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Accurate Trace Metal Analysis in Environmental Samples using Functionalized Sorbent Particles for Analyte Extraction and Pre- concentration prior to ICP-OES Measurement

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**“A bit of science distances one from God but
much science nears one to Him”**

Louis Pasteur

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Abstract

Trace metal analysis has been noticed since the hazards of their exposure to human body was realized. Several methods of analysis such as atomic absorption spectrometry (AAS), atomic emission/fluorescence spectrometry (AES/AFS), inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), neutron activation analysis (NAA), X-ray fluorescence (XRF), and anodic stripping voltammetry (ASV) have been applied over years. Although the sort of sample and the level of target metal concentration is the confining factor to select the analysis method, ICP-MS and ICP-OES techniques are the methods of choice because these techniques enable sensitive multi-elemental analysis with high accuracy and precision.

Owing to low concentration levels of target analytes in environmental or biological sample digests (usually in the range of ng L^{-1} or $\mu\text{g L}^{-1}$) a pre-concentration step is required prior to measurement. Furthermore, the presence of major sample constituents (sometimes in the range of g L^{-1}) demands isolation of the analytes from matrix components to reduce potential interferences in ICP-MS/OES analysis. In literature, several well-established techniques are reported for enrichment and/or isolation of target analytes. Among all applied methods like cloud point extraction (CPE), liquid-liquid extraction (LLE) and solid phase extraction (SPE) the latter one has been commonly used due to the ease of application, selectivity and high recovery. In solid phase extraction, the analyte-containing sample solution is passed through a column packed with a sorbent material. The analytes are trapped by the sorbent and thereby separated from sample matrix which does not interact with the sorbent. After a washing step, the retained elements are desorbed by elution with appropriate solvents. Nevertheless, this routine method suffers some deficiencies such as incomplete analyte elution, or the use of solvents not or only partially compatible with ICP analysis. Moreover, time effort and possibility of column contamination have to be considered. To solve these problems, an improved method for analyte enrichment has been developed recently at the Institute of Chemical Technologies and Analytics, which is named dispersed particle extraction (DPE). This method is based on the concept of solid phase extraction but it benefits from the use of fresh sorbent particles instead of packed columns, which results in faster reaction time, less chemical consumption and higher reproducibility.

In dispersed particle extraction the aqueous solution of analyte in its matrix, which can be natural water or digested soil/plant etc. is conditioned to reach the pH required for efficient analyte trapping by the adsorbent particles. Then, the μm -sized particles (in mg level) are added to this solution, and the target analytes are retained by the sorbent material. The particles are separated from the liquid by centrifugation, re-suspended in diluted acid or dissolved by microliters of concentrated acid and directed as suspension or homogeneous solution to ICP-OES or ICP-MS for analysis. The particles used in the mentioned works were house-made functionalized silica micro-particles.

In the present thesis, the idea is to further improve the extraction process and enhance accuracy and sensitivity of analyte measurement using ICP-OES. To achieve these goals, two kinds of adsorbent particles including magnetic nanoparticles and natural bioparticles were prepared. Furthermore, alternative sample introduction strategies were developed, including Electro-Thermal-Vaporization for measurement of organic bioparticles and flow-injection combined with a magnetic trap for analysis of Co-nanoparticles.

Magnetic and surface functionalized Co-nanoparticles were used for effective separation of Pb from drinking water, followed by ICP-OES analysis of the enriched particles. For this purpose, cobalt nanoparticles were silica-coated through sol-gel process and finally covered with a layer of ionic liquid acting as a cation exchanger. Applicability of this approach was demonstrated by the analysis of Pb in the reference material ERM-CA022a and tap water samples collected from different districts in Vienna.

In another application of dispersed particle extraction, solid sample introduction was performed using an electrothermal vaporization (ETV) system combined with ICP-OES for direct analysis of organic sorbent particles. These particles were prepared by coating the plant spores *Lycopodium clavatum* with ionic liquid. The method was successfully applied for determination of rare earth elements (REE) in ten different green tea samples.

Kurzfassung

Die Analyse von Spurenmetallen hat an Bedeutung gewonnen, seit die Gefahren bekannt wurden, die bei einem Kontakt mit diesen Metallen hervorgerufen werden können. Mehrere Analysenmethoden haben sich in diesem Bereich über die Jahre etabliert, beispielsweise Atomabsorptions-Spektrometrie (AAS), Atomemission/Atomfluoreszenz Spektrometrie (AES/AFS), Massenspektrometrie mit induktiv gekoppeltem Plasma (ICP-MS), optische Emissionsspektrometrie mit induktiv gekoppeltem Plasma (ICP-OES), Neutronenaktivierungsanalyse (NAA), Röntgenfluoreszenz (RFA), und anodic stripping voltammetry (ASV). Obwohl die Probenart und die Analytkonzentration bestimmende Faktoren für die Methodenauswahl sind, haben sich ICP-MS und ICP-OES als die Methoden der Wahl herausgestellt, da sie eine empfindliche Multielement-Analyse mit hoher Präzision und Richtigkeit erlauben.

Aufgrund der niedrigen Konzentrationslevels der Analyten in Umweltproben oder biologischen Probenaufschlüssen (typischer Weise im Bereich ng L⁻¹ oder µg L⁻¹), ist ein Aufkonzentrierungs Schritt vor der Analyse notwendig. Darüber hinaus erfordert die Gegenwart von Hauptkomponenten der Probe (manchmal im Bereich g L⁻¹) eine Isolierung der Analyten aus der Matrix, um mögliche Interferenzen in ICP-MS oder ICP-MS zu reduzieren. In der Literatur sind einige etablierte Methoden bekannt, die für diese Anreicherung und/oder Isolierung der Analyten verwendet werden können. Unter den am ehesten verwendeten Methoden wie Cloudpoint Extraction (CPE), flüssig-flüssig Extraktion und Festphasen Extraktion (SPE) hat sich letztere durchgesetzt, aufgrund ihrer einfachen Anwendung, Selektivität und hohen Wiederfindung. Bei SPE wird die analythältige Probelösung durch eine mit Sorbentmaterial gepackte Säule geleitet. Der Analyt wird auf dem Sorbent eingefangen und dadurch von der Probenmatrix getrennt, welche nicht mit dem Sorbent wechselwirkt. Nach einem Waschschrift werden die immobilisierten Analyten mit einem geeigneten Lösungsmittel eluiert. Diese Routinemethode hat jedoch Nachteile wie unvollständige Elution, oder die Verwendung von Lösungsmitteln, die nicht oder nur teilweise mit ICP-Analytik kompatibel sind. Darüber hinaus müssen der für SPE notwendige Zeitaufwand sowie mögliche Säulenkontamination berücksichtigt werden. Um diese Probleme zu lösen wurde unlängst eine verbesserte Methode der Analytanreicherung am Institut für chemische

Technologien und Analytik der TU Wien entwickelt, die unter der Bezeichnung dispersed particle extraction (DPE) läuft. Diese Methode basiert auf dem Konzept der SPE, aber sie hat den Vorteil, dass stets frisches Sorbensmaterial verwendet wird (anstatt gepackter Säulen), was zu einer schnelleren Reaktionszeit, weniger Chemikalienverbrauch und einer höheren Reproduzierbarkeit führt.

Bei der DPE wird die Probelösung (Analyt in der Matrix, beispielsweise Wasser oder aufgeschlossene Pflanzenproben) auf den korrekten pH-Wert gebracht, der für eine effiziente Analytretention auf den Sorbenspartikeln notwendig ist. Anschließend werden μm große Partikel (in der Größenordnung von wenigen mg) zu dieser Lösung gegeben, und der Analyt wird auf der Partikeloberfläche immobilisiert. Die Partikel werden anschließend von der Flüssigkeit mittels einer Zentrifuge getrennt, in verdünnter Säure wieder suspendiert, oder in wenigen Mikrolitern einer konzentrierten Säure aufgelöst. Dadurch wird eine Suspension oder eine klare Lösung erhalten, die dann mittels ICP-OES oder ICP-MS analysiert werden kann. Bisher wurden dafür funktionalisierte Silika Mikropartikel am Institut selbst hergestellt.

In der vorliegenden Dissertationsschrift wurde die Methode weiter verbessert, mit dem Ziel eines verbesserten Extraktionsprozesses, und einer verbesserten Richtigkeit und Empfindlichkeit in Kombination mit ICP-OES. Um dieses Ziel zu erreichen wurden zwei neue Arten von Partikel verwendet: magnetische Nanopartikel und natürliche Biopartikel. Darüber hinaus wurden alternative Proben-Eintrags Strategien entwickelt: einerseits die elektrothermische Verdampfung für die Messung von organischen Biopartikeln, andererseits die Fließinjektionsanalyse in Kombination mit einer Magnetfalle für die Analyse von magnetischen Nanopartikeln.

Magnetische und oberflächenmodifizierte cobalt Nanopartikel wurden für die Isolierung von Pb aus Trinkwasser – in Kombination mit ICP-OES – verwendet. Dafür wurden cobalt-Nanopartikel mit einer Silicaschicht durch einen Sol-Gel Prozess beschichtet, und abschließend mit einer Schicht aus ionischer Flüssigkeit umgeben, die als Analyt-selektiver Kationentauscher fungiert. Die Anwendung dieser Methode wurde durch die Analyse von Pb im Referenzmaterial ERM-CA022a sowie in Trinkwasserproben aus verschiedenen Bezirken Wiens gezeigt.

In einer anderen Anwendung von dispersed particle extraction wurde elektrothermische Verdampfung verwendet, um organische Sorbenspartikel zu verdampfen, und die adsorbierten Analyten mittels ICP-OES zu analysieren. Diese Partikel wurden hergestellt, indem Bärlappsporen

(*Locopodium clavatum*) mit ionischer Flüssigkeit beschichtet wurden. Diese Methode wurde erfolgreich für die Bestimmung von seltenen Erden in zehn Grüntee-Proben angewendet.

Chapter 1. Introduction

The scope of the presented thesis is to improve the sensitivity of trace metal analysis in matrices by ICP-OES through improvement in sample introduction.

1.1. Trace element analysis in complex matrices

Since heavy metals with the proven toxic and carcinogen effects, either trace or ultra-trace, accumulate in environment they must be monitored according to the regulations. Analysis of trace elements in environmental, biological and medical samples is mostly performed by flame atomic absorption spectroscopy FAAS¹, graphite furnace atomic absorption spectroscopy GFAAS², inductively coupled plasma mass spectrometry ICP-MS and inductively coupled plasma optical emission spectrometry ICP-OES³. Definitely, ICP-MS is the best choice but it is much more prone to errors and more expensive than ICP-OES thus ICP-OES is a suitable technique for routine measurement. However, trace element analysis with AAS and ICP-OES requires enrichment and with ICP-MS needs matrix separation in advance. Because firstly, the concentration of trace element is very low in comparison with the matrix ingredients. Secondly, accuracy of measurement could be influenced by the presence of matrix induced spectral and non-spectral interferences. Thus, the environmental sample must be treated in a way to enable ICP-OES to detect the trace element. The treatment including separation and/or pre-concentration are performed through variety of methods such as liquid-liquid extraction (LLE)⁴ dispersive liquid-liquid micro-extraction (DLLME)⁵, cloud point extraction (CPE)⁶ and solid phase extraction (SPE)⁷. Among these methods, SPE is the most frequently used due to the ease of application and being less expensive. Yet, there are some impediments to the effective use of SPE.

In SPE, samples consisting of analyte in matrix are passed through compact cartridge of sorbent material, in most cases a strong cation-exchanger for retention of multiply charged cations, which should have been already preconditioned with suitable buffer to the required pH for extraction. In the ideal condition, the sorbent material retains only the target analytes, and matrix is isolated from the analyte and discarded. In the following step, the analyte is desorbed by elution and wash-

out with strong solvents and collected for measurement. Although, by this way the separation and enrichment of analyte is achieved, the process is tedious, prone to make contaminated samples and high chemical consuming. To tackle the imperfections with SPE a modified method has been introduced recently by our group as dispersed particle extraction (DPE).

Through this thesis, the concept of DPE has been further exploited. Improved approaches for analysis of derived slurry solutions were developed. Furthermore, two kinds of adsorbent particles including bio-particles and magnetic nanoparticles were assayed to hamper the aforementioned drawbacks of conventional SPE.

The first kind, bioparticles, are plant spore *Lycopodium clavatum* coated with ionic liquid to catch cations. Application of the organic particles enabled implementation of analysis by electrothermal vaporization inductively coupled plasma optical emission spectrometry ETV-ICP-OES where the programmed heating of the inserted sample provides separate vaporization of organic adsorbent and target elements in ETV part. This process lets the target analytes be measured away from interferences entered by organic material. ETV-ICP-OES was applied for analysis of rare earth elements in digested tea samples which were already enriched by the bioparticles and it is discussed in chapter 2.

The second one, magnetic adsorbents, are sulfonated silica coated iron nanoparticles applied for rare earth elements extraction and silica coated cobalt nanoparticles which were covered further by ionic liquid layer to react as cation exchanger. Determination of Pb in drinking water was done with the cobalt particles. The magnetic characteristic of the adsorbent made the possibility of assembling switchable electromagnet trap for improved slurry analysis with higher sensitivity using flow injection inductively coupled plasma optical emission spectrometry FI-ICP-OES. The results will be discussed in chapters 3 and 4.

1.2. Theoretical considerations

1.2.1. Concept of dispersed particle extraction (DPE)

In DPE method, the sorbent material is not packed in a column like the SPE, instead it is single-use house-made porous micro-particle. To enrich/extract analyte by DPE, sample aqueous solution

is preconditioned by addition of a buffer to reach the pH required for extraction. The selection of pH depends on the sorbent surface and type of analyte. After adjusting pH, a few milligrams of particles (in the range of 5-10 mg) are mixed with the sample solution and are sonicated or shaken for 5 min, the particles containing trapped analyte are separated by centrifuge from solution, re-suspended in some diluted mineral acid and finally the suspension is measured with a slurry ICP-OES procedure⁸. To overcome the main disadvantage of slurry analysis (potential of nebulizer clogging), the sorbent particles can also be dissolved with the use of mineral acids, followed by conventional liquid ICP-MS analysis of the derived solution^{9, 10}.

1.2.2. Inductively coupled plasma optical emission spectrometry (ICP-OES)

Compared to the other atomic spectrometries such flame atomic absorption spectrometry¹¹, ICP-OES analyzes samples in much higher temperatures resulting in more efficient excitation and ionization of the elements which in turn brings higher sensitivity of measurement. Unique properties of ICP has made it dominant against other flame-like electrical discharges such as the three-electrode direct current plasma (DPC) and the microwave-induced plasma (MIP). These properties are listed in table 1.1¹².

Table 1.1. Unique properties of ICP discharges.

- | |
|---------------------------------------|
| 1. The axial channel of the ICP |
| 2. The robustness of the plasma |
| 3. High gas and electron temperatures |
| 4. High electron number density |

Inductively coupled plasma is a kind of plasma which is produced as a result of rapid change in the magnetic field around tube containing neutral gas, argon that is seeded with few electrons by a spark from a Tesla coil. Resistance to the eddy current caused by change in magnetic field produces Joule heating. Instant ICP is formed following self-sustaining process as ionizing temperature is reached. This ICP is an inhomogeneous plasma in doughnut shape¹².

The explained process happens in the ICP torch that is consisting of three concentric quartz tubes. Although three gas streams flowing through the concentric tubes of the torch are sometimes

classified from outer to inner layer as coolant, intermediate and injector gases, such a distinct separation is not admitted, because all the three streams can sustain plasma. The tip of the injector tube (the inner tube) of the torch is placed close to the base of the plasma. Sample as gas, vapor or aerosol is introduced to the injector tube. When it is as aerosols, it is needed to be desolvated and vaporized before getting atomized, excited and ionized in different zones of the plasma with the range of 9000-11000 K from inner to outer depending on the ionization energy. These regions are illustrated in figure 1.1¹³. The nomenclature of the regions were suggested by Koiryohann et al¹⁴.

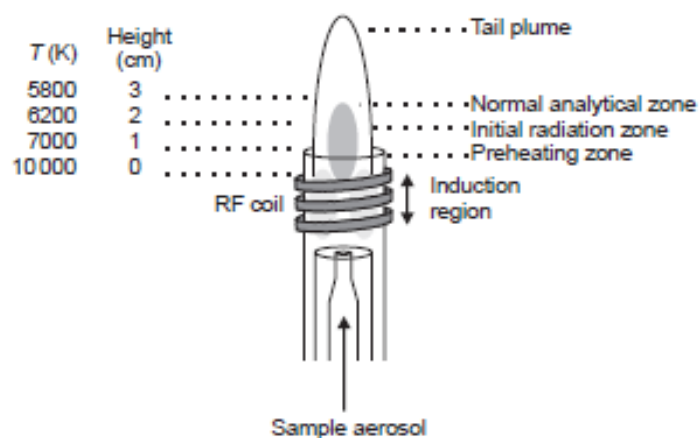


Fig 1.1. Schematic diagram of an ICP assembly showing the three concentric tubes composing the torch, the RF coil, the different plasma regions, and the temperature as a function of height above the load coil¹³.

The produced emissions are collected by a spectrometer to convert to data. Spectrometer in ICP-OES can observe atomic emissions from normal analytical zone of torch in two configurations including radial (side-on) and axial (end-on)¹⁵.

Even though, axial viewing results in better LOD due to better sensitivity rather than radial observation, spectral interferences are also strengthened there. The cooler plasma tail which is outside the optical path with the aid of the hot plasma gases flowing directly into the exhaust system, makes radially-viewed systems still ideal for routine analysis of complex sample matrices. Emissions for spectrometric measurements are collected from the normal analytical zone (NAZ) of the plasma. The NAZ is observed laterally in radial systems and the observation height is an important parameter for radial equipment. The heterogeneous spatial distribution of emitting species in radial plasma is one of the factors that affect the results. However, in axial plasmas, the

NAZ is extended because the entire plasma channel is observed¹⁶. In figure 1.2, both positions of torch are shown and the configuration of optics for them is illustrated in figure 1.3.

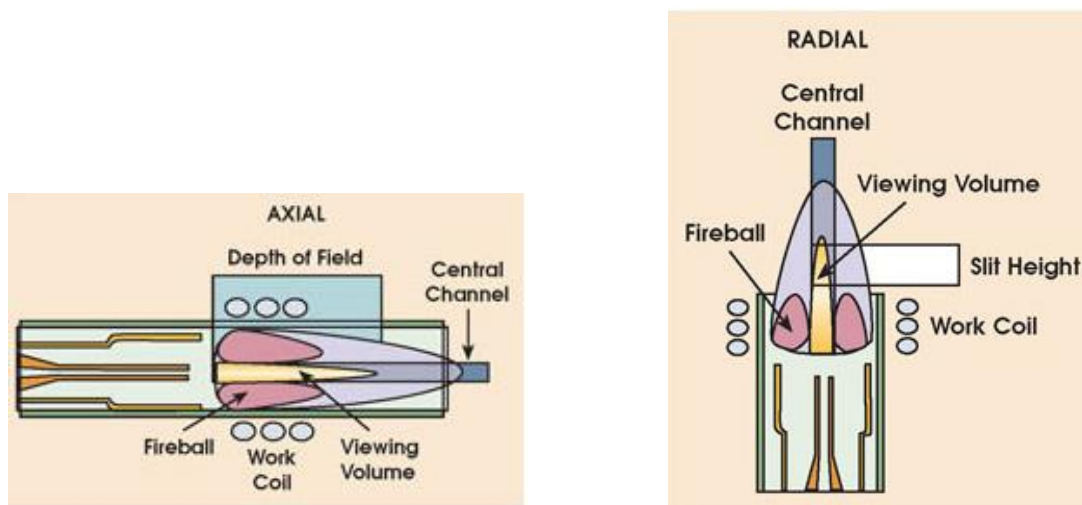


Fig 1.2. Comparison of axial and radial viewing in ICP torch in ICP-OES¹⁸.

Ionization interference, which is also known as ‘easily ionized element’ (EIE) interference is the most common type of matrix interference observed within the plasma. High concentrations of easily ionized elements in samples, especially the common alkali elements, potassium and sodium, and to a lesser extent, the alkaline earth elements, calcium and magnesium cause ionization interferences. These elements have low ionization energies and are easily ionized by the high plasma temperatures. When the concentration of the EIE is high, the atomization-ionization equilibrium of other elements is affected as a result of increase in the electron density within the plasma. Thus, to compensate the fluctuation in signal recording, the matrix matched calibration and sample solutions is required when it is possible¹⁷.

Furthermore, selection of a proper sample introduction system, use of robust operation conditions, selection of a proper observation height in radially systems and the use of an auxiliary correction method, such as internal standard or standard additions, are strategies that could be adopted to circumvent matrix effects¹⁷.

Whatever viewing position is selected, the radiations are measured by a sequential or simultaneous multichannel detector. In the second type of detector which is suitable for multi element analysis, grating polychromators pass the radiation to different slits; each one is responsible for a wavelength. Then, the reflection of the radiation to photomultiplier tubes or charge transfer devices

(CTDs) is performed by series of mirrors. Charge-coupled device (CCD) is a type of CTDs which functions based on electron-hole pair process in p-type silicon semiconductor. When photons hit the silicon substrate, electrons are collected by capacitors but positive holes migrate through the semiconductor material then the signal is read out¹⁸. All CCDs benefit from working at lower temperatures. Thermal energies alone is enough to excite extraneous electrons into the image pixels and these cannot be distinguished from the actual image photoelectrons. This process generates noise and is called ‘dark current’¹⁹.

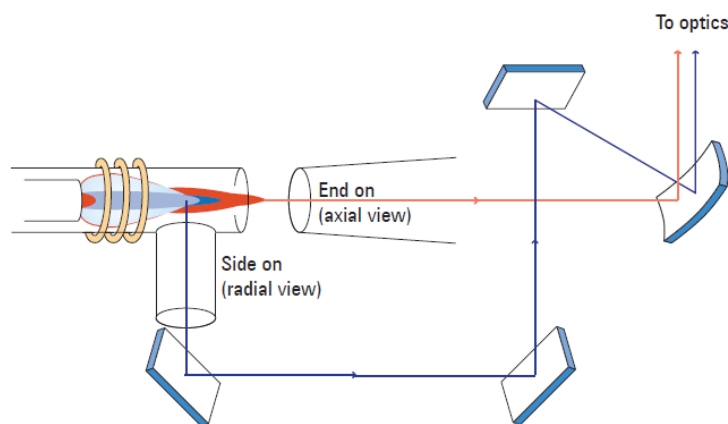


Fig 1.3. Diagram of the optics for two different plasma viewing; axial and radial¹⁷

1.2.2.1. Liquid analysis with ICP-OES

To introduce liquid sample into plasma, it is necessary to convert the liquid to aerosols. The conversion is done by nebulization of a solution with the help of a gas stream. Among different types of nebulizers such cross-flow, high pressure, concentric and Babington-type nebulizers, the last two are most commonly used, however, concentric nebulizer has possibility of getting blocked by particles in the case that, sample is in suspension form. Moreover, different samples with physical properties make variation of the aerosol droplet size which in turn, result variation in the efficiency of the nebulizer and the sample introduction.

Although, for suspension analysis operating parameters are similar with them of liquid analysis, a reduced nebulization carrier gas flow rate and high observation zone have been helpful to increase particle residence times and improve atomization efficiency¹². The resulted aerosols are passed

through a spray chamber to remove the large droplets before injection into the plasma. But this causes as well, losing majority of droplets as waste. Thus, only very small fraction of analyte stream reaches plasma. This is a disadvantage for liquid sample introduction in ICP-OES measurement. The sample introduction system is shown in figure 1.4.

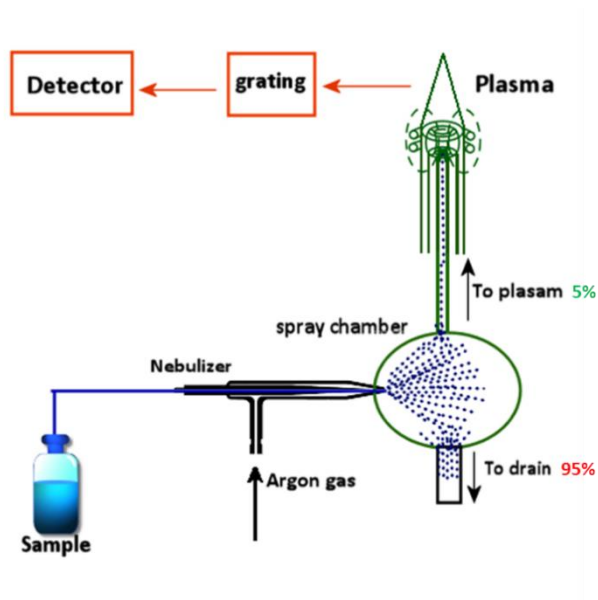


Fig 1.4. Diagram of conventional liquid sample introduction to ICP-OES²⁰.

1.2.2.2. Solid sample analysis with ICP-OES

For solid sample introduction, electrothermal vaporization (ETV) system is coupled with ICP-OES which provides analysis of sample without using nebulizer. Sample is transferred into a graphite boat, then the boat is replaced in the graphite tube, burned in the ETV oven via a controlled temperature program for the specific analyte and swept into the plasma by argon flow through a suited tube made of PTFE. The graphite boat and tube are shown in figure 1.5.



Fig 1.5. Graphite boat (sampling cell) and tube (combustion area) of ETV²¹.

For a precise temperature control the furnace is equipped with a very compact online-pyrometer ranging from room temperature up to 3000°C. The most important area of the system is the transition zone, where the sample is becoming oversaturated and by a well-defined gas flow regime is transferred into a dry aerosol. The principle is demonstrated in figure 1.6. The gas flow regime is determined by a defined mixing of the carrier gas stream transporting the evaporated sample and an auxiliary argon stream (bypass-gas). It is important that both gas streams have the same velocity to prevent turbulences²¹. Thus, sampling-vaporization process is separated from atomization-ionization-excitation which takes place in the ICP. This way of sample transport permits microvolume sampling and results in significantly higher detection limits than pneumatic nebulization. When ETV-ICP-OES is applied, signals are recorded in transient mode, that is, versus time profiles which in the more volatile elements' signals appear earlier. To promote analyte vaporization especially for refractory elements, Freon gas flow is added to injection gas¹².

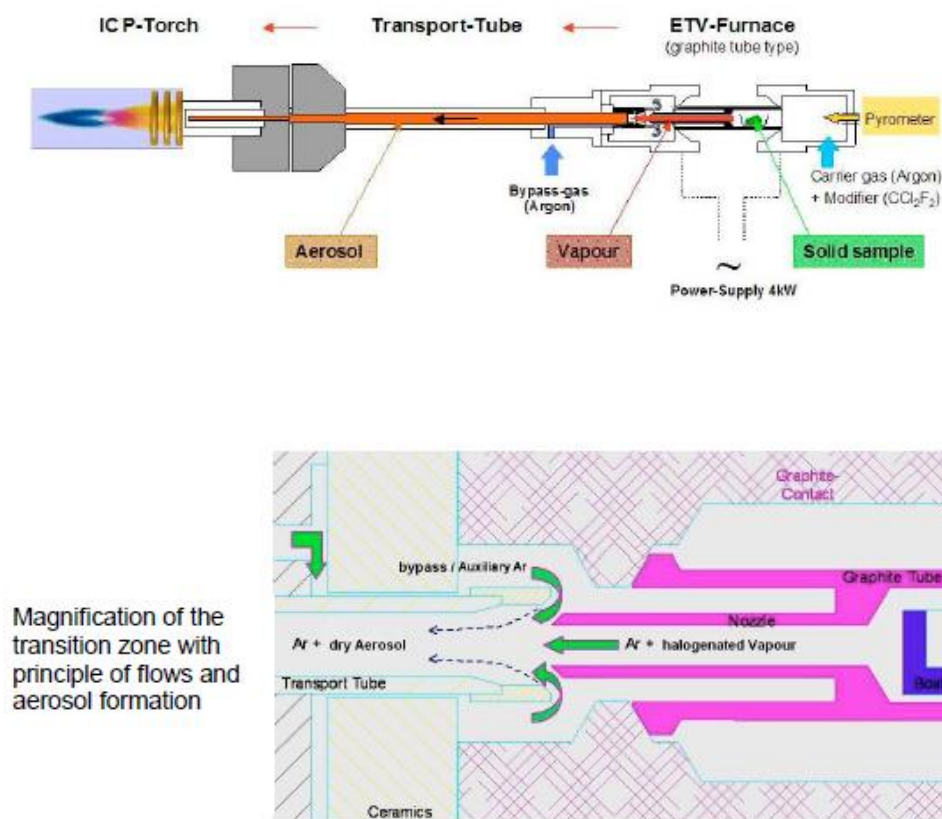


Fig 1.6. The principle of ETV-ICP operation and the magnification of the transition zone²¹.

1.2.2.3. Flow injection analysis (FIA)

Flow injection analysis (FIA) which was introduced in 1975 by Ruzicka and Hansen, is a kind of continuous-flow analyzer whereby samples are introduced at regular intervals into a liquid carrier stream transporting them to the detector. The basic components of flow injection analyser are a pump, a means for injecting the sample into the carrier system, and a detector.

Propelling unit maintains a constant flow of the carrier stored in a reservoir through a tubing system that makes the transport system. A peristaltic pump is the most common device is sued for transporting which consists of a set of rollers attached to the outside of a rotating drum. Tubing from the carrier reservoirs fits between the rollers and fixed plate. The tubing is squeezed as the drum rotates, which forces the contents of the tubing to move in the direction of the rotation. However, one limitation of using a peristaltic pump is that it produces a pulsed flow, particularly at higher flow rates, that may lead to oscillations in the signal²².

When a sample is injected to the carrier stream its rectangular flow profile at the beginning turns to parabolic flow profile in a while as a result of its dispersion. Two processes are involved in sample dispersion including convection and diffusion. Convection is owing to the flow of the carrier stream and diffusion is owing to the concentration gradient between the sample and the carrier stream. As the sample reaches the detector a signal is plotted as a function of time²².

The most important parameters of a recorded peak are peak height and return time. Peak height is related to the analyte's concentration and it determines the sensitivity of an FIA method. And, the importance of return time is due to determining the frequency of samples injection. Therefore, the time of transfer depends on flow rate, path length and the transferring tube diameter²². By using FIA, sample and solutions consumption and waste generation are reduced dramatically. Shown in figure 1.7 is the FIA schematic and the peristaltic pump.

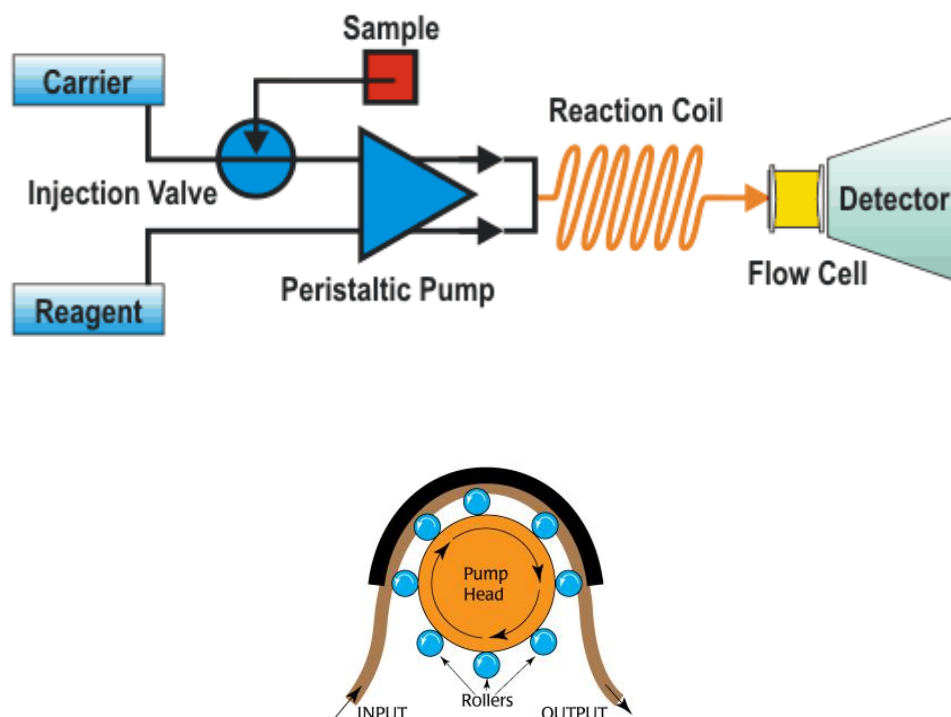


Fig 1.7. Schematic of flow injection system (up) and the structure of peristaltic pump (down)²³.

As it was mentioned in this introduction, the presented thesis consists of three chapters of practical work.

Chapter 2 explains determination of rare earth elements in tea samples with the modified bioparticles as adsorbent by ETV-ICP-OES.

Chapter 3 includes the experiments performed with functionalized magnetic iron nanoparticles as adsorbent which were preliminary tests for trace element analysis with stronger magnetic adsorbent; surface modified cobalt nanoparticles.

Chapter 4 explains the application of magnetic cobalt particles in FI-ICP-OES system for determination of Pb in drinking water.

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Chapter 2. Ionic liquid coated bioparticles for rare earth elements extraction from green tea prior to ETV-ICP-OES analysis

2.1. Introduction

This chapter includes determination of rare earth elements in digested green tea samples which were enriched by surface modified bioparticles through dispersed particle extraction and then measured by electrothermal vaporization inductively coupled plasma optical emission spectrometry.

Although REEs were unknown for general public until 2009, they have been dramatically come in use in all fields of industry, especially high tech instruments production¹. REEs are 17 elements including 15 lanthanides plus scandium and yttrium. In the periodic table of elements, lanthanides have located between barium and hafnium. Their atomic structure with *f*-orbitals provides trivalent (3^+) ions for all elements besides cerium possessing tetravalent (4^+) ions and europium, ytterbium and samarium with divalent (2^+) ions. Except for promethium as the only radioactive element, all REEs have stable isotopes.

Regarding large abundance of this group of elements in nature, rare earth element is not appropriate nomenclature. For instance, cerium as the 27th element in the earth's crust has abundance of six times compared to lead. Upon electron configuration of these elements, REEs are classified as light and heavy: Light REEs are including the elements from lanthanum ($Z=57$) to gadolinium ($Z=64$) and heavy group are elements from terbium ($Z=65$) to lutetium ($Z=71$). The light group includes yttrium but scandium is neither in the light nor the heavy group².

Due to direct dependence of an electron binding energy to its nucleus on its mass, there are strongly bound electrons in lanthanides. So, the decrease in ionic size is more strongly than expectation from increase in nuclear charge and orbital penetration³. These characteristics of lanthanides are resulted from a phenomenon called the *lanthanide contraction* which is the progressive reducing atomic and ionic radii by moving from left to right in the group. The trend of decrease in the radii are shown in figure 2.1.

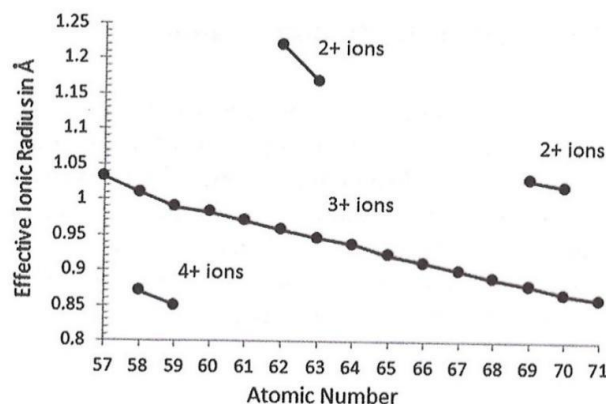


Fig 2.1 .Systematics of effective ionic radii of the lanthanides¹.

Recently, there has been increased tendency to apply REEs in several fields which include agriculture⁴, catalysts⁵ and cell phones⁶. The increased industrial use of REEs results in pollution of the environment, followed by accumulation of these elements in the biosphere and this accumulation causes an increased risk for human health. Based on reports, accumulation of REEs⁷ could cause serious problems in different organs of the human body⁸ especially in bones⁹ and the nervous system⁷. During plant growth, toxic elements present in soil or water can be taken up by the plant together with essential elements. Tea made from *Camellia sinensis* leaves, both black and green, is a common and popular non-alcoholic drink all around the world. Accordingly, it seems that the level of REEs should be monitored in tea. Up to now, data about REEs levels in tea is very sparse, and there are only a few studies published¹¹⁻¹⁴, which indicate that the level of REEs in tea is considerable, especially for La, Ce, Y, Pr and Nd.

For analysis of trace elements in environmental samples, the most appropriate techniques include inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES) and electro-thermal atomic absorption spectrometry (ET-AAS)¹⁵. However, accurate analysis of REEs in plant samples is challenging - REE levels in the range of a few ng g⁻¹ up to some 100 ng g⁻¹ combined with numerous interferences in the most sensitive analytical techniques are the major difficulties. To overcome limitations in sensitivity and/or selectivity (e.g. due to spectral interferences), the use of sample pre-treatment procedures for pre-concentration and quantitative separation of REEs from interfering sample constituents is recommended. Although

several enrichment processes have been reported in the literature, solid phase extraction (SPE) has received the most attention due to easy automation and being inexpensive. In SPE, the analyte-containing matrix is passed through a column of adsorbent on which the analytes of interest are retained. After a washing step to remove remaining matrix, the analytes are eluted with an appropriate solvent. Thus, besides analyte enrichment, also an effective removal of potentially interfering matrix can be achieved. Nevertheless, this way of enrichment has some disadvantages including time demand, column aging and large sample and solvent consumption¹⁶.

Regarding the aforementioned disadvantages of SPE, our group has recently introduced an improved approach called dispersed particle extraction (DPE). In this approach, adsorbent particles with surface modified functionalities are suspended in a liquid sample. Targeted analytes are trapped by the particles while the matrix remains in solution. After centrifugation, the supernatant solution is discarded, the sedimented particles are diluted with acid and finally the suspension is measured with a slurry ICP-OES procedure¹⁷. To overcome the main disadvantage of slurry analysis (potential of nebulizer clogging), the sorbent particles can also be dissolved with the use of mineral acids, followed by conventional liquid ICP-MS analysis of the derived solution^{18,19}. However, the dissolved sorbent material still increases the plasma load during ICP-MS measurement, which could affect atomization, excitation and ionization of the target analytes in the plasma.

In this chapter, an innovative approach is presented, which is based on enrichment of REE using DPE, followed by sensitive measurement of the analyte-containing sorbent particles by means of electro thermal vaporization (ETV) in combination with ICP-OES detection. ETV allows to first pyrolyze the adsorbent material, and only then to introduce the REEs into the ICP. In this way, an effective separation of particle matrix and analytes in time is enabled, thus plasma load from vaporization of the particles could be avoided during analyte measurement. Since the thermal behavior of REE and commonly applied silica particles¹⁷⁻¹⁹ is quite similar, DPE has been performed with organic sorbent particles in this work for the first time. The applied adsorbent is a natural bio particle with high porosity, *Lycopodium clavatum* spore, which was covered with a layer of ionic liquid salt. The ionic liquid acts as the cation exchanger. These natural plant spores with average size of 30 microns are an excellent choice as a core material because they are stable in strong acids or bases, inexpensive, easily approachable and ecological²⁰. Even though the particles are very porous, they do not swell in different

solvents²¹. Applicability of the method is demonstrated by the analysis of REE levels in different green tea samples.

2.2. Experimental

2.2.1. Reagents and standards

High purity water (18 MΩ cm) was prepared with an Easypure purification system (Thermo, USA) and was used in the whole process. Nitric acid 65% (Merck), hydrochloric acid 37% (Merck), hydrofluoric acid 40% (Merck), ethanol 99% (Chem-Lab) and acetone 99.8% (Acros Organics) were p.a. grade as purchased. Acetic acid 96% (Merck) and ammonium acetate (Merck) were used for buffering the samples prior to extraction. Single element ICP standards including La, Eu and Nd (Aristar, 1000 mg L⁻¹), In (Merck, 1000 mg L⁻¹) and a multi-element REE calibration standard (Agilent Technologies, multi-element calibration standard 1, 10 mg L⁻¹, 5% (v/v) HNO₃) were diluted to the concentration needed.

A set of ten different green tea samples was bought at a local market in Vienna (details on each tea are summarized in table 2.1). Prior to chemical digestion, samples were dried for 24 h at 60°C.

Table 2.1. description of tea samples		
sample ID	Origin	Description
Tea 1	China	gunpowder green tea
Tea 2	India	organic green tea
Tea 3	Fujian, China	organic Tiegunyin tea
Tea 4	China	Oolong tea
Tea 5	China	Chun-Mee
Tea 6	China	Sencha
Tea 7	China	"Teekanne" green tea
Tea 8	Japan	Genmaicha
Tea 9	China	fresh green tea
Tea 10	China	"grüner kimono"
Tea 11	China	fresh green tea

2.2.2. Instrumentation

ETV-ICP-OES measurements were performed with radial ICP-OES (Thermo iCAP 6500, Thermo Scientific, USA), coupled to an ETV 4000 unit (Spectral Systems, Germany). The plasma torch contained a corrosion-resistant ceramic injector tube of 1.5 mm inner diameter, and was connected to the ETV via 40 cm of PTFE tubing of 4 mm inner diameter.

For conventional ICP-OES analysis of liquid samples, a sample introduction kit consisting of a Babbington (V-groove) nebulizer, a glass cyclonic spray chamber with riser tube and a torch injector tube with 2 mm inner diameter was used.

Digestion of tea leaves was performed with microwave-assisted closed vessel treatment (Multiwave 3000, MF 100 vessels, Anton Paar, Austria).

Separation of particles during the enrichment process was performed by a Megafuge 16 Centrifuge (Thermo Scientific, Germany). The centrifuge was equipped with a FIBERLite F15-6x 100 angular rotor. The sample pretreatment procedure was carried out in 15-mL conical polypropylene centrifugation tubes with a V-bottom (maximum tolerable acceleration: 17000xg, VWR, Germany).

2.2.3. Preparation and characterization of sorbent particles

The ionic liquid used for the extraction of REEs consisted of the trihexyl(tetradecyl)phosphonium anion and the Di(2-ethylhexyl) phosphate cation (see figure S1, electronic supplementary material). Throughout this article, the nomenclature $[P_{66614}]^+ [BEHPA]^-$ will be used for the ionic liquid. Synthesis of $[P_{66614}]^+ [BEHPA]^-$ was carried out at the institute of applied synthesis chemistry of TU Wien, according to the following scheme: Trihexyltetradecylphosphonium chloride (5.19 g, 10 mmol), bis(2-ethylhexyl) hydrogenphosphate (3.54 g, 11 mmol) and potassium hydroxide (0.62 g, 11 mmol) were suspended in 100 ml of water:MeOH 1:1 and stirred for 2 hrs at room temperature. The solution was concentrated to approx. 60 ml and diluted with water. This mixture was repeatedly extracted with dichloromethane, and the combined organic layers were washed with water until no more chloride ions could be detected (checked by addition of an aqueous $AgNO_3$ solution). The organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Remaining solvent traces were removed under high vacuum (0.01 mbar, 48 h) with stirring at 50°C to yield

trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphonate as clear colorless liquid in 94% yield. Derived product was characterized with NMR (see electronic supplementary material).

To make a cation exchanger adsorbent, 990 mg of *Lycopodium clavatum* spores were added to the solution of 10 mg of ionic liquid salt $[P_{66614}]^+ [BEHPA]^-$ in 50 mL ethanol in a round bottom 100 mL flask. The mixture was shaken smoothly on a slow-moving platform shaker for 2 hours at room temperature. Ethanol was subsequently evaporated using rotary pump vacuum and the solid product was dried overnight under high vacuum.

Particles were characterized using Scanning Electron Microscopy (Quanta 200 MK2, FEI, USA) in the initial form and after coating with the ionic liquid. The SEM images of raw *Lycopodium clavatum* and the treated spores indicate no change in morphology after treatment. As it is shown in figure 2.2, the coated particles have a size of roughly 30 microns.

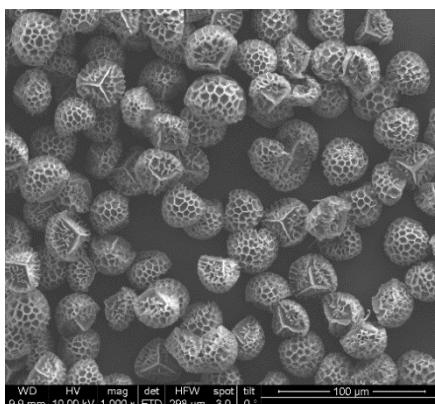


Fig 2.2. SEM images of $[P_{66614}]^+ [BEHPA]^- @ Lycopodium clavatum$, 10kV acceleration voltage and 100 μ m scale-bar.

2.2.4. Microwave assisted sample digestion

For complete decomposition of tea, 0.6 g of the dried leaves were transferred to clean microwave vessels and digested in a mixture of 3 mL HNO_3 (65wt%), 2 mL HCL (37wt%), 1 mL H_2O_2 (30wt%) and 0.1 mL HF (40wt%) under elevated pressure and temperature: 40 min heating ramp, 30 min hold time at 800 W power, maximum temperature of 190°C and maximum pressure of 20 bar. The obtained clear solutions were quantitatively transferred into PFA beakers (Nalgene, USA) and evaporated to dryness on a heating block at 140°C. Dried residues were treated for another 30 minutes with a mixture of 2 mL HNO_3 (65wt %) and 2 mL H_2O_2 (30wt %) at 90°C with closed caps. Then, the solutions were

again evaporated to dryness to remove any remaining $\text{HF}^{22,23}$. The residues were dissolved with 50 μL of 0.07 M HNO_3 in an ultrasonic bath (5 min) and then filled up to 35 mL with high purity water.

2.2.5. Dispersed particle extraction procedure

A graphical illustration of the developed sample pre-treatment procedure is presented in figure 2.3. For analysis 10 mL of sample solution was pipetted into conical 15 ml tubes, and ammonium buffer was added for pH adjustment. Dry sorbent particles were added to the sample solution (step I). After a reaction time of 5 minutes, necessary to retain the REE ions on the sorbent particles, the sample solution was centrifuged for separation of solution and analyte-containing particles. After removal of the supernatant solution (step II), the precipitated sorbent particles were re-suspended in diluted nitric acid (1% v/v) to obtain a final volume of 500 μL in case of ETV experiments (step III). For conventional slurry ICP-OES measurement, the volume was adjusted to a final volume of 2 mL. During step III, indium was added as internal standard with a final concentration of 6 mg L^{-1} .

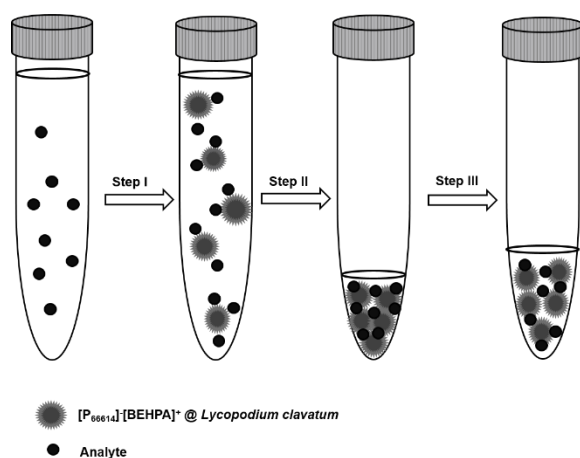


Fig 2.3. Illustration of the dispersed particle extraction (DPE) enrichment process.

2.2.6. Sample analysis

During method development, the slurry obtained after DPE extraction was analyzed via slurry nebulization ICP-OES. Measurement was done with the use of a Babington nebulizer with a sample

flow rate of 0.6 mL min⁻¹. Background-corrected signals were recorded in 5-fold replicate using an analysis time of 5 s per replicate.

For the final ETV ICP-OES method, 30 µL of the suspension obtained via DPE was transferred into a cleaned graphite boat. Before measurement, the solvent was evaporated by gentle heating with an infrared lamp. Then, the boat was placed in the ETV oven and heated following a defined program during 90 s. The boat was first heated to 400°C by a slow ramp in 40 s and was then held at that temperature for 30 s. Then, it was swiftly heated up to 2150°C and was held 20s at that temperature, followed by a cooling phase. Instrumental parameters of the applied analytical procedures are summarized in Table 2.2. Since the resolution of the time-axis is inversely proportional to the number of observed emission lines, only one emission line per element was selected. With those settings, “Timescan” mode was used to record the derived transient signals by collecting data points every 0.4 s.

Table 2.2. Instrumental parameters used for conventional and ETV measurement and analytical wavelengths			
		ETV sample introduction	Liquid sample introduction
Plasma power	W	1200	1200
Radial observation height	mm	11	11
Plasma gas (Ar)	L min ⁻¹	12	12
Nebulizer gas (Ar)	L min ⁻¹	-	0.9
Auxiliary gas (Ar)	L min ⁻¹	0.8	0.8
Freon R12 modifier	mL min ⁻¹	10	-
Bypass gas (Ar)	L min ⁻¹	0.38	-
Carrier gas (Ar)	L min ⁻¹	0.14	-
Element	λ (nm)	Element	λ (nm)
Ce	415.197	Nd	430.358
Dy	364.540	Pr	390.844
Er	369.265	Sc	361.384
Eu	381.967	Sm	360.949
Gd	364.619	Tb	350.917
Ho	339.898	Tm	342.508
La	333.749	Y	371.030
Lu	261.542	Yb	369.419
In*	325.609	* Indium was used as internal standard	

2.3. Results and discussion

2.3.1. Optimization of ionic liquid loading on plant spores

As it was mentioned, ionic liquid (IL) is added to the lycopodium core to obtain ion trapping material. The optimum proportion of IL was investigated by making four different weight percent of IL on Lycopodium surface including 0.5%, 1%, 5% and 10% w/w according to the method explained in 2.3 and the results of enrichment were compared for the three selected elements Eu, La and Nd. For each element three lines were investigated and among them one line is shown in figure 2.4. Based on the results, particles with 1% w/w of ionic liquid $[P_{66614}]^+ [BEHPA]^-$ had maximum retention of elements. Whereas, for both lower and higher amount of coating IL, the retentions deteriorate.

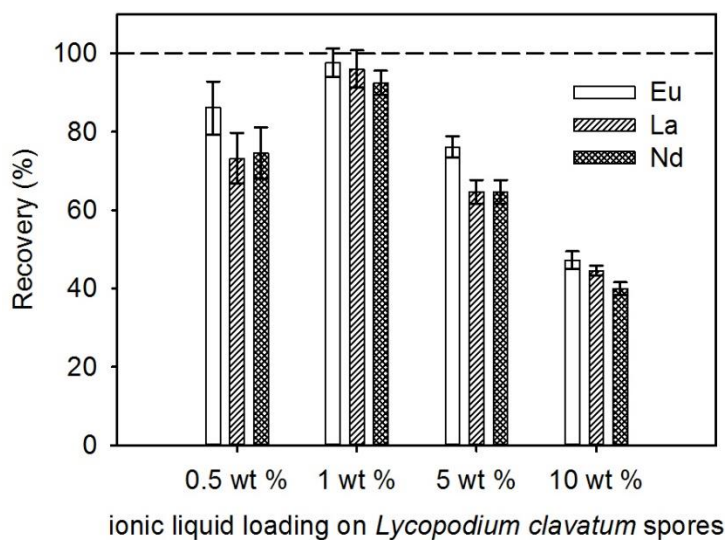


Fig 2.4. Recoveries of Eu, La and Nd on Lycopodium spores coated by different levels of ionic liquid in aqueous standards. (n=3, the values for ionic liquids are weight percent).

2.3.2. Optimization of extraction process

To optimize DPE procedure for REEs retention on Lycopodium@1% $[P_{66614}][BEHPA]$, several experiments were performed by changing the sample pH, reaction time, sample volume and adsorbent

amount. These preliminary experiments were done with $100 \mu\text{g L}^{-1}$ of three elements with high, medium and low sensitivity in ICP-OES including Eu, La and Nd respectively in 10 mL sample.

2.3.2.1 Sample pH

Sample pH is an important factor in this extraction procedure regarding to ionic characteristic of the coating layer $[\text{P}_{66614}]^+[\text{BEHPA}]^-$ of the adsorbent. Since the aim of this research is determination of REEs in tea samples, pH should be adjusted to enable particles to retain the target elements in presence of other common elements in the matrix of digested tea. Based on the various tests with different acidities by adjusting pH with different levels of ammonium acetate buffer, maximum retention for REEs was obtained at sample pH=5. By changing buffer amount between 0.002 - 0.02 mol L^{-1} , the recoveries reduce from 70 % to 30% for the three selected elements including Eu, La and Nd. So, the 0.002 mol L^{-1} buffer was used for 10 mL samples. However, for the tea digestion solutions the desired pH were obtained by adding 0.05 mol L^{-1} buffer which could be due to the matrix consists of inorganic and organic ingredients.

2.3.2.2. Reaction time

To achieve the optimum time for retention of analytes, 10 mL samples of $100 \mu\text{g L}^{-1}$ analyte with 5 mg particles and 0.002 mol L^{-1} buffer were shaken smoothly by hand for 2 to 10 min. Accordingly, 80% recovery for REE can be obtained in 5 min reaction time and longer time did not improve the analyte retention. It should be mentioned that ultrasonic agitation has quite the reverse effect on recovery because it probably destructs the physical connection between lycopodium's surface and ionic liquid.

2.3.2.3. Final volume of enriched analytes slurry

In the enrichment procedure, final volume of slurry after separation is important because it determines the theoretical enrichment factor. Therefore, the remaining volume after separation of supernatant should be as low as possible to achieve the highest enrichment factor but it shouldn't result in analyte loss. With the optimized conditions for centrifugation, 9 mL of the supernatant was withdrawn by

pipette and 1 mL remaining was diluted to 2 mL with 1% nitric acid and used for measurement in liquid measurement by ICP-OES. Because regarding the sample flow rate in liquid analysis the sample volume should be more than 1.5 mL. However, for ETV measurement there was no need for such a high sample intake (30 μL for each graphite boat). Therefore, 9.8 mL of supernatants were removed and the remaining were diluted to final volume of 0.5 mL.

2.3.2.4. Adsorbent amount

Since the adsorbent is added to the analyte solution in DPE procedure, optimization should be done to be sure that enough particles are available for retaining the target elements. On the other hand, excess amount of particles will be interfering during ICP-OES measurements by affecting the excitation in plasma. Even though this factor was removed using ETV coupled with ICP-OES but for liquid analysis in optimization process was troublesome. Therefore 1, 2.5, 5 and 10 mg of the particles were examined and the results showed that 5 mg adsorbent was sufficient to have 80% recovery for Eu, La and Nd from 10 mL sample solution.

2.3.2.5. Final optimized procedure

For summing up, the optimized conditions obtained from the mentioned tests for the three selected elements Eu, La and Nd with concentration of $100 \mu\text{g L}^{-1}$ were pH =5 by adding 0.002 mol L^{-1} buffer, 5 min reaction time, 1.5 mL final sample volume in liquid injection mode and 0.5 mL in solid introduction of sample and 5 mg adsorbent particles in 10 mL sample.

2.3.3. ETV-ICP-OES measurement

First, the ETV program was optimized for best performance in terms of matrix pyrolysis and analyte-release. To avoid extinguishing the plasma by the rapid formation of CO_2 (decomposition of the sorbent particles), it was found that a heating ramp from room temperature to 400°C during 40 s, followed by a plateau of 30 s at this temperature allowed for stable plasma conditions. Lower pyrolysis temperatures resulted sometimes in incomplete sample pyrolysis, which resulted in extinguishing the plasma during the following vaporization step, whereas higher pyrolysis temperatures can result in

analyte losses. The vaporization temperature was optimized in terms of quantitative analyte release, as well as in terms of graphite-tube life-time (too high temperatures result in reduced life-time of the tube). In order to vaporize refractory elements such as Y, a gaseous modifier (Freon R12) was added to the carrier gas. With optimized conditions, a second measurement of the same boat resulted in signals equal to the blank of an empty boat.

ETV analysis of samples was carried out as follows: in a first step, the loaded boat was heated up to the 400°C in 40 s, then was held for 30 s at that temperature. This step allows to pyrolyze slowly the organic material (lycopodium particles and ionic liquid) present in the investigated sample slurry, thereby a separation from the less volatile REEs could be accomplished. Then, by increasing the temperature to 2150°C with maximum heating rate, only the remaining inorganic sample constituents including the target elements are introduced into the plasma. The whole heating program requires 90 s and the analyte signals are continuously recorded with the software of the ICP-OES spectrometer. The amount of sample volume added into the graphite boats was first optimized (10 µL – 40 µL), and was found to be optimal at 30 µL. Higher sample volumes resulted in detector saturation for some elements (i.e., highest spiked standard-addition samples). The temperature program and typical time-resolved analyte signals are illustrated in figure 3. The analyzed samples were a digested tea sample (fig. 2.5a), as well as a method blank (all reagents, including microwave digestion, see fig. 2.5b). Both samples were pre-treated with the above mentioned DPE procedure and analyzed by means of ETV as described.

It is clear from figure 2.5 that during the first 70 s of the ETV program, there is no signal of the REEs or of the internal standard. The two inserts (fig 2.5c and 2.5d) show an enlarged version of the background. This shows that the method blank is negligible, and that matrix pyrolysis does not lead to earlier release of analytes. Upon elevating the temperature to 2150°C, analytes and internal standard are evaporated smoothly, resulting in sharp transient signals. Repeated analysis of one boat showed that the analytes are released quantitatively already during the first firing of the ETV program.

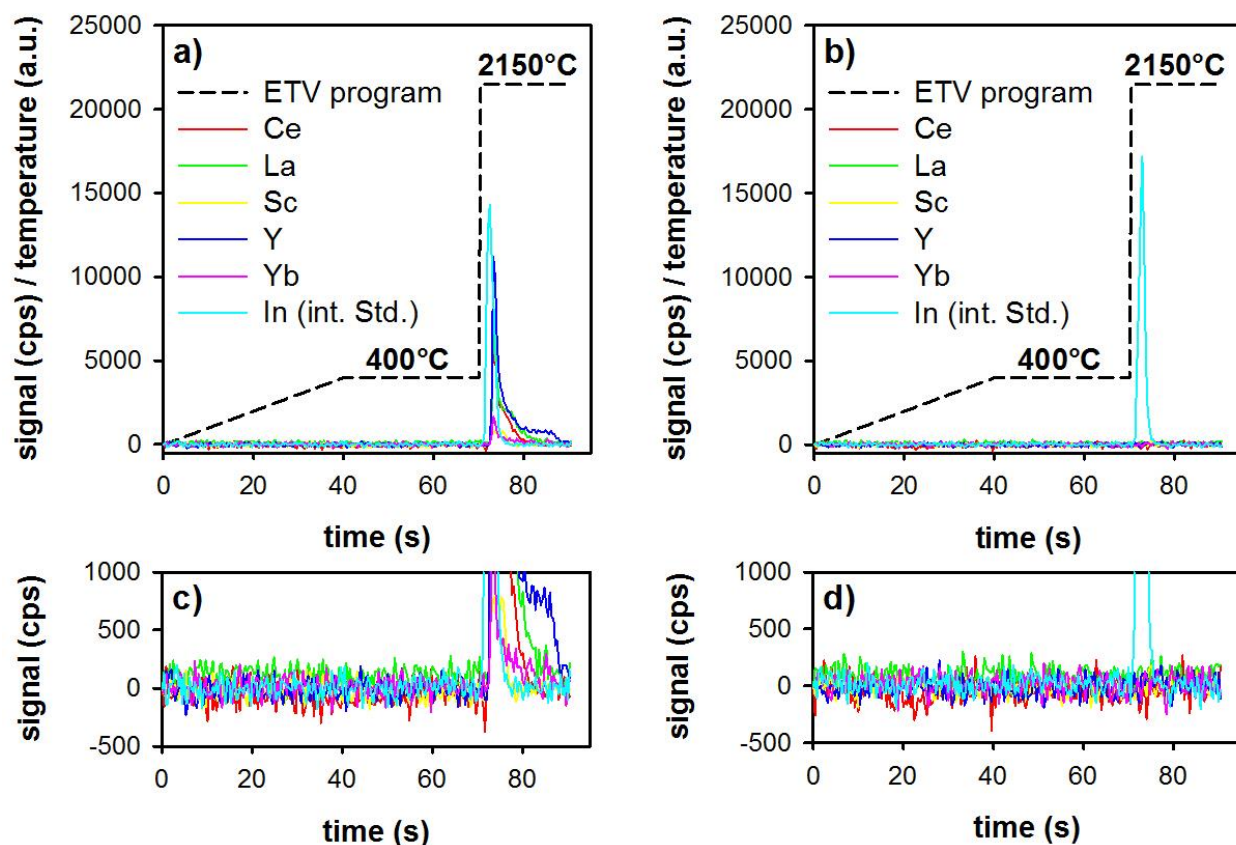


Fig 2.5. Heating program (dashed black line) used for ETV ICP-OES analysis and the recorded signals for Ce, La, Sc, Y, Yb, and In (as internal standard) in a tea sample pre-treated with the method presented here (a, c), and in a method blank (b, d). (c and d are enlarged versions of a, b, to see the background situation more clearly).

2.3.4. Figures of merit

By applying the optimized parameters obtained for REE retention on $[P_{66614}]^+ [BEHPA]^-$ @*Lycopodium clavatum*, enrichment factor, reproducibility and the limit of detection were calculated for all investigated elements. For this purpose, an aqueous calibration row was prepared, these solutions were then treated with the discussed DPE approach. Reproducibility of measurement was determined by replicate pre-concentration and measurement ($n=4$) of a sample solution containing 20 ng ml⁻¹ of the investigated REEs, leading to relative standard deviations ranging from 4% (Nd) to 18% (Dy). Based on the conditions used for sample pre-concentration – 10 mL applied sample volume and 500 µl final volume – it is possible to achieve a theoretical enrichment factor of 20. By comparing the

slopes of the calibration curves before and after pre-concentration, the actual enrichment factor was determined to be 17.8.

LOD was calculated from the standard deviation of 12 blank measurements, according to the 3s criterion. To obtain the LOD in the non-digested tea sample, a sample intake of 0.5 g dry tea, digested and diluted to a final volume of 35 mL was considered. As can be seen in table 2.3, typical detection limits are around 50 ng g⁻¹ in the dry tea samples.

Table 2.3. method LOD in case of ETV-ICP-OES (all data refers to concentration in the dry tea, ng g ⁻¹)								
Element	Ce	Dy	Er	Eu	Gd	Ho	La	Lu
LOD	30	8	20	9	60	50	40	2
Element	Nd	Pr	Sc	Sm	Tb	Tm	Y	Yb
LOD	90	40	5	80	40	30	4	5

2.3.5. Influence of sample matrix on DPE

In contrast to the synthetic aqueous standard solutions used for method development, real samples contain also sample matrix, which might have an impact on the enrichment procedure. To study the effect of the digested tea matrix on the recovery of REEs, the slope obtained by standard addition onto digested tea (tea sample 4, see table 1) was compared with the slope of aqueous standards. Both sets of samples were pre-concentrated with the described DPE approach and analyzed by means of ETV ICP-OES. For each calibration curve, also the standard uncertainty of the slope was calculated. The ratio of (standard addition slope / aqueous calibration slope) for all investigated elements is shown in figure 2.6, together with the corresponding expanded combined uncertainty ($k = 2$).

If there is no matrix effect, the ratio of both slopes is expected to be 1, which applies to Sm, La, Lu, Yb, and Ce. However, in the case of Er, Eu, Tb, Y, Ho, Nd, Gd, Tm, and Pr, the ratio is below 1, indicating that the slope of the standard addition curve was flatter than the slope of an aqueous calibration. This outcome indicates that the recovery of these elements is decreased in the presence of tea matrix. On the other hand, Dy and Sc showed the opposite trend revealing higher signals for aqueous standards than for matrix-containing tea digests. However, when accepting a deviation within

10% of the nominal ratio of 1, most elements could be quantified with external aqueous calibration (Nd, Gd, Tm, Pr, Sm, La, Lu, Yb, Ce).

For some elements, external calibration with aqueous standards might lead to under/overestimation of true contents. Matrix-adjusted calibration (i.e., a blank-corrected standard addition curve) was investigated as an alternative quantification approach to provide correct results for all elements investigated. Although this approach showed good results when performing spike-recovery experiments on one single tea sample (tea sample 4), with recoveries ranging from 90% to 124%, the analysis of different types of green tea showed that analyte-recovery also slightly changes due to variations in sample matrix. Therefore, the concept of two-point standard-addition was relied upon for correct quantification in all of the following experiments, since it is less work-intensive as matrix-matched calibration for every tea sample.

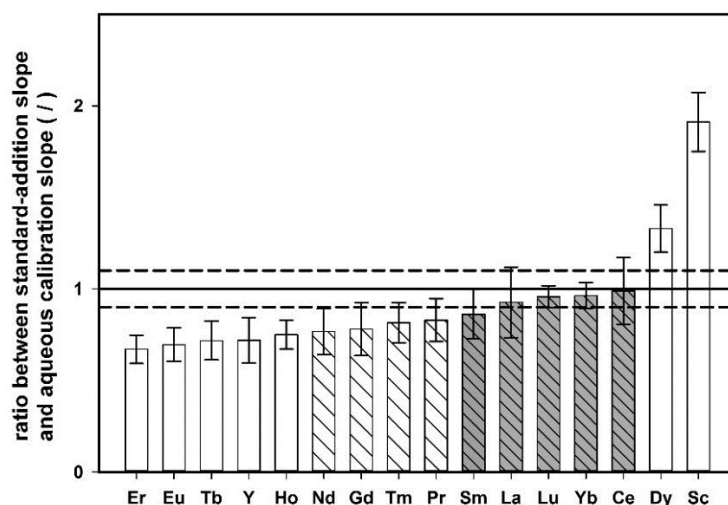


Figure 2.6. Ratio of the slopes obtained from standard-addition calibration and aqueous calibration (both in the range 0 – 10 $\mu\text{g L}^{-1}$, the error corresponds to the expanded combined uncertainty of the ratio, $k = 2$, the dashed lines correspond to $\pm 10\%$ deviation from a nominal ratio of 1).

2.3.6. Analysis of tea samples

For method validation, one tea-sample (tea-sample 11) was digested, and analyzed also with quadrupole ICP-MS in kinetic energy discrimination mode (KED-mode). Details regarding the ICP-MS method can be found in the electronic supplementary material. For this tea-sample, most elements

were below the respective detection limits, but for three elements, it was possible to obtain quantitative data with both methods. For those values, a good agreement between ICP-MS results (La: 720 ± 40 ng g⁻¹, Ce: 410 ± 20 ng g⁻¹, Y: 240 ± 20 ng g⁻¹) and the proposed ETV-ICP-OES procedure (La: 700 ± 80 ng g⁻¹, Ce: 440 ± 20 ng g⁻¹, Y: 180 ± 20 ng g⁻¹) was obtained.

Dispersed particle extraction was applied for enrichment of rare earth elements in ten different green tea samples (see table 2.1), followed by measuring the pre-concentrates by means of ETV ICP-OES. Quantification was carried out by means of standard-addition. To this end, one aliquot of the digested tea sample was pre-treated directly, whereas another aliquot was spiked with REEs and only then underwent the procedure. Table 2.4 summarizes the results for the investigated samples. For Ce, La, and Y all samples provided signals distinctly different from that of procedural blanks. In case of Gd and Tb contents were below the respective detection limits in all tea samples. For some elements (Dy, Eu), there was no significant variation observed in-between the samples, whereas other elements (Ce, La) showed concentrations differing for up to a factor of five. Obtained concentrations are generally in good agreement with typical REE-concentrations in tea samples. According to the results of green tea reference material GBW07605 analysis with ICP-OES²⁴, Ce, La, and Y have concentration of 0.92, 0.57 and 0.37 µg g⁻¹ in tea leaves. In another work regarding determination of REEs in four different tea samples by using ICP-MS¹¹ the range of concentration for Ce, La, and Y are respectively 0.62-0.99, 0.82-1.84 and 0.13-0.20 µg g⁻¹. These values are in similar order to the concentrations which are obtained in our work for Ce, La and Y including 0.340-1.800, 0.390-2.000, 0.090-0.540 µg g⁻¹ respectively²⁵⁻²⁷.

Table 2.4. Measured REE-concentrations in 10 different tea samples (all values in ng g ⁻¹ in the dry tea, n = 2, error corresponds to the standard deviation).				
	Ce	Dy	Er	Eu
tea 1	340 ± 5	< 8	< 20	< 9
tea 2	850 ± 360	270 ± 10	1200 ± 60	40 ± 10
tea 3	1500 ± 330	280 ± 30	800 ± 120	20 ± 5
tea 4	1700 ± 180	290 ± 10	< 20	< 9
tea 5	600 ± 130	< 8	< 20	< 9
tea 6	1800 ± 90	290 ± 10	880 ± 30	30 ± 5
tea 7	480 ± 160	240 ± 15	840 ± 30	20 ± 10
tea 8	180 ± 70	< 8	< 20	20 ± 5
tea 9	1000 ± 280	230 ± 5	1300 ± 10	20 ± 5
tea 10	850 ± 130	240 ± 5	< 20	20 ± 5

	Gd	Ho	La	Lu
tea 1	< 60	< 50	390 ± 10	10 ± 5
tea 2		1300 ± 170	870 ± 440	20 ± 5
tea 3		< 50	1400 ± 400	20 ± 5
tea 4		< 50	2000 ± 100	10 ± 5
tea 5		< 50	780 ± 120	10 ± 5
tea 6		830 ± 20	2000 ± 160	20 ± 5
tea 7		870 ± 120	540 ± 80	20 ± 10
tea 8		730 ± 100	370 ± 110	< 2
tea 9		1100 ± 70	750 ± 210	30 ± 20
tea 10		< 50	790 ± 110	20 ± 5
	Nd	Pr	Sc	Sm
tea 1	< 90	< 40	< 5	< 80
tea 2	7300 ± 480	< 40	70 ± 5	1000 ± 120
tea 3	5200 ± 400	260 ± 80	70 ± 5	< 80
tea 4	< 90	< 40	< 5	< 80
tea 5	3700 ± 400	< 40	30 ± 5	< 80
tea 6	5400 ± 250	180 ± 30	40 ± 5	< 80
tea 7	5000 ± 430	120 ± 10	50 ± 5	< 80
tea 8	4600 ± 330	< 40	< 5	< 80
tea 9	7800 ± 860	< 40	50 ± 5	1000 ± 190
tea 10	3700 ± 410	160 ± 5	40 ± 10	< 80
	Tb	Tm	Y	Yb
tea 1	< 40	< 30	140 ± 10	20 ± 5
tea 2		810 ± 150	460 ± 130	60 ± 10
tea 3		640 ± 100	240 ± 40	40 ± 10
tea 4		< 30	180 ± 5	30 ± 5
tea 5		< 30	160 ± 20	20 ± 5
tea 6		670 ± 50	540 ± 10	50 ± 10
tea 7		570 ± 20	400 ± 110	50 ± 10
tea 8		440 ± 10	90 ± 10	< 5
tea 9		880 ± 20	460 ± 10	50 ± 5
tea 10		490 ± 80	450 ± 80	60 ± 5

2.3.7. Summary and Outlook

In this chapter, the concept of dispersed particle extraction has been further explored by with ETV-ICP-OES for direct measurement of the analyte-containing sorbent particles. Compared to conventional slurry analysis, distinct improvements in sensitivity could be achieved, furthermore sample introduction with ETV allows to separate analyte and matrix in time. In order to achieve this goal, the use of an organic sorbent material instead of commonly applied silica based materials was necessary. For this purpose, *Lycopodium clavatum* spores coated with an ionic liquid acting as cation exchanger were used, which could be completely volatilized during the matrix-pyrolysis step in the ETV program.

The method was applied to the analysis of REE in digested tea samples, with typical detection limits in the range of 50 ng g^{-1} in the dry tea. The measurement procedure was shown to produce good results in terms of analyte recovery when performing spike-recovery experiments in combination with matrix-adjusted calibration. However, since slight differences in the matrix between different tea-samples persisted, two-point standard addition was relied upon for quantification. The results obtained for ten tea samples are in the same concentration range as reported by other authors^{11,24}.

The method presented here is a first proof of principle to show the applicability of natural bio-particles coated with ionic liquid for extracting and pre-concentrating REE elements. The method will be further optimized in terms of pre-concentration factor as well as digestion procedure, in order to mineralize the organic sample-matrix of the tea entirely. Then, it should be possible to rely upon aqueous external calibration, which would enhance sample throughput.

Furthermore, the procedure could be easily adapted to other tasks by simply changing the ionic liquid used for analyte extraction. With the use of task-specific ionic liquids, not only improvements in sensitivity but also selectivity are expected, compared to conventional SPE methods.

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Chapter 3. Sulfonated silica coated iron nanoparticles for rare earth elements enrichment

3.1. Introduction

Based on the previous works in our group¹⁻³ for trace element enrichment using dispersed particle extraction, in this chapter, magnetic nanoparticles were used as adsorbent for extraction. With these particles it is possible to reduce the time required for sample preparation because the particles can be separated by a magnet instead of centrifugation. This chapter is about application of functionalized silica coated iron oxide nanoparticles for pre-concentration of rare earth elements.

Materials with magnetic properties are classified as diamagnetic, paramagnetic and ferromagnetic. Diamagnetic and paramagnetic materials lose their magnetism by removal of external magnetic field but ferromagnetics are permanent magnets. When it is talked about magnetic materials commonly refers to ferromagnetics. Ferromagnetic samples consist of domains in which magnetization reaches its saturation. There are a few elements with ferromagnetic property in natural form including Fe, Co, Ni and their compounds and alloys with some other elements⁴.

Magnetic nano/micro particles have been immensely used in solid phase extraction as sorbent material prior to analysis by inductively coupled plasma optical emission spectrometry. Among them, iron oxide particles are the most used one due to the excellent paramagnetic properties, high dispersibility and ease of the surface modification⁵. To make the particles specific for target analyte(s), functionalization has to be done. This is possible when a reactive shell of a material surrounds the magnetic core which stabilizes it against oxidation and destruction by inorganic acids in one hand and makes a shield to avoid agglomeration on the other hand. Many different coatings including tunic acid⁶, manganese oxide and alumina⁸ have been used for magnetic particles. However, silica shell provides more alternatives due to the silanol groups on the surface which enable to anchor a variety of molecules as functional groups⁹⁻¹¹.

Due to lower electropositivity of silicon in comparison to the transition metals, it is not prone to be attacked by a nucleophile which results in stable and easy-handling compounds. The process of

making silica shell around the core is called Sol-gel process with steps including “(I) hydrolysis and condensation of the molecular precursors and formation of sols (II) gelation (sol-gel transition) (III) aging and (IV) drying”. One of the most common tetraalkoxysilanes used for sol-gel processing is tetraethoxysilane (TEOS) and since it is immiscible with water, ethanol is used as solvent to homogenize the reaction mixture. A mixture of a tetraalkoxysilane in water and alcohol would react very slowly. Therefore, acid or base catalysis is necessary to start the hydrolysis and condensation reactions. The time needed for gelation is reduced dramatically by using catalyzer¹².

3.2. Materials

For whole synthesis and analysis, high purity water 18 M Ω cm was used. Ferrous chloride tetrahydrate FeCl₂ · 4H₂O 99% (Sigma-Aldrich), ferric chloride hexahydrate FeCl₃ · 6H₂O (Merck), hydrochloric acid 37% (Merck), nitric acid 65% (Merck), Ammonia 25% (Merck), ethanol 99% (Chem-Lab), tri- sodium citrate (R. P. Normapur, VWR), tetraethyl orthosilicate TEOS (Merck), 3-mercaptopropyltriethoxysilane MPTS 95% (Sigma-Aldrich), trifluoroacetic anhydride TFAA (Merck); urea hydrogen peroxides UHP (Merck), acetic acid 96% (Merck) and ammonium acetate (Merck) were used as purchased. Dry acetonitrile and toluene were provided by TUWien solvents storage lab. REE multi-element calibration standard 1; 10 mg/L (Agilent Technologies), Rhodium ICP standard 1000 mg/L (Merck), single element ICP standards La, Eu and Nd 1000 mg/L (Aristar) were diluted upon the required concentrations.

3.3. Instrumentation

Analyses were performed by means of radial ICP-OES (Thermo iCAP 6500, Thermo Scientific, USA) including high solid nebulizer, a glass spray chamber with a riser and a torch tube with 2 mm inner diameter. The instrument parameters are shown in table 3.1.

Sample extraction procedure was performed in 15 mL conical polypropylene tubes with a V-bottom (VWR).

Table.3.1. ICP-OES parameters

ICP-OES parameters									
Plasma power		W		1200					
Radial viewing height		mm		11					
Plasma gas		Lmin ⁻¹		12					
Nebulizer gas		Lmin ⁻¹		0.8					
Auxiliary gas		Lmin ⁻¹		0.8					
Element	Ce	Dy	Er	Eu	La	Nd	Sc	Sm	Tb
λ (nm)	404.076	353.170	323.058	412.970	333.749	430.358	361.384	330.917	332.440
Element	Tm	Y	Yb	Rh*					
λ (nm)	346.220	371.030	369.419	343.489					

*Rh was used as an internal standard.

3.4. Iron oxide magnetic nanoparticles synthesis

Magnetic iron oxide particles were synthesized according to the literature¹³ with scaling up. The whole synthesis was performed under Ar protection. 50 mL of aqueous mixture of FeCl₂.4H₂O (0.4M) and FeCl₃.6H₂O (0.8M) in HCl (0.4M) was added dropwise to 500 mL of ammonia solution (28-30%) and it was stirred at room temperature for 2 h. The black produced particles were sonicated 20 min then, they were separated by external magnet from solution and washed three times with high purity water. To give the magnetic particles better dispersion, the method described in the article was followed¹⁴. 50 mL iron oxide nanoparticles suspension was stabilized with 60 mL of 0.16 mM sodium citrate solution by stirring at 60°C for 1h. The stabilized particles were washed with water as above. 30 mL of particles suspension was added to a mixture of 140 mL water, 140mL ethanol and 30 mL ammonia. A solution of 10 mL TEOS in 150 mL ethanol was added dropwise to the suspension and was stirred at room temperature for 72 h. The particles were centrifuged (13000xg, 5min) three times with ethanol and were separated by an external magnet from uncured particles. The silica coated magnetic particles were dried in oven at 90 °C overnight.

Functionalization of magnetite particles was performed as described in literature¹⁵. 6 g of the particles were hydrolyzed by stirring in 120 mL of 50% (v/v) HCl for 5h. The particles were washed with water to reach pH 7 and were dried in oven at 90 °C overnight. 4.5 g of the surface activated particles were transferred to a round flask which was dried and purged already with Ar. 6.75 mL 3-mercaptopropyltriethoxysilane (MPTS) and 225 mL absolute toluene were added and stirred for 2h at room temperature and then heated to reflux at 120 °C for 12 h. The resulting particles were washed with toluene and ethanol, and dried at 90 °C overnight.

Finally, to oxidize the thiol group on the surface to sulfonic acid, a mixture of 127 mL acetonitrile and 4.7 mL trifluoroacetic anhydride (TFAA) was cooled in an ice bath then 6.5 g urea hydrogen peroxide (UHP) was mixed with this solution. 4.2 g thiolpropyl-functionalized magnetite was added and stirred overnight at room temperature. The obtained sulfonated silica coated iron oxide nanoparticles were washed with ethanol and water, and dried at 90 °C overnight. The steps of the nanoparticles synthesis has summarized in figure 3.1.

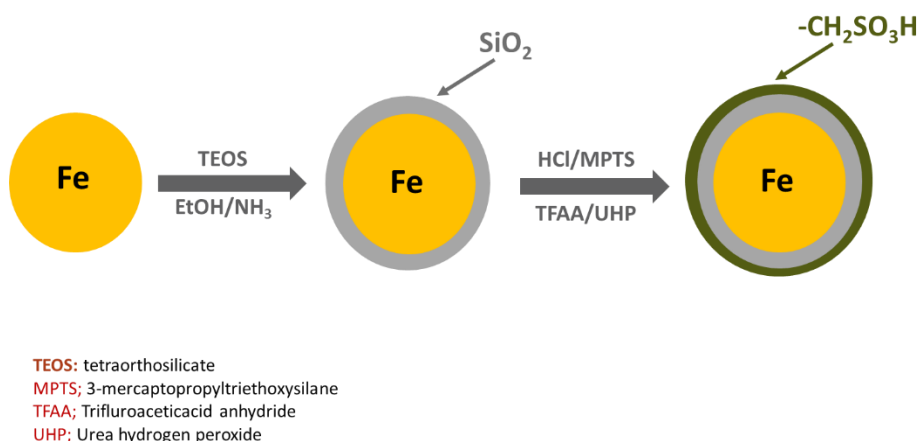


Fig 3.1. Schematic of sulfonated silica coated iron oxide nanoparticles

Structure and size of the synthesized nanoparticles were measured by transmission electron microscopy (TEM) which is presented in figure 3.2. The image shows 5 nm mono-dispersed functionalized nanoparticles. The surface area of the particles was determined 63.5 m²/g by BET analysis.

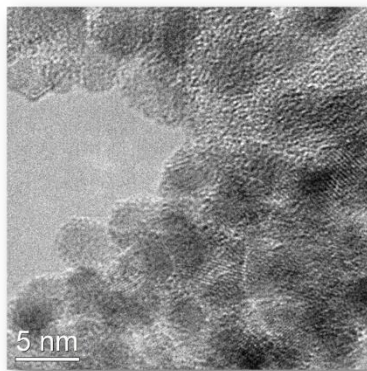


Fig 3.2. Transmission electron microscopy (TEM) image of functionalized silica coated iron oxide particles.

3.5. Optimization of dispersed particle extraction for retention of rare earth elements on the magnetite particles

Rare earth elements (REEs) are 17 elements, however, for optimization of affecting parameters, three elements including Eu, La and Nd which have respectively high, medium and low sensitivities in ICP-OES were chosen as representatives of whole group. Throughout the process, Rh was used as internal standard.

Different parameters which affect dispersed particle extraction were investigated and optimized. The parameters are including pH, buffer amount, adsorbent amount and reaction time.

3.5.1. Sample acidity

First of all, for efficient extraction, the acidity of sample solution has to be appropriate. Therefore, 10 mL samples containing 500 $\mu\text{g/L}$ Eu, La and Nd were acidified by HNO_3 to have different acidities including 0.01, 0.025, 0.075, 0.15, 0.23, 0.30, 1 and 3% (v/v). Then, 100 μL of 1M ammonium acetate buffer and 5 mg of the iron nanoparticles were added. The sample suspensions were sonicated for 10 min to give enough time for reaction between analyte and particles. After separating particles by a magnet, the precipitates were diluted to 2.5 mL with 1% HNO_3 and measured (Theoretical enrichment factor of 4). The results are summarized as a graph in figure 3.3. Based on the results, samples with 0.15% (v/v) acidity were found optimum. Accordingly, for

the next experiments sample acidity was chosen 0.15% (v/v). Relative standard deviation of measurements obtained from three replicates were 1-2%.

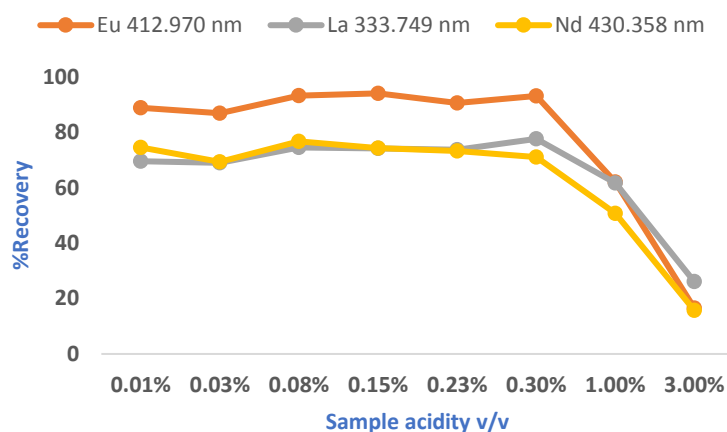


Fig 3.3. Effect of sample acidity on the recovery of selected REEs

3.5.2. Buffer amount

To stabilize sample pH, ammonium acetate buffer was added in different levels; 0.003, 0.03, 0.3 and 3 mL to 10 mL sample solutions of 12.5 µg/L the target elements in the same condition explained above. It was observed that the addition of buffer more than 0.3 mL (3% v/v) has reverse effect on the retention which can be a result of buffer ions interfering on the retention of target analytes. pH of the sample solution with maximum recovery was determined 3.5. As it is shown in figure 3.4, 0.1 mL buffer was the optimum volume. In case of Nd, the concentration was below its detection limit, then ICP-OES did not record the signal.

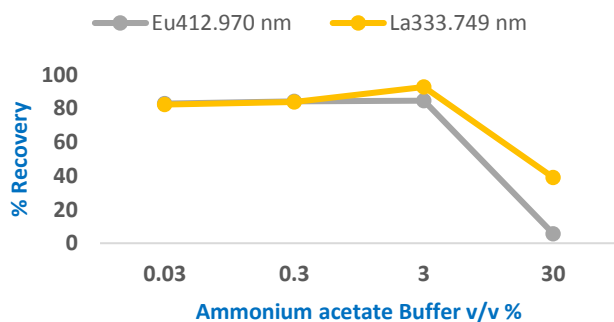


Fig 3. 4. Effect of ammonium acetate buffer amount on the recovery of selected REEs

3.5.3. Sorbent material amount

Sufficient sorbent material for maximum retention of the elements was investigated by addition of different mass of functionalized iron oxide particles including 2, 3, 4 and 5 mg and reaction for 10 min in ultrasonic bath with 12.5 $\mu\text{g/L}$ analyte solution in the chosen conditions for acidity and buffer amount (3 replicates,). As mentioned before, Nd did not show any peak because of low concentration. The trends for La and Eu is presented in figure 3.5. With the findings from this experiment, 5mg magnetic nanoparticles was chosen to reach maximum retention of analytes.

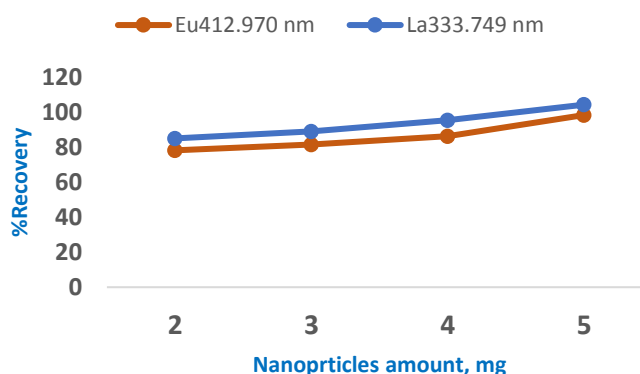


Fig 3.5. Effect of sorbent material amount on the recovery of selected REEs

3.6. Influence of co-existing ions

Since the optimized method will be used for determination of trace elements in environmental samples, the influence of ions in the sample matrix should be studied.

3.6.1. Single charged ions

For this, a set of samples (3 replicates) including 25 $\mu\text{g/L}$ of the analytes plus 0.1, 1, 10, and 100 mg/L of Na, K, and Rb were prepared in the optimized conditions; 0.15% v/v sample acidity, 0.1 mL ammonium acetate buffer, 5 mg adsorbent and 10 min reaction time. Particles were separated by magnet and suspended in 2.5 mL 1% HNO_3 . As it is illustrated in figure 3.6, by increasing the concentration of single charged ions, the recovery of the Eu and La increase. It means at this pH, single charged ions cannot compete with the multiple charged REE ions. Whereas they rise ionic

strength of the medium which improves the reaction conditions between sorbent particles and analytes.

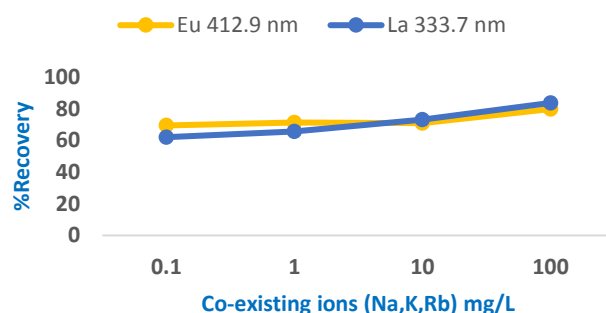


Fig 3.6. Effect of single charged ions on the recovery of the selected REEs.

3.6.2. Double charged ions

To investigate how double charged ions affect on the recovery, a similar sample set of 25 $\mu\text{g/L}$ Eu, La and Nd was made in the presence of 0.1, 1, 10, and 100 mg/L of matrix ions including Ca, Mg, and Sr (3 replicates). Despite single charged ions, the adsorbent particles cannot tolerate concentration above 10 mg/L of the double charged ions. Consequently, the recovery of REEs reduces above 10 mg/L. This is clear in figure 3.7 for Eu and La.

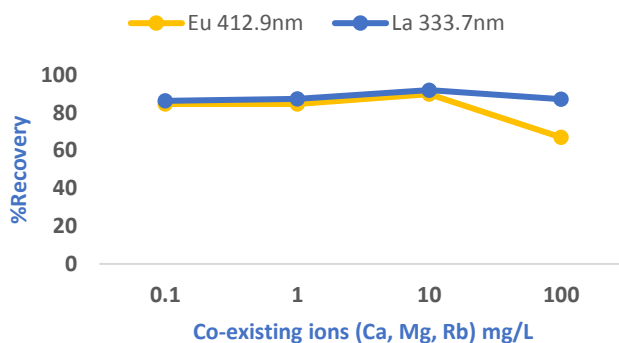


Fig 3.7. Effect of double charged ions on the recovery of the selected REEs.

3.7. Sample measurement with ICP-OES

Rare earth elements have lower sensitivity in ICP-OES compared to other trace elements. As a result, while they are analyzed in presence of an element like Fe, there are possibilities of getting interfered by strong iron emission lines. To reduce this probable spectrometric interferences, one approach can be removing iron particles from final sample suspension after enrichment.

Based on the silica coated iron particles structure, it is supposed that the analytes are retained by the functional groups on the silica shell. Therefore, if this shell is detached from the iron core, the core can be collected by an external magnetic field and removed. Thus, the measurand will only consists of analyte plus dissolved silica shell.

To show the efficiency of this method, samples containing 100 µg/L were analyzed in three different forms. In the first group, the enriched samples were analyzed as conventional slurry. In the second one, the silica shell was dissolved by 150 µL of 10% HF/HCl then after separation of the undissolved cores by magnet, the remaining solution was analyzed. In the last group, the whole particles were digested by addition of 400 µL concentrated HCl and heating then solution was measured.

As it is presented in figure 3.8, the recorded signals of the last group including the Fe is still the highest because it contains all the ingredients without any loss. But relative standard deviations (RSD) for this method were also the highest; about 40% against 2-10% for the other methods. Regarding the results, it seems the method of silica shell destruction is an appropriate way to increase the signal intensity with low RSD. However, it is not applicable for our goal because we need non-destructed magnetic particles for on-line enrichment.

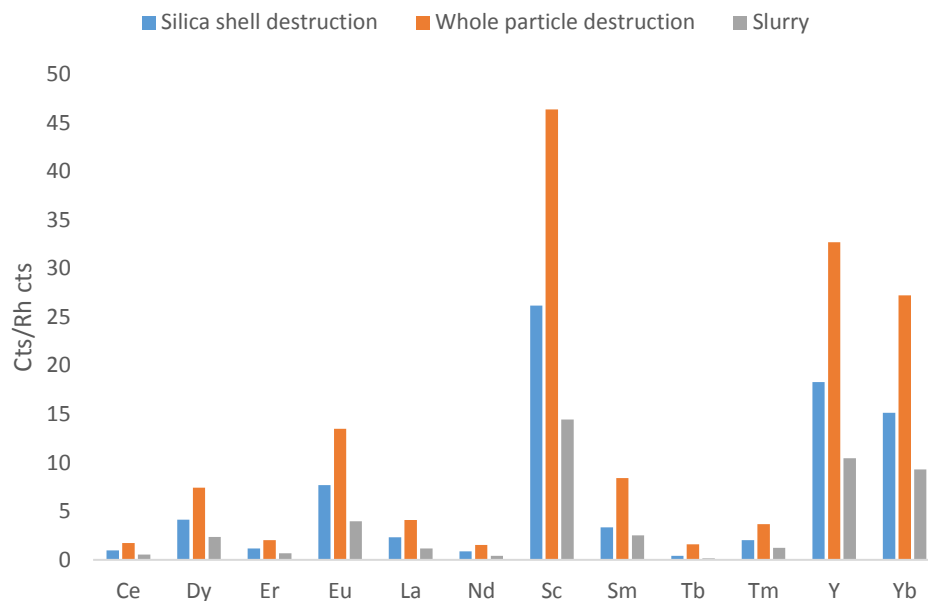


Fig 3.8. Comparison of REEs intensity in ICP-OES by using different methods of sample analysis.

3.8. Figures of merit

To determine limit of detection (LOD), a calibration function was made by 10 mL 0.15% HNO_3 standard solutions including 10, 20 and 50 $\mu\text{g/L}$ of rare earth elements respectively. The results were compared with calibration of the analogue solutions containing iron nanoparticles. The extraction of analytes was performed according to the optimized DPE and the final volume was reduced to 1.5 mL after discarding the supernatants and silica shell dissolution by 10% HF/HCl mixture. That is, the theoretical enrichment factor $10/1.5 = 6.7$ should be obtained in ideal case. Practical enrichment factor was calculated as slope of calibration with nanoparticles divided by slope of standard calibration. The results for REEs are shown in table 3.2. From the practical enrichment factor it can be judged that the recovery of REEs is done perfectly in the absence of matrix. LOD was obtained based on 3 times standard deviation of blank divided by slope. LOD for REEs was below 1 $\mu\text{g/L}$ except for Gd, La and Lu¹⁶⁻¹⁸.

Table 3.2. Parameters of calibration function made by aqueous standards and enriched samples.

	<i>PEF^I</i>	<i>LOD^{II}</i>	<i>Slope^{III}</i>	<i>Slope^{IV}</i>	<i>Intercept^V</i>
Ce	6.1	0.7	6.9	1.1	123
Dy	5.4	0.0	32.0	5.9	290
Er	5.7	0.9	9.3	1.6	71
Eu	5.2	0.1	51.1	9.7	539
Gd	6.2	3.3	4.9	0.8	36
Ho	5.3	0.7	10.6	2.0	80
La	7.0	1.6	9.3	1.3	147
Lu	5.9	10.2	7.3	1.2	46
Nd	4.5	0.8	5.7	1.3	54
Sc	6.3	0.1	150.6	23.8	176
Tb	9.2	0.7	5.3	0.6	29
Tm	5.6	0.7	16.7	3.0	139
Y	6.1	0.1	69.1	11.4	766
Yb	5.9	0.1	122.3	20.8	1187

I: Practical enrichment factor, II: Limit of detection, III: Slope of calibration with particles,

IV: Slope of standard calibration, V: Intercept of calibration with particles.

3.9. Conclusion

Sulfonated silica coated iron nanoparticles was synthesized to be applied as adsorbent for rare earth element via dispersed particle extraction. Although, the results of experiments were satisfying in case of LOD and recovery but the iron nanoparticles did not admit our expectation for on-line system because they did not possess strong enough magnetic characteristic as much as needed for flow injection analysis. Because, the nanoparticles cannot be trapped by external magnetic field quantitatively and some portions are lost, especially when they are supposed to be trapped from a flow of sample suspension. This might be due to small size of the particles besides their intrinsic weaker magnetic property than cobalt. Consequently, more studies were shifted to cobalt nanoparticles which are more compatible with our goal because of being magnetic, much stronger than iron.

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Chapter 4. Co@SiO₂@Ionic liquid magnetic particles for determination of Pb in drinking water with FI-ICP-OES

4.1. Introduction

Regarding the outcomes from last works of our group using dispersed particle extraction (DPE) with functionalized silica particles¹⁻³ and ionic liquid coated *lycopodium* spores⁴ and considering the deficiency of iron nanoparticles (chapter 3) for on-line application, functionalized cobalt particles were prepared to use in FI-ICP-OES.

When using DPE, capacity, as well as particle diameter of the resin must be optimized, to guarantee complete recovery and to avoid nebulizer blockage. Tuning the resin's properties has however its limitations: when using for example very small resin particles, it becomes difficult to effectively separate the analyte-loaded particles from the liquid sample by means of centrifugation, thus decreasing sample throughput.

In this chapter, magnetic particles (silica-coated cobalt particles) are therefore used for DPE extraction. These particles are covered with an outer layer of task-specific ionic liquid (TSIL) to extract the analyte, as such a layer of TSIL offers a higher analyte-capacity, compared to single-layer systems⁴. The magnetic properties of the particles allow for a swift phase-separation by applying an external magnetic field.

Likewise, iron nanoparticles with magnetic characteristic have been used in several researches⁵⁻⁷. To date, only one research from accessible references has presented the synthesis of cobalt nanoparticles (not in the composite form with other metals) for extraction⁸. Ionic liquid which was used on the outermost layer of the magnetic particle, acts as cation exchanger for trapping the analyte. Ionic liquids are a class of salts have melting point lower than 100°C with thermal stability and strong ionic characteristic that have been known beneficial for metallic elements extraction from environmental samples⁹⁻¹⁵.

To further improve repeatability and pre-concentration capacities of the method, a flow-injection (FI) system was conceived, which uses a switchable electromagnet to trap and release the analyte-

loaded particles as required. An additional advantage of the FI system developed is the fact that the analyte-loaded particles are released as sharp peak, thus introducing the entire amount of analyte in a short time, thus improving signal intensity and increasing the overall sensitivity of the method.

This FI-ICP-OES method using magnetic and ionic-liquid coated particles following the DPE-approach was applied for determination of Pb in certified reference material ERM-CA022a (soft drinking water UK-Metals) and in drinking water samples from Vienna, Austria. Due to toxicity of Pb^{16,17}, the permitted level in drinking water is 10 µg/L¹⁸. Thus, in sample preparation for optimization this value was taken into account.

4.2. Experimental

4.2.1. Reagents and materials

Throughout the synthesis and analysis, high purity water (18 MΩ cm) obtained from a purification system Easypure (Thermo, USA) was used. Cobalt powder (H. C. Starck GmbH), tri-Sodium citrate dihydrate (R. P. Normapur, VWR), tetraethylorthosilicate (Merck), ammonia 25% (Merck, Germany), ethanol 99% (Chem-Lab) and methanol (Merck) were used for particle synthesis. Hydrochloric acid 37% (Merck) was used for particle surface activation.

Sodium tetraborate 98% anhydrous (Acros Organics) and crystalline boric acid (Merck), sodium dihydrogenphosphate dihydrate extra pure (Merck), disodiumhydrogen phosphate dodecahydrate pro analysis (Merck), ammonium acetate (Merck) and acetic acid 96% (Merck) were used for buffer preparation. Nitric acid 65% (Merck) and ethanol absolute for analysis (Merck) were used for sample dilution and as carrier liquid for ICP-OES analysis respectively. Single element ICP standard Pb CertiPure (Merck, 1000 mg/L, 2-3% HNO₃) was applied with the required dilutions.

4.2.2 Instrumentation

ICP-OES measurements were assessed by means of radial ICP-OES (Thermo iCAP 6500, Thermo Scientific, USA) consisting of a high solid nebulizer, a glass spray chamber with a riser and a torch tube with 2 mm inner diameter for sample introduction. The ICP-OES conditions are presented in

table 4.1. In the finalized set-up to enhance the precision of analysis and signal intensity, the peristaltic pump was eliminated and nebulizer transferred the samples as self-aspirating.

Table.4.1. ICP-OES conditions with self-aspirated nebulizer

ICP-OES parameters			Element	λ (nm)
Plasma power	[W]	1550	Pb	220.353
Radial observation height	[mm]	15	Co	195.742
Plasma gas	[Lmin ⁻¹]	12	Co	221. 143
Nebulizer gas	[Lmin ⁻¹]	0.5	P	177.495
Auxiliary gas	[Lmin ⁻¹]	0.6		

In the initial optimization procedure with conventional analysis the instrument condition was a little different. Plasma power 1200 W, radial observation 11 mm, nebulizer gas flow 0.65 Lmin⁻¹, auxiliary gas flow 0.8 Lmin⁻¹.

For batch-wise separation of magnetic nanoparticles, Block magnet 40 x 20 x 10 mm, neodymium, N42, nickel-plated (Supermagnete, Germany) was applied. For flow injection system, the homemade electromagnet trap consisting of U- shape magnet, copper coil and AC power supply was used. Sample extraction procedure was performed in 15 mL conical polypropylene tubes with a V-bottom (VWR). Water samples were collected in 50 mL centrifuge tubes w. screw cap (BRAND, Germany).

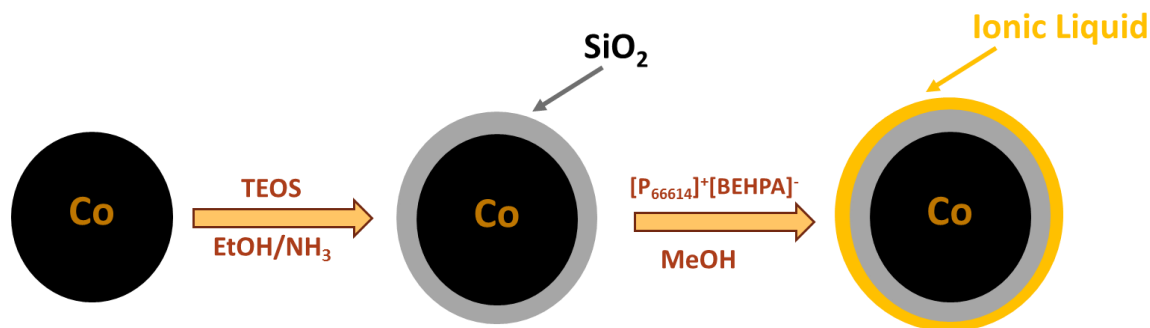
4.2.3. Magnetic particle synthesis

Synthesis of the silica coated particles was performed based on the method in literature¹⁹ with some modifications. High purity water and ethanol were deoxygenated in ultrasonic bath by flushing Ar into for 1 h and were consumed immediately in the synthesis. Whole synthesis was performed under Ar protection. At the first step, cobalt particles with the size of 300-400 nm were stabilized by 0.16 mM tri-sodium citrate solution in water to avoid agglomeration; 6 mL citrate solution was used for 1 g of particles already suspended in 20 mL water. The suspension was stirred for 1h at 60° C then the particles were washed with water. Silica shell formation around the cobalt core was done according to the reference²⁰ by scaling up. A mixture of 14 mL water, 14 mL

ethanol and 3 mL ammonia was prepared for suspension of 1g cobalt particles in water. Then, a solution of 1 mL TEOS in 15 mL Ethanol was added dropwise to the suspension. The mixture was stirred at room temperature rigorously for 72 h at 900 rpm. Silica shell stabilizes somehow the cobalt particles against oxidizing and dissolving in solvents and also enables to anchor functional groups to silanols on the surface after activation. Activation of silica surface was assessed according to the method reported, with a few changes²¹. 1g of the silica coated particles were dispersed in 20 mL 25% HCl and were stirred at room temperature for 2 h. The particles were washed with water to reach neutral pH and then dried under high vacuum overnight.

“The ionic liquid used as the external shell of the particles consisted of the trihexyl(tetradecyl)phosphonium anion and the Di(2-ethylhexyl) phosphate cation. Throughout this work, the nomenclature $[P_{66614}]^+ [BEHPA]^-$ will be used for the ionic liquid. Synthesis of $[P_{66614}]^+ [BEHPA]^-$ was carried out at the institute of applied synthesis chemistry of TU Wien, according to the following scheme: Trihexyltetradecylphosphonium chloride (5.19 g, 10 mmol), bis(2-ethylhexyl) hydrogenphosphate (3.54 g, 11 mmol) and potassium hydroxide (0.62 g, 11 mmol) were suspended in 100 ml of water:MeOH 1:1 and stirred for 2 hrs at room temperature. The solution was concentrated to approx. 60 ml and diluted with water. This mixture was repeatedly extracted with dichloromethane. The combined organic layers were washed with water until no more chloride ions could be detected in the wash solution (checked by addition of an aqueous $AgNO_3$ solution), dried over Na_2SO_4 and concentrated under reduced pressure. Remaining solvent traces were removed under high vacuum (0.01 mbar, 48 h) with stirring at 50°C to yield trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphonate as clear colourless liquid in 94% yield⁴. Derived product was characterized using NMR” (Supplementary data is shown in appendix).

To make the silica-coated Co particles selective for Pb extraction, 5 mg ionic liquid Trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate $[P_{66614}]^+ [DEHPA]^-$ was dissolved in 10 mL methanol and then 495 mg of the silica coated cobalt powder were added and shaken smoothly on a moving plate for 2 h. The resulted particles were dried primarily using rotary vacuum pump and then under high vacuum overnight. By this way, Cobalt @SiO₂ @ 1% ionic liquid was prepared. Shown figure 4.1 is the schematic of the particle synthesis.



TEOS: tetraethylorthosilicate

[P₆₆₆₁₄]⁺[BEHPA]⁻: trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphonate

Fig 4.1. Co @ SiO₂ @ [P₆₆₆₁₄]⁺[DEHPA]⁻ synthesis process

4.2.4. Sample collection and comparative measurements with ICP-MS

Tap water was collected from four households located in different districts of downtown Vienna, Austria. Water samples were collected in 50 mL centrifuge tubes w. screw cap (BRAND, Germany). The water samples were acidified with HNO₃ to 0.1% (v/v) immediately after collection to stabilize the contents. 8 samples were drawn at each location, 4 samples were analysed directly, and 4 samples were spiked to a level of 10 µg/L Pb prior to analysis, for the purpose of recovery-studies.

A portion of each of the samples was analyzed by means of ICP-MS (Thermo iCAP Qc) using standard parameters and an external aqueous calibration. Indium was used as internal standard in analysis with ICP-MS. The monitored isotopes were ¹¹⁵In, ²⁰⁶Pb, ²⁰⁸Pb, and the detection limit for Pb was determined to be 0.01 µg /L.

4.2.5. Sample preparation using dispersed particle extraction

To extract Pb from sample solution, the dispersed particle extraction was applied as it is explained. 14 mL of acidified pure (0.1% v/v) water with nitric acid was spiked with given concentration of Pb stock solution (in case of environmental sample, tap water was acidified as the same). The

sample solution was conditioned by addition of 1.02 mL of 0.75 M borax/boric acid buffer to reach $\text{pH} = 5.5 \pm 0.5$ for efficient extraction. Then, 1.5 mg of the cobalt particles, as adsorbent, were added to the solution and it was smoothly shaken by hand for 10 min. A strong magnet was used to separate the particles retaining Pb ions from the suspension. After discarding supernatant, the particles were re-suspended in 0.5 mL 2.5×10^{-3} M ammonium acetate/acetic acid buffer and were measured as suspension by ICP-OES. The ammonium buffer increases Pb signal intensity (25-50%) as a result of improvement in the excitation condition and plasma robustness²². The synthesis steps are illustrated in figure 4.2.

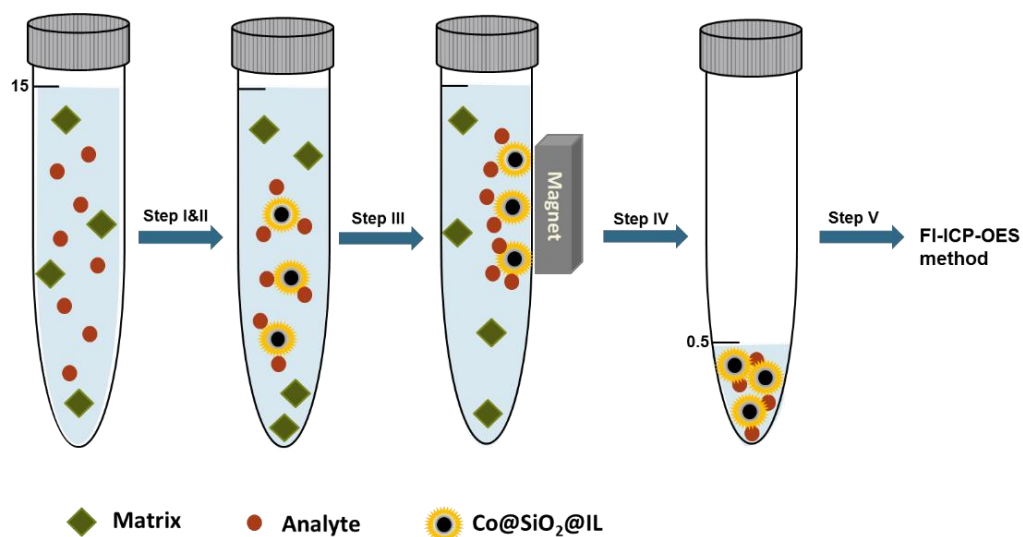


Fig 4.2. Dispersed particle extraction steps; step I: conditioning, step II: reaction with sorbent, step III: separation of particles by magnet, step IV: re-suspension in buffer, and step V: measurement by means of FI-ICP-OES method.

4.2.6. Flow injection analysis (FIA)

The samples which were prepared and pre-concentrated as described in section 4.2.5 were introduced to the ICP-OES detector by means of a flow injection set-up including an electromagnetic trap. The FI set-up has the advantage that all particles (and all analyte) present in one sample are used for one single measurement, yielding highest sensitivity. As the magnetic trap further pre-concentrates the particles and the analyte, a sharp transient peak is obtained. This peak

has optimal signal-to-noise ratio, compared to continuous sample uptake. Both aspects (complete sample consumption, and additional pre-concentration in the magnetic trap) are advantageous in terms of sensitivity, and in terms of repeatability.

Figure 4.3 shows the FI-ICP-OES set-up. Sample uptake is done by using the self-aspiring modus of the concentric nebulizer, thus avoiding possible pulsing of a peristaltic pump which might cause premature release of trapped particles.

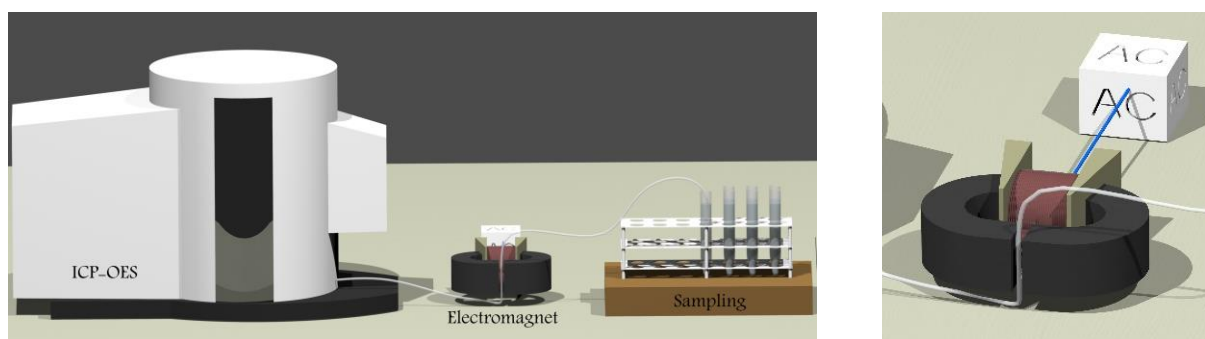


Fig 4.3. Left: configuration of FI-ICP-OES system, Right: closer view of electromagnet trapping device.

Measurement of one sample is carried out as follows (see also table 4.2): the sample suspension is taken up completely while the magnet trap is on. This causes the particles to pre-concentrate in the magnetic cavity, while the water/buffer mixture continues in the direction of the nebulizer. As soon as the sample container is empty, the line is switched to water, in order to wash the trapped particles in the trap. To help release the particles, a small air-bubble is now introduced, followed by a water-ethanol mixture. As the air-bubble reaches the magnetic cavity, the magnet is switched off. The combination of air-bubble and missing magnetic-field causes the particles to re-suspend in the water-ethanol mixture, and to continue their path towards the nebulizer. During initial method optimization, it was found that the water-ethanol mixture effectively prevents agglomeration of the particles which can cause nebulizer blockage.

At the end of each sample-run, the system is rinsed with 10% HNO_3 to dissolve any remaining cobalt particles in the system, and to make sure that the nebulizer is free from agglomerates. Then, the system is washed with water to remove remaining acid, and the next analysis can be started.

Table 4. 2. Sequence and operational conditions of the FI-ICP-OES system.

step no.	duration	magnet trap	action
1	2 min	on	rinse with water (18.2 MΩ cm)
2	~ 40 s	on	switch to sample-suspension, aspire entire volume
3	-	on	particles are trapped at the magnet
4	10 s	on	aspire water to wash particles
5	5 s	on	aspire air to create a small air-bubble in the FI line
6	-	on	switch to 1% ethanol in water
7	-	off	as air-bubble reaches magnet, switch off magnet
8	-	off	start signal acquisition
9	1 min	off	rinse with 10% v/v HNO ₃

4.3. Results and discussions

4.3.1. Optimization of the extraction procedure

Parameters which influence this extraction procedure including pH, buffer type and buffer concentration, sorbent material amount and sorbent-analyte interaction time were investigated prior to the first separation step (see section 4.2.5). All optimizations were performed for batch-wise analysis going through the initial sample volume of 10 mL and reducing to 2 mL after reaction and separation by a magnet then, measurement in conventional mode of ICP-OES. Since, cation exchanging process is pH dependent, pH range of 3-7 was investigated to find suitable pH for retention of Pb ions on the particle surface. Preliminary experiments for finding sufficient amount of buffer started by ammonium acetate buffer. Unexpectedly, there was weak signal of lead in spite of correct sample pH for enrichment. Owing to measurement in conventional ICP-OES mode, it was not possible to recognize whether ammonium acetate causes losing some part of cobalt nanoparticles before switching off the magnet. But, when the analysis was performed in timescan mode it showed that there were cobalt and simultaneously lead signals at the time which was not expected. This means part of particles and the adsorbed lead on their surface were missed before switching off the magnet. Therefore, three other buffers including 2 M citrate (trisodium citrate/nitric acid), 1 M phosphate (disodium hydrogen phosphate/sodium dihydrogen phosphate) and 0.75 M borate (borax/boric acid) were prepared and the required amounts of each were examined according to the values obtained in advance by calculations. To compare the efficiency

of each buffer for lead extraction, a set of aqueous samples with 100 $\mu\text{g/L}$ Pb were conditioned to $\text{pH}=5.5\pm0.5$ (the optimum pH for quantitative retention of Pb) by addition of 0.9, 1 and 1.5 mL of the buffers and then reacted with 5 mg of cobalt particles for 10 min by shaking with hand smoothly. The particles were separated by a magnet, re-suspended in 2.5×10^{-3} M acetate buffer and measured via FI system. As it is clear on figure 4.4, there are recorded signals of cobalt from 65 sec to 120 sec despite our expectation. Magnet was on till 130 sec and the particles could not have released from magnet trap. This could lead the conclusion that the buffers cause particles dissolving. However, compared to other three buffers, sample consisting borate buffer had the weakest signal at this period, then 1.02 mL of 0.75 M borate buffer was chosen for conditioning of the samples in DPE process. In figure 4.4, the enlarged view of the signals are shown as well.

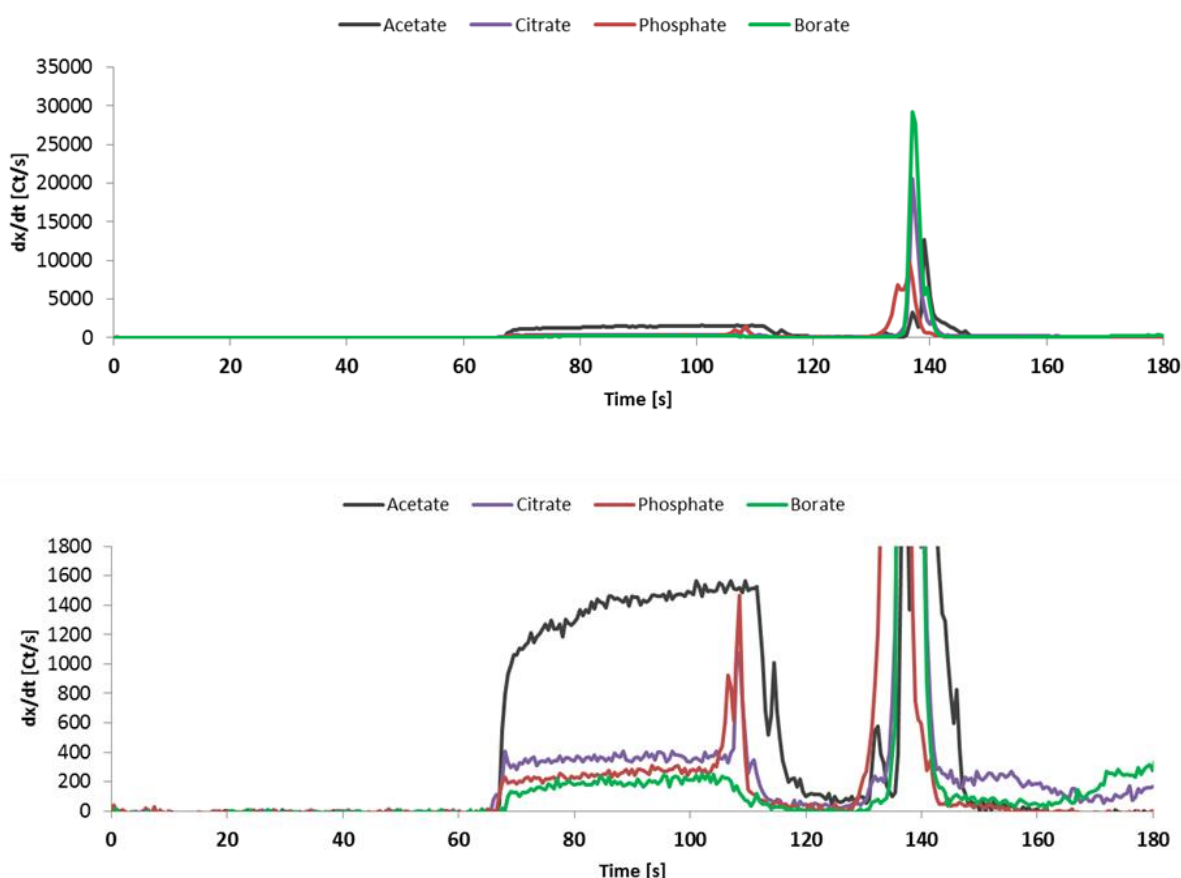


Fig 4.4. Comparison of four buffers for pH adjusting of aqueous samples in DPE by recording cobalt signal in timescan mode. The lower graph is illustrated as enlarged to clarify the preference of using borate buffer.

The sufficient amount of sorbent material was selected by addition of 1.5, 2.5, 5 and 10 mg of cobalt particles to sample solutions of 2 mg/L Pb and following DPE process. The optimum amount of sorbent particles was determined 5 mg in the adjusted pH. To let the cobalt particles retain Pb ions quantitatively, various interaction times including 2, 5, 10 and 20 min were examined and the outcome was that 10 min is enough to have highest recovery, 87%, in the sample with 2 mg/L Pb content. Accordingly, through analysis these conditions including sample pH of 5.5 ± 0.5 with 1.02 mL of 0.75M borax/boric acid buffer, 5 mg cobalt nanoparticles and reaction time of 10 min were applied.

4.3.2. Optimization of FI-ICP-OES measurement protocol

The ICP-OES system (Thermo iCAP 6000) in combination with the software used (iTEVA, Thermo Scientific) allow for two types of data recording. The first mode is the “conventional mode”, in which signal is recorded for a given acquisition time (on-peak, as well as background signal), and a background-corrected intensity is stored.

Conventional mode is the routine way but it is not proper when sample to be pumped is in slurry form. Because, the pulses produced by the pump reduce the precision of the slurry analysis greater than of homogenous solution. The particles move in the flow can be stopped at the intake tube holding points and released randomly. Therefore, as it was mentioned in section 4.2.6 the sample introduction was performed in the set-up without pump. Thus, the recorded steady state signals of Co and Pb had higher intensity. In figure 4.5, Pb signal obtained in conventional mode is illustrated.

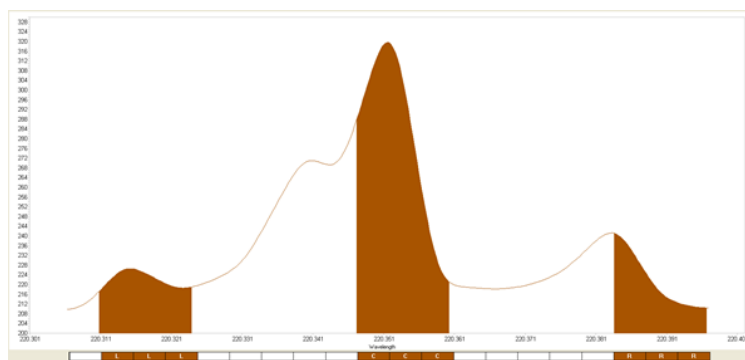


Fig 4.5. Pb signal of enriched aqueous sample spiked with 20 µg/L Pb in conventional ICP-OES analysis.

The second mode is the “time-scan” mode, which stores data in rapid succession, with given time-slices in the range of 0.5 - 2 seconds. Also with time-scan mode, background-corrected signals are obtained. Figure 4.6 shows a time-scan data-set for one measurement with the FI-ICP-OES system.

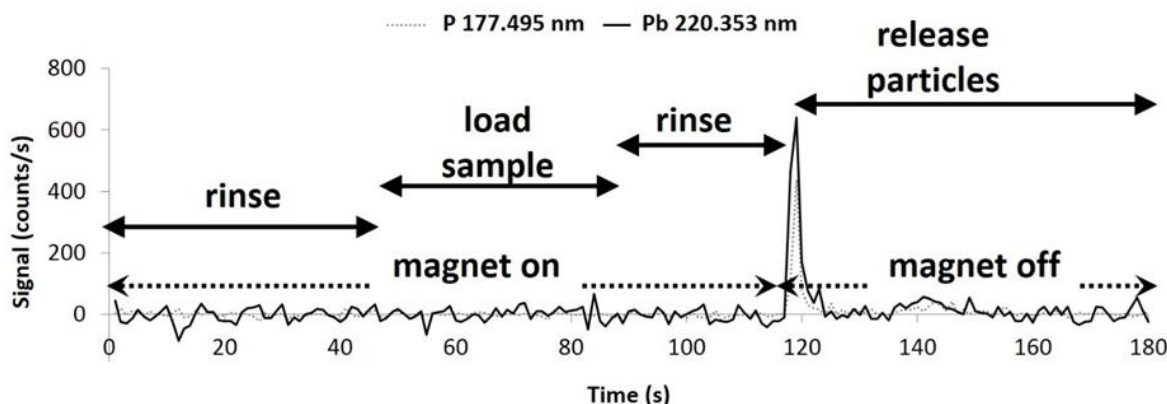


Fig 4.6. Time scan of sample analysis with magnet on/off states.

As can be seen from the data recorded, no lead-signal is observed during loading of the particle suspension, but as soon as the magnet is switched off, the analyte-loaded magnetic particles are released, causing a sharp peak in the lead signal. Simultaneously, the phosphorus signal rises, which is due to the phosphinate/phosphonium-nature of the ionic liquid coating. This confirms that the analyte is trapped on the coated particles throughout the FI-ICP-OES protocol.

Both acquisition modes (“conventional” and “transient”) were compared in terms of ease of data treatment, and sensitivity. Due to the fact that time-slices in transient mode are very short (As it is shown in figure 4.7 sometimes, the cobalt transient signal cannot be recorded entirely due to overloaded particles), the signal/background ratio for this mode was found to be inferior, compared to the “conventional” mode, which uses an integration time of 6 seconds. Therefore, conventional mode was used for all further measurements. Furthermore, as it was stated Pb signal is corrected by normalizing to the Co signal intensity in this work, it was required to have cobalt signals entirely which can be obtained by conventional mode.

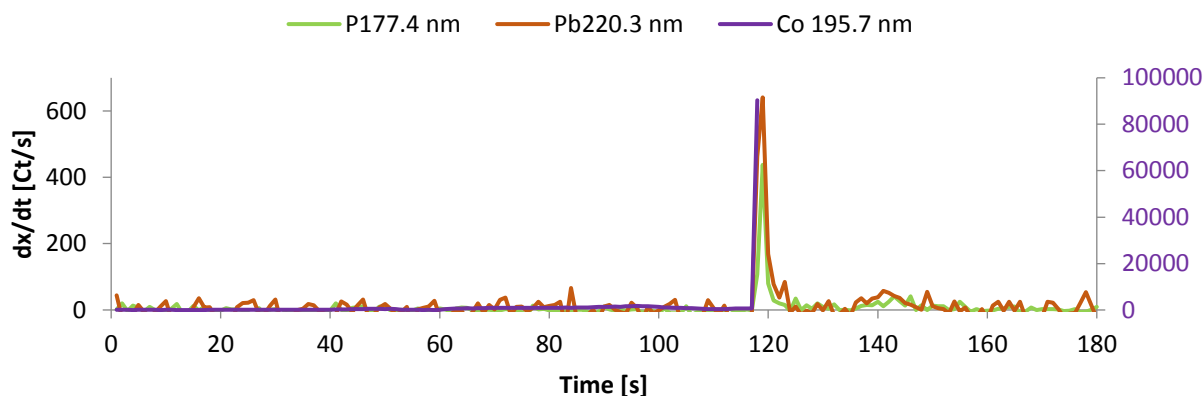


Fig 4.7. Transient signal of sample analysis with magnet on/off states in timescan mode. Signal of Co is not recorded entirely due to overloaded ions on plasma.

4.3.3. Figures of merit

The optimized conditions for extraction of Pb by Co @ SiO₂ @ [P₆₆₆₁₄]⁺[DEHPA]⁻ particles and analysis by FI-ICP-OES were applied to obtain limit of detection (LOD), relative standard deviation (RSD) and linear range. To determine LOD, a calibration curve was prepared by set of aqueous standard solutions including six blanks and spiked samples with 5, 10 and 20 µg/L Pb (n=4). LOD = 3 µg/L was calculated by three times standard deviation of blank divided by slope. The similar set was prepared with non-spiked 1:10 diluted tap water samples and spiked ones with 7.5, 15 and 30 µg/L Pb which yields LOD of 4 µg/L. Linear range for both series is up to 30 µg/L Pb with correlation factor R² of 0.95. RSD of the method obtained from the six blanks is 20%. This imperfect precision is the result of high blank values which is originated from impurity in cobalt metallurgic substrate. Although the care has been taken in all synthesis steps but it was released that the impurity is due to the raw cobalt cores before addition of any reagents. The raw cobalt particles show unexpected Pb background in ICP-OES recorded signals. The high value of LOD can be explained as well by non-zero blank signals. Furthermore, the increased LOD obtained from tap water calibration reveals the matrix influence on the extraction of Pb. As it was reported by Vienna's municipality the average concentrations of Ca and Mg in tap water as competitor ions to occupy the positions on the sorbent surface are 62 and 16 mg/L. These matrix

ions cause the difference between the slopes of aqueous standard and tap water samples calibration curves.

4.3.4. Method validation

To validate the introduced method for Pb determination, certified reference material ERM-CA022a (soft drinking water UK-Metals) was analysed. The concentration of Pb in the CRM was calculated by the calibration function made of both tap water and CRM. Co signals were used for background correction by dividing all responses to those values. Consequently the average concentration of Pb in CRM was obtained $29 \pm 3 \mu\text{g/L}$ which is comparable to the certified value $26 \pm 0.9 \mu\text{g/L}$.

4.3.5. Application of method

The method applied for determination of Pb in drinking water collected from four different district in Vienna, Austria; 1040 Wieden, 1060 Mariahilf, 1100 Favoriten and 1150 Rodulfsheim-Fünfhaus. The water samples were collected in centrifuge tubes w.screw cap and acidified immediately with HNO_3 to have 0.1% (v/v) acidity stabilize the contents in the optimized acidity required for quantitative extraction. Two sets of samples were prepared based on the method of enrichment explained in section 2.4 with 4 replicates of non-spiked and spiked ($10 \mu\text{g/L}$ Pb) solutions of each districts. A portion of the same non-spiked and 10 ppb spiked samples were analysed with ICP-MS to verify the method. To calculate the limit of detection, calibration sample solutions were made in both ICP-OES and ICP-MS measurements including non-spiked and 7.5, 15 and $30 \mu\text{g/L}$ Pb spiked to tap water (district 6th, Vienna). Indium was used as internal standard in analysis with ICP-MS and all data were corrected to ^{115}In . For ICP-OES, the signals of Co 221.143 nm were used for normalization.

According to the results obtained from ICP-MS analysis, concentration of Pb in the non-spiked waters of districts 4, 6, 10 and 15th are respectively 0.24 ± 0.04 , 1.98 ± 0.3 , 0.43 ± 0.2 and $0.3 \pm 0.05 \mu\text{g/L}$. These concentrations are far below the LOD of $4 \mu\text{g/L}$ obtained by ICP-OES.

4.3.6. Conclusion

In the current study, a new configuration of flow injection analysis was applied for determination of Pb in drinking water by ICP-OES. Magnetic particles were used to retain the analyte on their surface in a first step. Then, the particle-suspension was passed through a magnetic trap, for further pre-concentration. When switching off the magnetic trap, the particles and the analyte are released in one sharp peak, causing maximal sensitivity of the instrument. With the proposed method, certified reference material ERM-CA022a (soft drinking water UK - Metals) was successfully analysed. Different tap water samples from four districts in Vienna were also analysed by FI-ICP-OES and the results were in accordance with parallel ICP-MS determination, although the Pb content in the water samples was below LOD of the FI-ICP-OES method. With the findings, first recommendation for future research is to increase the initial sample volume from the current 15 mL to have larger enrichment factor. The second approach could be to apply a more selective ionic liquid on the particle surface for Pb retention. Also, the method could be applied to alternative analyte/matrix systems, or in combination with other detectors such as F-AAS (coupling the method to ICP-MS will most likely cause problems due to high particle-load of the suspensions).

4.4. References

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Chapter 5. Summary and conclusion

In the recent decades trace element screening in environmental samples has become important due to their proven risks for human health. Because, even in the case of trace amount, the accumulation of the elements in the environment raises the level of exposure. Compared to other methods of trace element analysis, inductively coupled plasma optical emission spectrometry (ICP- OES) offers ability for fast multi-elemental analysis with sufficient precision. However, challenging research tasks cannot be measured without pre-treatment because the concentration of the analytes are often below detection limits or the presence of highly abundant matrix constituents interferes analysis. Thus, a step of enrichment and/or separation is required prior to measurement. Here, an efficient, easy and fast sample preparation method was applied for enrichment that is named dispersed particle extraction (DPE). In DPE, which is based on the concept of solid phase extraction (SPE), firstly a solution of analyte plus matrix is pH adjusted by addition of a suitable buffer. Then, a few milligrams of the house-made adsorbent particles (surface modified silica) are added to the solution and the extraction of the analyte is done within 5-10 min by agitation in ultrasonic bath. The particles with the retained analyte on their surface are separated by centrifuge and re-suspended in 1% mineral acid for direct measurement by ICP-OES.

However, there were two unfavorable matters which were improved by the presented works in the thesis. First thing is related to the poor sample introduction efficiency of conventional nebulizer/spray-chamber systems in ICP-OES, usually less than 2% of the applied sample solution were introduced the plasma. In the presented thesis, two alternatives of sample introduction system were applied to overcome sample loss and intensity decline of the signal. Those methods were electrothermal vaporization (ETV) and flow injection (FI) coupled with ICP-OES, both allowed a more efficient sample utilization. Second thing is that, separation of sorbent material through DPE by centrifuge is time consuming. To reduce the time needed for sample treatment, magnetic nanoparticles were synthesized and applied. Therefore, the separation step was shortened by application of external magnetic field.

In the whole monography, DPE was applied for sample enrichment prior to analysis.

In chapter 2, for extraction of rare earth elements (REEs), surface modified bioparticles were prepared by coating *lycopodium clavatum* plant spores with ionic liquid $[P_{66614}]^+ [BEHPA]^-$. Green tea samples were converted into an aqueous sample solution using a microwave-assisted digestion procedure. The bioparticles were added to the sample and interacted according to the DPE procedure and finally the content of REEs were measured using ETV-ICP-OES. Combination of DPE method (analyte enrichment) with ETV (solid sample introduction) resulted in increased sensitivity of REE analysis by ICP-OES. ETV provided matrix-free analyte vapor for measurement in ICP by stepwise vaporization of matrix and analyte. Moreover, the concentration of analytes were not reduced by dilution whereas sample digests require dilution prior to conventional ICP analysis. Instead, each analysis run was performed with 30 μ L of the sample suspension and consequently was no need for much dilution. With this method, detection limits of 50 ng/g were obtained for REEs in the dry tea.

In chapter 3, sulfonated silica coated iron oxide nanoparticles were synthesized and applied for pre-concentration of REEs with DPE and slurry analysis by flow injection ICP-OES. The efficiency of enrichment obtained with these particles were perfect with 90% recovery but the magnetic characteristic of the particles was not sufficient to use them for on-line slurry analysis with ICP-OES due to small size of the particles around 5 nm which changes the magnetic behavior. Thus, the experiments were shifted to application of cobalt particles with strong magnetic property.

In chapter 4, cobalt particles were coated with silica shell and further covered by ionic liquid to function as cation exchanger for enrichment of Pb in drinking water via DPE process. The treated samples were analyzed in flow injection system (FI) coupled with ICP-OES. Strong magnetic characteristic of cobalt particles enabled firstly to use an external magnet for separation in batch-wise sample preparation instead of centrifuge which resulted in saving time. And, secondly it made possible to apply an electromagnet in FI-ICP-OES for further enrichment of analyte containing particles by controllable trap-release when magnet is on/off respectively prior to online measurement. More importantly, with this sample introduction system lower amount of adsorbent particles were needed for extraction which decreased the nebulizer clogging possibility. In the introduction system applied here, the peristaltic pump was removed to minimize the risk of particle loss and increase the precision of the analysis by eliminating pulsation effect. Thus, intensive

signal of Pb was recorded in steady state mode by injection of sample slurry. The method was validated by analysis of drinking water reference material.

Chapter 6. Outlook

The concept of dispersed particles extraction (DPE) was successfully applied for pre-concentration of trace elements in combination with two different sample introduction systems including electrothermal vaporization (ETV) / flow injection (FI) coupled with ICP-OES for sensitive analysis of the trace elements. Ongoing research should focus on synthesis of sorbent particles with better selectivity/capacity as well as further improvement of applied analytical techniques.

The adsorbent particles used in DPE were self-made materials which can be modified to have alternative functionalities for diverse numbers of analytes with enhanced selectivity and they can be optimized in size for higher surface area of adsorption.

The kind of ionic liquid as functional group can be changed regarding enormous variety of available cationic and anionic parts in their structure. Combination of different positively and negatively charged sections in the structure of ionic liquid changes the affinity of the material for specific cationic or anionic analyte namely, it makes ionic liquid selective.

The size of particles, are to act as sorbent, affect on the efficiency of analyte retention. It is a big challenge to obtain particles with optimum size. The smaller particles lead to higher efficiency due to increased surface area but minimizing has adverse result because it changes the characteristics of the material. For instance it diminish the magnetic property. Furthermore, conventional separation of the sorbent particles from liquid sample solutions becomes more difficult.

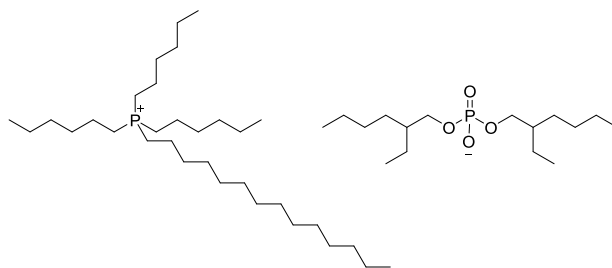
Further goals will be complete automation of flow injection procedure, and utilization of this approach for multi-element analysis. In case of ETV-analysis further improvements in sensitivity are possible by using ICP-MS for analyte detection.

Appendix. Characterization of ionic liquid

General:

All reagents were purchased from commercial suppliers and used without further purification unless noted otherwise. ^1H and ^{13}C NMR spectra were recorded from CDCl_3 solutions on a Bruker Advance UltraShield 400 (400 MHz) spectrometer and chemical shifts (δ) are reported in ppm using tetramethylsilane as internal standard coupling constants (J) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, m = multiplet, brs = broad. Infrared spectra were recorded on a Perkin-Elmer Spectrum 65 FT IR spectrometer equipped with a specac MK II Golden Gate Single Reflection ATR unit.

Trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphate [P_{66614}][DEHPA], [P_{66614}][B2EHP]



Trihexyltetradecylphosphonium chloride (5.19 g, 10 mmol), bis(2-ethylhexyl) hydrogenphosphate (3.54 g, 11 mmol) and potassium hydroxide (0.62 g, 11 mmol) were suspended in 100 ml of water:MeOH 1:1 and stirred for 2 hrs at room temperature. The solution was concentrated to approx. 60 ml and diluted with water. The mixture was repeatedly extracted with dichloromethane. The combined organic layers were washed with water until no more chloride ions could be detected (checked by addition of aqueous AgNO_3 solution), dried over Na_2SO_4 and concentrated under reduced pressure. Remaining solvent traces were removed under high vacuum (0.01 mbar, 48 h) with stirring at 50 °C to yield trihexyltetradecylphosphonium bis(2-ethylhexyl)phosphonate as clear colourless liquid in 94% yield.

^1H -NMR (400 MHz, CDCl_3): δ_{H} = 3.70 (dd, 4H), 2.39 m (8H), 1.47 (m, 20 H), 1.27-1.21 (m, 46), 0.85 (m, 24H). ^{13}C -NMR (400 MHz, CDCl_3): δ_{C} = 67.04, 40.55, 32.00, 31.27, 30.94 (d, $J_{\text{P-H}}$ = 15.0 Hz), 30.61 (d, $J_{\text{P-H}}$ = 14.7 Hz), 30.20, 29.77, 29.73, 29.64, 29.44, 29.18, 23.42, 23.28, 22.78, 22.40, 22.06 (d, $J_{\text{P-H}}$ = 4.6 Hz), 19.13 (d, $J_{\text{P-H}}$ = 48.5 Hz), 14.24, 14.20, 14.04, 11.11. IR: $\tilde{\nu}(\text{cm}^{-1})$ = 2956.0, 2923.8, 2855.5, 1462.0, 1378.5, 1244.5, 1044.6, 973.1, 810.3, 723.2.

The synthesis of this ionic liquid is based on bis(2-ethylhexyl)hydrogenphosphate (DEHPA), which is a well-known ligand for REE or uranium extraction on industrial scale and currently produced by the

company Cytec. Normally, DEHPA is used as solution in kerosene or other hydrocarbons, sometimes also in combination with tributylphosphate.

By combining it DEHPA (as anion) with a very hydrophobic cation (P66614+) should give a very hydrophobic and good ionic liquid for REE extraction. Whether it would be specifically suited for Sc and/or Y I do not know – but there might be literature available with pure DEHPA that might help here I hope this helps!