2006). "Fractionation of calcium and magnesium in honeys, juices and tea infusions by ion exchange and flame atomic absorption spectrometry." *Talanta* **69**(5): 1227-1233.

Prohaska, T. (2009). "Course: Training in Metrology in Chemistry."

Prohaska, T., G. Kollensperger, M. Krachler, et al. (2000). "Determination of trace elements in human milk by inductively coupled plasma sector field mass spectrometry (ICP-SFMS)." *Journal of Analytical Atomic Spectrometry* **15**(4): 335-340.

Prohaska, T., C. Latkoczy, G. Schultheis, et al. (2002). "Investigation of Sr isotope ratios in prehistoric human bones and teeth using laser ablation ICP-MS and ICP-MS after Rb/Sr separation." *Journal of Analytical Atomic Spectrometry* **17**(8): 887-891.

Pupin, A. M., M. J. Dennis, I. Parker, et al. (1998). "Use of Isotopic Analyses To Determine the Authenticity of Brazilian Orange Juice (Citrus sinensis)." *Journal of Agricultural and Food Chemistry* **46**(4): 1369-1373.

Radovic, B. S., R. Goodacre and E. Anklam (2001). "Contribution of pyrolysis-mass spectrometry (Py-MS) to authenticity testing of honey." *Journal of Analytical and Applied Pyrolysis* **60**(1): 79-87.

Remaud, G. S., Y. L. Martin, G. G. Martin, et al. (1997). "Authentication of mustard oils by combined stable isotope analysis (SNIF-NMR and IRMS)." *Journal of Agricultural and Food Chemistry* **45**: 1844-1848.

Renou, J. P., G. Bielicki, C. Deponge, et al. (2004). "Characterization of animal products according to geographic origin and feeding diet using nuclear magnetic resonance and isotope ratio mass spectrometry. Part II: Beef meat." *Food Chemistry* **86**(2): 251-256.

Robinson, R. W. and D. S. Decker-Walters (1997). "Cucurbits Volume 6 of Crop production science in horticulture." *CAB International*.

Rodrigues, C. I., R. Maia, M. Miranda, et al. "Stable isotope analysis for green coffee bean: A possible method for geographic origin discrimination." *Journal of Food Composition and Analysis* **In Press, Corrected Proof**.

Rodushkin, I., T. Bergman, G. Douglas, et al. (2007). "Authentication of Kalix (N.E. Sweden) vendace caviar using inductively coupled plasma-based analytical techniques: Evaluation of different approaches." *Analytica Chimica Acta* **583**(2): 310-318.

Rodushkin, I., F. Ödman and P. K. Appelblad (1999). "Multielement Determination and Lead Isotope Ratio Measurement in Alcoholic Beverages by High-Resolution Inductively Coupled Plasma Mass Spectrometry." *Journal of Food Composition and Analysis* **12**(4): 243-257.

Rossano, E. C., Z. Szilagyi, A. Malorni, et al. (2007). "Influence of Winemaking Practices on the Concentration of Rare Earth Elements in White Wines Studied by Inductively Coupled Plasma Mass Spectrometry." *Journal of Agricultural and Food Chemistry* **55**(2): 311-317.

Rossmann, A., G. Haberhauer, S. Hölzl, et al. (2000). "The potential of multielement stable isotope analysis for regional origin assignment of butter." *European Food Research and Technology* **211**(1): 32-40.

Rousk, J., E. Bååth, H. Göransson, et al. (2007). "Assessing plant-microbial competition for 33P using uptake into phospholipids." *Applied Soil Ecology* **36**(2-3): 233-237.

Rummel, S., S. Hoelzl, P. Horn, et al. "The combination of stable isotope abundance ratios of H, C, N and S with 87Sr/86Sr for geographical origin assignment of orange juices." *Food Chemistry* **In Press, Corrected Proof**.

Sacco, D., M. A. Brescia, A. Sgaramella, et al. (2009). "Discrimination between Southern Italy and foreign milk samples using spectroscopic and analytical data." *Food Chemistry* **114**(4): 1559-1563.

Sauvage, L., D. Frank, J. Stearne, et al. (2002). "Trace metal studies of selected white wines: an alternative approach." *Analytica Chimica Acta* **458**(1): 223-230.

Schachtman, D. P., R. J. Reid and S. M. Ayling (1998). "Phosphorus Uptake by Plants: From Soil to Cell." *Plant Physiol.* **116**(2): 447-453.

Schmidt, O., J. M. Quilter, B. Bahar, et al. (2005). "Inferring the origin and dietary history of beef from C, N and S stable isotope ratio analysis." *Food Chemistry* **91**(3): 545-549.

Serapinas, P., P. R. Venskutonis, V. Aninkevicius, et al. (2008). "Step by step approach to multi-element data analysis in testing the provenance of wines." *Food Chemistry* **107**(4): 1652-1660.

Sewenig, S., U. Hener and A. Mosandl (2003). "Online determination of 2H/ 1H and 13C/ 12C isotope ratios of cinnamaldehyde from different sources using gas chromatography isotope ratio mass spectrometry." *European Food Research and Technology* **217**(5): 444-448.

Shintu, L. and S. Caldarelli (2005). "High-Resolution MAS NMR and Chemometrics: Characterization of the Ripening of Parmigiano Reggiano Cheese." *Journal of Agricultural and Food Chemistry* **53**(10): 4026-4031.

Shintu, L., S. Caldarelli and B. M. Franke (2007). "Pre-selection of potential molecular markers for the geographic origin of dried beef by HR-MAS NMR spectroscopy." *Meat Science* **76**(4): 700-707.

Shiraishi, K. (1998). "Multi-element analysis of 18 food groups using semi-quantitative ICP-MS." *Journal of Radioanalytical and Nuclear Chemistry* **238**(1): 67-73.

Simpkins, W. A., G. Patel, M. Harrison, et al. (2000). "Stable carbon isotope ratio analysis of Australian orange juices." *Food Chemistry* **70**(3): 385-390.

Spangenberg, J. E. and N. Ogrinc (2001). "Authentication of Vegetable Oils by Bulk and Molecular Carbon Isotope Analyses with Emphasis on Olive Oil and Pumpkin Seed Oil." *Journal of Agricultural and Food Chemistry* **49**(3): 1534-1540.

Statistik (2009). "Guidelines Diskriminanzanalyse." *http://www2.hu-berlin.de/psychologie/ingpsycscw/MethWiki/pmwiki.php?n=Guidelines.Diskriminanzanalyse* (25.Oktober.2009).

Steiger, R. H. and E. Jã¤Ger (1977). "Subcommission on geochronology: Convention on the use of decay constants in geo- and cosmochronology." *Earth and Planetary Science Letters* **36**(3): 359-362.

Stewart, B. W., R. C. Capo and O. A. Chadwick (1998). "Quantitative strontium isotope models for weathering, pedogenesis and biogeochemical cycling." *Geoderma* **82**(1-3): 173-195.

Suhaj, M. and M. Korenovska (2005). "Application of elemental analysis for identification of wine origin - A review." *Acta Alimentaria* **34**(4): 393-401.

Suzuki, Y., Y. Chikaraishi, N. O. Ogawa, et al. (2008). "Geographical origin of polished rice based on multiple element and stable isotope analyses." *Food Chemistry* **109**(2): 470-475.

Swoboda, S., M. Brunner, S. F. Boulyga, et al. (2008). "Identification of Marchfeld asparagus using Sr isotope ratio measurements by MC-ICP-MS." *Analytical and Bioanalytical Chemistry* **390**(2): 487-494.

Taylor, V. F., H. P. Longerich and J. D. Greenough (2003). "Multielement analysis of Canadian wines by inductively coupled plasma mass spectrometry (ICP-MS) and multivariate statistics." *Journal of Agricultural and Food Chemistry* **51**(4): 856-860.

Terrab, A., A. F. Recamales, M. L. González-Miret, et al. (2005). "Contribution to the study of avocado honeys by their mineral contents using inductively coupled plasma optical emission spectrometry." *Food Chemistry* **92**(2): 305-309.

Terrab, A., A. F. Recamales, D. Hernanz, et al. (2004). "Characterisation of Spanish thyme honeys by their physicochemical characteristics and mineral contents." *Food Chemistry* **88**(4): 537-542.

Thiel, G., G. Geisler, I. Blechschmidt, et al. (2004). "Determination of trace elements in wines and classification according to their provenance." *Analytical and Bioanalytical Chemistry* **378**(6): 1630-1636.

Thomas , R. (2001(a)). "A Beginner's Guide to ICP-MS Part I & II." *Spectroscopy* **16**(4): 38-42.

Thomas, R. (2001(b)). "A Beginner's Guide to ICP-MS Part III & IV." *Spectroscopy* **16**(6): 57-60.

Thomas, R. (2001(c)). "A Beginner's Guide to ICP-MS Part VI." *Spectroscopy* **16**(10): 44-48.

Thomas, R. (2002). "A Beginner's Guide to ICP-MS Part X." *Spectroscopy* **17**(4): 34-39.

Thomsen, V., D. Schatzlein and D. Mercuro (2003). "Limits of Detection in Spectroscopy." *Spectroscopy* **18**(12): 112-114.

Tyler, G. (2004). "Rare earth elements in soil and plant systems - A review." *Plant and Soil* **267**: 191-206.

Voerkelius, S., G. D. Lorenz, S. Rummel, et al. (In Press). "Strontium isotopic signatures of natural mineral waters, the reference to a simple geological map and its potential for authentication of food." *Food Chemistry* **In Press, Accepted Manuscript**.

Wen, B., D.-A. Yuan, X.-Q. Shan, et al. (2001). "The influence of rare earth element fertilizer application on the distribution and bioaccumulation of rare earth elements in plants under field conditions." *Chemical Speciation and Bioavailability* **13**: 39-48.

Wiedemann, S. C. C., H. Abbes and W. G. Hansen (2004). "Direct analysis of Ca, P, and Fe in oleochemicals by inductively coupled plasma MS." *Journal of the American Oil Chemists Society* **81**(5): 437-440.

Wu, M. C., S. J. Jiang and T. S. Hsi (2003). "Determination of the ratio of calcium to phosphorus in foodstuffs by dynamic reaction cell inductively coupled plasma mass spectrometry." *Analytical and Bioanalytical Chemistry* **377**(1): 154-158.

Wyttenbach, A., P. Schleppi, J. Bucher, et al. (1994). "THE ACCUMULATION OF THE RARE-EARTH ELEMENTS AND OF SCANDIUM IN SUCCESSIVE NEEDLE AGE CLASSES OF NORWAY SPRUCE." *Biological Trace Element Research* **41**(1-2): 13-29.

Xu, X., W. Zhu, Z. Wang, et al. (2002). "Distributions of rare earths and heavy metals in field-grown maize after application of rare earth-containing fertilizer." *The Science of The Total Environment* **293**(1-3): 97-105.

Yang, C. H. and S. J. Jiang (2004). "Determination of B, Si, P and S in steels by inductively coupled plasma quadrupole mass spectrometry with dynamic reaction cell." *Spectrochimica Acta Part B-Atomic Spectroscopy* **59**(9): 1389-1394.

Yang, L. and R. E. Sturgeon (2003). "Comparison of mass bias correction models for the examination of isotopic composition of mercury using sector field ICP-MS." *Journal of Analytical Atomic Spectrometry* **18**(12): 1452-1457.

You, C. F., B. S. Wang, C. S. Chung, et al. (2009). "Determination of the strontium isotope ratio by ICP-MS ginseng as a tracer of regional origin." *Food Chemistry* **115**(1): 387-387.

Zhang, S. and X.-Q. Shan (2001). "Speciation of rare earth elements in soil and accumulation by wheat with rare earth fertilizer application." *Environmental Pollution* **112**(3): 395-405.

# Curriculum Vitae

| | |
|---|---|
| **Angaben zur Person** | |
| Name | Gerlinde Grabmann |
| Adresse | Knollnhof 8<br>4284 Tragwein<br>Österreich |
| Geburtsdatum | 21.08.1983 |
| **Schulbildung** | 2003-2009<br>Universität Wien<br>1997-2002<br>BORG Perg<br>1993-1997<br>Hauptschule Tragwein<br>1989-1993<br>Volksschule Reichenstein |
| **Muttersprache** | Deutsch |
| **Fremdsprachen** | Englisch (fließend)<br>Französisch (Basics)<br>Spanisch (Basics) |
| **Auslandsaufenthalt** | 2002-2003<br>Au Pair, Washington DC |
| **Hobbies** | Klettern, Lesen, Reisen, Kochen |