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Privat Doz. Dr. Andreas Limbeck

Development of advanced methods for the determination of Platinum Group Elements in plant material

Diplomarbeit

Ausgeführt am

Institut für Chemische Technologien und Analytik

der Technischen Universität Wien

unter der Anleitung von

Privat Doz. Dr. Andreas Limbeck

Univ.Ass. Dipl.-Ing. Mag. Dr. Marie-Alexandra Neouze

durch

Winfried Nischkauer

[redacted]

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Winfried Nischkauer

ABSTRACT

Platinum, Palladium and Rhodium are members of the Platinum group Elements (short PGEs); these elements are used in large quantities as catalysts in the chemical industry as well as in automobile catalysts. The latter reduce the emission of noxious gases like carbon-monoxide, nitrogen oxides and non-combusted fuel and have been widely applied both in passenger cars and in freight vehicles since the mid-1980ies. The catalytically active PGEs are finely dispersed on a ceramic material; due to thermal stress, mechanical shock and high gas-flow rates abrasion of the carrier material and the PGEs takes place. The resulting particles are co-emitted with the vehicle's exhaust gases and are deposited along roadsides. Due to environmental conditions (rain, wind) and their incorporation in biomass, they can gain additional mobility. Knowledge about PGE's toxicity and/or carcinogenic behaviour is still scarce; as long as the actual infliction of PGEs on living species is not totally understood and their respective potential to enter the food chain is unknown, monitoring of these elements is required.

The analysis of PGEs in environmental samples is a rather challenging task, as several factors hamper their correct determination. Firstly, the natural background-concentration of these elements is very low. Even soils collected along heavily frequented highways contain PGEs in concentrations of only some µg per kg. Secondly, many analytical methods are interfered by elements or compounds inherent to environmental surroundings like crustal elements, other trace metals and organic material. These interfering agents are found to be several orders of magnitude higher in concentration than the PGEs. It is obvious that the removal of these interferences respectively the correction of their negative effects is considered a major task in trace metal analysis.

In this Diploma Thesis two methods for the assessment of PGEs in plant material are presented; the instruments used throughout the process are well introduced to analytical laboratories therefore it should be easy to actually implement the methods in routine analysis.

The work is structured in three main parts, the first (chapter 1) providing general information about the technological use of PGEs and the faith of these elements in the environment. Analytical methods commonly applied for the assessment of PGEs are compared. In the second part (chapter 2), a novel approach in sample pre-treatment using a

modified solid phase extraction method is introduced which allows the enrichment of palladium from aqueous solutions. Due to this enrichment, it was possible to quantify comparatively low concentrations of Palladium in digested plant material using ET-AAS; the spatial distribution of this analyte in various parts of the plants could therefore be determined and a significant difference in Pd- content between leaves, stem and roots was discovered.

In order to enable the analysis of plants that show restricted growth (low sample mass), direct sampling of PGE containing plant material using electro thermal vaporisation ICP-OES is presented in the third part (chapter 3). The major advantage of this direct sampling approach lies in the reduction of time consuming sample pre-treatment steps and the avoidance of potentially dangerous chemicals. Furthermore, the inevitable dilution of the target analytes after sample digestion is eliminated since no dissolution of the samples is required. The results are compared with the results of a conventional ICP-OES analysis using digested plant material and are found to be in good accordance if correct quantification is applied.

ZUSAMMENFASSUNG

Platin, Palladium und Rhodium zählen zu den Platin- Gruppen Elementen (PGE). Diese Metalle werden in großen Mengen als Katalysatoren in der chemischen Industrie und in Kraftfahrzeugen eingesetzt. KFZ- Katalysatoren ermöglichen es, die Emission von Kohlenmonoxid und Stickoxiden sowie von nichtverbranntem Treibstoff zu reduzieren. Sowohl in PKWs als auch in LKWs werden Katalysatoren seit Mitte der 1980er Jahre vermehrt eingesetzt. Die katalytisch aktiven PGEs sind als feindisperse Partikel auf einem keramischen Trägermaterial verteilt; aufgrund von thermischer Wechselbeanspruchung und mechanischen Erschütterungen, verstärkt durch hohe Gasflüsse, kommt es zum Verschleiß dieses Trägermaterials. PGE werden somit freigesetzt und lagern sich in unmittelbarer Umgebung von Verkehrsflächen ab. Aufgrund von Umweltbedingungen wie Regen und Wind und durch Bio- Akkumulation können die Metalle zusätzlich verfrachtet werden. Über die Toxizität und/oder die krebserzeugende Wirkung dieser Metalle ist noch wenig bekannt. Solange die tatsächliche Auswirkung der PGE auf Lebewesen noch nicht vollständig geklärt ist und auch über eine eventuelle Anreicherung in der Nahrungskette keine ausreichenden Daten zur Verfügung stehen, sollte diesen Elementen vermehrte Aufmerksamkeit zukommen.

Die Analyse von PGE in Umweltproben gestaltet sich oft schwierig, da sich mehrere Faktoren negativ auf deren korrekte Bestimmung auswirken. Zunächst wäre zu erwähnen, dass die natürliche Hintergrundkonzentration dieser Elemente sehr niedrig ist. Selbst Bodenproben, die direkt neben stark befahrenen Straßen gesammelt wurden, enthalten PGE nur in Konzentrationen von wenigen µg/kg. Als zweiter Punkt kommt erschwerend hinzu, dass die meisten analytischen Methoden durch Komponenten, die in Umweltproben allgegenwärtig sind, stark negativ beeinflusst werden (zum Beispiel Mineralien, andere Spurenmetalle und organische Substanzen). Die interferierenden Komponenten liegen meistens um Größenordnungen höher konzentriert vor als die eigentlichen Analyte. Das Entfernen dieser störenden Komponenten oder das Korrigieren ihrer negativen Einflüsse stellt die größte Herausforderung in der Analytik von Spurenmetallen dar.

In dieser Diplomarbeit werden zwei Methoden präsentiert, die eine Analyse von PGE in Umweltproben ermöglichen; alle verwendeten Geräte gehören zum Standardinventar von

analytischen Labors, somit sollte längerfristig auch eine Anwendung der vorgestellten Methoden in der Routineanalytik möglich sein.

Die vorliegende Arbeit ist in drei Abschnitte gegliedert: im ersten Teil (chapter 1) wird die technologische Verwendung der PGE sowie der Verbleib dieser Elemente in der Umwelt diskutiert. Analytische Methoden, die üblicher Weise in der Analyse von PGEs Verwendung finden, werden vorgestellt und miteinander verglichen. Im zweiten Teil (chapter 2) wird eine neue Art der Probenvorbereitung mittels einer modifizierten Festphasenextraktion präsentiert, die eine Anreicherung von Palladium aus wässrigen Lösungen ermöglicht. Aufgrund dieses Anreicherungsschrittes konnten mit Hilfe von ET-AAS Messungen vergleichsweise niedrige Pd- Konzentrationen in aufgeschlossenen Pflanzenproben bestimmt werden, wodurch eine Verteilungsanalyse dieses Metalls in unterschiedlichen Pflanzenorganen möglich wurde. Es ergab sich ein signifikanter Unterschied im Pd- Gehalt zwischen Blättern, Stängel und Wurzeln.

Im dritten Teil (chapter 3) wird eine Methode zur direkten Feststoffanalyse von Pflanzenmaterial mittels ETV ICP-OES beschrieben, die eine drastische Reduzierung des Probenverbrauchs im Vergleich zu herkömmlichen Verfahren ermöglicht, wodurch auch die Analyse von sehr kleinen Pflanzen möglich wurde. Der große Vorteil der ETV Methode besteht darin, dass kein Aufschließen notwendig ist, wodurch einerseits der Einsatz von bedenklichen Chemikalien vermieden werden kann und andererseits eine verbesserte Nachweisstärke erzielt wird, da die Proben nicht durch einen Aufschluss verdünnt werden. Es wird gezeigt, dass die mit der hier präsentierten ETV ICP-OES Methode erzielten Ergebnisse gut mit den Ergebnissen einer konventionellen ICP-OES Messung übereinstimmen, sofern bei der Quantifizierung auf die Einflüsse der Pflanzenmatrix Rücksicht genommen wird.

DANKSAGUNG

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1. INTRODUCTION

1.1. PGES IN TECHNOLOGY

Due to their good chemical stability, their high melting points and their good electric conductivity, PGEs are nowadays widely used in electronic devices as well as in human medicine and jewellery. Besides these undoubtedly important applications, the great majority of the annual PGE production is being dedicated to the construction of catalysts in the chemical industry and in cars (automotive catalysts) (see figure 1).

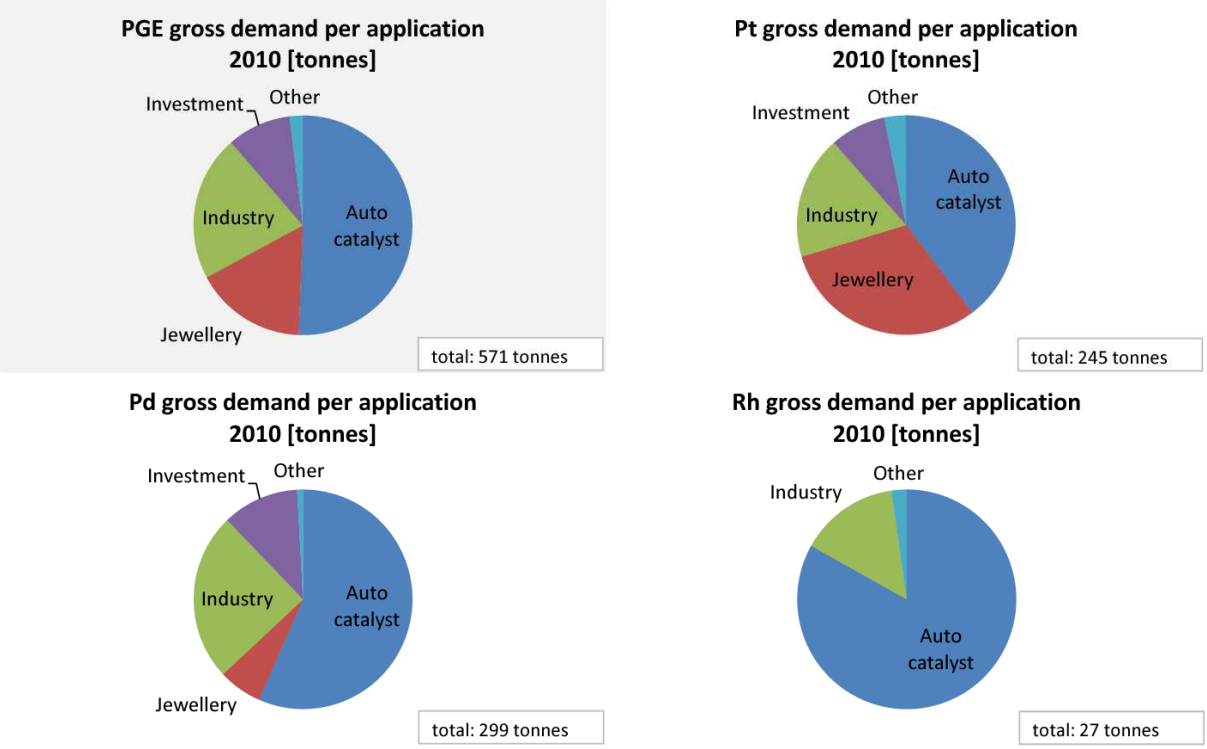


Figure 1 World-wide demand for PGEs in the main fields of application, all values in metric tonnes[1]

Industrial processes like the production of nitric acid, hydrogen peroxide, caprolactame, cyclohexane, acetaldehyde ... necessitate PGEs in the form of heterogeneous or homogenous catalysts. Despite the amount of PGEs that are annually required for the construction of these catalysts is significant (see figure 1), recycling of the precious metals is nearly quantitative due to economical reasons. However, recovery of PGEs that are manufactured into automotive catalysts is low since the spent catalyst material is very heterogeneous and recycling procedures are costly (Kim 2000).

[1] Adapted from (Platinum 2011)

1.2. PGES IN THE ENVIRONMENT

The natural abundance of PGEs in the earth crust is low (1-5ng/g Pt, 15ng/g Pd and 0.1ng/g Rh in the lithosphere, (Ravindra 2004)). Due to anthropogenic emission of PGEs into the environment, the overall concentration of these elements in the biosphere increased over the last forty years (see figure 2). Besides other man-made emission sources like nickel smelters or mining of rare earths, PGEs emitted from automotive catalysts contributed majorly to this effect. Bench tests showed that PGEs are being emitted from automotive catalysts in the ng/km range, the actual amount depending on parameters such as driving velocity, age and type of catalyst as well as meteorological conditions (Moldovan 1999). Considering the annual vehicle traffic, the total amount of PGEs that are emitted in the period of one year in a major European city (Madrid) could be estimated from these experiments to be 610g Pt, 390g Pd and 190g Rh (Moldovan 2002)). Concentrations of PGEs in the vicinity of heavily frequented roads (Zereini 2007) and in city centres (Napoli, (Cicchella 2002)) are significantly higher than in rural surroundings. Furthermore, PGEs can gain additional mobility through wind (Schaefer 1998a) and due to their partial solubility in surface waters (Limbeck 2006). The incorporation of PGEs into plants is found to depend on the plant species and on soil conditions (Schaefer 1998b, Verstraete 1998). In the presence of complexing agents (e.g. humic substances), the lipid solubility of PGEs is significantly enhanced; an accumulation in the food chain is possible and experiments have shown bio- accumulation of PGEs in zebra mussels (Zimmermann 2003).

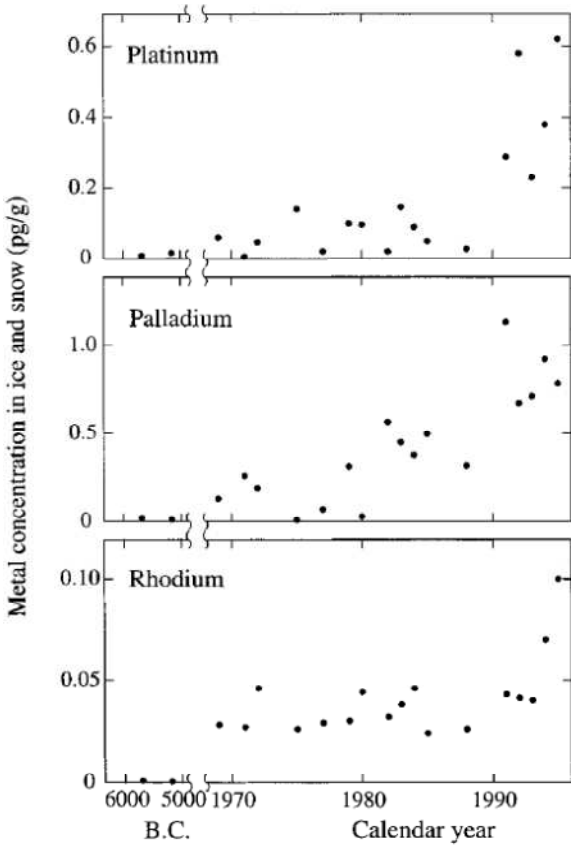


Figure 2 Changes in Pt, Pd, and Rh concentrations in central Greenland ice and snow as a function of the age[2]

[2] From (Barbante 2001)

1.3. ANALYTICAL ASSESSMENT OF PGES

In consideration of the low concentration of PGEs in environmental samples and the inherent presence of potentially interfering agents, one may wish for a method that is at the same time very sensitive and very selective; sensitivity allows for low concentrations of the target analytes; selectivity provides for results free of interferences. Modern spectroscopic methods meet these conditions close enough, yet every method has its own specific shortcomings (Bencs 2003). In table 1 four of the most popular spectroscopic methods in PGE analysis are compared regarding their respective sensitivity and selectivity.

Table 1. Spectroscopic methods commonly used for Pd determination

	Sensitivity (average concentration range)	**selectivity**
ICP-MS	**<< ng/g**	**-**
ICP-OES	**ng/g***	**~**
ET-AAS	**ng/g**	**+****
F-AAS	**µg/g**	**~**
*depending on sample introduction even < ng/g, ** with Zeemann background correction		

One method of great interest is ICP-MS, allowing the direct analysis of ions formed in the inductively coupled plasma via quadrupole mass spectrometry. This method is bound to be very sensitive, as in theory even single atoms can be detected. Nevertheless ions that have about the same mass to charge ratio as the analyte may cause severe interferences (Rauch 2000); appropriate sample pre-treatment and the use of a reaction/collision cell can help to reduce this problem. High mass resolution on its own cannot solve the problem because high resolution results in low ion intensity and therefore the sensitivity of the method suffers.

Atomic Absorption spectroscopy (AAS) uses element- specific radiation which is absorbed by the analyte to gain qualitative and quantitative information. With Zeeman- background correction, the method is literally free of interferences caused by molecular absorption. Also line overlap is rarely observed and can usually be tackled by changing to another line or by optimizing the temperature program (Brzezicka 1999). Yet AAS suffers from comparatively low sensitivity; pre- concentration steps prior to the actual analysis may help to overcome this disadvantage (Limbeck 2003).

Due to the high sample throughput in Flame AAS, the lowest sensitivity of all compared methods is obtained. The big advantage of ET-AAS, namely the long residence time of the analytes in the graphite furnace, does not exist in F-AAS and therefore low detection limits are observed.

In Optical Emission Spectroscopy (OES) the radiation emitted by thermally excited atoms is used for quantitative and qualitative elemental analysis. For many elements spectral interferences are observed and cautious correction for these has to be done (Todoli 2002); fortunately, OES interferences are not as severe as in ICP-MS. In terms of selectivity and sensitivity, ICP-OES lies in between ICP-MS and ET-AAS, with the possibility to gain additional sensitivity by using efficient sample introduction.

1.3.1. ET-AAS

Atoms have the ability to absorb photons with energies that relate to their unique orbital structure. This effect, discovered independently by Fraunhofer and Wollaston at the beginning of the 19th century may be used to perform qualitative as well as quantitative elemental analysis. The application of quantitative AAS has been thoroughly developed in the past decades. One reason for this is the fact that absorption spectra- as compared to emission spectra- feature only a few lines; therefore interferences by coinciding lines are very unlikely. If interferences are expected, different lines of the same element may be used and problems are readily avoided. The electromagnetic radiation used for AAS is produced in a hollow cathode lamp by the decay of thermally excited states of the element which is being analyzed. The energy required is procured by noble gas ions hitting the target cathode. On de- excitement, the atoms in the cathode emit light of discrete wavelengths which are specific for the chemical element. The intensity of the emitted light is a function of the applied voltage and the current as well as of the element itself. Therefore mostly single-element lamps are in use as it has proven to be difficult to procure ideal conditions for more than one element. This implicates that only one element may be measured at a time; AAS has to be regarded as a single- element technique, although great effort has been put into developing systems which are able to analyze more elements in parallel. Moreover, since ET-AAS is an absorption technique, the law of Lambert- Beer has to be applied which restricts the linear range of the method to comparatively low concentrations (see chapter 1.3.5. for details on quantification).

In order to achieve atomic absorption, the sample has to be atomized; the high temperatures needed for this process may either be reached by a combustion process (Flame- AAS) or by electro thermal heating (ET-AAS); the latter principle was used during this work. The liquid sample is introduced in a graphite tube which is subsequently heated by resistance heating. To allow uniform heating of the whole sample, it is deposited on a platform inside the tube (L'vov Platform see figure 3) which is heated indirectly by thermal radiation emanating from the tube's walls. During this heating program the liquid evaporates and organic components are decomposed, removing the majority of interfering matrices as well as volatile inorganic compounds. To avoid oxidation of the graphite tube, argon is used as protective atmosphere. After matrix removal, the temperature is increased rapidly which causes molecules to dissociate and the target analyte is consequently evaporated in the form of single atoms. The vaporisation temperature is usually reached within one second; due to this high heating rate, all the atoms are in the gas phase at the same time which accounts for maximum sensitivity.

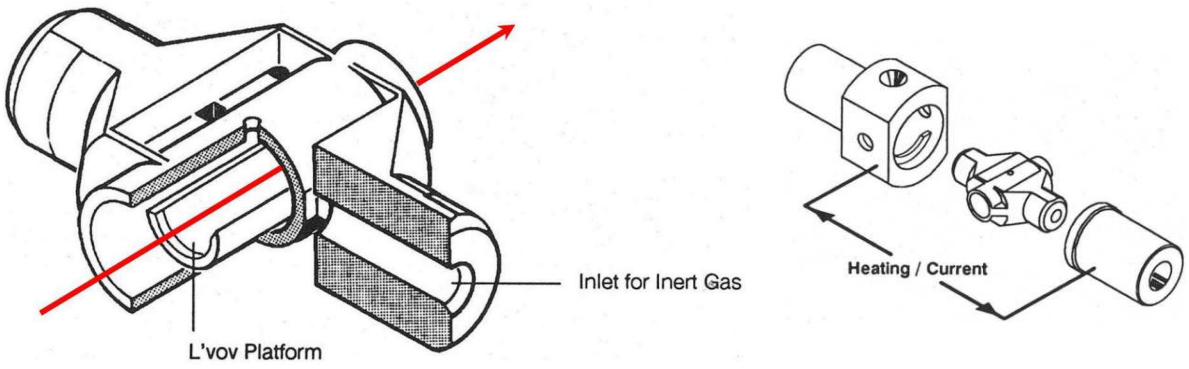


Figure 3 Construction scheme of the graphite tube[3]

The radiation produced in the hollow cathode lamp enters and leaves the graphite tube parallel to the L'vov platform. Afterwards the light is dispersed by a monochromator and the wavelength of interest is focused on a detector (see figure 4). The instrument determines the ratio between the weakened intensity due to atomic absorption and the initial intensity. This output can be directly related to the concentration of atoms in the path of the beam (see chapter 1.3.5. for details on the Lambert- Beer law).

[3] Adapted from (Perkin Elmer 1991)

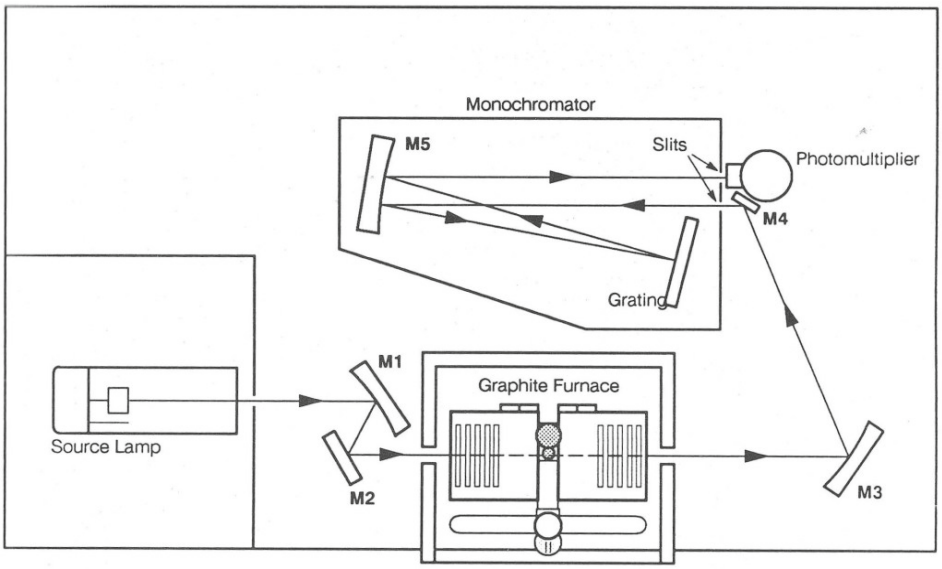


Figure 4 Optical assembly of the Perkin Elmer 4100ZL instrument[4]

Thermal inertia of the furnace and the tube leads to transient signals; the amount of atoms in the gas phase increases to a maximum and then decreases again (see figure 5).

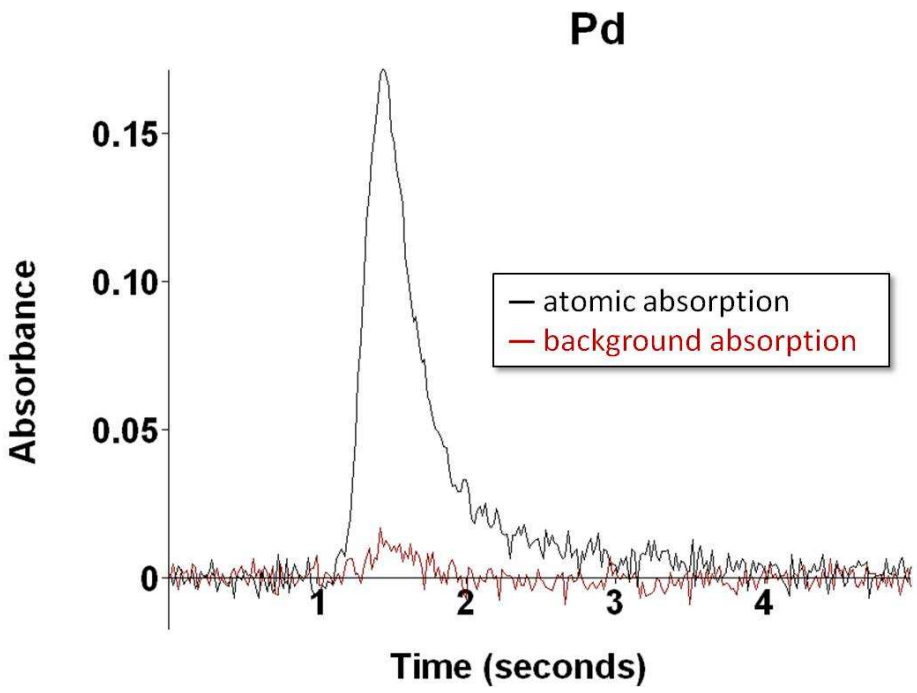


Figure 5 Typical output file showing the analyte signal (Pd, 5ng) and the background signal

As can be seen in this figure, there is not only a signal related to atomic absorption of the target analyte but also unspecific background absorption. This signal is usually subtracted from the signal to yield the net signal. The presence of absorption other than that of the

[4] From (Perkin Elmer 1991)

atoms may at first be unexpected; as stated above, line- coincidence is very unlikely and the AAS- process is not prone to spectral interferences. Yet there are gas molecules (carbon dioxide, nitrogen oxides, silicon oxide …) in the optical path and these compounds can absorb light by exciting rotation and/or vibration states. Due to the quasi- continuity of these states, molecules may absorb a broad spectrum of light, leading to specific absorption spectra which are used to characterize substances via UV/Vis absorption (see fig 6 (a)). Atoms absorb radiation of a discrete energy content leading to sharp absorption lines (b). During AAS measurements molecular absorption is not wanted because the registered signal is the sum absorption of the molecules and the atoms of the target analyte (c).

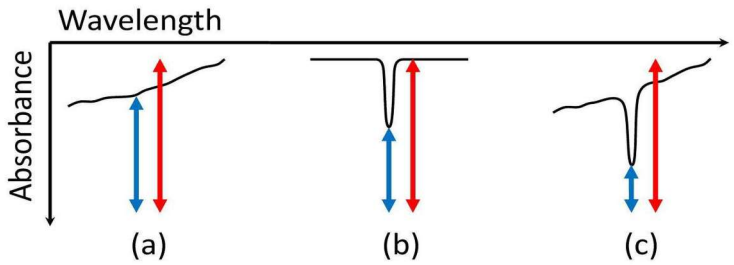


Figure 6 Influence of molecular absorption on the recorded absorption signal; initial radiation intensity (red), weakened radiation intensity due to absorption (blue)

To distinguish these two contributions, the Zeeman- effect can be successfully made use of. In the presence of a strong magnetic field, the atomic orbitals split and therefore more absorption lines are observed. Orbital transitions where the magnetic quantum number is not changed may only be excited by linear polarized light. Other transitions absorb circular polarized light. If the magnetic field is parallel to the optical path, those lines that react to linear polarized light cannot absorb any radiation and disappear from the absorption spectrum because light can only propagate in the direction of its magnetic vector (see fig 7)

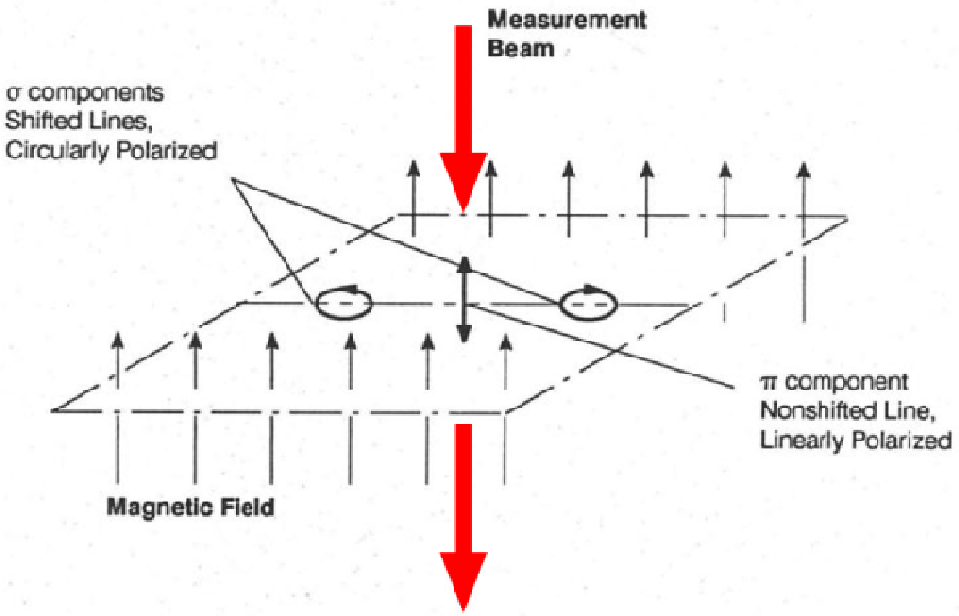


Figure 7 Principle of the Zeeman background correction[5]

The absorption spectra of molecules are not changed by the magnetic field; although shifting occurs, the effects are small and may not be resolved by the spectrometer. To be able to distinguish between absorption of atoms and molecules, two consecutive measurements are required: in a first step, no magnetic field is applied and the sum of both absorption processes is measured (see fig 8 (a)). In a second step, the magnetic field is applied in such a way, that atomic absorption is eliminated and only molecular absorption is registered (b). The difference between those two measurements yields the atomic absorption.

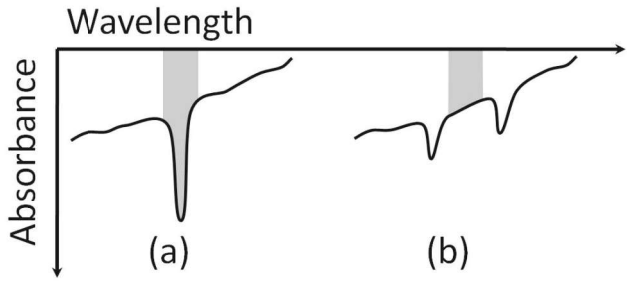


Figure 8 Influence of the Zeeman- effect on the obtained absorption signals

Yet another source of disturbance has to be considered: scattered light from outside the instrument and light produced by thermal emission of the glowing graphite tube and gases

[5] Adapted from (Perkin Elmer 1991)

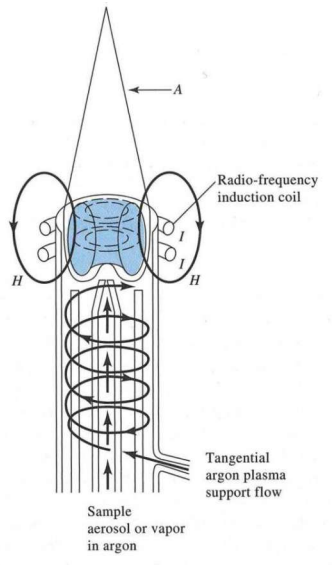
inside the furnace may have the same energy as the line to be observed. This problem can be easily solved by periodically intermitting the light of the hollow cathode lamp either by means of a mechanical chopper or by modulating its voltage. Radiation that is registered while the hollow cathode lamp is turned off may be easily attributed to scattering or to thermal emission processes.

1.3.2. ICP-OES

The analysis of radiation that is emitted by atoms due to the decay of excited states is possible using an Optical Emission Spectrometer (OES). Following the Boltzmann distribution (equation 1), the number of atoms in the excited state n increases significantly with increasing temperature T; that means that temperatures reached in flames only suffice to produce radiation from alkaline or earth alkaline elements which need a small amount of energy to reach the excited state. To excite elements with higher excitement energy ΔE, plasma temperatures are needed (k: Boltzmann constant).

$$n \approx e^{\frac{\Delta E}{kT}}$$

Equation 1



In ICP-OES argon is used as a "burning" gas (it is a noble gas and therefore it cannot burn...). By applying a high voltage spark, some atoms of the gas are ionized; these charged particles can couple with a high frequency radio signal that is produced by a coil surrounding the gas stream. This coupling effect raises the temperature of the gas and more ions are produced, a chain reaction starts. After reaching stable plasma conditions, average temperatures of 7000 to 10000K are attained, depending on the power supplied and the presence of other gases than argon.

Figure 9 ICP Plasma torch, A indicates the point that is being analyzed by the spectrometer's optics (radial observation height)[6]

[6] Adapted from (Skoog 2007)

The design of the torch aims at a homogenous gas flow and stable plasma conditions in order to guarantee constant temperature and therefore a reproducible method. The liquid sample is nebulised and introduced in the plasma by means of a carrier gas via the injector tube placed in the centre of the torch. This tube is surrounded by two other tubes made of transparent quartz glass which procure the main gas flow and a tangential gas flow that helps in cooling the tubes and directs the flame in order to keep it compact and in place. See figure 9 for a detailed sketch of the torch. As mentioned above the intensity of radiation produced in the plasma depends on the element to be analyzed and the actual plasma temperature. Elements that emit easily are observed in a colder part of the flame, elements that procure weak radiation are observed in the core of the flame where maximum temperature is reached. Choosing the appropriate radial observation height can help to avoid detector saturation; nevertheless one has to account for all elements that are to be measured and compromises have to be made.

The emitted radiation enters the optical system via the ceramic cone next to the flame; a purging gas flow perpendicular to the optical axis removes fumes and dust. In a next step, the radiation is dispersed according to its wavelength (qualitative information) and the intensity is measured (quantitative information). If radiation in the UV is analyzed, care has to be taken in order to remove any oxygen from the spectrometer as it readily absorbs UV light; this task is usually achieved by using a protective gas such as argon or nitrogen or by evacuating the whole system. It is obvious that such a system- which has to be moreover kept at constant temperatures to avoid thermal drift- is very difficult to sustain. The smaller the system, the more constant conditions will be achieved.

Old systems use optics following the Rowland geometry (see figure 10). In this arrangement, the radiation meets a grating and is dispersed; the detector moves along the Rowland- circle and collects radiation that relates to a small wavelength- window. Unless several detectors are used, this process takes some time which means time-resolved measurements are difficult to carry out. When CCD line-detectors are used, a small wavelength- window can be analyzed simultaneously which allows for faster measurements; yet in order to cover a larger range of the spectrum, several detectors are needed.

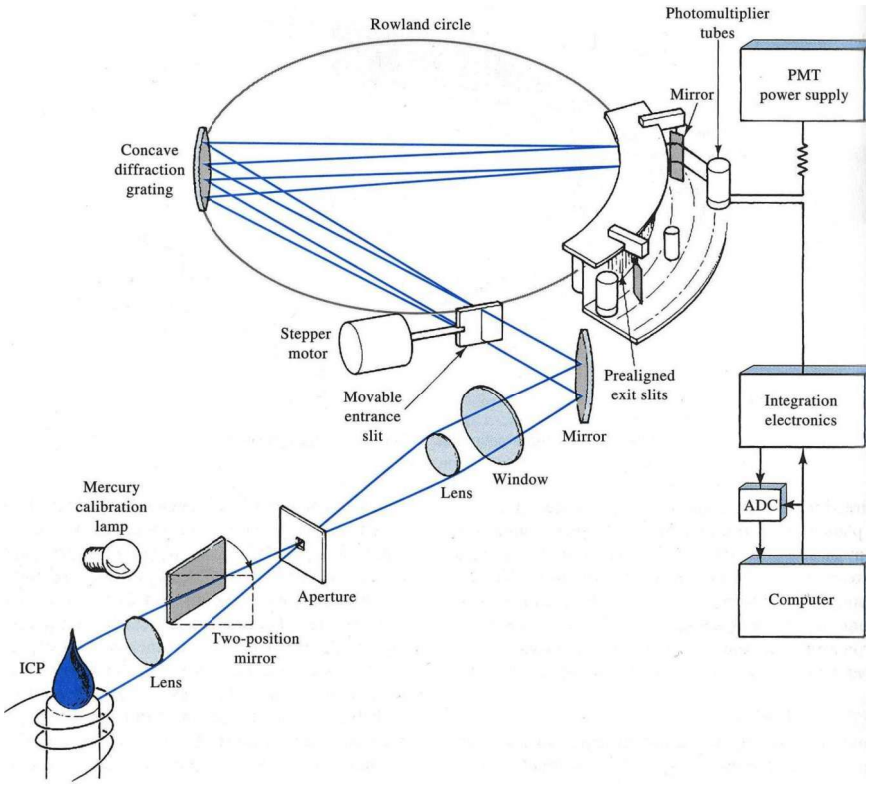


Figure 10 Optical system using the Rowland circle[7]

With an Echelle system the disadvantages of the Rowland assembly such as bulky spectrometers and long measurement times can be overcome. The incident light meets two dispersing elements, a grating and a prism; in a first step, the radiation is dispersed by a blaze grating, and then this spectrum is dispersed once more by the prism, yielding a 2D plot which is projected onto one CCD detector (see figure 11). This arrangement allows measuring the whole spectrum in one step; moreover, several diffraction orders are recorded. This means that many lines are redundant and therefore it becomes possible to correct interferences in one diffraction order by using one order that is not interfered.

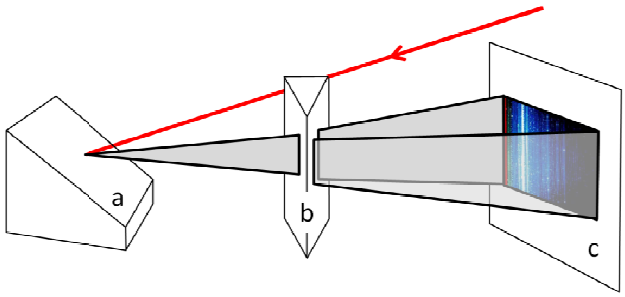


Figure 11 Echelle optic, schematic alignment of dispersive elements

[7] From (Skoog 2007)

Reading time of the CCD is very short and therefore high time- resolution can be achieved. Transient signals as observed in chromatography, Flow Injection systems and electro thermal vaporisation (see chapter 3.1.4.) can therefore be readily analyzed.

1.3.3. SLURRY ANALYSIS

All methods described so far require the samples to be in liquid form. To convert solid samples into liquid, usually digesting procedures are applied. Depending on the nature of the solid, different dissolving agents are possible, ranging from distilled water to highly aggressive mixtures of mineral acids. Nevertheless, there are sample matrices that cannot be dissolved; although the samples may be dissolved in highly concentrated agents, they precipitate upon dilution. The dilution process is required in most of the cases, since the introduction of concentrated chemicals is disadvantageous for the majority of analytical instruments; also the aspect of work safety has to be regarded.

If a sample can therefore not be dissolved, the un- dissolved material has to be analyzed in order to gain the desired information. Since the direct introduction of solids into analytical instruments is difficult- the samples have to be very fine to ensure homogeneity and usually only small sample aliquots are required- the sample is introduced in the form of a suspension. To create this slurry, the finely ground sample is mixed with a solvent and vigorously shaken (Ferreira 2010). This suspension is introduced into the instrument by means of the conventional sample introduction unit and no further accessory is required (in some cases though, modified sample introduction systems are required, e.g. high- solid nebulizers with a larger tip- diameter). If the particles are fine enough to prevent immediate sedimentation, or if chemicals that hinder sedimentation are added to the slurry, even auto-samplers may be used for the analysis. The solvent can be totally inert, but in some cases, partial dissolution of the solid or leaching of the analytes is observed; this effect is beneficiary in terms of higher reproducibility.

1.3.4. ETV

Electro Thermal Vaporisation allows direct analyzing of solid samples without any digestion step. The samples are evaporated and the vapours are introduced into the plasma of an ICP-OES or an ICP-MS instrument. The ETV process is comparable to the electro thermal process used in the ET-AAS system, organic matrix is easily removed by an appropriate temperature

program. The solid sample is placed in a graphite boat (see figure 12 (a)) which is transferred inside a graphite tube (b). This tube is heated by resistance heating (the current is applied through connection pieces (c) and (d)); thermal radiation emanating from the walls causes homogenous heating of the sample. Argon is used as a carrier gas (1); it is mixed with small amounts of "Freon" which dissociates at high temperatures and produces highly reactive components which enhance the formation of volatile species and ensure the quantitative evaporation of the target analytes. The vaporized analyte leaves the hot graphite tube (b) and it is very likely that it will re-condense on colder spots in the system. Therefore, a cooling gas (2) is injected tangentially to the main carrier flow which ensures that the vapour cools down without touching any walls. By doing so, particles with a very small diameter are produced and transferred into the plasma (3); due to the very small size of these particles, sedimentation is avoided and the transport efficiency from the ETV system to the plasma torch increases.

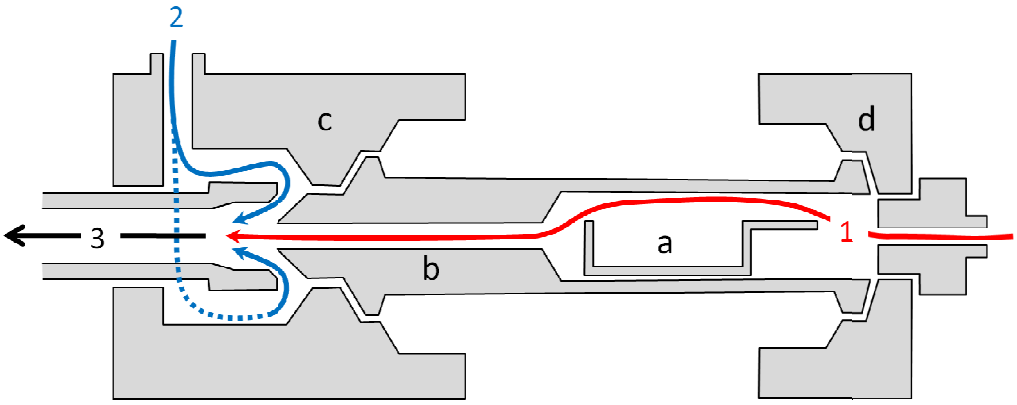


Figure 12 Section view of the ETV unit

1.3.5. QUANTIFICATION

To relate the signal obtained with an instrument (be it ET-AAS or ETV-ICP-OES) to the concentration of the target analyte, a calibration is generally employed. The signals obtained from samples of well-known concentration are plotted against their concentration. In most cases, a linear relation between signal and concentration is obtained, described by a linear equation similar to equation 2.

$$y = k \cdot x + d$$ **Equation 2**

Due to variations in signal generation and pure statistical variation an overall deviation from the ideal straight line is observed. To compute a linear equation that fits the data points in a

most appropriate way, the least-squares method is employed. The algorithm yields at minimizing the (square of the) deviation between a data point y and the value found by equation 2 for a given concentration.

By minimizing the sum of these deviations, a straight line is obtained which represents the data set in the best possible way (see equation 3 with N being the total amount of data points).

$$k = \frac{\sum_i \left(x_i - \bar{x}\right) \cdot \left(y_i - \bar{y}\right)}{\sum_i \left(x_i - \bar{x}\right)^2}$$

$$d = \bar{y} - k \cdot \bar{x}$$

$$\bar{x} = \frac{\sum_i x_i}{N}$$

$$\bar{y} = \frac{\sum_i y_i}{N}$$

Equation 3

Having established the calibration curve, quantification of an unknown sample can readily be performed: the signal is entered in equation 2 and the corresponding concentration is obtained. This linear approach holds true for emission spectroscopy up to comparatively high concentrations; in absorption spectroscopy the linear approach is restricted to a limited concentration range. Absorption processes are described by Lambert Beer's law (equation 4) which states that the absorption A is proportional (via the extinction coefficient ε) to the concentration c and the length of observation x.

$$A = \log\left(\frac{I_0}{I}\right) = \varepsilon \cdot x \cdot c$$

Equation 4

Two assumptions limit the concentration range: the absorbing particles have to be independent (higher concentration increases interaction) and the refractory index should be independent of concentration (which is only true for small concentrations). Therefore, if the concentration of a sample is high and hence the linearity range is exceeded, the sample either has to be diluted, the observation length x has to be shortened (which is in most cases rather difficult to achieve), or a less sensitive wavelength has to be chosen.

For both absorption and emission spectroscopy, the slope of the calibration curve defines the detection power of a given method; in the case of a steep graph, small variations in sample concentration yield a large change in signal intensity. For statistical, electronic (background noise from amplifiers) and methodical (contamination) reasons, a sample containing definitely no analyte (blank) still produces a signal. The standard deviation of this blank signal (equation 5) can be utilized to establish Limit Of Detection (LOD) and Limit Of Quantification (LOQ).

$$\sigma_{blank} = \sqrt{\frac{\sum\left(y_{blank} - \bar{y}_{blank}\right)^2}{N-1}} \qquad \text{Equation 5}$$

The LOD is the value above which an obtained signal can be attributed with statistically satisfying certitude to the presence of the target analyte. The actual concentration may only be calculated above the LOQ. These two values are computed from the mean of the blank signal and its standard deviation according to equation 6.

$$LOD = \frac{3 \cdot \sigma_{blank}}{k}$$
$$LOQ = \frac{10 \cdot \sigma_{blank}}{k} \qquad \text{Equation 6}$$

These values are converted to concentrations by means of the linear calibration function (equation 2)

LOD and LOQ can be calculated for the instrument and for the method. The instrumental LOD ($LOD_{instrumental}$) describes the amount of analyte that has to be present in the instrument to produce values significantly different from blank values. The methodological LOD ($LOD_{methodological}$) takes into account all enrichment and dilution steps that are performed with the sample. If for example an enrichment process is performed, the amount of analyte that is found in a large sample mass is concentrated to a small volume. This extract is introduced into the instrument and a signal is obtained if the concentration in the enriched phase is higher than the $LOD_{instrumental}$. Taking into account the enrichment factor, the $LOD_{methodological}$ is obtained.

2. DISPERSED PARTICLES EXTRACTION (DPE) IN COMBINATION WITH ET-AAS ANALYSIS

2.1. ENRICHMENT PROCEDURES

To overcome the problem of low PGE concentration in environmental samples, an enrichment step can be introduced before the actual measurement takes place. Although a large number of different enrichment procedures are reported in the literature, they are usually connected to time consuming and laborious sample manipulation that may introduce contaminations and therefore can produce high blank values. The main tasks in developing a new enrichment procedure are therefore to ensure quantitative recovery of the analyte using a minimum of manipulation steps to reduce the risk of contaminations and to increase the reproducibility of the analysis.

2.1.1. MISCELLANEOUS ENRICHMENT PROCEDURES

To extract PGEs from solid samples, the fire assay method uses the principle of metal- in-metal solubility (Shibuya 1998). A collector phase (nickel sulphide) is mixed with the solid sample, a flux component is added and the mixture is heated in a crucible. Due to gravity, the collector metal segregates to the bottom of the container and after cooling down, a small button of collector metal is found which is manually separated from the rest of the material and holds an elevated concentration of the analytes. Great effort has to be exerted to procure non-contaminated metal reagents but the big advantage of the fire-assay method lies in the large sample intake which results in comparatively high analyte concentrations in the enriched phase.

PGEs that are dissolved in a liquid sample matrix can be collected by co- precipitation (Messerschmidt 2000). An excess of mercury or tellurium ions is added to the solution and the metals are precipitated by adding a reducing agent (e.g. formic acid). Noble metals like gold or PGEs are reduced as well. Since they have a high solubility in the collector metals they may be quantitatively extracted from the sample by removing the precipitate.

Electrochemical enrichment of PGEs is possible as well: one possibility is to electrochemically reduce the metals by supplying an electrical current and depositing them on the surface of a graphite tube (Komarek 1999). Afterwards, the tube is dried and inserted into an ET-AAS system. Unfortunately, the longevity of the graphite tube greatly suffers from these

proceedings. A slightly modified method uses a tungsten tube instead of a graphite tube. Besides better long-term stability, the deposition process is facilitated by employing a magnesium electrode and thus forming an electrochemical cell (Mg/W) (Ohta 1997). Reducing the PGEs and depositing them on a graphite electrode was reported to yield good recovery in a flow-through cell (Godlewska-Zylkiewicz 2002). By passing by the electrode, PGEs are deposited and extracted from a large volume of sample. When the flow is stopped and the current changed to oxidizing conditions, the analytes are dissolved in a much smaller sample volume and thus enriched.

Conventional liquid-liquid extraction can be performed if appropriate complexing agents are used to capture the analytes and to help in transferring them into the organic phase (Terada 1991, Patel 2000). To reduce the effect of solvent losses due to the low vapour pressure of organic solvents, the resulting organic phase is generally evaporated to dryness and the analytes are taken up with inorganic solvents such as diluted acids (Brzezicka 1999). Another method that avoids any phase separation and the problem of emulsification is cloud-point extraction (Sanz-Medel 1999); a surfactant is added to the sample and the analytes are captured inside the micelle that are formed by the surfactant. Upon changing the temperature, the surfactant instantaneously agglomerates and can be easily retrieved.

2.1.2. SOLID PHASE EXTRACTION

Besides the more extravagant methods described so far, generally solid phase extraction (SPE) is applied in trace metal enrichment. The method offers high enrichment factors combined with high sample throughput; automatic sample treatment is possible as well avoiding any laborious sample manipulations. In figure 13 the SPE procedure is shown schematically.

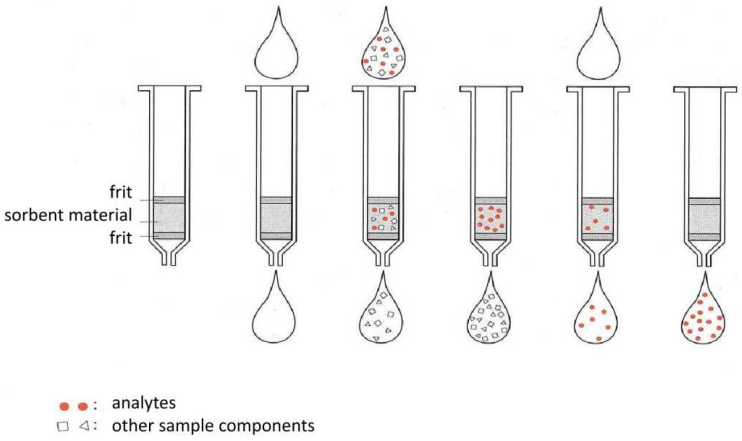


Figure 13 Operating steps for conventional SPE[8]

The liquid sample passes through a cartridge equipped with a sorbent material; the analyte is retained on the surface of the material. After removing excess liquid, a small volume of an appropriate solvent is used to elute the analyte. The resulting solution now holds a higher concentration of the target analyte.

SPE was initially devised for the analysis of organic compounds and therefore aliphatic chains were grafted on the sorbent material (C18 cartridges). Organic compounds are readily retained by this material but for inorganic trace analysis, the analytes have to be masked with appropriate complexing agents to obtain sufficient retention (Vlasankova 1999). For the elution from C18 cartridges, organic solvents like ethanol or methanol are required; this means that after the enrichment process the inorganic analytes are dissolved in organic solvents. The latter are in most cases not compatible with the instruments; for example the plasma of an ICP-OES or ICP-MS is severely disturbed if large quantities of organic solvents are introduced. A subsequent solvent change is feasible but increases the possibilities of sample contamination.

[8] Adapted from (Cammann 2001)

To overcome the disadvantages of C18 columns in the analysis of trace metals, ion exchanger materials can be used to retain the analytes. This approach can aim at the retention of cations or the retention of anions, depending on the analytes of interest. In the case of PGEs, anion exchanger resins can be applied because in aqueous solution and in the presence of chloride ions PGEs form negatively charged chlorocomplexes. These complexes adhere to strong anionic exchangers (SAX, e.g. quaternary ammonium groups) (Kovacheva 2002); to elute the adsorbed ions, two approaches are feasible. Either, the analytes are removed by concentrated mineral acids (Colodner 1993) or complexing agents are used (Kovacheva 2002). In the case of PGEs, usually thiourea is applied and allows for excellent recovery; unfortunately, this reagent is potentially carcinogenic and its use in chemical laboratories should therefore be minimized, if possible.

Although the SPE- method is being widely used, it has some major shortcomings arising mainly from the fact that due to economical reasons the columns are generally re- used several times. Because the removal of the analyte is never quantitative, memory- effects are often encountered. As mentioned above, strong acids are used to remove the PGEs from the resin; this causes on the one hand corrosion of the sample introduction system and on the other hand the surface of the ion- exchanging material gets damaged with every elution step (Ruzicka 1999). This means that the retention capacity of the column deteriorates over time which is bound to have a negative influence on the reproducibility of the whole analytical process (Wang 2000). If this effect is to be avoided, potentially dangerous complexing agents have to be employed which raises legitimate safety concerns. Lastly, if high enrichment factors are required, the time for the SPE process increases.

To overcome these problems, a modified form of SPE was introduced which supplies fresh sorbent material for each sample, the so- called “renewable surfaces” approach (Ruedas Rama 2005, Miro 2003). Here, the ion- exchanging material is manufactured into macroscopic beads which are added to the sample. The solution is stirred, the beads are removed from the solution and the analytes are subsequently eluted from the beads. This process avoids all the negative effects of deteriorated and contaminated surfaces since for each analysis, fresh sorbent material is procured. Yet, the analyte still has to be eluted from the beads afterwards; potentially dangerous and corrosive agents are needed.

2.1.3. DISPERSED PARTICLES EXTRACTION

In this work, the principle of renewable surfaces is extended and the elution process is completely omitted. The main idea behind this approach can be summarized as follows: if the ion- exchanging particles were sufficiently small, there would be no need for removing them prior to analysis. By performing slurry analysis, a complete recovery would be obtained. The main advantages of this approach compared to conventional SPE with packed columns are

RENEWABLE SURFACES: avoidance of memory- effects and deteriorating sorbent capacity

SLURRY ANALYSIS OF THE SORBENT MATERIAL: avoidance of harmful eluting agents and quantitative recovery

Of course, an analytical method has to be chosen that tolerates high solid load; due to its straight- forward sample introducing system, ET-AAS is the method of choice here, although the use of plasma methods like ICP-OES or ICP-MS should be possible as well.

The enrichment procedure is performed in three steps: at the beginning, the sorbent material is added to the sample solution. To facilitate the manipulation of the sorbent material, it is suspended in water and can be easily dispended by means of a pipette (see figure 14 (a)). The mixture is mixed vigorously to allow for maximum retention of the analytes. This process can be easily accomplished by applying ultrasonic energy which also helps in destroying residual agglomerates and prevents premeditate sedimentation. Afterwards, the sorbent material is separated from the liquid in a gravity field (centrifuge, (b)). The majority of the particles are found on the bottom of the vial and excess liquid can be removed by means of a pipette (c). Finally the particles are suspended in the small volume that remains and the slurry is analyzed (d).

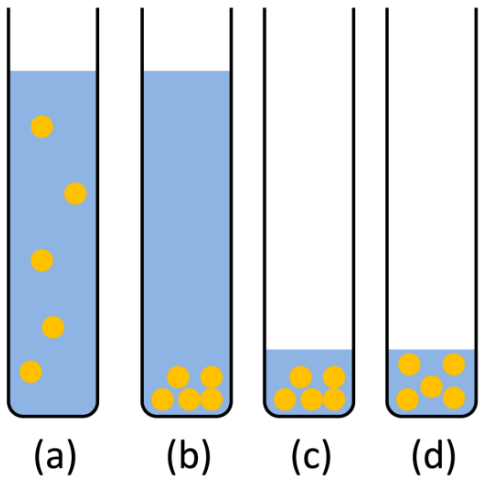


Figure 14 Operating steps for the DPE method

2.2. EXPERIMENTAL

Throughout the analytical process of dispersed particle extraction and the consecutive measurement of the slurry via ET-AAS several parameters have to be optimized in order to achieve sensitive and reliable results. After describing the instrumentation and the reagents used throughout this process, chapter 2.2.4. will treat the synthesis of the sorbent material. ET-AAS parameters will be given and the pre-treatment of the samples will be described. Various factors that influence the enrichment process will be studied in chapter 2.2.6.

As a matter of fact, the investigations presented in chapter 2.2 were not carried out consecutively but in parallel and a steady learning process took place; yet, for the sake of clarity, these topics will be discussed separately.

2.2.1. INSTRUMENTATION

A Perkin Elmer 4100ZL graphite furnace AAS with Zeeman background correction was used throughout this work.

Samples were digested in a Multiwave 3000 (Anton Paar) in eight high pressure Teflon vessels (HF 100 set) in a rotor equipped with 16 positions. Every other rotor position was left vacant to ensure homogeneous heat distribution. The heating program (see table 2 for a general schema) was operated in power- mode. To monitor the pressure and the temperature inside the vessels, a sensor was introduced into one vessel, reducing the number of digests per run to seven. To gather temperature information about each vessel, the external infrared radiation was recorded. To avoid destruction of the instrument, maximum temperatures (240°C internal temperature, 210°C IR temperature) and a maximum pressure rate (0.5bar/sec) are monitored by the software.

Table 2. Temperature Program Multiwave 3000

	Time [min]	Power [W]
Heating ramp	20	1200
Hold time	30	1200
Cool down	20	-

In the case of aqueous soil- extracts, organic matrix was decomposed by means of UV digestion. The eight vessels employed for this process were made of quartz glass, the liquid

samples were mixed with inorganic acids and hydrogen peroxide and a sealed glass vial containing cadmium metal was added to the solution. Due to the microwave radiation this metal emits UV light that enhances the oxidation of organic matrix in acid solutions in the presence of hydrogen peroxide. The temperature program was the same as described in table 2.

For performing the enrichment step, 15mL Polypropylene tubes (Sarstedt) were used, an EBA20 centrifuge (Hettich), a Vortex 2 (Scientific Industries) and a Sonorex TK30 ultrasonic bath (Bandelin) were further employed during sample enrichment. A Sartorius H110 balance was used throughout the process, very small sample aliquots (see chapter 2.3.2.) were weighed on a Sartorius MC-210 P balance.

2.2.2. REAGENTS

The water was deionised by means of reversed osmosis and further purified with an Easipure system (Thermo Scientific), a specific conductivity of 18MΩcm^{-1} was obtained. All reagents used during the synthesis of the SAX MCM-41 particles were of synthesis grade or higher. All chemicals used throughout the analytical process were of p.a. grade or higher as indicated in table 3.

Table 3. List of used Chemicals

	purity	**supplier**
Nitric acid, 65%	p.a.	Merck, Germany
Hydrochloric acid, 37%	p.a.	Merck, Germany
Hydrofluoric acid, 48%	p.a.	AppliChem, Germany
Hydrogen peroxide, 30%	Suprapur	Merck, Germany
Perchloric acid, 70%	p.a.	AppliChem, Germany

Standard solutions of PGEs were purchased from FLUKA, Germany (see table 4).

Table 4. List of standard solutions

	Standard	**concentration [mg/L]**
Pd	FLUKA 77091	1001 ±2
Rh	FLUKA 04736	999 ±3
Pt	FLUKA 19078	1000 ±2

2.2.3. SAMPLE DIGESTION

Plant material was digested by adding a mixture of concentrated mineral acids and hydrogen peroxide according to table 5 and performing a microwave digestion following the program given in chapter 2.2.1. For the clean- out step, a less aggressive mixture of chemicals was employed.

Table 5. Digesting agents for Multiwave 3000

	Sample digestion	Clean Out
Nitric acid, 65% [mL]	3	3
Hydrochloric acid, 37% [mL]	1	1
Hydrofluoric acid, 48% [mL]	0.1	-
Hydrogen peroxide, 30% [mL]	1	1

To perform an UV digestion, the liquid sample was mixed with the required reagents according to table 6 and digested according to the abovementioned temperature program.

Table 6. Digesting agents for UV digestion

	Sample digestion	Clean Out
Sample or water	13.8	13.8
Hydrochloric acid, 37% [mL]	0.5	0.5
Nitric acid, 65% [mL]	0.5	0.5
Hydrogen peroxide, 30% [mL]	0.2	0.2

2.2.4. SYNTHESIS AND CHARACTERIZATION OF SAX MCM-41

The synthesis of the SAX MCM-41 material was carried out at the Institute of Materials Chemistry under the guidance of Univ.Ass. Dipl.-Ing. Mag. Dr. Marie-Alexandra Neouze.

Ion exchanging materials with a high specific surface are ideal for the slurry- approach described in chapter 1.3.3. Due to the high number of ligands per unit surface, very small amounts of the resin are sufficient to reach quantitative retention of the target analyte. In this work, silica was used as carrier- material since it is inert to most chemical environments and may easily be modified. In practice, MCM-41 silica was employed and synthesized according to (Grün 1997); this compound possesses many open surface- pores and the particles are very small in diameter (approximately 500nm). The synthesis was carried out by

hydrolysis of tetraethyl orthosilicate (TEOS) in the presence of ammonium hydroxide (base), water and cetyltrimethylammoniumbromide (CTAB), a cationic surfactant. The silica produced by the hydrolysis of the TEOS- precursor gathers around the micelle formed by the surfactant, leading to the formation of larger particles with pores of the diameter of the micelle. After collecting the material and washing it, a drying step (24h, 90°C) was carried out, followed by calcination which removes remaining solvents and the surfactant (5h, ramp 1°C/min, 550°C). The reaction yielded a white, very fine powder (99.4% yield). The subsequent surface modification was carried out according to (Tian 2009) (see figure 15).

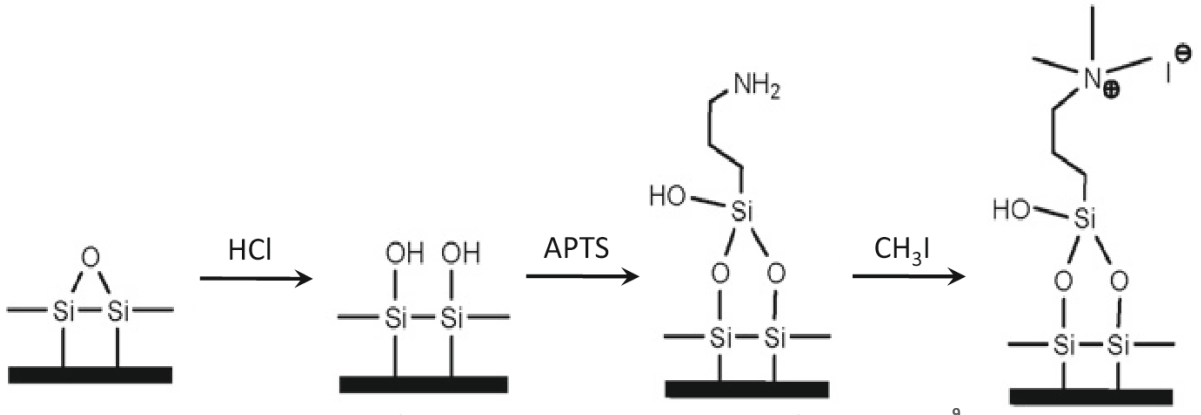


Figure 15 Modification steps during the synthesis of SAX MCM-41[9]

To hydrolyze the surface of the MCM-41 material in order to introduce the new functionalities, the material was stirred for 5h in 50% (v/v) hydrochloric acid. The material was filtered, washed until complete removal of the acid (pH 7) and dried (48h, 120°C, 97.8% yield). 2g of the material were used for further modification; under argon atmosphere the silica was mixed with dry toluene and 3-aminopropyltriethoxysilane (APTS) and stirred for 2h. The mixture was then heated to reflux for 16h, filtered, washed with toluene and ethanol and subsequently dried (120°C, 24h), yielding a whitish material. Agglomerates were destroyed with a glass rod; the material was suspended in dry ethanol, mixed with methyl iodide and stirred at moderate temperatures (23h, 55°C). After washing with ethanol and drying (120°C, 24h), a slightly yellow powder was obtained. The colour is probably due to iodide ions still present in the material; when wet, the material gains significantly in colour intensity.

[9] Adapted from (Tian 2009)

To characterize the obtained SAX MCM-41 material, three methods were applied. Firstly, nitrogen sorption isotherms were recorded on an ASAP 2000 instrument at 77K using the BET model (Brunauer, Emmett and Teller (Brunauer 1938)) in order to obtain information about the specific surface of the material and the pore diameter (results see table 7).

Table 7. Results of BET measurements

	Non hydrolized MCM-41	hydrolized MCM-41	SAX MCM-41
BET Surface Area [m²/g]	1084	930	66
BET diameter [nm]	2.5	2.5	3.7

As can be seen in this table, MCM-41 silica has a very high specific surface of approximately 1000 m^2/g and an average pore- diameter of 2.5nm. After the chemical modification, the BET Surface significantly decreases which is probably due to formation of new surface layers containing the diethyl- aminopropyl- group; the longer and the more complex the newly introduced group, the greater the loss in BET surface (Kimura 1998).

The mean particle diameter was measured[10] by Scanning Electron Microscopy (SEM) on a Quanta 200 mK2 (FEI) and was found to be approximately 0.5µm (see figure 16). The raw material shows slightly larger particles (650 ± 200nm) than the surface-modified particles (500 ± 50nm).

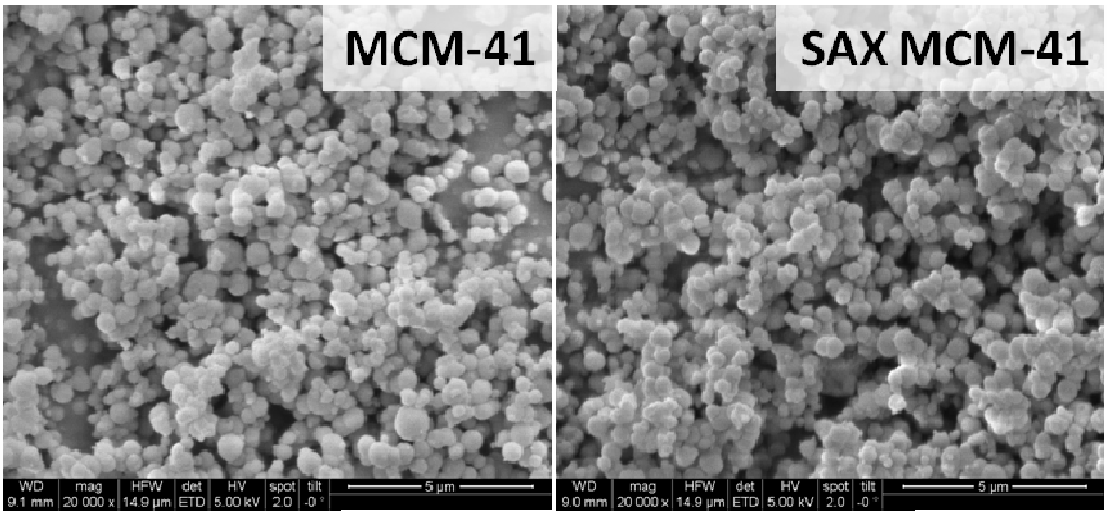


Figure 16 SEM micrographs of the synthesized particles (5kV, measuring bar = 5µm)

[10] Special acknowledgement to Elisabeth Eitenberger for performing the SEM measurements

In order to further determine the pore diameter, X-ray diffraction was performed[11] on the particles because the regular distribution of the pores on the surface leads to diffraction phenomena, as reported in (Beck 1992, Sayari 2001 and Cai 2000). The X-ray radiation was generated with a Cu anode (Cu Kα1 = 1.5405980nm, Cu Kα2 = 1.5444260nm) and the diffractograms were recorded on a Philips X'Pert instrument (see figure 17). The resulting data is in poor accordance with the data found in the literature; yet the diffraction patterns are reported to greatly depend on the concentration of the surfactant during the synthesis of the MCM-41 material (Sayari 2000).

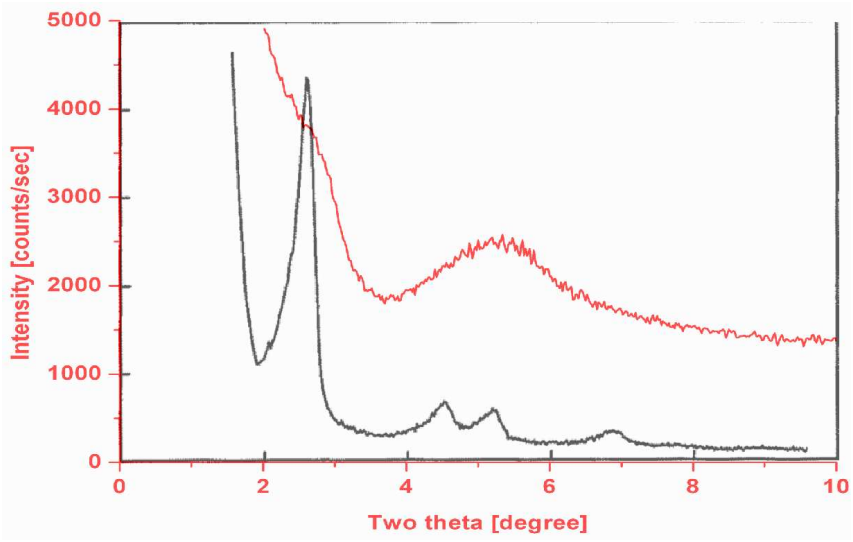


Figure 17 Comparison of a diffractogram found in the literature (Cai 2000) (black curve) and the diffractogram of the synthesized MCM-41 material (red curve)

2.2.5. OPTIMIZATION OF THE ET-AAS PARAMETERS

The specification of the hollow cathode lamps and their respective operating parameters are summarized in table 8. No lamp was available for the analysis of Rh, therefore only Pt and Pd analysis was performed with the ET-AAS.

Table 8. Hollow cathode lamps used for all measurements

	Platinum		**Palladium**	
Specification	Photron Ltd.		Photron Ltd.	
Wavelengths [nm]	265.9	306.5	247.6	340.5
Slit width [nm]	0.7	0.7	0.2	0.7
Lamp current [mA]	10		15	

[11] Special acknowledgement to Ass.Prof. Dipl.-Ing. Dr.techn. Erich Halwax for performing the XRD measurements

For the actual ET-AAS measurements, wavelengths have to be chosen and temperature programs have to be optimized in order to obtain results with sufficient reproducibility. For Pt and Pd, four lines are free of interferences and of sufficient intensity. In a first experiment, aqueous standards were used to investigate the signals obtained when using these four wavelengths. From the graphical output files in figure 18 it becomes obvious, that Pd measurements should be carried out using the line at 340.5nm as the other line shows very weak response. The Pt line at 265.9nm gives a slightly higher signal than the Pt line at 306.5nm; further experiments proved that the RSD using the 265.9nm line is significantly better.

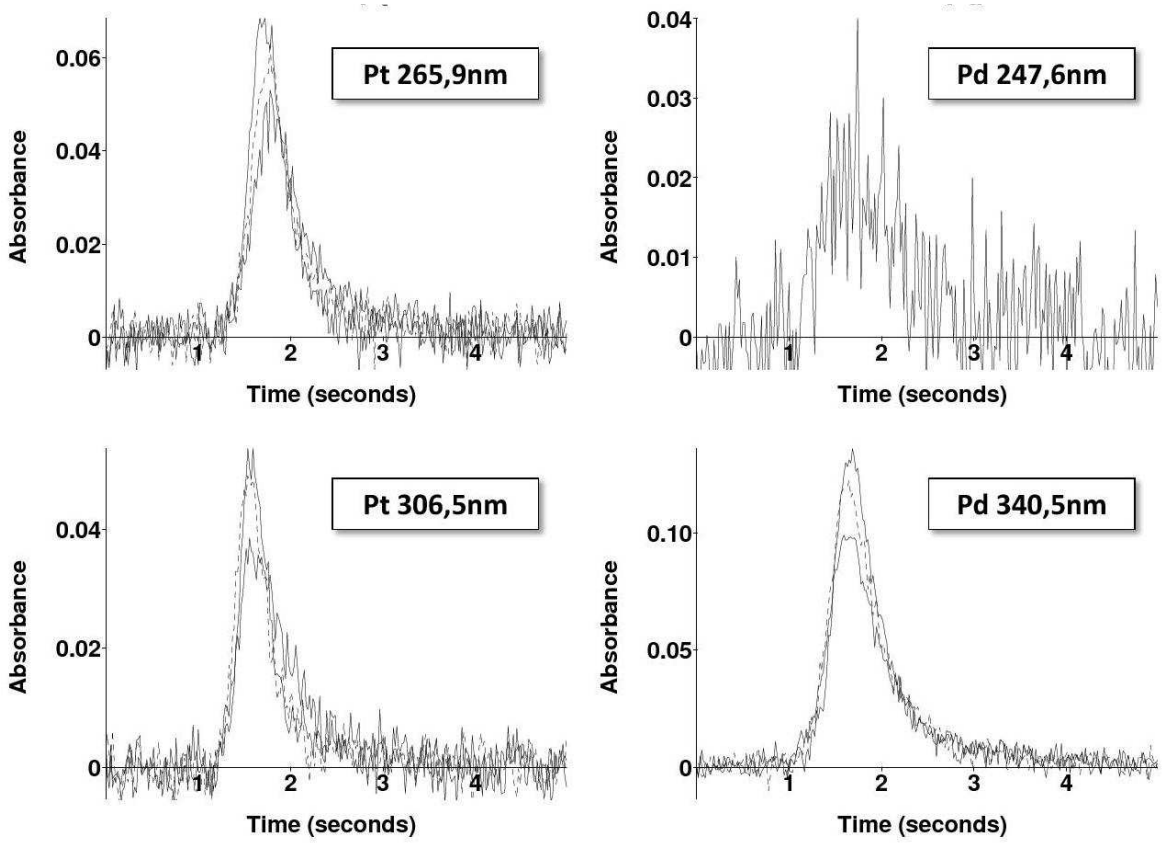


Figure 18 ET-AAS signals obtained using different vaporization temperatures (total analyte mass: 3ng in the tube); Pt: 2300°C (solid line, smallest peak), 2350°C (dashed line) and 2400°C (solid line); Pd: 2150°C (solid line, smallest peak), 2200°C (dashed line) and 2250°C (solid line).

With higher vaporisation temperatures, the peak area and the peak height increase (see fig. 18). At the same time, the relative standard deviation (RSD) decreases. Yet, with too high a temperature, the RSD increases again, making it necessary to find a temperature- window

where optimal conditions are met. Following the results in table 9, optimal vaporisation temperatures are 2200°C and 2350°C for Pd and Pt, respectively.

Table 9. RSD of Peak Area and Peak Height at different vaporisation temperatures

	Line [nm]	vaporisation Temperature [°C]	Peak Area RSD [%]	Peak Height RSD [%]
Pt	265,9	2300	6.7	1.0
		2350	0.8	2.7
		2400	4.6	1.7
Pt	306,5	2300	8.2	8.6
		2350	5.0	2.5
		2400	8.7	4.4
Pd	247,6	2150	10.0	8.0
		2200	10.1	6.9
		2250	27.8	12.3
Pd	340,5	2150	5.7	5.2
		2200	1.5	1.4
		2250	4.7	5.0

The temperature programs and wavelengths used for all further analysis of the two analytes are therefore established (see figure 19).

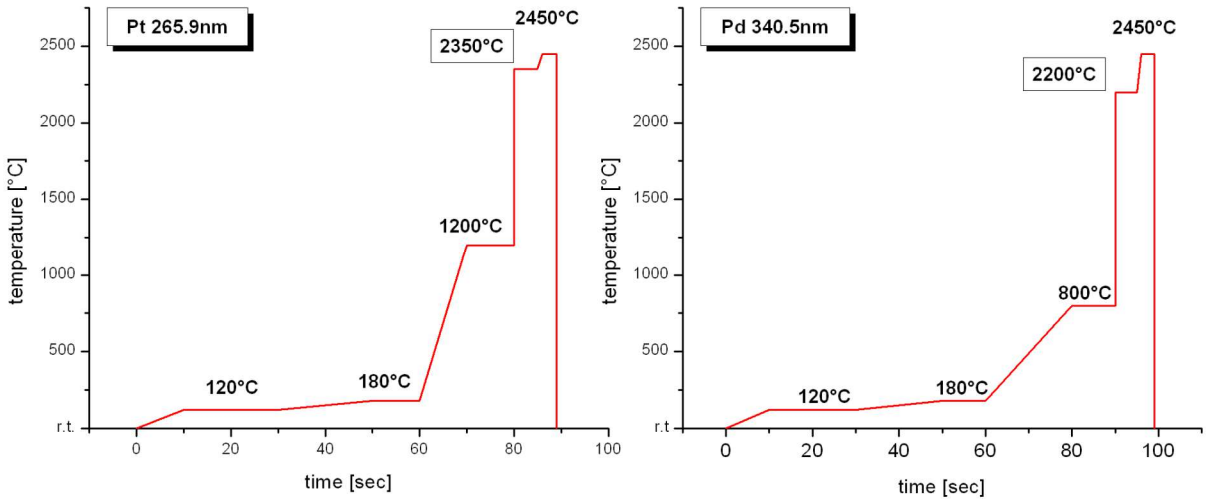


Figure 19 optimized temperature programs for Pt and Pd

When adding the SAX MCM-41 particles to the solution, interferences during ET-AAS measurements may be expected due to vaporizing silica. Especially in the case of Pt where higher vaporisation temperatures are applied, the background dramatically rises in the

presence of the particles (see figure 20 (b)). The addition of hydrofluoric acid (10% v/v) helps in reducing the background to an acceptable size (see figure 20 (c)-(e)). Obviously, the Palladium measurements are not interfered by the silica material; nevertheless addition of 5µL HF (10% v/v) seems appropriate in order to remove the silica quantitatively and to avoid its accumulation in the graphite tube.

Either the peak area or the peak height may be used for calibration purposes. The calibration curve of the peak height signal is much steeper than the peak area curve; in a first conclusion, a steeper slope should yield better results: small variations in analyte concentration produce large changes in the signal (see also chapter 1.3.5.). Yet in the presence of the particle slurry and after the enrichment process, the slopes of both calibration curves become more or less the same. Moreover, the blank values of peak height calibrations are much higher because one outlier determines the height of the peak, whereas the peak area is integrated over the whole analysis time; outliers become thus less predominant. Therefore, the peak area was used for quantification throughout this investigation because of yielding a better LOD.

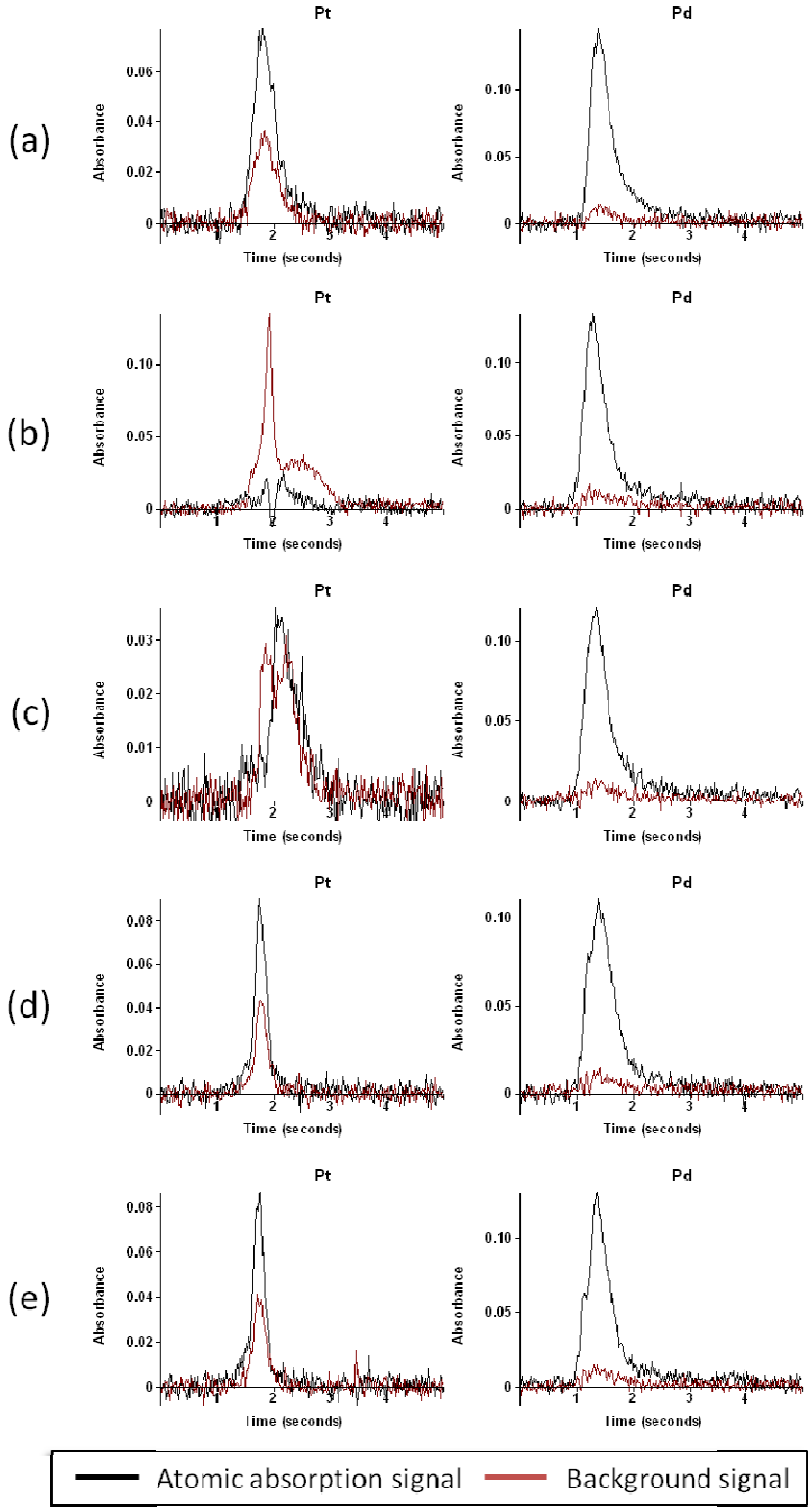


Figure 20 The signal of 3ng analyte in the tube (a) drastically changes in the case of Pt in the presence of 0,1mg MCM-41 particles (b). The addition of small amounts of HF (2µL (c), 4µL (d) and 6µL (e)) successfully removes this additional background

2.2.6. OPTIMIZATION OF THE ENRICHMENT PROCESS

Despite having optimized AAS parameters both for Pt and Pd, only the enrichment of Pd from aqueous solutions was further explored and will be described in the following chapter; Pt can be readily analyzed with ICP-MS which offers outstandingly good sensitivity.

Optimal conditions have to be established in order to quantitatively adsorb the Palladium-chlorocomplex on the SAX MCM-41 material. In a first attempt, ideal systems (aqueous standards, pure chemicals and bi-distilled water) were used for studying these parameters. After establishing a method that allows for maximum recovery and low RSD, the influence of organic and inorganic matrix components on the process was examined.

The ACID CONCENTRATION most obviously interferes in the enrichment process: if there is a high concentration of hydrochloric acid, the surface of the sorbent material will be completely covered with chloride ions. Hence the analytes are not retained quantitatively. On the other hand if the solution is not sufficiently acidic, the Palladium- chlorocomplex is likely to dissociate and again incomplete recovery is obtained (see figure 21).

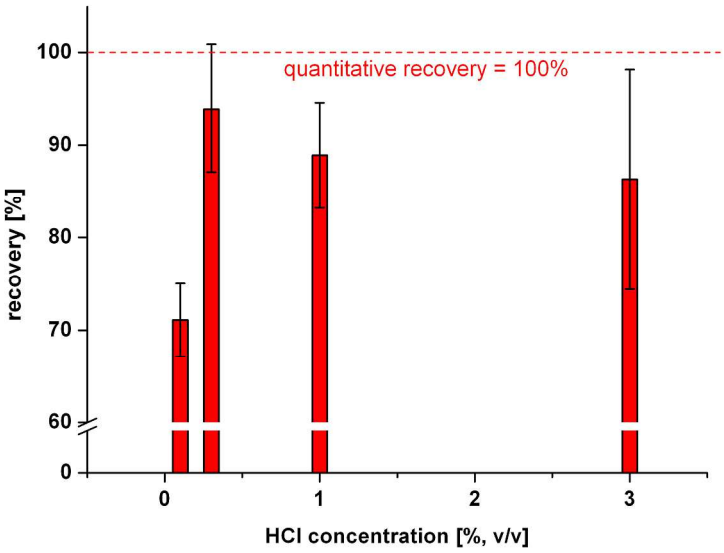


Figure 21 Influence of the sample acidity on the recovery, optimal conditions at 1% HCl

The recovery was calculated by adding Palladium standard (equal to 50ng Pd) to 12mL of a solution with the desired acidity and performing the enrichment procedure (40µL 50g/L SAX suspension, final volume: 0,4mL, theoretical enrichment factor: x30). The ET-AAS- signal that can be expected in the case of 100% recovery was obtained by mixing the same amount of

analyte with the sorbent material and diluting to a final volume of 0,4mL; the ratio between these two signals yields the recovery. Recoveries of about 80% are usually obtained with conventional SPE methods; the proposed slurry method yields comparable recoveries (around 80 to 85%). By varying the acid concentration, an amount of 1% (v/v) of hydrochloric acid in the aqueous solution was found to be optimal since it yielded the lowest RSD values and a high recovery.

The AMOUNT OF SORBENT material also influences the recovery; obviously, a higher amount of particles yields a higher recovery (see figure 22). By further increasing the particle amount beyond 2mg, no significantly higher recovery was obtained. Furthermore, too high a particle concentration may even enhance possible interferences in the instrument. Therefore the particle amount was set to 2mg, respectively 40µL of a 50g/L suspension.

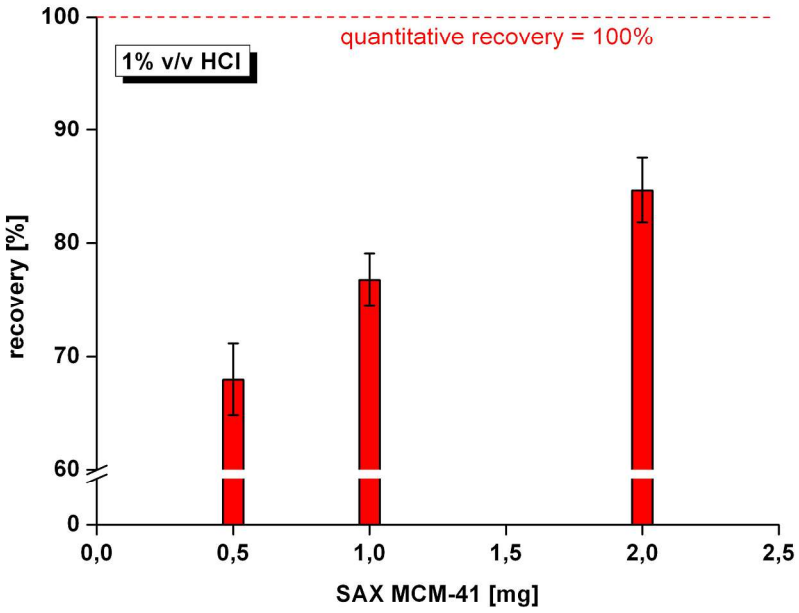


Figure 22 Influence of the amount of sorbent on the recovery

The VOLUME RATIO (initial volume/final volume) should be maximal in order to increase the theoretical enrichment factor. The enrichment effect becomes obvious, when the sample (25ng Palladium standard in 10mL initial volume) is reduced to different final volumes (0.2, 0.3, 0.4 and 0.5mL). The signal increases linearly with decreasing final volume as expected (see figure 23, left).

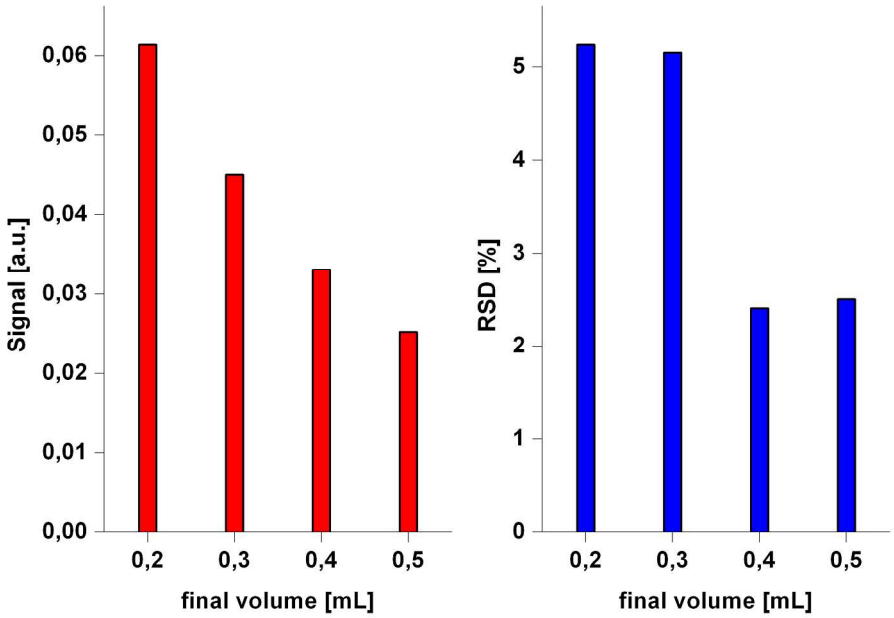


Figure 23 Influence of the final volume on the signal (left) and on the RSD (right)

Although the highest signal intensity is achieved with the smallest final volume, also the RSD increases over two-fold (see figure 23, right). The decrease in reproducibility is probably due to difficulties in manipulating such small sample volumes; one other disadvantage of very small final volumes is a reduced number of repeat analyses.

The TIME of interaction between sorbent material and analyte was found to have no influence on the recovery (reaction times of 1 and 10 minutes were examined). This means that the adsorption process takes place immediately as the analytes are being mixed with the sorbent material.

The way of REMOVING THE SUPERNATANT SOLUTION after centrifugation is crucial: if the final volume is reached by removing the supernatant solution in one step, large particle losses are observed. This leads to low recovery and high RSD values. To overcome this problem, a two-step procedure was established; with this procedure, a dramatic increase of the recovery was observed compared to the one-step enrichment (see table 10).

Table 10. Comparison of both ways of removing the supernatant solution		
One-step enrichment	**Two-step enrichment**	**parameters**
Initial volume 10mL	Initial volume 10mL	
Centrifugation	Centrifugation	3000 rpm, 3min
ultrasonic bath	ultrasonic bath	10sec
Centrifugation	Centrifugation	3000 rpm, 1min
Removal of supernatant solution (9.6mL)	Removal of supernatant solution (8.6mL)	
-	Vortex, ultrasonic bath	10sec, 1min
-	Centrifugation	3000 rpm, 3min
-	Removal of supernatant solution (1mL)	
Vortex, ultrasonic bath	Vortex, ultrasonic bath	10sec, 1min
Final volume 0.4mL	Final volume 0.4mL	
52.0 ± 0.9 % recovery	80.7 ± 2.0 % recovery	

SEDIMENTATION of the SAX MCM-41 particles can be a problem although the particle diameter is very small. After some time the particles tend to sediment on the bottom of the vials which eventually leads to a loss in signal intensity and increased RSD. To overcome this problem, Triton X and ethanol were tested as suspending agents (Ferreira 2010); either the handling of the substances was troublesome (the surfactant TritonX produced large amounts of foam) or the additives caused even faster sedimentation (Ethanol, see figure 24). Because of these adverse effects of the tested additives, only aqueous solutions were used and the particles were re-suspended every 15 minutes by means of an Eppendorf- pipette.

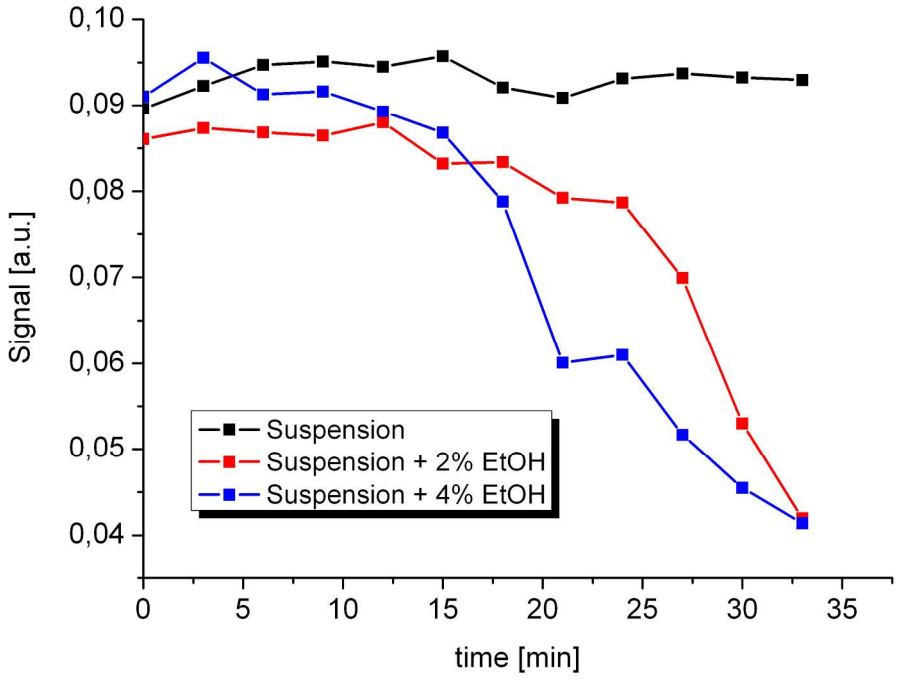


Figure 24 Addition of Ethanol to the suspension increases the sedimentation of the sorbent material

The SAMPLE INTAKE of the ET-AAS instrument for one measurement should be as large as possible to allow for maximum sensitivity. To enhance the sample intake, the surface tension of the sample can be modified by adding ethanol; this allows better wetting of the L'vov platform and improved spreading of the sample drop. Yet, the addition of ethanol greatly enhances the sedimentation of the SAX MCM-41 particles in the autosampler vials. Therefore the sample intake was restricted to 30µL per analysis.

In all experiments that were described so far aqueous standard solutions, pure reagents and bi-distilled water were used. In "real-world" samples, other constituents like organic compounds and high concentrations of other ions are present.

The influence of ORGANIC SAMPLE CONSTITUENTS on the enrichment process was examined by mixing soil- extracts and UV-digested soil extracts with varying volumes of distilled water, spiking the resulting solution with a constant amount of palladium and observing the recovery (see figure 25). As expected, the recovery largely depends on the concentration of organic matrix; palladium is readily complexed by organic compounds (e.g. humic acids) and may therefore not be retained on the SAX MCM-41 material. The complete destruction of organic matrix is therefore vital for the success of the enrichment procedure.

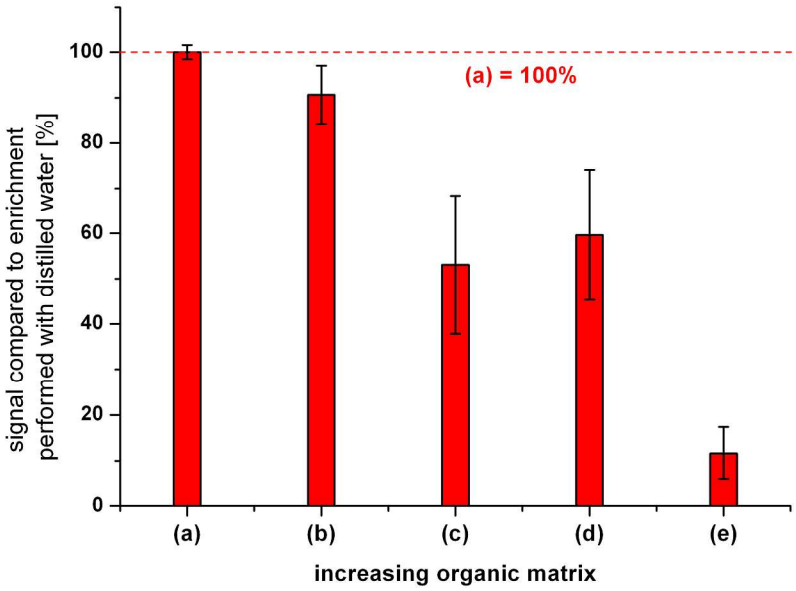


Figure 25 Pd was added to 10mL aqueous sample (25ng). The samples consisted of: (a) distilled water, (b) 2mL digested soil- extract and 8mL water, (c) 10mL digested soil- extract, (d) 2mL crude soil- extract and 8mL water and (e) 10mL crude soil- extract. All samples were acidified to 1% HCl (v/v) and 2mg sorbent material was used.

The influence of INORGANIC SAMPLE CONSTITUENTS was examined using plant digests that were prepared as described in chapter 2.2.3. Due to the microwave digestion using concentrated mineral acids, organic matrix will be quantitatively destroyed; only inorganic compounds remain. Three different amounts of Palladium were added to the digests, the enrichment process was performed on the resulting solutions and a calibration was recorded. Comparison with an aqueous calibration shows that no influence on the slope of the calibration curve is observed when inorganic matrix components are present. This proves that the SAX MCM-41 material is very selective to PGEs and interferences of other anions can be neglected.

ANALYTE LOSSES due to adsorption on the walls of the Polypropylene tubes are possible in the case of insufficient acidity. Yet, with a concentration of 1% HCl no significant losses- even over a period of 72 hours at room temperature- were observed. Therefore the use of PP tubes was considered feasible.

THE OPTIMIZED PARAMETERS described in this chapter were used for all further measurements and are summarized in table 11.

Table 11. Summary of all optimized parameters		
ET-AAS	Wavelength [nm]	265.9 (Pt) 340.5 (Pd)
	Vaporisation temperature [°C]	2350 (Pt) 2200 (Pd)
	Dispensed sample volume [µL]	30
	Hydrofluoric Acid 10 % v/v Modifier [µL]	5
Enrichment process	Hydrochloric acid [% v/v]	1
	Amount of sorbent material [mg]	2
	Final Volume [mL]	0.4
	Removal of supernatant solution	2-step procedure
	Additives against Sedimentation	None
	Organic sample constituents	Complete removal required

2.3. RESULTS

2.3.1. FIGURES OF MERIT

Having optimized the procedure, LOD and LOQ are distinctly lower as compared to conventional ET-AAS measurements. A factor of approximately x20 was gained in LOD and LOQ through the enrichment process; however theoretically a factor of x25 to x30 would be possible according to the volume ratio (initial volume/final volume). Since the values of LOD and LOQ largely depend on the reproducibility of blank measurements, the values given in table 12 are subjected to variation and should therefore be regarded merely as guidelines. Further examples for LOD and LOQ values are given in table 13 on page 44.

Table 12. Figures of Merit			
		Conventional ET-AAS	**ET-AAS after enrichment process**
LOD	**[ng/mL]**	3.40	0.14
LOQ	**[ng/mL]**	10.70	0.47
RSD (one sample, n=4)	**[%]**	2.40	2.70
RSD (three samples)	**[%]**	5.00	6.10

The RSD of one measurement (repeat analysis) and the RSD of several replicates show satisfactory values in the lower percent range. Since the RSD depends on the analyte

concentration (low concentrations yield higher RSD values), the values were calculated at 5times the LOQ for both methods.

2.3.2. APPLICATION EXAMPLE: SPATIAL DISTRIBUTION OF PALLADIUM IN PLANTS

In order to monitor the uptake potential of PGEs in plants, green-house experiments[12] with *Brassica Napus Californium* were carried out under standardized conditions. Since the soil chemistry of PGEs is very complex, the plants were grown in hydroponic setup to avoid any unwanted influences. Four contamination levels were chosen (blank, 0.5, 1 and 5µg/mL) and PGEs were added to the nutrient solution in the form of chlorides (platinum and palladium: salts, Sigma Aldrich; rhodium: ICP standard, Merck). The nutrient solution was kept at constant pH = 7 by means of a buffer (MES, 2-(*N*-morpholino)ethanesulfonic acid, Sigma Aldrich M0895). To guarantee a constant level of nutrients and PGEs, the solutions were changed twice a week. In a first experiment, the plants were grown for four weeks in non-contaminated nutrient solution; afterwards they were contaminated and harvested after four weeks. To remove any superficially adsorbed PGEs, after harvesting the plants were washed with 0.05M $CaCl_2$ solution and distilled water in an ultrasonic bath and subsequently dried at 60°C. Since these plants had sufficient time to grow and prosper before contamination, rather large specimens were obtained. In a second experiment, the contamination process was started right after germination; due to the increased stress, these plants showed restricted growth. The dry mass of these plants was about 300mg each; in the first experiment, average masses of 10g per plant were achieved.

Due to the restricted growth, it is very difficult to analyze the samples of the second experiment; usually, an aliquot of 200mg plant material was digested and conventional ICP-OES measurements were performed (see chapter 3.1.3. for a detailed description). A lower sample intake is not possible with this method because the sensitivity of the ICP-OES measurements does not allow for such low analyte concentrations.

With the ET-AAS method, there is no restriction in terms of sample intake since the LOD is significantly lower. Therefore it was not only possible to measure the Pd concentration in the samples of the second plant experiment, but it was even possible to divide each plant

[12] The author is indebted to Mag. Esther Herincs for supplying the plant material.

into sub-samples (see figure 26). The spatial distribution of Palladium in each plant could thus be determined.

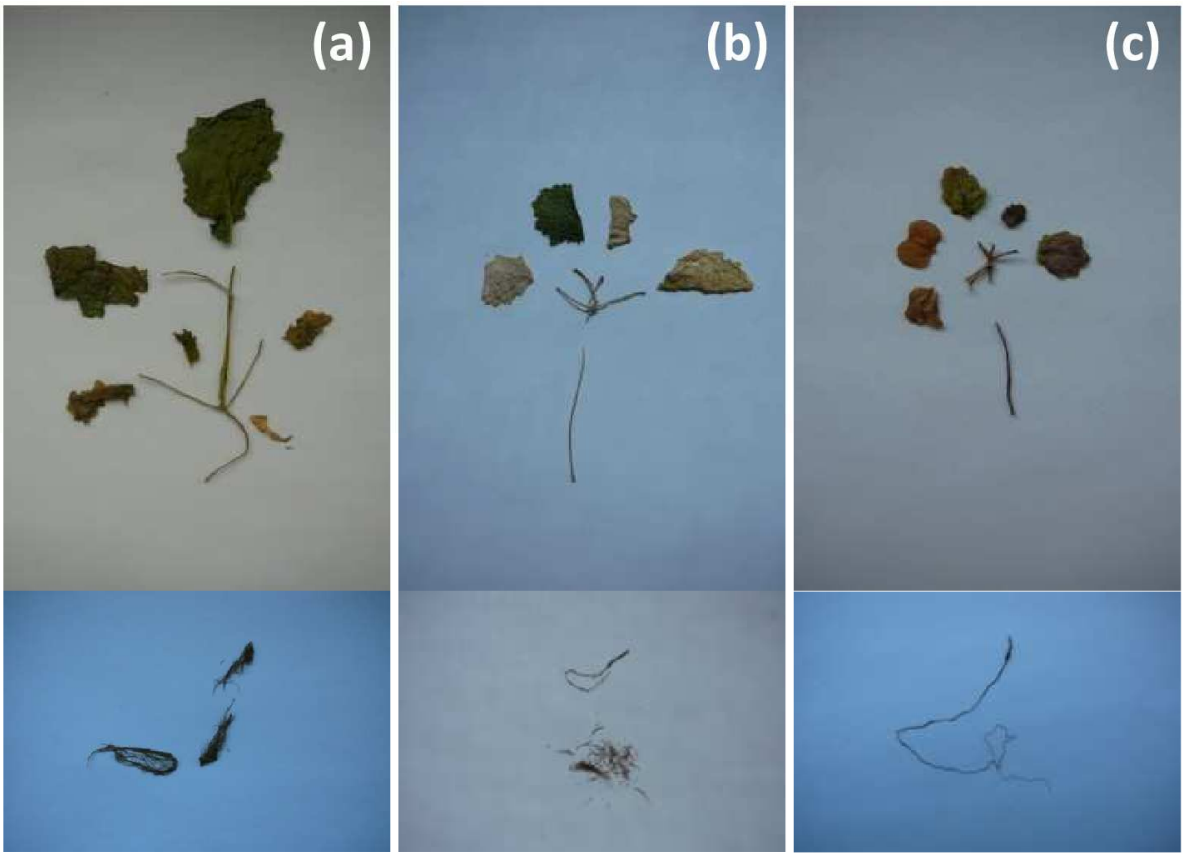


Figure 26 Sub- divisions of the samples (MES 0.5: (a), MES 1: (b) and MES 5: (c))

The plant sub- samples of about 5mg to 50mg each were weighed and transferred into Teflon recipients. Concentrated mineral acids and Hydrogen peroxide were added and a microwave assisted digestion was performed according to chapter 2.2.3.

Up to this point the samples contain highly concentrated acids; this mixture is not compatible with the SAX MCM-41 sorbent material since hydrofluoric acid readily dissolves silica. In order to reduce the acid concentration, an evaporation step was introduced: after cooling down, the solutions were quantitatively transferred to smaller Teflon vessels; the initial vessel was rinsed twice with 0.2mL concentrated hydrochloric acid and this solution was added to the rest of the sample to ensure a complete transfer of the analyte. Then the samples were heated to 110°C in an aluminium heating block for approximately 8 hours. To avoid complete evaporation of the solvent which may cause the unwanted conversion of the analyte into less soluble forms, a small amount of perchloric acid (50 µL) was added to the samples prior to evaporation. The low vapour pressure of this compound ensures that the

samples never run dry completely. Additionally, perchloric acid helps in the destruction of remaining organic or inorganic carbon and converts Palladium completely into the Palladium-chlorocomplex.

After the evaporation step, the samples were diluted to a volume of 12mL using 1% HCl yielding a clear aqueous solution with less than 0.4% perchloric acid; this acid concentration was shown not to hamper the enrichment process which was performed as described in chapter 2.2.6.

Since several dilution steps and one enrichment step were performed during the entire analysis procedure, care has to be taken in order to correctly determine the concentration of Palladium in the plant material.

To calculate the net concentration in the dried plant material, the concentration of the digest solution c_{digest} has to be converted to the absolute amount of palladium present in the sample by multiplying with the digest volume V_{digest}. Dividing by the dry mass m_{plant} of the sample yields the desired concentration c_{plant} (see equation 7).

$$c_{plant}[ng/g] = \frac{c_{digest}[ng/mL] \cdot V_{digest}[mL]}{f \cdot m_{plant}[g]} \qquad \text{Equation 7}$$

Digesting the roots always yielded highly concentrated solutions; hence no enrichment step was needed but instead the solutions were diluted by a factor 10 to 100 and conventional ET-AAS measurements were performed. The dilution factor f can be calculated from the aliquot $V_{aliquot}$ taken from the digested Volume and the Volume $V_{diluted}$ to which it was diluted (see equation 8).

$$f = \frac{V_{aliquot}[mL]}{V_{diluted}[mL]} \qquad \text{Equation 8}$$

In the case of the leaves and the stems, no dilution was necessary and therefore the dilution factor becomes unity.

The detailed results are given in table 13 at the end of this chapter (page 44).

The concentration in the ROOTS was very high; a differentiation between fine and coarse roots shows significant differences (see figure 27). However, no difference was observed between roots that grow near the stem and far from the stem.

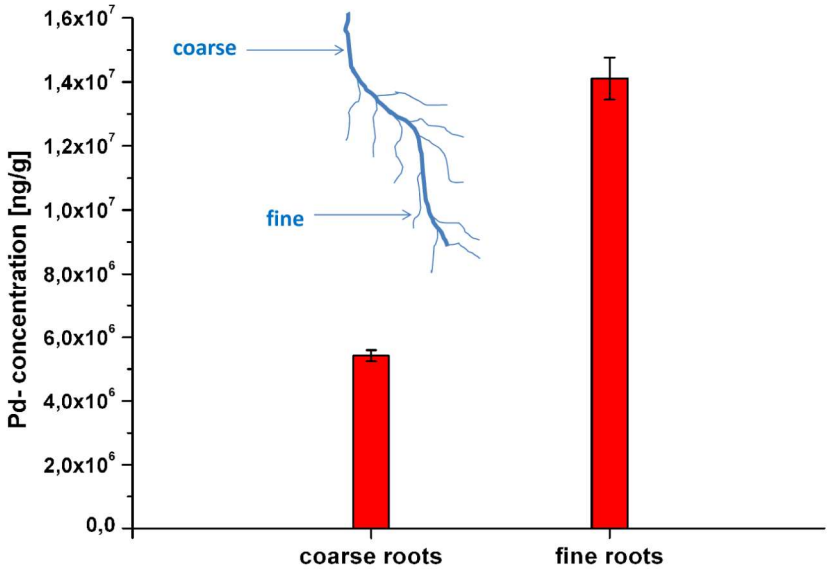


Figure 27 Different Pd- concentration was observed in coarse and fine roots (sample MES 1)

The concentrations of the LEAVES are plotted in graph 28; to allow for straight-forward comparison, the y-axis is scaled logarithmically.

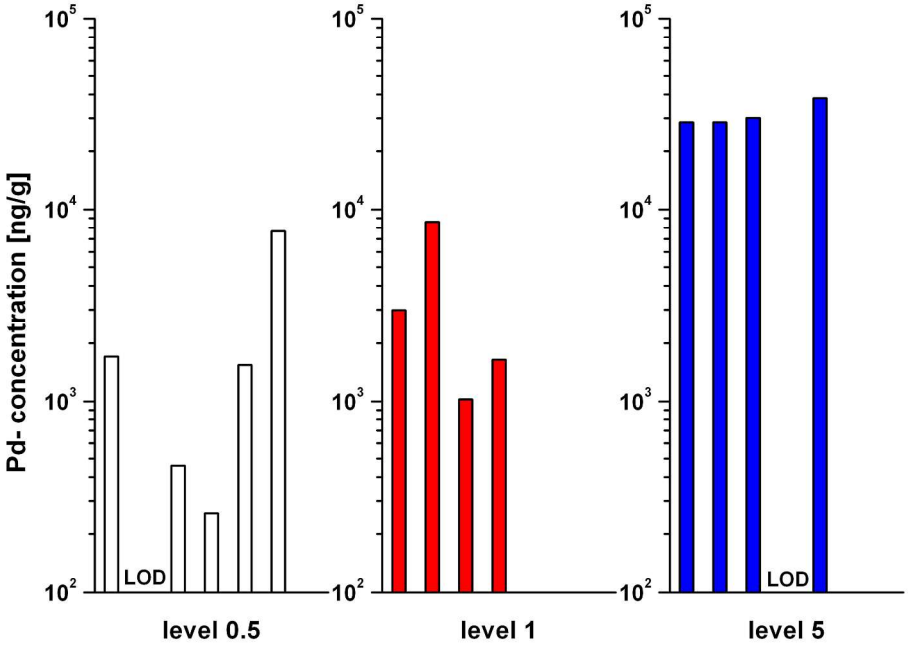


Figure 28 Pd- concentration in the leaves, logarithmical scale (LOD: the concentration of the digest was below the LOD of the method)

The strong variation between measurements at first seems strange (the variation due to instrumental RSD can be omitted because of the larger variation in-between the samples). Upon comparison of the Pd- concentration of the leaves and the physical appearance of the plants, no correlation was observed; in the case of the lowest contamination level (see figure 29 (a)) the yellow leaves show the highest Pd- concentration and in the case of the highest contamination level (figure 29, (c)), the green leaf shows the highest concentration.

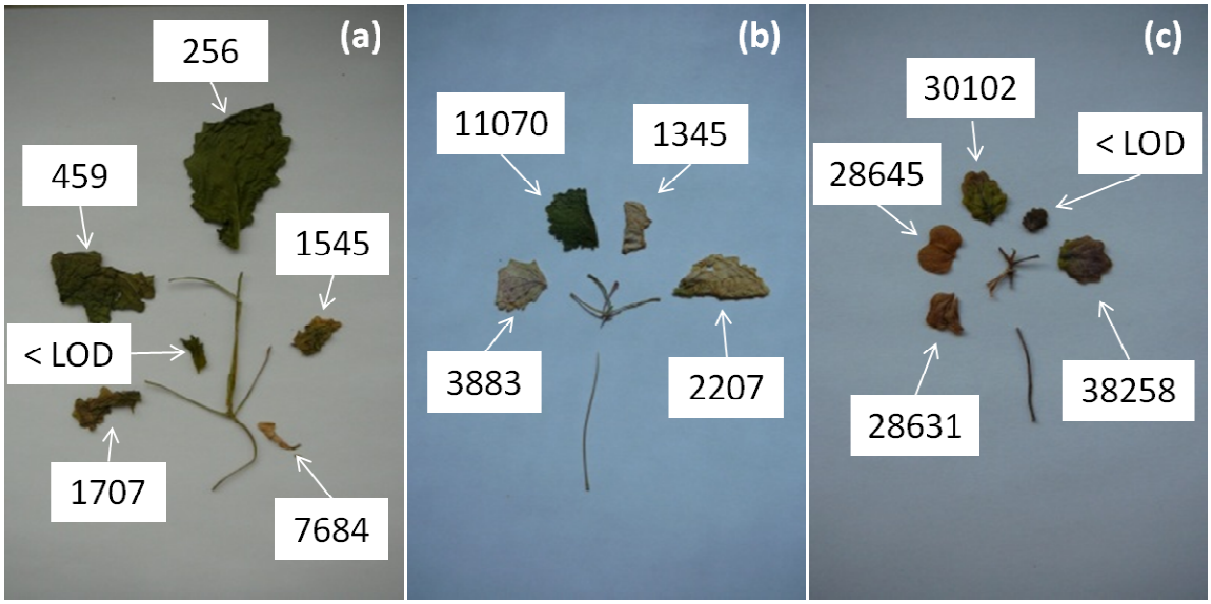


Figure 29 Concentrations in the leaves, all values in [ng/g] (samples: MES 0.5: (a), MES 1: (b), MES 5: (c))

The variations in-between measurements have to be accepted as inherent to the plant experiment. The fact that the green plant material ("shoots") is inhomogeneous regarding the Pd- content will be of major interest in the ETV-ICP-OES method, where sample homogeneity plays a major role (see chapter 3).

Nevertheless, a good linear correlation between contamination and uptake can be established when the mean concentration of Palladium in the leaves, the stem and the roots for each contamination level is calculated and plotted against the contamination level (see figure 30).

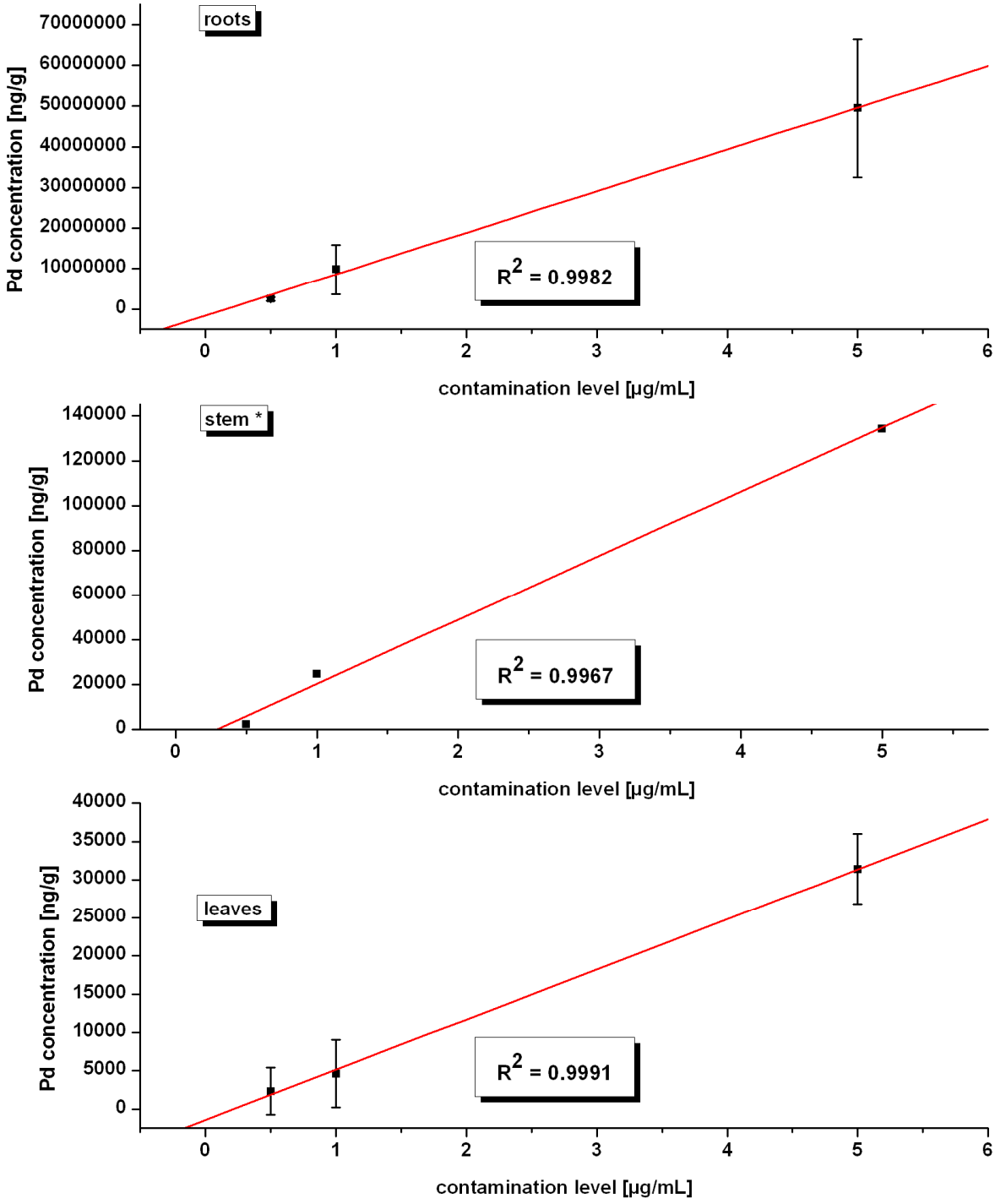


Figure 30 Influence of the contamination on the uptake (mean values; error bars: standard deviation in-between analyzed sub-samples; * stem: no standard deviation could be calculated; only 1 sample per stem was prepared)

Table 13. Results of the determination of Pd in digested plant material using the DPE method

	sample	m_{sample} [g]	V_{digest} [mL]	LOD [ng/mL]	LOQ [ng/mL]	c_{digest} [ng/mL]	RSD [%]	dilution factor [/]	c_{plant} [ng/g]
MES buffer, level 0.5	stem	0.05562	13.62	0.19	0.64	9.28	6.63	1.00	2271.6
	leaf 1	0.01613	12.90	0.19	0.64	2.14	0.73	1.00	1707.5
	leaf 2	0.00604	13.04	0.19	0.64	< LOD	n.n.	n.n.	n.n.
	leaf 3	0.04890	13.12	0.19	0.64	1.71	4.97	1.00	459.0
	leaf 4	0.05538	12.96	0.19	0.64	1.09	7.15	1.00	255.7
	leaf 5	0.00908	13.00	0.19	0.64	1.08	3.56	1.00	1545.2
	leaf 6	0.00634	12.94	0.19	0.64	3.76	6.40	1.00	7684.7
	roots near the stem	0.00681	10.11	4.14	13.79	219.18	2.43	0.12	2791630.7
	roots- middle part	0.00880	11.75	4.14	13.79	243.87	0.38	0.12	2756774.1
	roots far from stem	0.01107	9.79	4.14	13.79	260.19	0.19	0.12	1906615.3
MES buffer, level 1	stem	0.00473	13.23	0.07	0.23	8.81	2.21	1.00	24662.6
	leaf 1	0.00658	13.11	0.07	0.23	1.95	4.54	1.00	3883.4
	leaf 2	0.00481	13.10	0.07	0.23	4.07	2.86	1.00	11070.0
	leaf 3	0.00632	13.07	0.07	0.23	0.65	14.80	1.00	1345.8
	leaf 4	0.00360	13.24	0.07	0.23	0.60	18.97	1.00	2207.7
	coarse roots	0.00202	12.16	4.14	13.79	86.58	3.23	0.10	5419050.9
	fine roots	0.00574	12.68	4.14	13.79	59.09	4.66	0.01	14106084.1
MES buffer, level 5	stem- lower part	0.00084	13.30	0.19	0.64	13.34	0.99	1.00	211228.2
	stem- upper part	0.00211	13.14	0.19	0.64	9.25	2.34	1.00	57591.5
	leaf 1	0.00290	13.07	0.19	0.64	6.36	1.71	1.00	28631.0
	leaf 2	0.00400	12.96	0.19	0.64	8.85	1.23	1.00	28644.6
	leaf 3	0.00320	13.14	0.19	0.64	7.33	0.80	1.00	30101.9
	leaf 4	0.00125	13.06	0.19	0.64	< LOD	n.n.	n.n.	n.n.
	leaf 5	0.00307	13.06	0.19	0.64	8.99	2.77	1.00	38258.4
	roots near the stem	0.00022	10.49	4.14	13.79	82.05	3.75	0.12	33741648.8
	roots- middle part	0.00020	10.29	4.14	13.79	104.59	2.10	0.11	47270387.9
	roots far from stem	0.00018	9.95	4.14	13.79	144.49	2.90	0.12	67468443.5

3. ETV-ICP-OES METHOD FOR THE DETERMINATION OF PGES IN PLANTS

Although the ET-AAS method presented in chapter 2 allows the accurate determination of palladium in plant material, there are two facts that limit this approach: firstly, the samples have to be digested. Secondly, AAS offers only single-element information. In order to assess all three PGEs, one sample would have to be analyzed three times which of course increases the time of the analysis. In ETV ICP-OES there is no need to digest the samples since the finely ground plant material can be directly introduced in the graphite boat (Detcheva 2009); after pyrolytic matrix removal the analytes are abruptly evaporated and transported to the ICP-OES instrument which offers simultaneous multi-element analysis. Owing to the small sample intake, the homogeneity of the sample material is very important as will be discussed in chapter 3.1.3.

3.1. EXPERIMENTAL

Instrumentation and reagents will be described in chapters 3.1.1. and 3.1.2. Details on the sample preparation can be found in chapter 3.1.3. The sample introduction via the ETV- unit and the actual measurements in the ICP-OES depend on various parameters which were optimized regarding signal intensity and RSD; these experiments will be described in chapter 3.1.4.

3.1.1. INSTRUMENTATION

An iCAP 6500 RAD ICP-OES spectrometer (Thermo Scientific) in combination with iTEVA software was used for all measurements. The instrument possesses an echelle optic (grating: 77lines/cm, 64° blaze angle) and records the emission spectrum on a SpectraCam CID86 detector (540x540 pixels). For each of the three PGEs two emission lines were selected according to their intensity and to potential spectral interferences (see table 14).

Table 14. Emission lines for all three PGEs

	Palladium	Platinum	Rhodium
wavelength	229,6 nm	214,4 nm	233,4 nm
	340,4 nm	265,9 nm	343,4 nm

Although some lines are in the UV range, all lines may still be analyzed with one spectrometer setting (high wavelengths) because no hard UV light is being analyzed. This

allows for high time resolution since the optical settings do not need to be changed during measurements. To avoid unwanted absorption of UV radiation by oxygen and carbon dioxide, the optical system has to be purged with argon to remove these gases.

Plasma conditions, radial observation height and gas flow rates were optimized in order to achieve maximum signal for a given analyte concentration. Not only ETV measurements were carried out but conventional liquid sample introduction was done as well. The plasma settings for both sample introduction modes are summarized in table 15.

Table 15. Operating parameters of the ICP-OES system

	ETV- ICP-OES	**Conventional ICP-OES**
Plasma power [W]	1300	1400
Radial observation height [mm]	12	11
Plasma gas flow rate [L/min]	12	12
Nebulizer gas flow rate [L/min]	-	0.7
Auxiliary gas flow rate [L/min]	0.6	0.6

In the case of the ETV- method both plasma power and radial observation height differ from the conventional method because dry gas is being introduced into the plasma; less power is consumed for solvent evaporation and therefore the thermal emission process is more efficient (Kántor 2001). The observation height is changed to a higher value since the plasma becomes hotter which implicates that the plasma power can be reduced.

Sample introduction of solid samples was done via an ETV 4000 instrument (Spectral Systems) with an argon flow rate of 0.5L/min. Freon modifier (Freon 12, CCl_2F_2) was added to the carrier gas with a flow rate of 10mL/min in order to guarantee a swift and quantitative evaporation process.

Sample introduction of liquid samples was performed with an APEX E nebulizer (Elemental Scientific) to enhance the sample aerosol yield by evaporating the majority of the solvent; the sample flow rate was set to 0.8mL/min. Higher sample flow rates would not be compatible with the solvent evaporation unit in the APEX E instrument (the heating and cooling power is limited).

Microwave assisted sample digestion was done in a Multiwave 3000 (Anton Paar) instrument according to the procedure already given in chapter 2.2.3. The plant material was pulverized by means of a MM400 mixer mill (Retsch).

A Sartorius MC-210 P balance was used to weigh the samples into the graphite boats and the ashing process- which reduces the sample's carbon content to an acceptable amount- was done in a Nabertherm – LE 4/11/RG muffle furnace.

3.1.2. REAGENTS AND SAMPLES

All chemicals and reagents were of p.a. grade or higher (see table 16), the water was purified with an Easipure system (Thermo Scientific, 18MΩcm^{-1}) as already described in chapter 2.2.2.

Table 16. List of used Chemicals

	purity	**supplier**
Nitric acid, 65%	p.a.	Merck, Germany
Hydrochloric acid, 37%	p.a.	Merck, Germany
Hydrofluoric acid, 48%	p.a.	AppliChem, Germany
Hydrogen peroxide, 30%	Suprapur	Merck, Germany

Standard solutions of PGEs were purchased from FLUKA, Germany (see table 17).

Table 17. List of standard solutions

	Standard	**concentration [mg/L]**
Pd	FLUKA 77091	1001 ±2
Rh	FLUKA 04736	999 ±3
Pt	FLUKA 19078	1000 ±2

The plant material used in this investigation was obtained from green-house experiments; *Brassica Napus Californium* plants were grown in hydroponic setup. Four contamination levels were chosen (blank, 0.5, 1 and 5µg/mL) and PGEs were added to the nutrient solution in the form of chlorides. The nutrient solution was kept at constant pH = 7 by means of MES buffer. The plants were grown for four weeks in non-contaminated nutrient solution; afterwards they were constantly contaminated during four weeks and harvested after this

time. After washing and drying the plants, they were coarsely ground (see chapter 2.3.2. for further details of the plant experiment).

3.1.3. SAMPLE PREPARATION

Samples were prepared for the conventional analysis using liquid sample introduction and for the ETV analysis.

For the CONVENTIONAL ANALYSIS using liquid sample introduction, sample aliquots of 100mg were digested by applying the same microwave- assisted digestion process as described in chapter 2.2.3. with a slightly modified digesting agent (see table 18).

Table 18. Digesting agents for Multiwave 3000

	Sample digestion	**Clean Out**
Nitric acid, 65% [mL]	2	2
Hydrochloric acid, 37% [mL]	3	3
Hydrofluoric acid, 48% [mL]	0.1	/
Hydrogen peroxide, 30% [mL]	1	1

The changes in digesting agent (increased content of hydrochloric acid) aim at the quantitative decomposition of the organic material. The homogeneity of the sample aliquots was shown to be within the range of the instrumental RSD which means the sample intake of 100mg was sufficient. After digestion, the solution was diluted to a volume of 30mL and consecutively analyzed. Calibration was carried out by means of aqueous standards; these standards were prepared using 2% HNO_3 and 5% HCl solution which yields about the same acidity and density as the digested samples. This matrix modification ensures equal tribological behaviour of samples and standards in the nebulizer. All liquid samples and standard solutions were introduced into the plasma by means of an APEX E nebulizer which removes the majority of the solvent by heating the aerosol and cooling it down again. The solvent re- condenses in the cooler; the dried sample- aerosol is not affected by this condensing process and is transferred to the ICP-OES. Interferences due to aerosol size and plasma disturbances due to solvent evaporation are thus minimized.

For the ETV ICP-OES ANALYSIS, very fine sample powder is required. Therefore the coarsely ground plant material was further pulverized by means of a mixer mill; 200mg

sample were put into small polypropylene tubes and four ceramic beads (0.2mm diameter, material: alumina) were added. The milling process was performed by shaking the tubes at a frequency of $30sec^{-1}$ for 10 minutes (5x 2 minutes to avoid sample heating due to friction).

The dried and finely ground plant material was weighed into the graphite boats and consecutively ashed in the muffle furnace under oxygen atmosphere (Detcheva 2009). A maximum temperature of 340°C was applied (heating ramp: 1.5 hours, hold- time 2 hours) with an oxygen flow rate of 2L/min. This process aims at the complete conversion of all organic carbon into inorganic carbon. The graphite boats are not burnt because inorganic carbon is stable well beyond 400°C in oxygen atmosphere.

The ashing procedure does lead to increased preparation time per sample but experiments showed that the introduction of non- ashed material into the ETV unit causes severe disturbances: firstly, large amounts of gas are produced by the formation of carbon dioxide and due to the evaporation of residual humidity. The plasma is destabilized or even destroyed because of the abrupt introduction of these gases. Secondly, volatile organic compounds lead to the formation of elemental carbon in the transport line and in the ETV unit which causes severe changes in transport efficiency over time.

Because only very small amounts of the samples are weighed into the boats, the homogeneity of the material is paramount to ensure good reproducibility. As the results in chapter 2 showed, the Palladium content significantly differs between stems and leaves; a variation of the other two PGEs also seems very likely. The grinding process with the mixer mill yields sufficiently fine material; without this second grinding process, RSD values of more than 30% were obtained in-between analyses, after grinding the samples these RSD values decreased to an average of 2%.

The weighing of the plant material is crucial since amounts of 5mg are difficult to handle; to ensure constant weighing conditions the material was put in the boats, transferred onto the balance and the displayed value was taken down 20 seconds after the balance reached equilibrium. By doing so, always the same time was used for the weighing process which should account for a reproducible weighing error.The complete preparation of the samples for ETV ICP-OES analysis is summarized in figure 31.

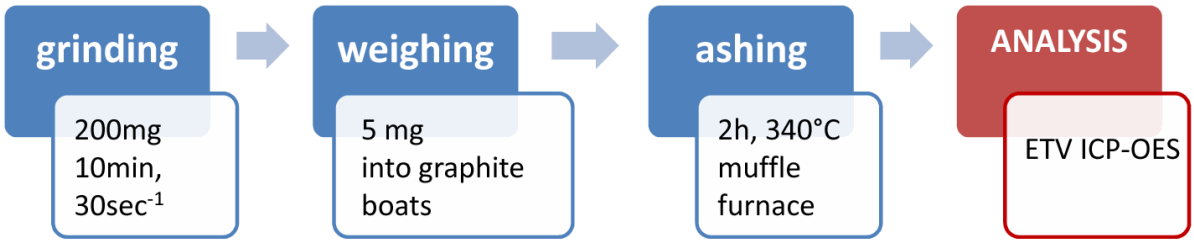


Figure 31 Schematic structure of the sample preparation in ETV ICP-OES

3.1.4. OPTIMIZATION OF THE ETV PARAMETERS

In this chapter, the optimization of four parameters that greatly influence the ETV ICP-OES system will be discussed: the software offers two different ways of data acquisition and a decision has to be made which of the two modes gives better results; a temperature program has to be established and optimized. Furthermore, the use of the Freon modifier has to be evaluated and the sample intake has to be optimized- large sample intakes are advantageous because they produce a good methodological LOD, but at the same time the RSD of the measurements increases because the abrupt evaporation of the analytes is hindered.

Two MEASURING MODES are possible with the iCAP 6000 instrument: either the light intensity is accumulated on the detector during a chosen period of time (conventional mode) or the detector signal is read in very short intervals and the change of the signal over time is observed (time scan mode). Both methods have their advantages and their disadvantages:

In the conventional mode, a large number of pixels can be processed, making it possible to gain information about how the emission spectrum looks like in the vicinity of the observed lines. The signal is accumulated on the detector during a measuring time of 10 seconds which produces a good signal to noise ratio. The high number of pixels allows the immediate detection of baseline shifts due to interfering elements. The precise position of the background pixels (see figure 32 “L” and “R”) can be set in this mode as well. Unfortunately, the period of time in which the signal is recorded can only be set before the actual measurement is performed; if- by one reason or another- the temperature program of the ETV unit is not sufficiently synchronous with the ICAP software, information is inevitably lost.

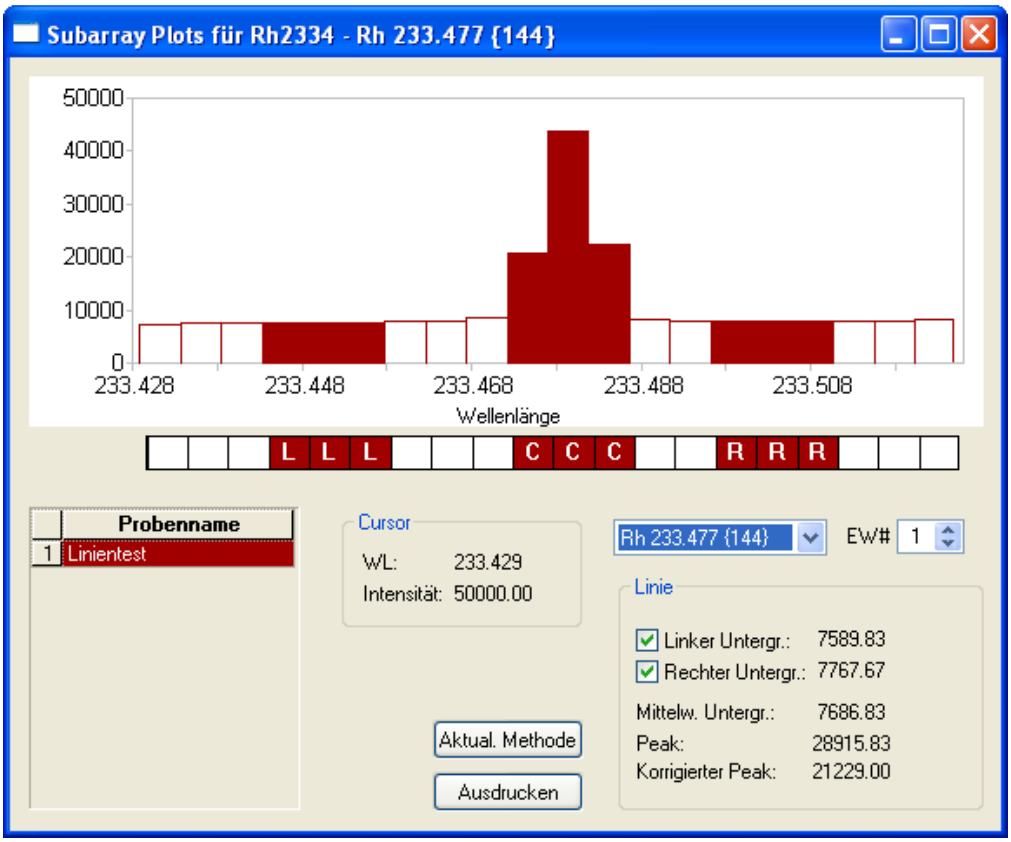


Figure 32 Result- window in conventional mode; left (L) and right (R) background pixels, centre (C) pixel

Due to the high rate of data acquisition in time- scan mode, the number of pixels that may be processed by the software is limited; only a few pixels per emission line are recorded, namely the left and the right background as well as the centre-peak. These pixels are needed for background correction; the rest of the spectrum (white pixels in figure 32) is not measured, therefore no full spectrum can be recorded in time-scan mode. The pixels used for signal detection have to be selected prior to the measurement which makes it impossible to correct instrumental drifts and varying background after the measurement has been recorded.

In the time-scan mode, the entire transient signal is recorded and the actual signal used for quantification is generated after the analysis by integration; integration boundaries may be freely selected. The signal is recorded as accumulated intensity over time (see figure 33 (a)). After integration, peak shapes are obtained (b), the area beneath these peaks is proportional to the analyte concentration.

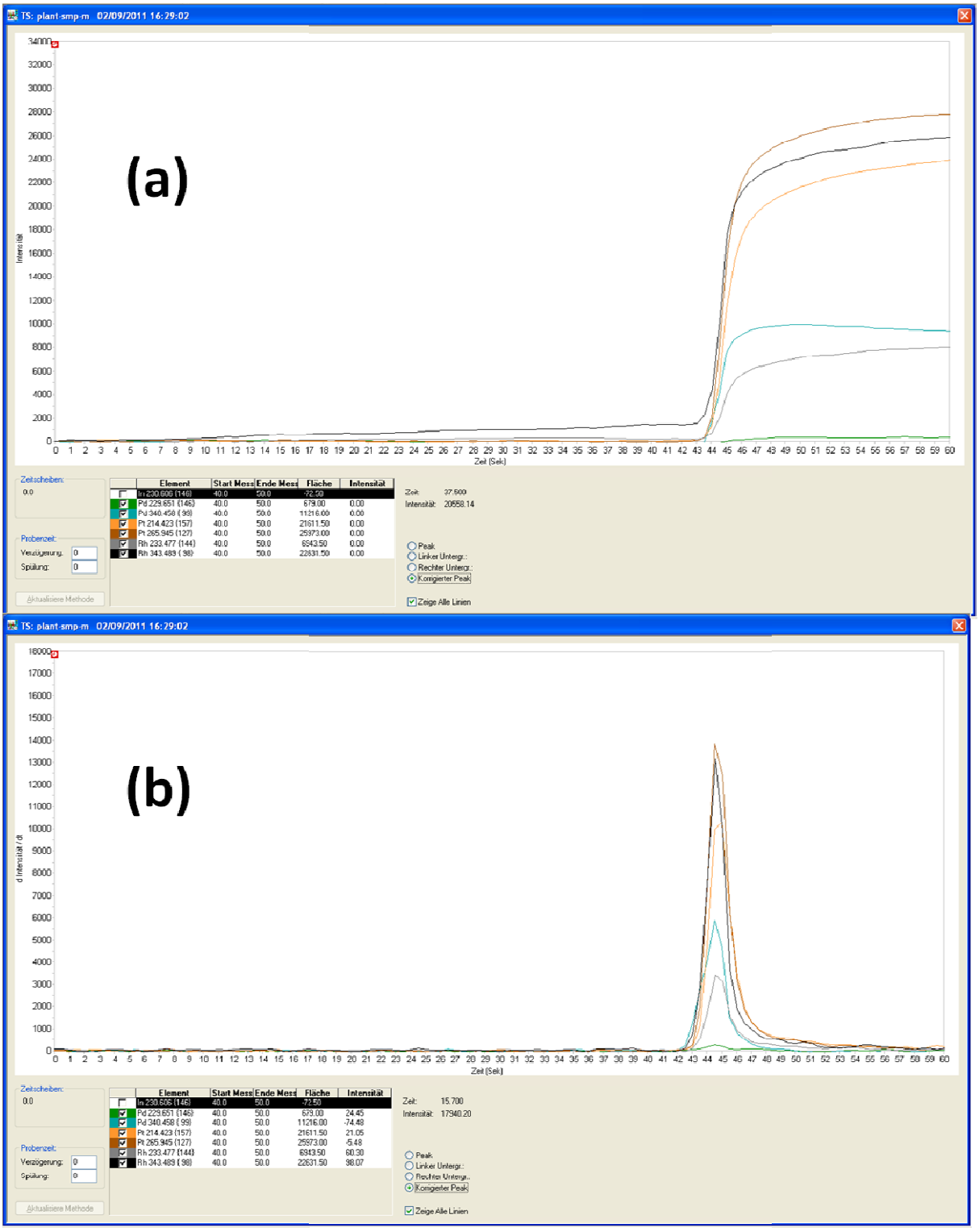


Figure 33 Result- window in time scan mode: differentiated signal (a) and integrated signal (b)

To compromise, the conventional mode was used to record a “line test” which allows detecting small shifts in the settings of the monochromator and spectral interferences: an aqueous standard mixture of all elements that are about to be measured was employed for the “line test”. Pixels for background correction and for the centre peak can thus be selected

and repositioned if necessary. The actual sample analysis was carried out in time- scan mode using only these previously selected pixels.

A high density of DATA POINTS ("time slices") should allow the correct description of the transient signal (see figure 34). On the one hand a high number of data points offers an improved time resolution; on the other hand, increased observation time per data point yields better sensitivity because the signal to noise ratio of the detector is ameliorated at longer observation times.

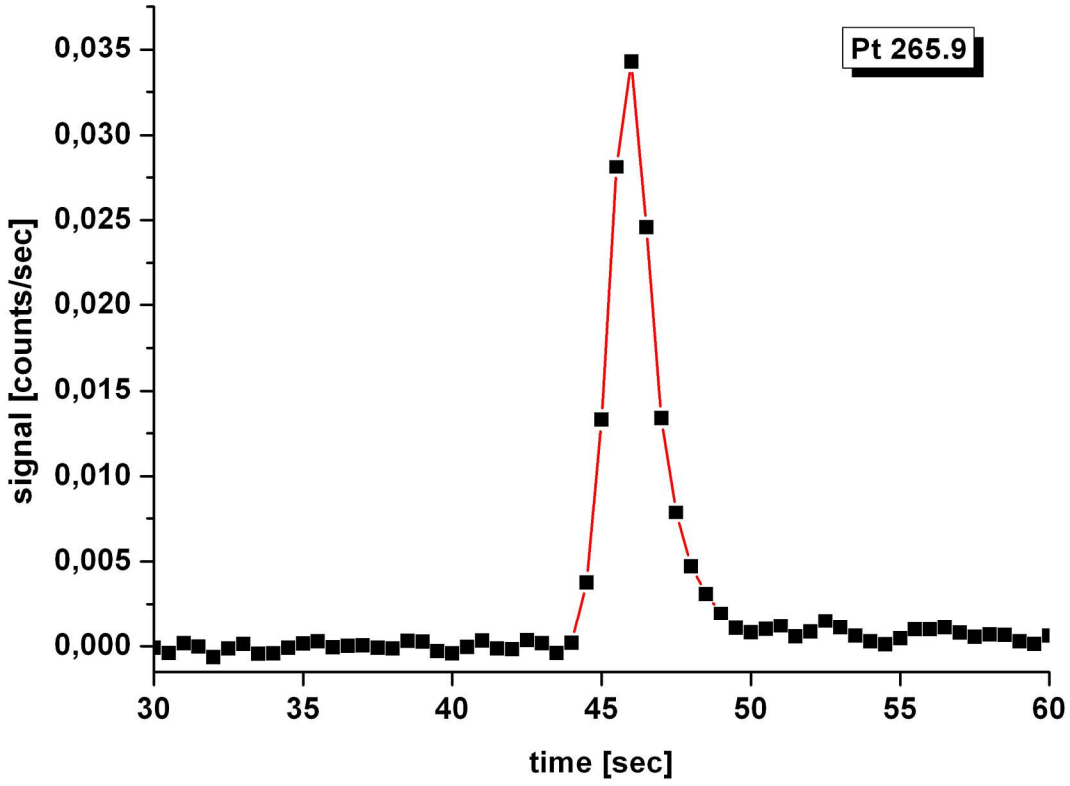


Figure 34 Data points (time- slices: 0.3 sec)

The main advantage of long time slices is the accumulation of radiation on the detector over a longer period of time which means that the signal to noise ratio of the detector will be better. If the time slices are too long, the peak-shape of the transient signal will not be resolved completely. A compromise has to be made in order achieve maximum sensitivity and at the same time obtain good peak shapes. Transient signals using three different lengths of the time slices were recorded (see figure 35).

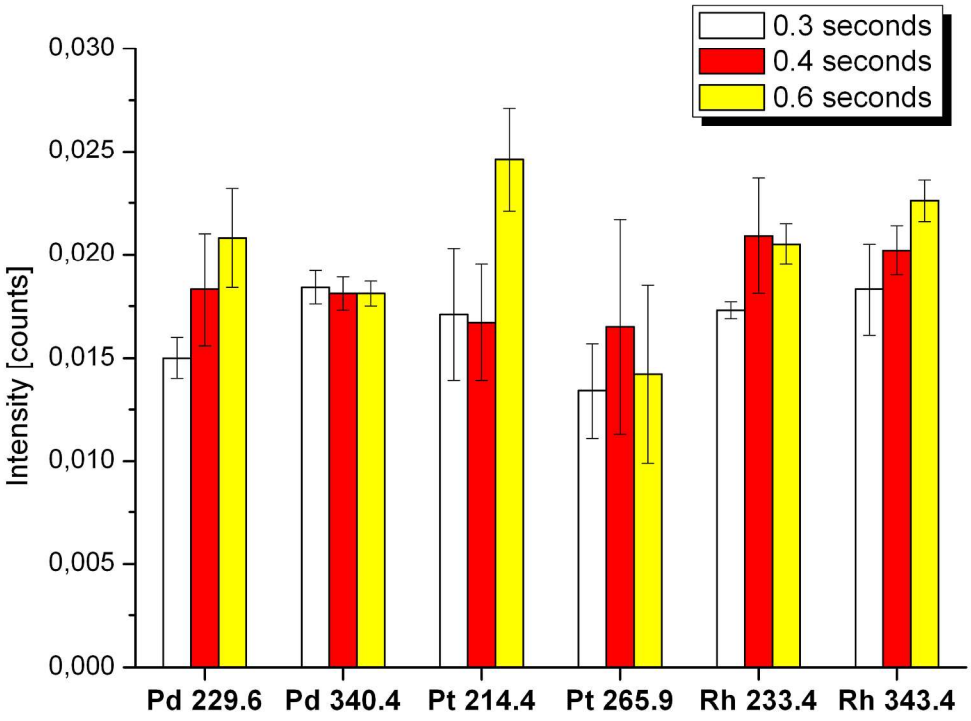


Figure 35 integrated signal for 20ng of PGEs, integration boundaries: 40 to 60 seconds, time-slices of 0.3, 0.4 and 0.6 seconds

The influence of the better signal to noise ratio at longer time slices becomes obvious when the RSD values are compared: the longer the time slice, the better the RSD. Most interestingly, the net signal increases with longer time slices in the case of most of the recorded emission lines; this may be due to a constant reading time in-between the time slices during which no data is recorded. Time slices of 0.5 seconds proved to be optimal in terms of signal intensity, RSD and density of data points.

By choosing an appropriate TEMPERATURE PROGRAM, unwanted sample constituents (organic and inorganic compounds) can be removed prior to analysis; they no longer interfere with the actual measurement because the analyte itself is being evaporated later on. Regarding the thermal stability of the analytes, two factors have to be considered: on the one hand, no analyte losses should occur prior to the analysis, hence the pyrolysis-temperature should allow matrix removal but no premeditate analyte vaporisation. On the other hand, the evaporation- temperature should be chosen in such a way that the analyte is evaporated instantly and quantitatively to account for maximum signal and to avoid any carryover between analyses. The general schema of a temperature program is shown in

figure 36 indicating these two temperatures and showing the resulting analyte signals. Owing to the time-scan mode, it is possible to detect premeditate analyte losses during matrix pyrolysis.

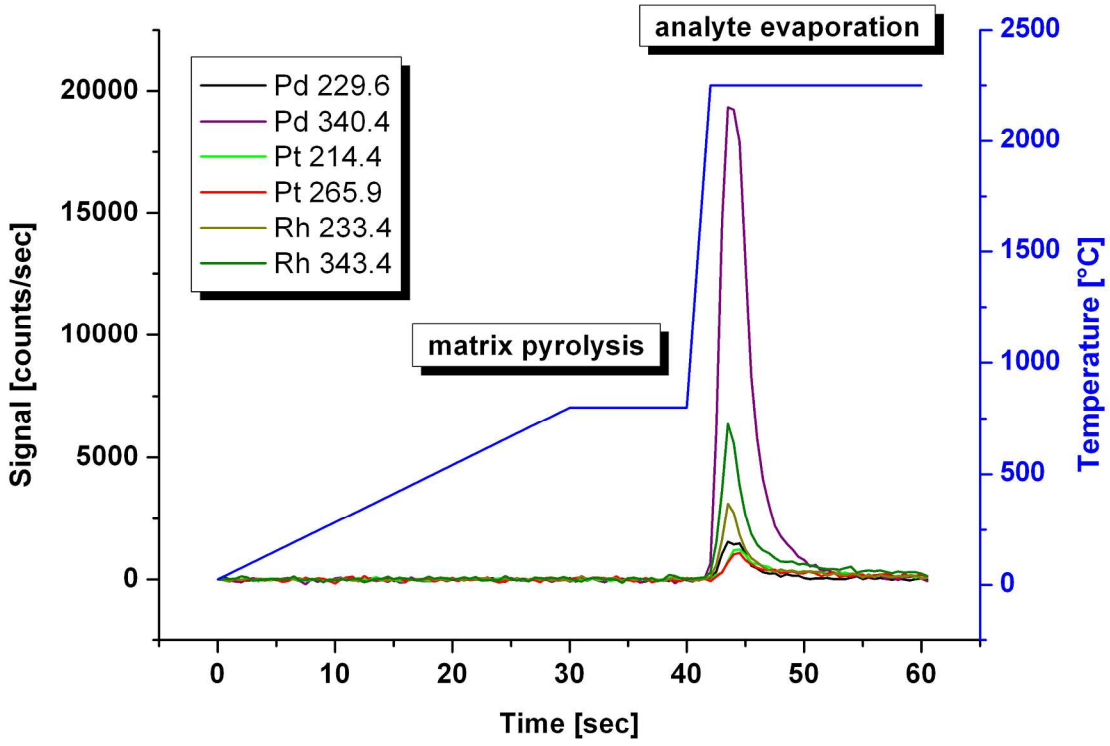


Figure 36 Typical temperature program (800°C pyrolysis- temperature, 2250°C vaporization temperature)

In order to find the optimum pyrolysis- temperature, measurements were performed with temperatures varying between 400 and 1200°C (see figure 37). From these graphs it can be seen that even at 1200°C pyrolysis temperature no premeditate analyte losses occur.

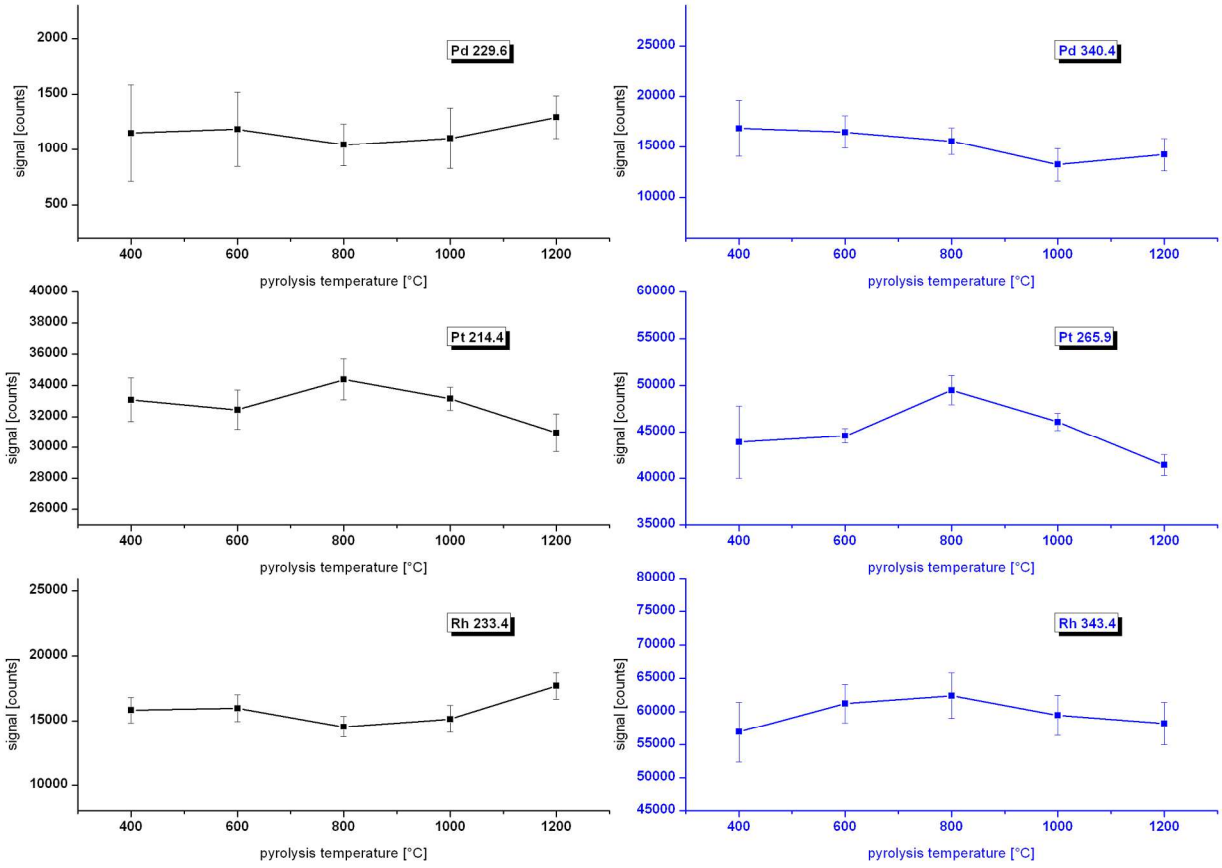


Figure 37 Influence of the pyrolysis- temperature on the obtained signal (integration boundaries 40 to 60 sec, time- slices: 0.5 sec)

Within the boundaries of the RSD, the peak area stays constant at all temperatures in the observed range. Only for Pt a slight decrease at the highest pyrolysis- temperature is observed. Generally, high temperatures are optimal to guarantee quantitative matrix removal; yet they have negative effects on the longevity of the graphite tube. 800°C were chosen as optimum pyrolisis- temperature since at this temperature, the instrumental RSD is minimal and the signal intensity is maximal.

The vaporisation temperature was set to 2250°C: although higher temperatures yield slightly better results concerning the instrumental RSD, the longevity of the tubes is significantly reduced at elevated temperatures. The gain of some tenth of percents in RSD does not outbalance the loss in tube life. The completeness of the evaporation was verified by analyzing the same graphite boat twice; upon the second analysis, blank values were reached. This indicates that no measurable amounts of PGEs remain after the vaporisation step.

The use of a MODIFIER is recommended (Amberger 2010, Kántor 2001) because it facilitates quantitative evaporation. As opposed to solid modifiers (e.g. Teflon powder), gaseous modifiers can be easily dosed. Freon, a fluorinated hydrocarbon (CCl_2F_2), was therefore employed as gaseous modifier; due to the high temperatures in the graphite tube, the molecule dissociates and sets free highly reactive products which readily form volatile compounds with the analytes. The necessity for the use of Freon becomes obvious when calibration curves are recorded with and without the modifier (see figure 38).

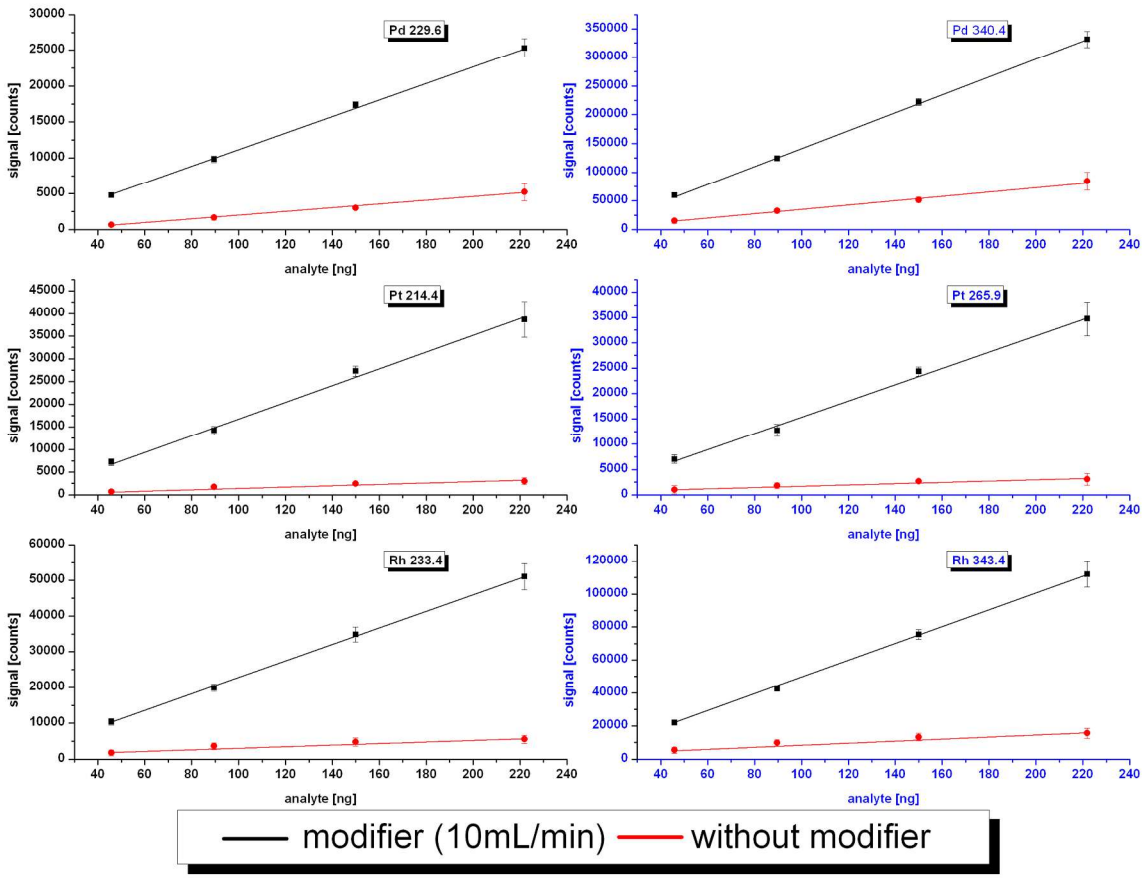


Figure 38 Influence of the Freon modifier on the slope of the obtained calibration curves (aqueous standard solutions)

Throughout the calibrations, an approximately tenfold signal suppression is observed in the absence of the modifier; at the same time the instrumental RSD increases to values well above 20%. Since the sensitivity of a calibration is connected to the slope of the calibration curve, steep curves are required for optimal sensitivity (see chapter 1.3.5.). Without the modifier, the curves are significantly flatter than in its presence, hence the use of the

modifier appears to be vital for the sensitive detection of PGEs. Freon was added to the carrier gas during all measurements (modifier flow rate 10mL/min).

The SAMPLE INTAKE cannot be held constant since it is literally impossible to transfer exactly the desired amount of sample into the boats. Small variations in the range of 0.2mg were tolerated; correction for the different weights was carried out by multiplying the obtained analyte concentration by a factor according to equation 9.

$$c_{corrected}[ng/g] = c_{uncorrected}[ng/g] \cdot \frac{5.00[mg]}{m_{sample}[mg]}$$ Equation 9

This approach assumes a linear relation between signal and sample intake; up to sample weights of 15mg sufficient linearity was observed for all emission lines (see figure 39), therefore the correction according to equation 9 is feasible.

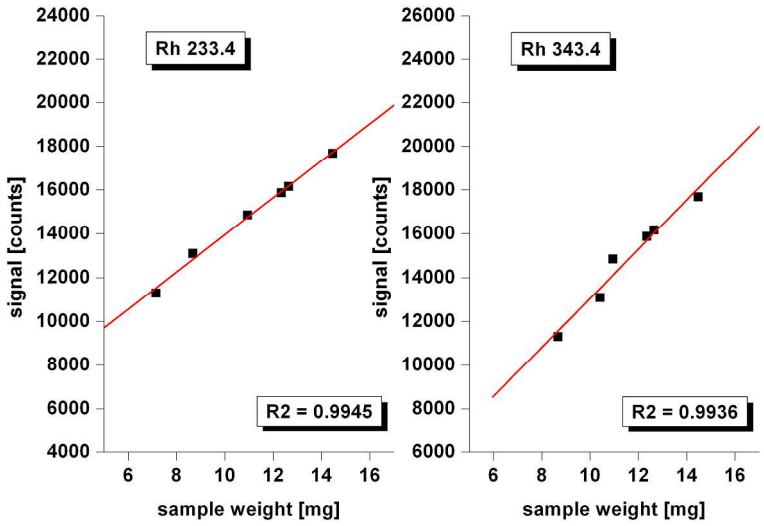


Figure 39 Linearity of sample intake

The observed linear relation between signal and sample intake could be used to increase the methodological LOD: if the sample intake is higher, the total amount of analyte in the graphite boat is higher as well. Yet, experiments showed that the ideal sample intake is indeed around 5mg: if the sample weight is increased over 12mg, the evaporation process cannot take place as rapidly as desired; the peak of the transient signal becomes broader and hence the instrumental RSD increases significantly.

To summarize, the ETV sample introduction was performed under the conditions given in table 19.

Table 19. Summary of all optimized parameters		
Measuring mode	Conventional (line- test) Time- scan (sample analysis)	
Length of time- slices	[sec]	0.5
Pyrolysis- temperature	[°C]	800
Evaporation temperature	[°C]	2250
Freon modifier	[mL/min]	10
Sample intake	[mg]	5

3.2. RESULTS

Since no certified reference material is available for the determination of PGEs in plant material in the desired concentration range, the developed ETV- method is validated by comparing the results with the results of well- established conventional ICP-OES measurements using digested plant material and liquid sample introduction.

3.2.1. QUANTIFICATION & FIGURES OF MERIT

Quantification of the ETV ICP-OES method was carried out by analyzing aqueous standards of known concentration and performing a linear calibration. The standard solutions were prepared in 1% (v/v) hydrochloric acid to guarantee the stability of the solution. After pipetting a small volume of the standard solution (30µL) into the graphite boat, the solvent was slowly evaporated by means of an IR lamp. To avoid contamination, the boats were transferred into a petri dish; the upper part of the glass made sure that no contaminants could enter from above (e.g. dust). Only a small gap was left open in order to let the solvent evaporate. This process took about 15 to 20 minutes; if the samples are located close to the IR lamp, the evaporation process is faster but concerns remain that analyte might be lost due to vapour formation inside the solution. A slightly higher RSD was obtained at faster evaporation rates, although the difference is merely statistically significant. Nevertheless, the evaporation process was performed slowly to avoid losses.

The plant samples were prepared as described before and measured. Introduction of the graphite boats into the ETV unit was done via a pair of tweezers (stainless steel); blank

measurements did not indicate any additional contamination arising from the metal tweezers.

Both the instrumental and the methodological LOD[13] were determined from the standard deviation of blank measurements (see table 20). Due to the digestion process, the dry sample mass is dissolved in a large volume of solvent, hence the instrumental LOD (which considers the concentration in the digest) is about three times higher than the methodological LOD (which considers only the dry mass).

Table 20. LOD of the conventional measurements (digestion, liquid sample introduction)

		Pd 229.6	Pd 340.4	Pt 214.4	Pt 265.9	Rh 233.4	Rh 343.4
$LOD_{instrumental}$	**[ng/mL]**	1.1	2.9	1.7	1.0	3.7	2.1
$LOD_{methodological}$	**[ng/mg]**	0.3	0.9	0.5	0.3	1.1	0.6
RSD (40ng/mL, n = 5)	**[%]**	3.4	1.0	3.4	2.8	1.6	0.6

Upon comparison of the results obtained from the conventional measurements with those of the ETV- measurements (see table 21) a general decrease of the LOD is observed. This effect is due to the fact that sample digestion can be avoided in the ETV method and therefore the net amount of analyte that is introduced in the ICP-OES instrument per measurement is higher. Furthermore, the atomisation efficiency is higher in the case of dry aerosol introduction which means that the signal obtained with ETV sample introduction will be higher.

Table 21. LOD of the ETV measurements

		Pd 229.6	Pd 340.4	Pt 214.4	Pt 265.9	Rh 233.4	Rh 343.4
$LOD_{instrumental}$	**[ng]**	0.297	0.067	0.227	1.193	0.639	0.163
$LOD_{methodological}$	**[ng/mg]**	0.059	0.013	0.045	0.239	0.128	0.033
RSD (40ng, n = 3)	**[%]**	1.7	1.6	0.6	6.0	3.9	1.0

[13] The LOQ was not entered in the tables for the sake of clarity since it can be easily calculated by multiplying the LOD by a factor of 10/3

The RSD of repeat analyses ranges around 1 to 5% for both methods and is therefore mainly influenced by the actual ICP-OES measurements and not so much by the way of sample introduction.

In conclusion it can be stated that the ETV sample introduction system allows for distinctly lower methodological LOD: in the case of the plant material a factor x10 to x20 was gained. This increase in detection power is partly due to enhanced plasma conditions but mainly it is caused by the increased net sample intake for one analysis. Nevertheless, the total sample consumption is reduced by a factor x5 to x10 in the case of ETV sample introduction (a four-fold replicate requires only 20mg of sample, one conventional digest requires 400 to 800mg sample). The repeatability of both methods is excellent, RSD values are obtained in the lower percent range.

3.2.2. METHOD COMPARISON

The results of the ETV- measurements are promising regarding LOD and repeatability; in order to determine the reliability of this new method, the results have to be compared with a method that is well- established.

Conventional measurements were performed using the previously digested plant material. To achieve the desired method comparison, one sample was repeatedly digested and measured in the conventional mode by varying operators[14] and on different days. The resulting PGE concentration is given in table 22, first column (see page 64). No significant variation in-between operators or measuring day (calibration) were observed, thus these results can be accepted as reliable.

In a first experiment, the plants were analyzed with the ETV method and quantification was performed with AQUEOUS STANDARD solutions. Unfortunately, all sample concentrations resulting from this experiment are significantly higher than the values achieved with the reference method (see table 22, second column). This can be due to various matrix influences since the calibration was performed with aqueous standards and the samples contain high concentrations of crustal elements.

[14] The author would like to specially acknowledge the help of Mag. Esther Herincs and Armin Eitzenberger, BSc for performing these measurements

To compensate for these effects, a MATRIX MATCHED calibration was performed: the matrix of the standards is changed in a way that guarantees similar analyte behaviour in the samples and in the calibration standards. This task was accomplished by weighing blank plant material into the graphite boats and preparing them the same way as the samples. After the ashing process, aqueous standards were added to the blanks and dried under the IR lamp. By doing so, the ashed plant matrix is present in the samples as well as in the calibration standards. Quantification was performed by means of a linear calibration. The slope of the calibration curve is steeper for the majority of the emission lines; nevertheless, the results obtained with the matrix matched method are still higher than the reference values although some amelioration can be observed (see table 22, third column)

Up to now the matrix matched calibration ensures similar matrix but the treatment of samples and standards is still slightly different: PGEs that are inherent to the samples experience the ashing process in the muffle furnace; PGEs that are added for calibration purposes do not undergo this treatment. If the metals are in some way transformed during the ashing process in the muffle furnace, different behaviour in the ICP plasma may be the result; differences in the calculated concentration of the PGEs in the samples will be observed (Grünke 1997). By adding the calibration standards prior to the ashing process and comparing the obtained results, this theory was shown to be inaccurate: no difference was observed and the results were still significantly higher than the results of the reference method.

The high concentrations obtained with the ETV measurements should not lead to the conclusion that PGEs are mysteriously formed during measurements. Since it was shown during method optimization (chapter 3.1.4.) that the evaporation of the PGEs is quantitative, the only reason for higher signals can be due to a better transport efficiency between the ETV unit and the plasma and/or an enhanced emission process in the plasma when sample matrix is present.

To further explore the nature of the matrix effect a calibration was done that avoids any use of aqueous standards: since the concentration of the sample is well-known due to the repeat analysis via the conventional method, the sample can be used as "IN-LAB" REFERENCE MATERIAL. Prior experiments have shown that the sample intake can be varied between 1 and 15mg with optimal results at approximately 5mg. This allows a calibration

process by varying the sample intake of the “in-lab” reference material between 3 and 7mg. As the PGE concentration of the reference material has been meticulously determined, the sample intake can easily be converted to the absolute amount of analytes in the boat according to equation 10.

$$m_{analyte}[ng] = m_{sample}[mg] \cdot c_{sample}[ng/mg] \qquad \text{Equation 10}$$

Most interestingly, the obtained calibration curve differs from the calibration curve obtained with matrix matched calibration at all observed emission lines (see figure 40). This means, the matrix effect cannot be fully compensated by performing the matrix matched calibration.

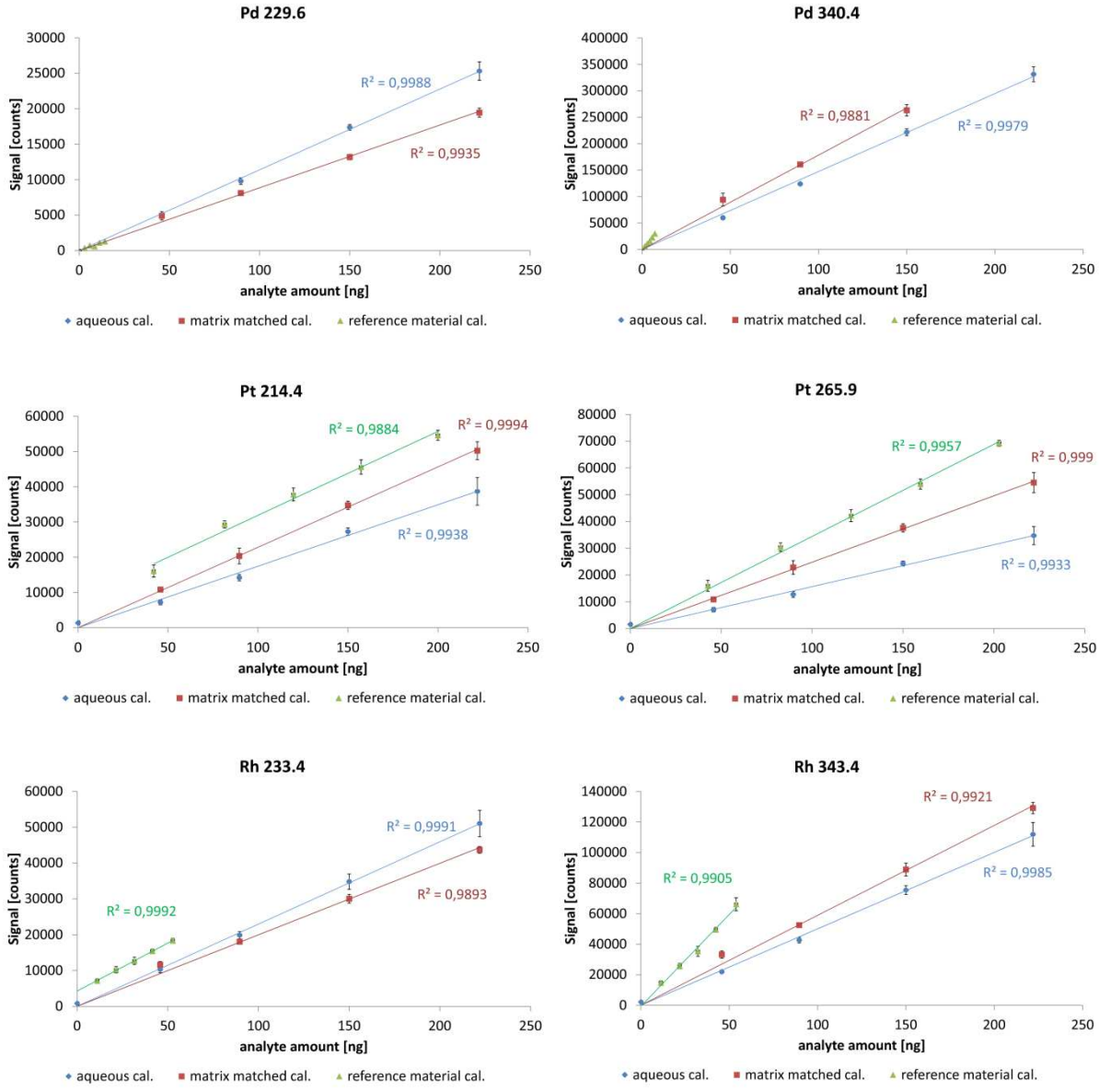


Figure 40 Influence of the calibration mode on the obtained slopes

If the samples are quantified with the calibration curve obtained with the “in-lab” reference material, the results are in excellent accordance to the reference determinations using the conventional liquid sample introduction (see table 22, fourth column).

Table 22. Comparison of quantification methods

Wavelength	conventional mode			aqueous calibration			matrix matched calibration			reference material calibration		
[nm]	[ng/mg]			[ng/mg]			[ng/mg]			ref		
Pt 214.4	27.64	±	1.08	47.15	±	2.34	35.94	±	1.78	27.76	±	1.04
Pt 265.9	27.1	±	1.04	60.17	±	1.57	37.51	±	1.02	26.84	±	0.62
Pd 229.6	1.43	±	0.82	1.88	±	0.71	-0.27	±	1.13	1.56	±	1.08
Pd 340.4	0.65	±	0.18	3.18	±	0.33	-5.99	±	1.42	0.95	±	0.13
Rh 233.4	7.57	±	0.43	12.22	±	0.71	12.8	±	0.82	7.53	±	0.58
Rh 343.4	7.52	±	0.51	16.5	±	1.76	12.92	±	1.74	7.01	±	0.72

In this special case, the determination of palladium is not satisfactory since the Pd concentration of the “in-lab” reference material is very low; therefore the obtained Pd-calibration curves cover only a very small signal range. Regarding the RSD, the results obtained for Pt and Rh show good reproducibility (about 2 to 5% RSD) which means that the proposed ETV ICP-OES method was successfully optimized for the analysis of PGEs in dried plant material.

3.2.3. OUTLOOK

To resolve the problem of steeper calibration curves in the presence of sample matrix, the following approach is suggested: an aqueous calibration is recorded and the slope is corrected by analyzing a sample with a known PGE concentration. By doing so, the calibration process is drastically simplified; instead of using more than 20 graphite boats for the construction of a matrix matched calibration curve, the majority of the boats can be dedicated to ashing sample material. The aqueous calibration can be recorded while the ashing process is being performed which helps in minimizing the net time for one analysis. The time consumption for the sample preparation can be reduced since pipetting of aqueous standards can be done quickly whereas weighing blank material into the boats takes a considerably longer time.

In the near future, the ETV ICP-OES method will be extended in such a way that the spatial distribution of PGEs inside one leaf can be assessed. The leaf is going to be cut into representative aliquots of approximately 5mg (see figure 41), transferred into the graphite boats without any further grinding process, ashed and consecutively analyzed using the method described in this work which yields good LOD and repeatability for the analysis of PGEs in dried plant material.

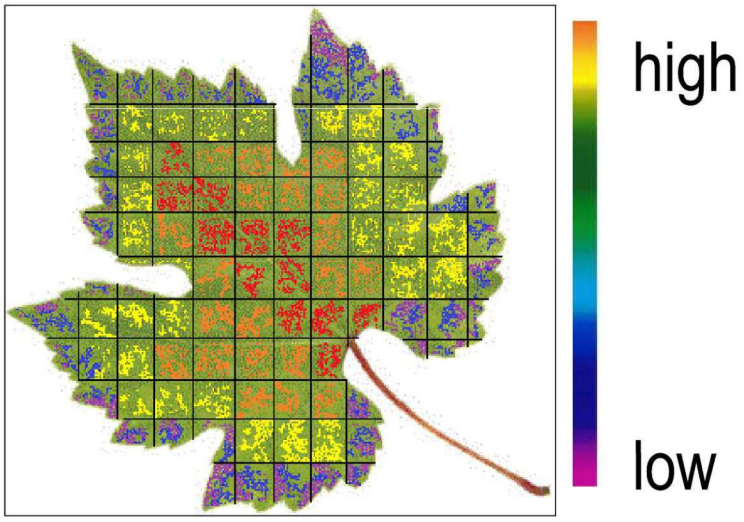


Figure 41 Outlook: assessment of spatial PGE- distribution inside one leaf[15]

To gain better spatial resolution, the leaves could theoretically be cut into even smaller aliquots. It goes without saying that the detection power of the ICP-OES instrument will not suffice to determine such low amounts of PGEs. Since ICP-MS offers LODs that are approximately two to three orders of magnitude lower than those of ICP-OES, coupling the ETV unit to an ICP-MS can be a possible solution to this problem.

[15] Graphic by Armin Eitzenberger, Bsc

SUMMARY

Platinum Group Elements are used throughout the chemical industry because they offer unique properties regarding chemical and mechanical stability as well as catalytic activity. The majority of the yearly primary production of PGEs is being dedicated to the construction of automobile catalysts. The number of passenger cars has continuously been growing in the last decades; to reduce part of the unwanted side- effects of increasing vehicle traffic, exhaust gasses have been treated in Europe for the last thirty years in order to reduce the production of noxious gasses. Classical three-way catalysts use a mixture of PGEs supported by a ceramic carrier material. Due to degradation and mechanical wear during operation of the vehicle's catalyst, the noble metals are continuously co-emitted with the exhaust gases. The total PGE emission per kilometre largely depends upon the type and age of catalyst but also upon the driving conditions like speed and vehicle status as well as on meteorological conditions. As a result of economical considerations and pending patents, the composition of the catalytically active metal layer is subjected to continuous modifications: in the last decade, the amount of palladium was increased since this element is considerably cheaper than the other PGEs. Moreover, palladium offers enhanced catalytic performance: with a sufficiently high Pd content, the temperature needed for the catalyst to become active can be decreased which enables an immediate exhaust gas treatment right after igniting the engine. The increased deposition of PGEs and especially palladium in environmental departments raises concerns about possible adverse effects on human health. Although no precise knowledge about the toxicity of PGEs is available at the moment, it is known that high concentrations of PGEs as they are experienced for example at certain workplaces are the cause of adverse health effects. Furthermore, platinum is being successfully employed as anti-cancer drug but it exhibits severe side-effects. The solubility in hydrophilic and hydrophobic systems greatly determines the bio- accessibility of PGEs and their potential to be transformed into potentially toxic forms. Of all PGEs, palladium shows the highest solubility and mobility under ambient conditions. Recent research showed that the bio-accessibility of Pd is over tenfold higher than the bio- accessibility of Pt or Rh. Since the natural abundance of PGEs in the earth crust is very low, man-made contamination has been shown to be the major contributor to raised concentration of these elements in the environment.

The assessment of trace and ultra-trace concentrations of PGEs is challenging since many factors hamper the correct determination of these elements in samples of biological provenience. All analytical instruments that are currently available for this task either suffer from interferences of matrix constituents (ICP-MS) or they do not offer the required sensitivity (ET-AAS). In both cases, proper sample preparation can help to overcome these disadvantages: interfering sample constituents can be removed or the net analyte concentration can be raised. Numerous methods for sample preparation have been established but Solid Phase Extraction is the most commonly used one since it can easily be automated. Unfortunately, the SPE method does not offer quantitative recovery and the use of harmful chemicals is required in order to elute the analytes from the sorbent material.

To overcome these major shortcomings of SPE, a novel enrichment procedure that allows the selective enrichment of palladium from aqueous solutions was described in the first part of this diploma thesis (chapter 2). Since the major disadvantage of conventional SPE lies in the necessity to elute the adsorbed analytes from the sorbent material after having them successfully extracted from the liquid samples, this contribution aims at completely omitting the elution step. An anionic ion- exchanger material (SAX MCM-41) with a very small particle diameter of about 0.5µm and a high specific surface of approximately 100m^2/g was synthesized. The sorbent material was suspended directly in the liquid samples; as PGEs form negatively charged chlorocomplexes, they readily adsorb on the surface of the ion- exchanger resin. In the gravity field of a centrifuge the particles sediment to the lower part of the sample vessels and the supernatant solution can be easily removed. After re-suspending the particles in the remaining volume, the resulting slurry is directly introduced in an ET-AAS instrument; owing to the applied temperature program, solvent is evaporated and matrix elements from the sample or from the sorbent material are easily removed. After complete matrix removal, the analytes are still present in the graphite furnace of the instrument; by applying a very steep heating ramp, the analytes are evaporated abruptly and form an atomic gas inside the furnace which is used for quantification by means of an atomic absorption spectrometer. Since the sorbent material consists mainly of silica which is not evaporated during the matrix removal step, a small

amount of hydrofluoric acid (6µL of a 10% v/v solution)[16] was added each time to the sample aliquot (30µL) to facilitate the evaporation of silica. After optimization of the parameters needed for good performance of the ET-AAS instrument such as temperature program, analytical wavelengths and the addition of hydrofluoric acid, the enrichment procedure was stepwise optimized. Various parameters were found to influence the recovery: sample acidity (1% HCl v/v), the amount of sorbent material (2mg) and the precise procedure of removing the supernatant solution were optimized. Especially the way of removing the supernatant solution after centrifugation proved to be paramount for good recoveries and high reproducibility: if the solution is removed in one big step, uncontrollable particle losses lead to very low reproducibility. But if the solution is removed in two steps and the particles are re-suspended and centrifuged before the second step, good reproducibility and high recoveries are obtained. The final volume to which the sample is reduced was found to be optimal at 0.4mL. Larger volumes reduce the attained enrichment factor, smaller volumes are difficult to handle and also the number of replicate analyses with ET-AAS is limited. The selectivity of the enrichment process was proved to be good even in the presence of other inorganic sample constituents. However, experiments have shown that the complete decomposition of organic matrix is vital to ensure good recovery: PGEs are readily complexed by these organic compounds and therefore they cannot interact with the sorbent material.

Owing to the optimized enrichment procedure, the sensitivity of the ET-AAS measurements was enhanced by a factor of 20. Theoretically, even higher gains in sensitivity should be possible but since the samples have to be prepared manually, a certain restriction regarding the sample volumes cannot be circumvented. Automated sample preparation could help to overcome this limitation. Recoveries of approximately 80 to 85% were obtained under optimized conditions. These recoveries are in good accordance with comparable SPE methods.

The enrichment procedure was successfully applied to determine the concentration of palladium in plants that were grown in a nutrient solution containing this metal in a soluble form. The intent of this contamination experiment was to estimate the uptake potential of

[16] Values in brackets indicate optimized conditions

Pd (and the other two PGEs) in plants. When the plants were transferred into the contaminated solution right after germination, very restricted plant growth was observed. It is not possible to quantify the Pd concentration of these small plants by conventional ICP-OES methods since large sample intakes are required for this approach. The presented enrichment process was very well suited to solve this dilemma as it allows the determination of very low Pd concentrations. It was even possible to further divide the small plants into leaves, stem and roots and to analyze these parts separately. By doing so, a significant difference in Pd concentration between leaves, stem and roots was found.

The optimized enrichment procedure and the results obtained from analyzing the plant samples were presented orally at the EUROanalysis conference 2011 in Belgrade, Serbia. The abstract can be found in the appendix.

In the second part of this diploma thesis (chapter 3), a solid sampling approach for the analysis of the same plant material is presented. Since the samples have to be transformed into liquid in order to perform sample pre-treatment steps as for example the enrichment process just described, large quantities of digesting agents are required which can contribute to sample contamination. The digesting procedure as such is a time-consuming and costly step. By employing solid sampling techniques like ETV ICP-OES, this laborious procedure can be completely skipped. The samples are introduced into a graphite furnace, matrix constituents are removed by a temperature program and the remaining analytes are swiftly evaporated. The vapour is re-condensed in such a way that very small solid particles are formed which can be quantitatively transported via a tubing into the plasma of an ICP-OES instrument where they are again evaporated, atomized and thermally excited to produce element- specific radiation. An important advantage of the ICP-OES instrument over ET-AAS measurements is its ability to simultaneously acquire multi- element information.

The sample intake with the proposed ETV ICP-OES method is very low which on the one hand allows the analysis of samples where only a restricted amount of material is available; on the other hand, the analyzed aliquots have to be representative parts of the sample entity. Sample homogeneity was shown to be of great influence for the reproducibility of the results. To guarantee homogeneous samples, the plant material was specially pulverized with a mixer mill that produces a very fine powder. Then an aliquot (5mg) was transferred

into a graphite boat and was subjected to an ashing procedure: the sample was heated in a muffle furnace in an oxygen-rich atmosphere (2h, 340°C, 2L/min O_2). After this treatment, all organic carbon is decomposed which is important to avoid formation of elemental carbon in the transport tubing connecting the ETV unit to the ICP-OES instrument. Furthermore, the rapid formation of gaseous combustion products in the graphite furnace can cause severe disturbances in the plasma. To guarantee complete evaporation of the analytes, a gaseous modifier was added to the transport gas (10mL/min Freon 12 modifier). The temperature program, the signal recording mode of the instrument's software and the sample intake were optimized. The latter can be varied around 5mg and a linear relation between signal and sample intake is obtained; however, if a maximum sample mass of 12mg is exceeded, thermal inertia of the sample prevents the rapid vaporisation of the analytes which results in decreased reproducibility.

Even though the sample intake was reduced by a factor of 40 in the ETV- method, a 5-fold amelioration of the limit of detection was obtained in comparison to conventional ICP-OES measurements that use liquid sample introduction and require sample digestion. The main advantage of the presented method lies in the complete avoidance of any digestion step. Although the ashing of the sample material and the weighing of the samples into the graphite boats are time consuming steps (5min of weighing for each sample, 3h muffle furnace including gentle heating ramp), the sample throughput could be considerably increased. The time demand for one conventional microwave assisted digestion is 3h (sample digestion: 1.5h, clean out: 1.5h) and the sample dilution step takes about 5-10 min for each sample. Yet, within one digestion run only eight samples can be processed, whereas the muffle furnace can hold at least 20-30 graphite boats; a 3 times higher sample throughput was therefore obtained with the ETV ICP-OES method.

Comparison of the obtained results with the results of a conventional analysis using digested samples and liquid sample introduction at first showed large discrepancies: the ETV method overestimates the PGE- concentrations over 2-fold when aqueous standards are used for quantification because of substances inherent to the sample matrix. It was possible to somewhat reduce this effect by performing a matrix matched calibration but the results were still not convincing. To further explore this unwanted effect, one sample of well-known analyte content was used for calibration purposes: aliquots of increasing mass were put into

graphite boats, ashed and analyzed. Since the analyte content increases linearly with the sample intake, calibration curves were obtained. When these curves were used for quantification of the samples, the obtained results were found to be in excellent accordance with the reference method using liquid sample introduction.

Further experiments are required to fully understand why the ETV ICP-OES method overestimates the analyte content when a conventional calibration with aqueous standards is applied. For the time being, a straight-forward correction for this effect can be obtained by measuring the signals obtained with a sample of known concentration ("in-lab" reference material). The slope of a conventional aqueous calibration can then be corrected to match this referenced concentration. Future projects will aim at the assessment of the spatial distribution of PGEs in single leaves of the plants using the presented ETV ICP-OES method.

The work described in the second part of this diploma thesis was presented in the form of a poster at the EUROanalysis conference 2011 in Belgrade, Serbia. The abstract can be found in the appendix.

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APPENDIX

DEVELOPMENT OF AN ELECTRO-THERMAL VAPORISATION INDUCITIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY - PROCEDURE FOR THE DETERMINATION OF PLATINUM GROUP ELEMENTS IN PLANTS

W Nischkauer[1], E Herincs[1,2], A Limbeck[1]

[1] *Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-IAC, 1060 Vienna, Austria*

[2] University of Natural Resources and Life Sciences, Department of Forest- and Soil Science, Institute of Soil Science, Peter Jordanstr. 82, 1190 Vienna, Austria

e0525056@student.tuwien.ac.at

In order to reduce noxious gas emissions of hydrocarbons, carbon monoxide and nitrogen oxides in exhaust fumes of modern vehicles, platinum group elements (PGEs) have been employed as catalysts in automobile catalytic converters in Europe since the late 1980s. Even though the air quality improved, concentration of PGEs in the environment increased significantly over time, caused by abrasion of the catalyst material during vehicle operation [1]. Despite PGEs being rather inert themselves, reactive and bio-available species arise by environmental transformations. This may lead to accumulation of PGEs in soil, sediments and plants, evoking concerns about their possible impact on the biosphere. Although elevated PGE levels were determined in road dusts and soils along heavily frequented roads [2], there is a lack of information on the availability of these metals to the biosphere [3]. The main reasons being difficulties in analysis, since relatively low PGE concentration levels in the presence of complex plant matrix have to be determined.

This contribution presents the development of an ETV-ICP-AES procedure for the direct analysis of PGE in *Brassica napus*. The plants were grown in a hydroponic setup containing incremental concentrations of Pt, Pd and Rh to study their respective uptake potential. Prior to ETV-ICP-AES analysis the dried and grinded plant samples were treated in a muffle furnace for two hours in an oxygen atmosphere to decompose organic material. For signal quantification three different strategies were investigated; namely external calibration with aqueous standard solutions, application of an internal standard and matrix-matched calibration. Compared to traditional approaches for analysis of PGEs in plants, the proposed ETV-procedure offers enhanced sensitivity, since the digestion step required for sample dissolution and the inherent dilution could be omitted. Furthermore the developed approach allows analysis of limited sample amounts which in some cases is due to restricted plant growth.

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ENRICHMENT OF PALLADIUM FROM AQUEOUS SAMPLE SOLUTIONS USING FUNCTIONALIZED NANO- PARTICLES

W Nischkauer[1], M A Neouze[2], A Limbeck[1]

[1] *Vienna University of Technology, Institute of Chemical Technologies and Analytics, Getreidemarkt 9/164-IAC, 1060 Vienna, Austria*

[2] *Vienna University of Technology, Institute of Materials Chemistry, Getreidemarkt 9/BC/02, 1060 Vienna, Austria*

e0525056@student.tuwien.ac.at

Pd is widely used in today's automotive catalytic converters. Thermal and mechanical stress cause surface abrasion of the catalytic material, releasing Pd in the environment [1]. Due to its potentially harmful properties, it has become necessary to perform analysis of very low concentrations of Pd in environmental samples. The methods at hand for this task are ICP-MS, ICP-AES or ET-AAS [1]. Unfortunately, when using these methods, Pd is either strongly interfered by other elements (ICP-MS) or sensitivity does not allow measurements in the desired concentration range (ICP-AES, ET-AAS). To improve detection limits and to eliminate interferences usually sample pre-treatment techniques like solid phase extraction (SPE) with ion-exchangers are applied. Although being well established, SPE suffers from several shortcomings such as time consuming conditioning steps, incomplete recovery of the adsorbed ions and memory effects. One of the major drawbacks of SPE is the necessity to elute the analyte after adsorption using appropriate solvents.

In this work a novel sample pre-treatment procedure for enriching Pd from liquid samples is presented, featuring the idea of renewable surfaces and eliminating any elution process. Porous nano- spherical silica was functionalized with quaternary ammonium groups [2], yielding a strong anion exchanging material with a mean particle size of 700nm. Due to the high specific surface of the silica, very low amounts of this compound are sufficient to obtain nearly quantitative recovery for Pd from aqueous solutions. After separating the particles from the sample volume by means of a centrifuge and removing excess liquid, an aliquot of the remaining suspension is analyzed using ET-AAS. This straight- forward slurry approach helps to overcome the problems associated with the elution process. On that account it is possible to enrich Pd from aqueous solutions or sample digests, propelling the limit of detection in the 100ng/L range.

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