Thesis for the Master's
degree in chemistry

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Development of methods for separation and determination of platinum, palladium and rhodium, utilizing solid phase extraction, ICP-OES and ICP-MS

60 study points

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Preface

This graduate study has been carried out at the Department of Chemistry, University of Oslo, in the period from August 2011 to June 2013. My supervisors have been Professor Grethe Wibetoe and Ph.D student Dejene Kifle.

I would like to sincerely thank my supervisors for giving me an interesting and challenging problem to work with in my study as well as providing guidance and support during the past two years. I would also like to thank the people at K.A.Rasmussen and SINTEF for letting me take part in project meetings for the project “Gjenvinning og raffinering av lavgehaltige platinametaller”. It was a great experience that I am sure will be helpful later in life.

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In the end I want to thank my loving and supporting family who have always been there for me. Mom and dad, thank you so much for being amazing parents, teaching me responsibility and the value of critical thinking. Thanks to my three younger sisters, Marianne, Renate and Pia Sophie. You have all tested my patience through the years but I could not have asked for better siblings. Finally, I want to thank to my grandparents; “Ammi”, “Far” and “Besta”. It means the world knowing you are proud of me. I love you all very much.

Oslo, Norway, June 2013

Tina Bryntesen

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Abstract

The platinum group elements (PGMs) Pt, Pd and Rh are used extensively in different industrial and technological applications. Particularly important is their use in autocatalysts in order to reduce emissions of harmful pollutants from car exhaust. Increased use of the PGMs has resulted in high interest of their recovery from spent autocatalysts in addition to determination of low concentrations of the PGMs in different sample matrices.

In this study, separation of the PGMs (and selected base metals) in HCl solutions have been studied using solid phase extraction. Strong anion exchange (SAX) and strong cation exchange (SCX) resins was tested due to the PGMs forming (mostly) anionic chlorocomplexes in HCl solution, while the base metals are present as cations. Cyano (CN) and dioctyl sulphide (DOS) modified reverse phase was tested due to the PGMs having a large affinity towards N and S. The differences in adsorption due to HCl concentration and storage time of the solutions was investigated on SAX and SCX and optimum results were found using fresh solutions with 0.15 M HCl, in which Pt and Pd were quantitatively adsorbed on SAX and the base metals quantitatively adsorbed on SCX. Pd was found to be selectively retained on CN and DOS modified resin. Recovery of the analytes was tested using several elution solutions. Thiourea was found to be needed in order to recover Pt from SAX and Pd from DOS modified resins. 3 M HCl could be used for recovery of Pd from SAX, recovery of base metals from SCX and recovery of Pd from CN. None of the tested resins adsorbed Rh to any large degree. A separation scheme was proposed using SCX and SAX and a good, although not quantitative, separation was obtained. Additionally, high pressure liquid chromatography (HPLC) was tested using a SAX column and the ICP-MS as a detector, with a mobile phase containing a maximum of 2 M HCl. High background of Pt and Pd was found in the HPLC method, presumably due to previous contamination of the column. Rh was the only PGM showing peaks not present in the blank.

Analyses of the samples were performed using inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Both were found to be good techniques for determining low concentrations of PGMs in HCl solutions with detection limits ~ 0.1 – 0.9 ng mL^{-1} for ICP-MS and ~ 10 - 15 ng mL^{-1} for ICP-OES. Determination of the selected base metals on the ICP-MS was problematic and this instrument was therefore only used for analysis of the PGMs.

Abbreviations

CN	Cyano
DOS	Dioctyl sulphide
HPLC	High performance liquid chromatography
ICP-MS	Inductively coupled plasma mass spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
LLE	Liquid-liquid extraction
LOD	Limit of detection
LOQ	Limit of quantification
M	Mol L^{-1}
MP	Mobile phase
PGM	Platinum group metal
RP	Reverse phase
SAX	Strong anion exchange
SCX	Strong cation exchange
s	Standard deviation
SP	Stationary phase
SPE	Solid phase extraction
TDS	Total dissolved solids
TU	Thiourea

1 Introduction and background

1.1 Platinum Group Metals

1.1.1 General

Platinum group metals (PGMs) is a term given to the metals Ru, Rh, Pd, Os, Ir and Pt. The PGMs are part of the noble metals, which “resist chemical action, do not corrode and are not easily attacked by acids” [1]. Several of the PGMs have important properties, most importantly a high catalytic activity, which makes them important in many industrial processes and new technologies [2].

The PGMs are usually found in sulphur rich minerals, particularly in Ni, Fe and Cu sulphides [2-4]. The refineries have different approaches towards refining the metals depending on if they are seen as the main product (with Ni/Cu as bi-products) or as a bi-product itself in the Ni-Cu refining [2]. In addition, other transition metals are often found together with the PGMs, with gold, copper and iron being examples [5].

As with the other precious metals (Au, Ag), the amount of PGMs in the Earth's crust is low (approximately 1 ng g^{-1} per element) [4]. The demand for the PGMs, especially for Pt, Pd and Rh, is very high, as they have many important properties that are useful in industrial processes [6]. The process for refining and extracting the PGMs is a complex process [2] which in addition to the high demand and the scarcity of the elements makes them very expensive. There is therefore an increased interest in their recovery from waste products like spent catalysts, electronic scrap and metal wastes, due to the natural deposits getting exhausted [6, 7].

1.1.2 Applications

The most important elements of the PGMs are Pt, Pd and Rh. The distribution of their demand by application in 2012 can be seen in Figure 1. The main demand is their use in autocatalysts which in 2012 comprised of approximately 40, 65 and 80 % of the total demand of Pt, Pd and Rh, respectively [8]. Additionally, they are used in several other applications due to their different properties. They are resistant to corrosion and oxidation in addition to having excellent mechanical properties, which is important for high temperature processes in the industry [2, 4, 9]. The elements are good catalysts and Pt based catalysts can eliminate volatile organic compounds that are emitted from many industrial processes [9, 10]. Platinum is among other used as a catalyst in organic synthesis [7] and the good electrical conductivity and high melting point of the PGMs makes them useful in the electrical industry [2, 4, 9]. Other applications are in ceramic capacitors, fuel cells, as catalysts in the chemical industry and in glass manufacturing [11]. Additionally, platinum is used in chemotherapy where cisplatin, $[PtCl_2(NH_3)_2]$, has been used as an anticancer agent [12]. Platinum is also used in jewellery due to its shiny and silvery appearance [7, 9, 13].

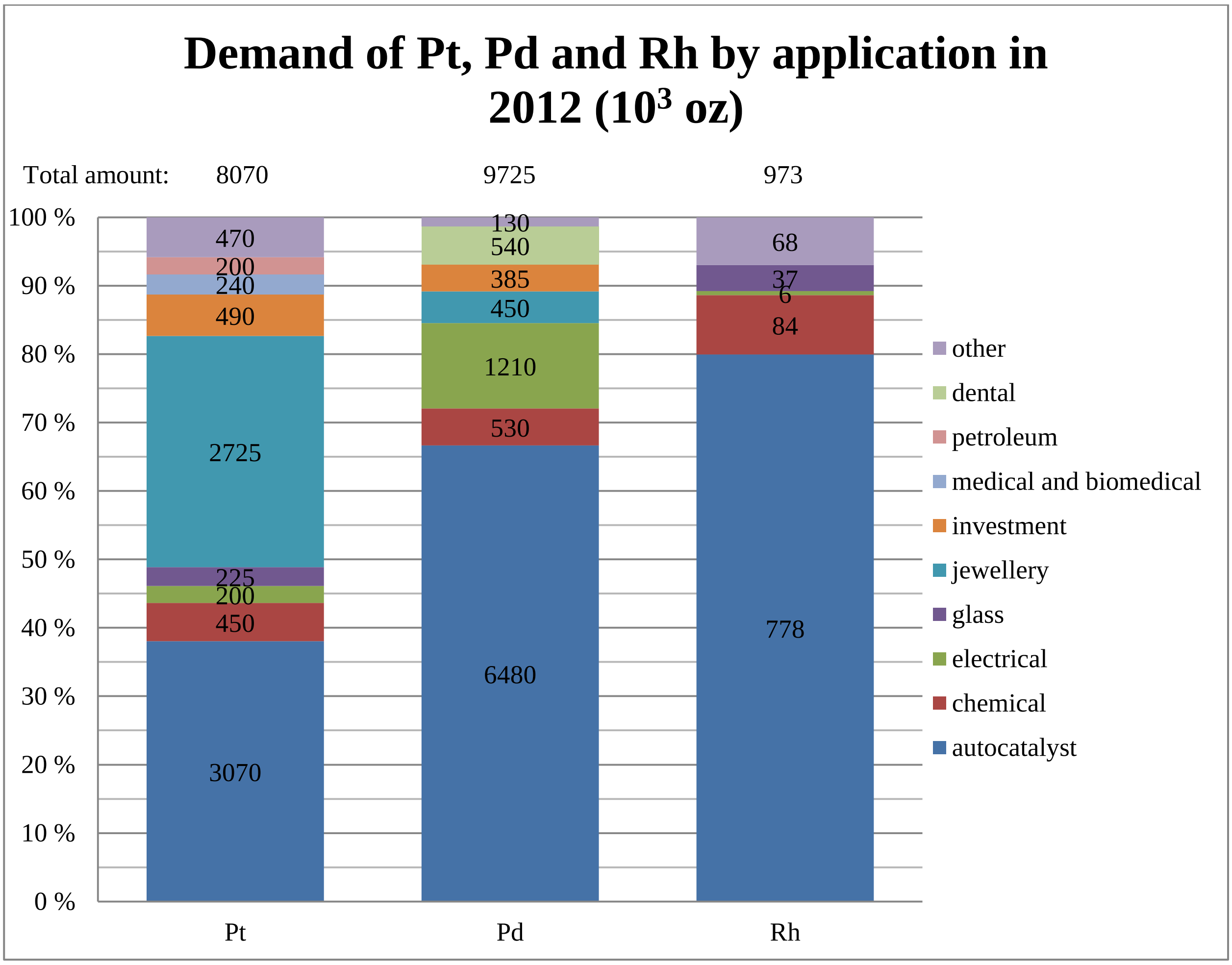

Figure 1 Total demand of Pt, Pd and Rh by application in 2012, values are in 10^3 oz [11]

1.1.3 Autocatalysts

Increased awareness of environmental pollution from car exhaust has led to implementation of catalytic converters in cars. These autocatalysts reduces levels of carbon monoxide from petrol engines as the catalytic activities of Pt and Pd enables the complete combustion of hydrocarbons and convertion of CO into CO_2. The three-way converters, which have Rh in addition to Pt and Pd also remove nitrogen oxides (NO_x) by reducing them to N_2. The catalysts are thermally stable and operate at relatively low temperatures [5, 10, 13-18]. The three-way autocatalysts has been the most important application for Pt, Pd and Rh the last 20 years [4].

Although the PGMs in the autocatalysts have a positive impact on the environment by greatly reducing the amount of harmful pollutants and emissions released in nature, small amounts of PGMs are released from the autocatalysts by abrasion and thermal cracking due to the hot exhaust gases flowing through the catalytic converters [4, 15, 19, 20]. The emitted PGMs are mainly released in their biologically inert metallic state while still bound to metal oxides. Transformation into soluble forms can, however, occur in nature, which in turn can lead to bioaccumulation [12, 21]. The number of redox and complexation agents in soils and sediments can affect this mobilization greatly [12]. Increased levels of PGMs have been observed in ambient air and dust particles close to highways [4, 5, 12, 22]. Releases can also originate from point sources of production and recycling of the PGMs although the release from autocatalysts exceeds the other sources [4, 9, 12].

1.1.4 Chemistry

The chemistry of the PGMs in solution is depending on the hydrochloric acid concentration and the oxidation state of the elements. The oxidation state of rhodium can be **Rh(III)** or Rh(IV), palladium can be found as **Pd(II)** and Pd(IV) while Pt can exist as Pt(II) and **Pt(IV)**. The most stable oxidation states are noted in bold [7, 13, 22, 23]. They all form chlorocomplexes in strong hydrochloric acid solutions, creating mostly anionic complexes, with distribution depending on the pH and temperature in the addition to the concentration of HCl/chloride and the metals in the solution [7, 24, 25].

For platinum, the octahedral complex hexachloroplatinate, $[PtCl_6]^{2-}$ predominates in strong acidic HCl solution (> 3 M) but with dilution, complexes of Pt(II) appear and coexist in solution as their square planar $[PtCl_4]^{2-}$ equivalent. The increased pH also allows aquation and hydrolysis to take place, where one or more chloride is exchanged by H_2O or OH^-. This is what is known as the "ageing" effect of the PGM solutions, which means that over time the speciation of the PGMs in a solution will change from its original composition. Normally, more aquated and hydrolysed complexes will appear and this effect is especially pronounced in weakly acidic solutions. It will lead to a mix of PGM chlorocomplexes with various degrees of aquation and hydrolyzation, which can make their separation challenging [7, 26, 27].

Palladium is mainly present as Pd(II) and there are limited knowledge of the chemistry of Pd(IV) complexes [28]. The Pd(II) oxidation state forms square planar $[PdCl_4]^{2-}$ complexes in hydrochloric solutions. The square planar complexes generally have a higher degree of ligand exchange than their octahedral counterparts, as they have less steric hindrance. Rhodium is present as the $[RhCl_6]^{3-}$ complex in strong HCl (> 6 M) solutions although lowering of the acidity causes many transformations, most importantly the aquation of the complexes, where one or more chloride is exchanged with a water molecule [23, 25]. Rhodium is more affected by this aquation than the other PGMs [16]. The aqua and hydroxo complexes are kinetically inert, which can lead to them being less readily extracted by ion exchange extractants [7, 25]. Due to the wide variety of possible complexes, it is hard to predict the distribution via thermodynamic constants although there is qualitative agreement that chlorocomplexes of Pt and Pd will occur in highly oxidizing, acidic solutions [22].

The PGMs have a large affinity to sulphur and nitrogen-containing ligands. This can be explained by the hard and soft acids and bases theory. The precious metals in their low oxidation state belong to the "soft acids" and has a strong affinity for the "soft base" donor atoms in the order of $S \sim C > I > Br > Cl \sim N > O > F$ [22, 29, 30].

1.2 Separation and preconcentration

There are several reasons why separation of platinum, palladium and rhodium from both each other and from accompanying metals is an important area of research. The increase of PGMs in the environment has led to an increased interest in determining the elements in trace amounts from different matrices including environmental and biological samples. In order to increase sensitivity of the detection methods, it is often needed to remove matrix elements to minimize background noise and interferences. Additionally, there is often a need to preconcentrate the PGMs in the sample in order for the PGM concentration to reach the instrumental limit of detection [12, 15, 31, 32]. This is especially important when measuring for increased pollution of the metals in the environment as the PGMs are present only in trace amounts.

There is also pressure from the industry to develop easier and less expensive ways of obtaining the pure metals, both from natural deposits and in regards to their recycling. A regular tree-way converter contains 1 - 5 g of the PGMs [22] and because of the rarity in nature and the high demand of these elements, it is important to find good methods of recovery [6, 25]. For this to be cost effective, generally a recovery higher than 95 % is needed [16]. The similar chemistry of the different PGMs and their complexes makes their separation challenging [33] and much research have been made in this field. Several review articles have summarized work that has been done so far in regards to separation and preconcentration of the PGMs [2, 4, 32, 34].

1.2.1 Traditional refining methods

The refining of PGMs has traditionally been achieved with the use of a series of precipitations. Due to poor selectivity and contaminant PGMs, several intermediate and cleaning steps have to be made in order to obtain the pure metals. This makes the process prolonged and labour intensive. Liquid-liquid extraction (LLE) was implemented in the 1970s, with the use of dialkyl sulphides as a complex forming selective extractant for Pd in addition to the use of anion exchange solvents to extract the metal chlorocomplexes [2]. LLE gives a higher selectivity than the precipitation methods, in addition to a higher purity of the PGMs and more complete removal of metals. This causes LLE to be superior to precipitation methods both in terms of refining time and production costs. The main downside of solvent extraction is the use of large amounts of organic solvents which needs to be recycled [2, 35].

1.2.2 Solid phase extraction (SPE)

In solid phase extraction, analytes are extracted from a liquid phase to a solid phase. The solid phase usually consists of particles made of either silica or polystyrene-divinylbenzene with added functional groups. Several types of these resins are commercially available and can be bought in bulk weight or pre-packed in syringe barrels or cartridges. The extraction can be done in batch mode, where a certain amount of resin is mixed with the solution containing the analyte and left to equilibrate. Agitation will usually decrease the time needed before equilibrium is reached. More practical is using a "column mode", where the sample is passed through a column or cartridge containing the resin. This mode is faster, more user-friendly and it is easier to back extract the analytes from the resin than for the batch mode. The extracted analytes can be removed from the solid phase by passing an appropriate eluent through the resin and collecting the effluent. SPE is more practical than LLE, as it is easier to separate the phases. Additionally it is faster, less labour intensive and can be easily automated.

Normally there are four steps in the method of solid phase extraction [36]. The first is to condition the resin to activate the functional groups for analyte adsorption and to ensure a good contact between the mobile phase and the stationary phase. This is especially important for hydrophobic resins, as they often contain long chains of hydrocarbons which can collapse when the resin is dry. The second step is the sample application, where the sample is passed through the resin and the analytes are adsorbed. Normally a wash solution is then applied as the third step, to remove matrix components that may be adsorbed together with the analytes. Finally, the eluent is applied, to elute the analytes from the resin. Ideally the analytes are eluted in a small volume, as this ensures a preconcentration of the analytes. SPE can also be used to extract matrix components from the samples while the analytes pass through unhindered.

For the PGMs, several sorbents have been used for adsorption of either the analytes or the matrix components. Most often used is anion exchange resins, in order to adsorb the anionic chlorocomplexes of Pt and Pd [6, 7, 24-26, 32, 37-40]. The tendency for the PGM chloro complexes to form ion pairs with anion exchangers is reported to be $MCl_6^{2-} > MCl_4^{2-} \gg MCl_6^{3-}$ [16]. In order to quantitatively adsorb the PGMs, the HCl concentration in the sample should be kept low, as the chloride ions compete with the analyte anions for the active sites of the sorbent. The downside to using this type of sorbent is the lack of selectivity, in addition to it being difficult to back extract the adsorbed platinum. Thiourea is often used in the eluent as it is a strong complexing agent for Pt [4, 9, 28, 41] and occasionally the resin is burned in order to recover the adsorbed elements [24, 32]. In weak acidic solutions, Rh do not adsorb to the anion exchange resins, presumably because of the many aquated species that are present in solution. These are more kinetically inert than the hexachloro complex and consequently less easily extracted [39]. Cation exchange resins have been used to adsorb matrix elements in the sample, as most of the other transition metals do not form stable chlorocomplexes as easily as the PGMs [38, 42, 43]. Other types of sorbents used are chelating or complexing sorbents, often containing sulphur donor atoms which have a particular affinity for the PGMs. These sorbents can either be synthesized or a reverse phase resin can be impregnated with a complex forming agent before sample application [21, 32].

1.2.3 High performance liquid chromatography (HPLC)

High performance liquid chromatography works by the same principles as SPE, with the analytes interacting with the resin. The difference between HPLC and SPE is that in SPE a relatively large amount of sample is applied to the column and the analytes are completely retained before they are eluted with an appropriate eluent. With HPLC, however, a small amount of sample is applied as a plug in a continuous flow of mobile phase (MP) which is chosen so that the analytes move through the column at different speeds according to their affinity to the resin. This ensures a separation of the different analytes, as they will elute separately in time from the column. The column is also longer than for SPE, and the stationary phase (SP) consists of smaller particles which results in a high pressure over the column.

For PGM separation, strong anion exchange HPLC has been used, although a strong eluent like sodium perchlorate or high amounts of HCl is often needed in the mobile phase in order to elute the analytes completely. Reverse phase HPLC has also been used. The SP in reverse phase HPLC is hydrophobic and the analytes are retained due to their hydrophobic parts. As the PGMs are not hydrophobic themselves, the sample has to be treated to form PGM chelates before application on the column. Another way to use reverse phase HPLC is to use an ion pairing agent in the MP. These ion pairing agents have a hydrophobic part that interacts with the SP and a cationic part that interacts with the anionic PGM chlorocomplexes [19, 31, 44].

1.3 Analytical methods

As previously mentioned, there is an increased need for determination of low concentrations of PGMs in different sample matrices. Several techniques have been used, including adsorptive voltammetry, neutron activation analysis, electrothermal atomic absorption spectroscopy, inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) [12, 15, 21, 41]. Common for the techniques are low limits of detection, although preconcentration of analytes and/or separation from the matrix is often needed. Most applicable are the ICP-OES and ICP-MS, although both have challenges that need to be overcome.

1.3.1 Inductively coupled plasma optical emission spectrometry (ICP-OES)

In ICP-OES, liquid samples are usually aspirated through a concentric nebulizer into radio-frequency generated argon plasma. The analytical zone in the plasma reaches temperatures up to 8 000 K and this high temperature causes the sample components to atomize and ionize, before the atoms and ions are excited. The emission originating from the relaxation of the atoms and ions are then detected at specific wavelengths, chosen by the analyst. Around 60 - 70 elements can be detected with this technique, with detection limits ranging from < 10 – 300 ng mL^{-1} [45].

ICP-OES has been applied to determination of trace concentrations of PGMs, although low analyte levels and complicated matrices means that preconcentration and/or matrix separation steps are often needed for their determination. Non-spectral interferences are usually not a big problem if the calibration solutions are acid matched to the matrix of the samples [15, 20]. Spectral interference may be a problem if a high concentration of matrix elements is present in the sample matrix. This is most easily overcome by pre-treatment of the sample in order to remove the interfering elements [20, 23].

1.3.2 Inductively coupled plasma mass spectrometry (ICP-MS)

ICP-MS uses the same plasma source as the ICP-OES but in this technique the purpose of the plasma is to generate mono charged ions. These ions are then transferred into a mass spectrometer and separated according to their mass to charge ratio, before they are converted into electrical pulses which is counted by the instrument [46].

This technique is one of the few which can be directly applied for determining the ultra-trace levels of PGMs in the environment [15]. The main limitations for analysing trace level PGMs by ICP-MS is spectral interference arising from ions with the same mass to charge ratio as the analytes. These ions can be isotopes of other elements or molecular and doubly charged ions created in the plasma source [46]. This is further discussed in the method development section (3.3.1). The extent of the spectral interference depends on the concentration of elements present in the plasma gas and the sample matrix. Non-spectral interferences can arise from high concentrations of matrix elements, and can either suppress or enhance the analyte signal. This type of interferences is assumed to be less significant for analysis of PGMs [15].

Modification of the sample introduction by using a membrane desolvator [47] or a cooled spray chamber to give “dry” plasma conditions can reduce O and OH-containing polyatomic interferences from samples with a complicated matrix [12]. An increase in plasma power has been found to be of advantage in order to reduce the polyatomic interferences, although this will also increase the amount doubly charged ions [15, 48]. If the size of the analyte ion is significantly less than the polyatomic ions, a collision cell can be advantageous [12, 15, 46] although this seems to not be ideal for the PGMs [19]. The use of a reaction cell may also be an advantage, especially for the measurement of some of the base metals. In general, a chemical separation of the PGMs from the interfering elements seems to be the preferred choice [12, 49].

1.3.3 HPLC-ICP-MS

It is of interest to use ICP-MS coupled with HPLC in order to have an on-line separation of the sample components before the analysis. The coupling of HPLC to ICP-MS is easy, by using a switching valve between the LC column and the ICP-MS sample introduction components. This way, the mobile phase of the HPLC can be sent to waste during the column conditioning and rinsing steps while being directed into the ICP-MS for the analysis. It is, however, important to keep the tubing lengths as short as possible and to have a small dead volume in the connections, fittings and switching valves, in order to reduce band broadening [46].

The HPLC principle used for separation of the PGMs is most often anion exchange. The high affinity of some of the PGMs towards the anion resins means that the MP must contain high acid concentrations (> 1 M HCl) or ions like ClO_4^- which has a strong affinity to ion exchanger sorbents. Complexing agents like thiourea and ethylenediaminetetraacetic acid have also been used in the MP to elute the PGMs [19, 27, 37, 44]. Short eluting times of approximately 3 min have been found when using $NaClO_4$ concentrations of 300 mM coupled with UV detection [50] but this amount of sodium perchloride causes problems with the ICP-MS, as the total dissolved solids (TDS) in solution should not exceed 0.2 % when a concentric nebulizer is used [46]. This corresponds to 17 mM of $NaClO_4$. Mobile phases containing 1.1 M HCl and 50 mM of $NaClO_4$ have given elution times up to 45 min for Pt [19]. The problem of excess amounts of dissolved solids can be overcome by using post-column dilution and the retention time can be reduced by using a short guard column instead of an analytical column [27, 44].

1.4 Objective of the study

The aim of this work was to study and develop methods for separation of the PGMs from both each other and from the matrix elements. This was done using mainly SPE, with analysis of the samples using ICP-OES and ICP-MS. In order to find a method that can be applied to a larger scale refining of recycled car catalysts, it is necessary to find sorbents that can selectively retain specific PGMs or eluents that can selectively elute the PGMs. Because of the similar chemical properties of the elements, this is a great challenge. Ideally, a HPLC method would be implemented coupled with the ICP-MS, using the findings from the SPE trials. In order to determine the purity of the separated metals, ICP-OES and ICP-MS was used, as these are specific detectors and have low limits of detection. The focus of the study was shifted from HPLC methods towards SPE, as the HPLC-ICP-MS coupling and subsequent analysis proved more difficult than originally hoped.

2 Experimental

2.1 Vessels and reagents

Borosilicate glass volumetric flasks were used throughout the study for preparing and collecting the PGM solutions and samples in order to minimize any possible adsorption of analytes to the vessels [12, 15]. A few samples were prepared in centrifuge tubes made from polypropylene with a high density polyethylene screw cap (SARSTEDT AG & Co, www.sarstedt.com) although this was only done for dilution of samples shortly before analysis on the ICP-MS. The polypropylene tubes were also used for preparation of some of the eluent solutions which did not contain any PGMs.

Ultra-pure, deionized water from a Millipore Milli-Q system (Bedford, USA) was always used. Suprapur 30 % (m/m) HCl, Suprapur 65 % (m/m) HNO_3, pro analysi 25 % NH_3 and 99 % pure thiourea were from Merck (www.merck.de). Dioctyl sulphide (96 %) was from Sigma Aldrich (www.sigmaaldrich.de). 99.8 % HPLC-gradient grade BDH PROLABO methanol and 95 % (m/m) Rectapur BDH PROLABO H_2SO_4 was from VWR (www.vwr.com). The analyte containing solutions were prepared using commercial single element stock solutions and their specifications can be seen in Table 1. All the single element solutions were from Teknolab (www.teknolab.no).

Table 1 The specifications of the single element stock solutions in which the analyte solutions were prepared from.

	Conc. (µg mL^{-1})	**matrix**
Pt	1000 ± 0.5	4.9 % HCl
Pd	1001 ± 2	3.3 % (abs) HCl
Rh	1000 ± 2	4.9 % HCl
Al	1000 ± 3	2.5 % HCl
Fe	1003 ± 2	1.4 % (abs) HNO_3
Zn	1000 ± 3	2.5 % HNO_3
Cu	1000 ± 3	2.5 % HNO_3
Cr	1000 ± 0.5	2.5 % HNO_3 + 0.04 % HCl

Real converter sample was obtained from K.A.Rasmussen AS (www.ka-rasmussen.no) and the elemental composition specifications are given in Table 2. This sample was microwave digested with aqua regia by Dejene Kifle and the obtained digested solution consisted of 5 mg total converter material per mL of 10 % aqua regia solution.

Table 2 The given specifications for the real converter sample.

Fe	Ni	Cu	Pt	Pd	Rh	Slag
69.00 %	7.20 %	0.45 %	3.60 %	2.00 %	0.86 %	16.84 %

2.2 Solid phase extraction setup and materials

A Minipuls 3 peristaltic pump (Gilson, Paris) was used together with tubing of 0.76 mm inner diameter and 0.86 mm outer diameter. The tubes and SPE barrels were made from polypropylene which is tolerable to high acidic environment. Polypropylene could possibly adsorb Pd [4] but this was assumed not to be a problem over the short contact times between the PGM solutions and the materials. A picture of the setup can be seen in Figure 2. All experiments were carried out at room temperature, using a flow rate of 1 mL min^{-1} as a higher flow rate may result in lower ion exchange efficiency [30, 43]. The resins were always conditioned by a minimum volume of 10 mL water unless otherwise stated. All effluents were collected in borosilicate glass volumetric flasks and appropriate amounts of concentrated HCl was added before filling the flasks with water up to the volume indicated by the flask.

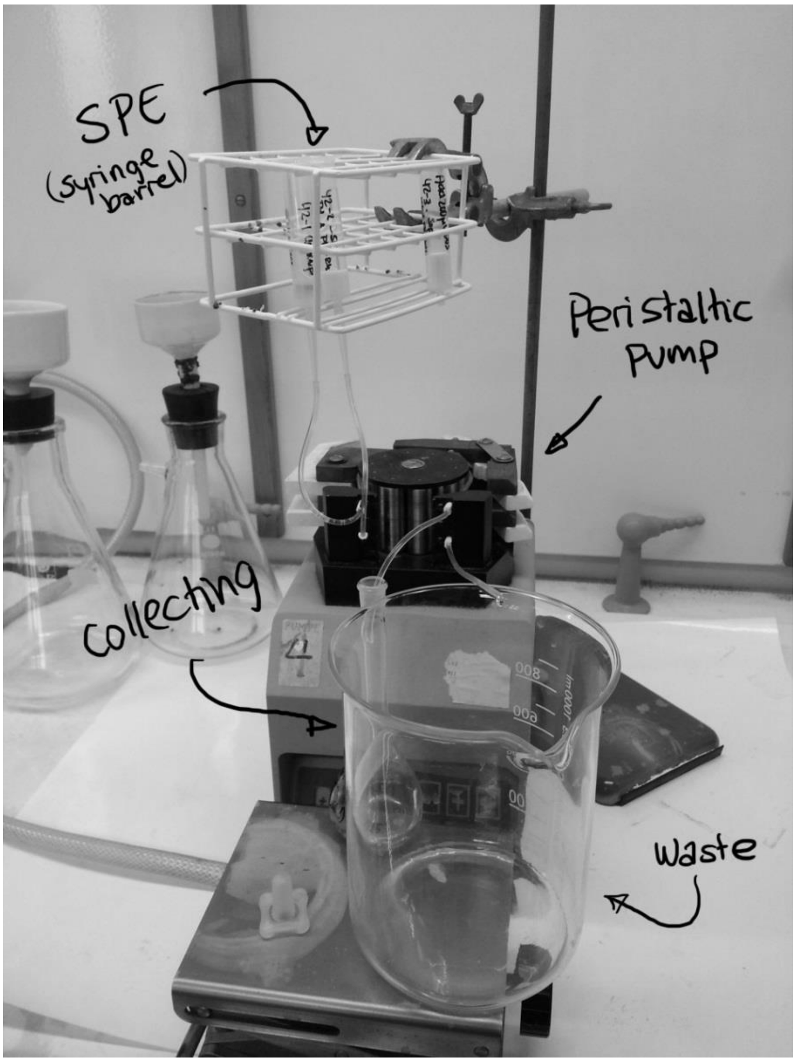

Figure 2 The setup for the solid phase extraction experiments.

The SPE resins used were strong anion exchange (SAX), strong cation exchange (SCX), cyano (CN) and reverse phase (RP), obtained from Phenomenex (www.phenomenex.com) or Agilent (www.home.agilent.com) and some of their specifications are seen in Table 3. A picture of the SPE's can be seen in Figure 3 and illustrations of the resins can be seen in Figure 4. The RP resins were modified using 200 μL Dioctyl Sulfide (DOS), which corresponds to 0.65 mmol DOS. The cartridges were initially conditioned with 10 mL methanol, then 10 mL water before applying the 200 μL DOS. This was either done with the help of a syringe (to pull the conditioning solutions and DOS through the cartridge) or by a peristaltic pump at 1 mL min^{-1}. Immediately after the DOS had gone through the cartridge, the sample was applied.

Table 3 Some specifications of the SPE cartridges used.

	Serial or part number	Mass (mg)	Capacity (meq g^{-1})	Average particle size (µm)	Pore size (Å)
Bond Elut SAX Jr, Agilent					
	12162044B	500	0.7 – 0.9	47 - 60	60 - 87
Strata SCX, Phenomenex					
	144802	500	1.0	56	70
Strata CN, Phenomenex					
	141275	500	N/A	56	70
Strata-X polymeric RP, Phenomenex					
	102613	500	N/A	28 - 34	81 – 91

Figure 3 The SPE cartridges used, showing SAX, SCX, CN and RP, from left to right.

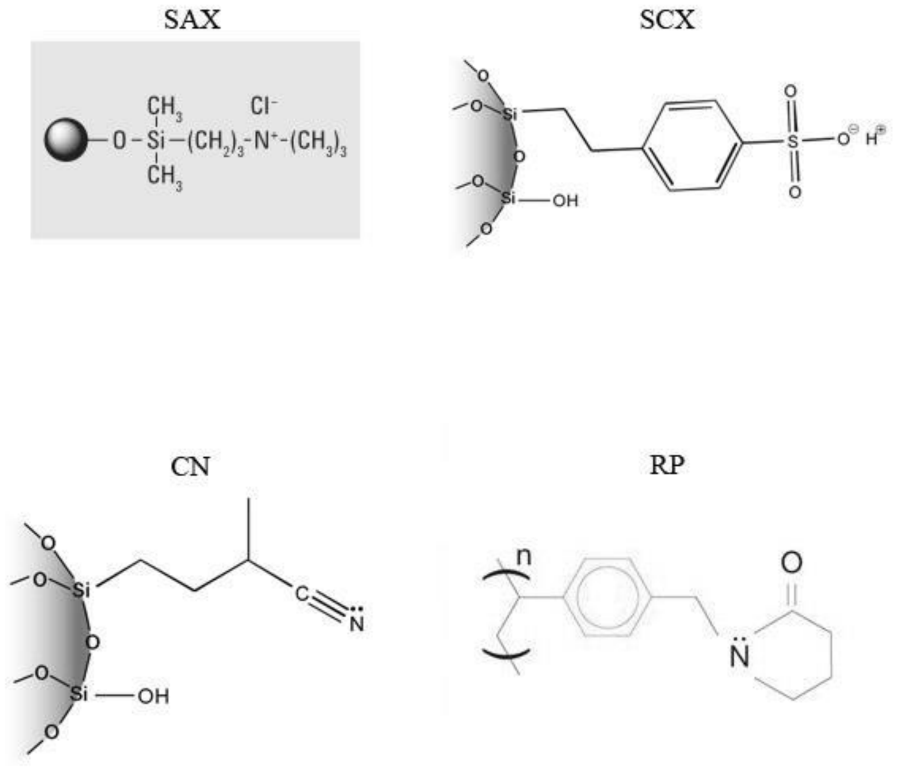

Figure 4 Illustrations of the SPE resins used.

3 Method Development

In this work, both ICP-OES and ICP-MS were used for analysis of the samples. Most often used was the ICP-OES as this could often be applied without additional dilution of the samples containing approximately 1 µg mL^{-1} of analytes. For samples with lower concentration of analytes (~ 100 ng mL^{-1}) the ICP-MS was used. The ICP-MS was also used in some experiments where the collected sample would have too high concentration of analytes for analysis on the ICP-OES with the pre-made calibration solutions and therefore had to be diluted in any case.

3.1 Limit of detection and limit of quantification

The limit of detection (LOD) and limit of quantification (LOQ) is calculated from the minimum distinguishable analytical signal of the instruments. This can be found by measuring the blank signal multiple times, finding the standard deviation (s) of this signal and multiplying it with an integer. When using an analysis method that reports concentrations directly, the LOD can be found by calculating 3s of the concentration given for the blank samples. The LOQ is often set as 10s [45, 51]. In order to find the LOD and LOQ of the entire method, the instrumental LOD and LOQ has to be corrected for dilutions of the sample previous to the analysis. As the samples analysed in this study were mainly model solutions made from single element standards, only the instrumental values were calculated.

3.2 ICP-OES method

The instrument used was a Varian (Australia) Vista AX CCD simultaneous axial view ICP-OES equipped with V-groove nebulizer and a Sturman-Masters spray chamber. Figure 5 shows a picture of the instrument. Fitted background correction was used in order to subtract the background emission and the standard operating conditions used can be seen in Table 4.

Four multielement calibration standards were made, with analyte concentrations of 0.2, 0.5, 1.0 and 1.5 μg mL^{-1} in addition to a blank standard. A 2.0 μg mL^{-1} standard was also made, in order to increase the range of the calibration for analysis of a diluted solution of the real sample in an SCX experiment (see section 4.8). Initially, the matrix used for the calibration solutions consisted of 1.2 M HCl, in order to matrix match the SPE samples eluted with high concentration of HCl. Later, calibration solutions with 0.4 M HCl were made, as high concentration of acid was no longer used. Blank samples were regularly analysed after samples with high concentration of PGMs in order to check for any memory effects, as the analytes are known to easily adsorb to surfaces so that prolonged rinse times have been needed [41]. In general there did not seem to be any memory effects with the PGM concentration used in this study.

Figure 5 Picture of the ICP-OES instrument used for analysis.

Table 4 The operating conditions for the ICP-OES.

Parameter	Value
RF Power (kW)	1.00
Plasma gas flow (L min^{-1})	15.0
Auxiliary gas flow (L min^{-1})	1.50
Nebulizer gas flow (L min^{-1})	0.75
Sample flow rate (mL min^{-1})	1.0
Replicate time (s)	1.000
Number of replicates	3

3.2.1 Wavelength selection

In order to select the best wavelengths for analysis, four wavelengths from each element were initially monitored (five, in the case of Al). These were selected according to the wavelengths recommended by the ICP-OES software and can be seen the appendix, section 7.1.1. The selected wavelengths were then narrowed down to two wavelengths for each element, after careful consideration of the possible interferences, the spectra, calibration curves and the limit of detection of each wavelength. One of the wavelengths for each analyte was chosen as the best and used for reporting the concentration, while the other was monitored to ensure that no interferences were present. The spectra of the blank and the 1.5 μg mL^{-1} standard for the two monitored wavelengths can be seen in the appendix, section 7.1.2 – 7.1.4, together with the calibration curves and statistics of the wavelengths selected for the analytical result (7.1.5 – 7.1.6).

The selected analytical wavelengths are given in in Table 5. In most cases, they correspond to the analysis wavelength recommended in the instrument software, except from Al and Cr, which was the second most recommended wavelength. Images from the software showing possible interferents of the analytical wavelengths can be seen in the appendix, section 7.1.7. The PGM wavelengths used are also the same that are regularly used in the literature [3, 10, 41]. While there are a few possible interferences from other metals, this is not a problem as long as the interfering elements are not present in several orders of magnitude higher than the analytes. In real samples, however, the PGMs are normally present in a low concentration compared to the more common metals, and possible interferences should be carefully considered.

Table 5 The wavelengths selected as the analytical wavelengths for the ICP-OES.

Al:	396.152	**Cu:**	327.395	**Cr:**	205.560	**Fe:**	238.204
Pd:	340.458	**Pt:**	214.424	**Rh:**	343.488	**Zn:**	213.857

3.2.2 LOD and LOQ

The literature gives LOD for the PGMs ranging from 10 to 300 ng mL^{-1} using ICP-OES [3, 21, 32]. In order to check this limit, the blank solution was measured ten times and the LOD and LOQ were calculated from the standard deviation of these measurements. The replicates and the s values can be seen in the appendix, section 7.4.1, and the resulting instrumental LOD and LOQ for the elements are seen in Table 6.

Table 6 The instrumental LOD and LOQ for the analytes on the ICP-OES (ng mL^{-1}).

	LOD	LOQ		LOD	LOQ
Pt	14.8	49.4	**Al**	4.5	15.2
Fe	1.5	5.1	**Cu**	2.5	8.3
Rh	15.2	50.6	**Cr**	5.9	19.6
Pd	10.6	35.4	**Zn**	1.3	4.3

3.3 ICP-MS method

For the ICP-MS analysis a NexION 300 instrument from PerkinElmer (Norwalk, USA) was employed, equipped with three quadrupole mass analysers, a cyclonic spray chamber and a concentric nebulizer. The peristaltic pump of the ICP-MS was fitted with PVC flared pump tubing with an inner diameter of 0.38 mm and the pump used a fixed rotation of 20 rpm for the analysis. This corresponds to a flow rate of 0.3 - 0.5 mL min^{-1}. An image of the instrument can be seen in Figure 6. The ICP-MS was controlled via a PC running the NexION software.

Daily performance was performed using a Smart Tune solution (PerkinElmer) consisting of 1 µg mL^{-1} Be, Ce, Fe, In, Li, Mg, Pb and U in 1 % HNO_3. The daily performance adjusts the nebulizer gas flow in order to minimize the formation of oxides ($^{156}CeO^+/^{140}Ce^+ \leq 2.5$ %) and adjusts the auto lens voltage to maximize ion transmission of Li, Mg, In, Ce, Pb and U. The daily performance check is passed if the criteria $^{9}Be > 3000$, $^{24}Mg > 20\,000$, $^{115}In > 50\,000$ and $^{238}U > 40\,000$ are met, in addition to $^{70}Ce^{2+}/^{140}Ce \leq 3$ % and the previously mentioned oxide criteria. The average operating conditions of the method can be seen in Table 7.

Figure 6 Picture of the ICP-MS instrument used for analysis.

Table 7 Average operating conditions of the ICP-MS.

Operating conditions	
RF power (W)	1000
Plasma gas flow (L min^{-1})	13.0
Auxiliary gas flow (L min^{-1})	1.2
Nebulizer gas flow (L min^{-1})	0.94
Running vacuum (torr)	7.80 x 10^{-7}

For the method development, isotopes of all the sample analytes were initially included in the analysis, but poor calibration curves for the base metals resulted in a decision to use the ICP-MS only to determine the PGMs. As the ICP-OES showed good results for the base metals it was decided to use the optical instrument for determining these elements. Analysing trace levels of certain elements by ICP-MS can be challenging due to interferences and the use of a reaction gas in a dynamic reaction cell could possibly have been of interest. A study by

Danadurai et al. [49] showed that of 43 measured elements, more accurate and precise measurements was found for Al, V, Cr, Fe, Ni, Cu and Zn when using a reaction cell with NH_3 as the cell gas. This includes all of the 5 base metals used as analytes in this work. Another possible reason for the poor calibration curves of the base metals is contamination. Fe, Al, Cu, Cr and Zn are all common elements and the low concentration (ng mL^{-1}) in the solution is easily affected by contamination.

External calibration were used, with four multielement standards of concentrations 25, 50, 75 and 100 ng mL^{-1} and a matrix of 0.3 M HCl. Initially, simple linear calibration curves were used, but this resulted in a negative intercept. As the signals from the ICP-MS can never be negative, this resulted in the blank solutions showing positive values of 2 - 3 ng mL^{-1}. “Linear through zero” calibration curves was then used instead, as the correlation coefficients still had values above 0.9999 and this resulted in blank values of approximately zero ng mL^{-1}.

The rinse time was increased from the standard settings in order to leave enough time for the sample to reach the spray chamber. The read delay was also increased so it would serve as a continued rinse period. As the sample was analysed without an autosampler, the wash step is not significant, since the analyst has to manually introduce wash solution between analyses. It was still included in case an autosampler were to be used during one of the analyses. The total analysis time is determined by the timing parameters, which can be seen in Table 8 together with the sampling parameters. The selected timing parameters were the same parameters as set in a standard quantitative analysis method included in the NexION software.

Table 8 The timing and sampling parameters for the ICP-MS method.

Timing parameters		**Sampling parameters**		
Sweeps/reading	20		**seconds**	**rpm**
Readings/replicate	1	**Sample flush**	25	30.0
Replicates	3	**Read delay**	25	20.0
Dwell time per amu	50 ms	**Analysis**	-	20.0
Integration time	1000 ms	**Wash**	30	30.0
Scanning mode	Peak hop transient			

Memory effects have been reported for the PGMs in ICP-MS analysis, resulting in a need for extended wash periods or the use of more aggressive cleaning solutions, including aqua regia or high concentration of HCl [42, 48]. In order to check for any memory effects, blank samples were analysed after the standards of higher concentration. A small possible memory effect could sometimes be seen for Pd, although as the blanks always showed concentrations below 1 ng mL^{-1} it was seen as negligible for the samples analysed in this study.

3.3.1 Isotope selection and possible interferences

The selected isotopes can be seen in Table 9. ^{103}Rh was monitored as it is monoatomic and ^{195}Pt was monitored as it is the most abundant isotope in addition to it having the least interferences of all the Pt isotopes. ^{105}Pd was monitored because the two more abundant isotopes (^{106}Pd and ^{108}Pd) have isobaric overlap from Cd isotopes. The three isotopes used for the analysis is also the ones regularly used in the literature [3, 38, 48]. The potential interferences are also shown in Table 9 together with the relative abundance [12, 15, 18].

Table 9 Mass, abundance and possible interferences for the isotopes chosen for analysis.

Analyte mass	Abundance (%)	Interferences
Pt 195	33.832	HfO
Pd 105	22.33	SrO, YO, ArCu, RbO, SrO, Cl_3
Rh 103	100	SrO, ArCu, SrOH, Pb^{2+}, ArZn, RbO

If high amounts of Cu are present in the sample matrix, the $ArCu^+$ ions can be important interferences and cause a false positive on the Pd and Rh signals. For most of the ICP-MS analyses, however, the base metals had been previously separated from the PGMs. More importantly, the concentration of base metals did not exceed the concentration of PGMs in the calibration solutions, so any interference would be negligible. For real samples, however, this can be a major source of interference, as Cu is a common element and would likely be present in a much higher concentration than the PGMs. Matrix separation before detection would therefore be strongly suggested. Cation exchange seems to be a good way to remove the metals that may cause intereference.

3.3.2 LOD and LOQ

A blank sample was measured ten times over a period of 80 minutes, between regular samples and with a recalibration after about half the time. The LOD and LOQ were calculated in the same way as for ICP-OES. The raw data from the ten replicates can be seen in the appendix, section 7.4.2, and the LOD and LOQ are seen in Table 10. Possible memory effects was found for the first two replicates of Pd, which accounts for the increased LOD and LOQ values of this element. The parenthesis show the values if the first two replicates are omitted, which could possibly be obtained with the use of a longer rinse period in the method.

Table 10 Instrumental LOD and LOQ for the ICP-MS (ng mL^{-1}), calculated from 10 blank measurements. The parenthesis show the LOD and LOQ for Pd if replicates with memory effects are omitted.

	LOD	**LOQ**
Pt 195	0.13	0.4
Rh 103	0.08	0.3
Pd 105	0.94 (0.12)	3.1 (0.4)

3.4 HPLC-ICP-MS

For the HPLC, a four channel Flexar LC pump equipped with a vacuum degasser was used together with a Flexar LC Autosampler. The pump had been converted to an inert system in order to allow for introduction of highly acidic mobile phases. An Agilent (USA) Zorbax SAX 250 mm x 4.6 mm silica based analytical column was used, containing 5 µm particles. This was coupled to the ICP-MS via PEEK tubing and a switching valve, in order to allow for the mobile phase to go directly to waste during conditioning and rinsing steps.

Two mobile phases, C and D, were used in order to create a gradient system. The MP compositions were 2 M HCl (C) and ultrapure, deionized water (D). A mobile phase composition of 5 % C and 95 % D is therefore equal to 0.1 M HCl. This was chosen as the MP for the equilibration and rinsing steps, as it is similar to the sample solution of 0.15 M HCl. After a 10 min equilibration step, 10 µL of the sample was injected using the autosampler. The entire pump program can be seen in Table 11.

Table 11 The pump program used in the HPLC method. The 1.0 value of the curve means a linear change in MP.

Step	Step type	Step time (min)	Flow (mL min^{-1})	% C	% D	Curve
0	Equil	10.0	0.5	5.0	95.0	1.0
1	Run	4.0	0.5	5.0	95.0	1.0
2	Run	2.0	0.5	100.0	0.0	1.0
3	Run	18.0	0.5	100.0	0.0	1.0
4	Run	1.0	0.5	5.0	95.0	1.0
5	Run	5.0	0.5	5.0	95.0	1.0

4 Results and discussion

4.1 Adsorption effects of storage in different vessels

It is known from literature that Pd and Pt can be adsorbed to different polymers under long storage in weak acidic conditions. According to literature, Pd will adsorb to both polypropylene and polyethylene [4] and Pt adsorbs to polyethylene [15]. Quartz vessels are seen to be the best choice of storage for these analytes [4, 12, 15]. The autosampler for the ICP-MS uses tubes made from polypropylene with a high density polyethylene cap, so adsorption effect was checked by storing part of a 30 ng mL^{-1} multielement calibration solution (matrix was approximately 0.2 M HCl) for two weeks in one of these tubes. It was then analysed as a sample. The 30 ng mL^{-1} calibration solution which had been stored in a borosilicate glass flask was also analysed as a sample. The result (including the instrumental standard deviation) can be seen in Table 12.

Table 12, The concentration of analytes (ng mL^{-1}) in an initially 30 ng mL^{-1} PGM solution, after 2 weeks of storage in different vessels.

Analyte	Stored in quartz flask	Stored in polypropylene tube
Rh	30.1 ± 0.48	29.9 ± 0.33
Pt	30.2 ± 0.15	29.1 ± 0.15
Pd	30.2 ± 0.20	15.7 ± 0.12

As seen in Table 12, the amount of Pd in the solution has decreased by almost 50 % over the two weeks of storage. This is likely adsorbed to the walls of the polypropylene tubes. It also seems as some Pt has been adsorbed, although this effect is much less significant than for Pd. The result shows that the vessels are inappropriate for storage of the PGM solutions, at least when using low acidity solutions (0.2 M HCl). The borosilicate glass volumetric flasks were as such used for all PGM solutions that were going to be stored for more than a few hours.

4.2 Strong anion exchange (SAX)

Strong anion exchange has been used for adsorption of the PGMs because they form anionic complexes with chloride in solution. Pd and Pt are strongly adsorbed to the SAX resin, while Rh is often unretained. This is likely due to the speciation of Rh in the chloride solution. As previously discussed, the Rh chlorocomplexes are more prone to aquation, which could lead to neutral aqua-chloro complexes [6, 25]. Most other transition metals are present as cationic species and will flow freely through the resin [38]. Elution from strong anion exchangers is normally performed using solutions with high amounts of ions in order to exchange the adsorbed chlorocomplexes from the sorbent. This can be done using acidic solutions, although the strong adsorption of the PGM chlorocomplexes necessitates a high acid concentration for the substitution of $[MCl_x]^{n-x}$ by the anions in the acid [39]. An often used approach is the addition of thiourea (TU) in the eluent, as this is a stong complexing agent for the PGM. A mix of thiourea and HCl is often applied [7, 16, 25, 41].

4.2.1 Adsorption

4.2.1.1 Effects of sample solution acidity

Differences in adsorption depending on the acid content in the sample solution were investigated using four 5 µg mL^{-1} multielement feed solutions with different HCl concentrations; no added acid (called 0 M), 0.15 M, 0.5 M and 1.0 M HCl. 5 mL of the feed solution was applied to a SAX cartridge and the effluent was collected and analysed on ICP-OES. Reference solutions were obtained from each of the four feed solutions and the adsorbed percentage was calculated as described in the appendix, section 7.3. Figure 7 shows the adsorbed percentage of all the elements in the four feed solutions.

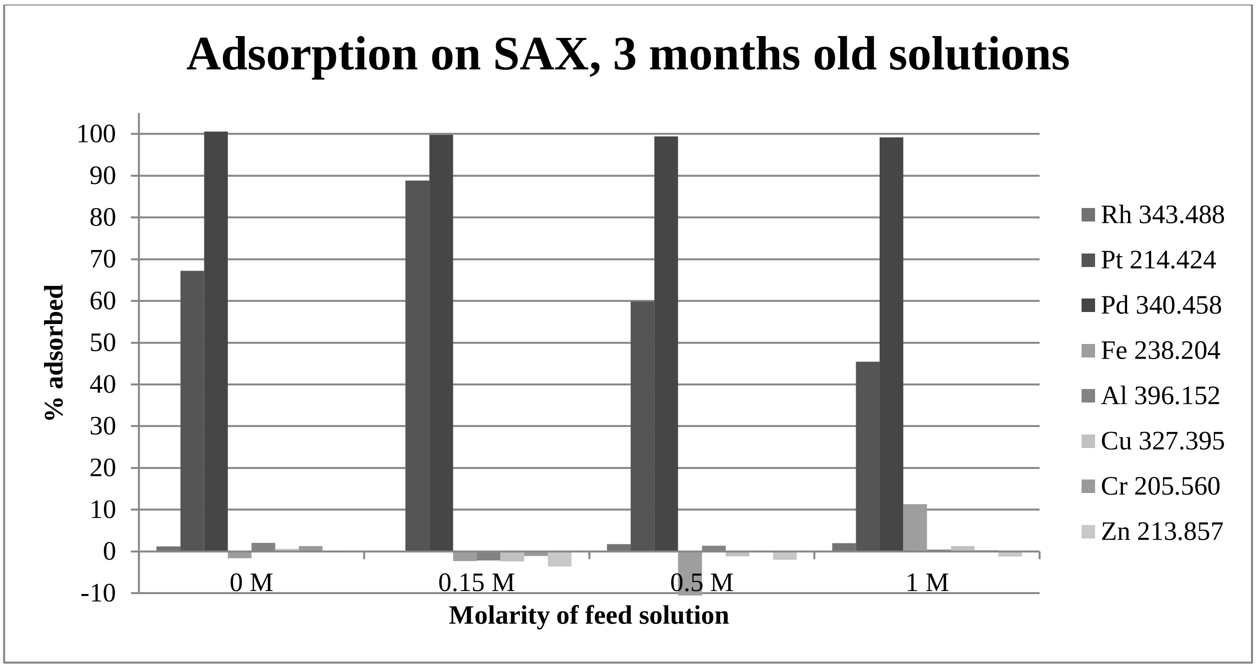

Figure 7 The effect of sample acidity on the adsorption of analytes in HCl solution by SAX sorbent (one replicate).

As can be seen by the figure, the acidity of the feed solution is an important factor for the adsorption of Pt. Pd is still quantitatively adsorbed over the range of acid concentrations tested. This is similar to results found in the literature [6, 16]. With a higher amount of HCl in the feed solution, however, it is likely that Pd will be less adsorbed as well. Too low concentration of Cl^- in the feed solution will hinder the formation of PGM chloro complexes while a high concentration of Cl^- will cause increased ion strength in the solution, resulting in less adsorption of the analytes. The experiment was only done with one replicate for each feed solution but gave an indication that 0.15 M HCl is close to the optimal amount of HCl in the feed solutions. This concentration of HCl was therefore used in the feed solution in most of the later experiments. The literature also indicates that a limited amount of HCl should be used in the feed solution and have been explained by an increase of HCl_2^-, which is a strong ion displacer, in the solution [16, 24, 25].

The base metals are generally not retained on SAX although a small amount of Fe seems to be adsorbed from the 1 M HCl feed solution. This indicates that iron may form chlorocomplexes when the chloride concentration is increased. Where the adsorbed percentage is negative, this means that the concentration of elements in the effluent was higher than in the reference solution. This can be explained by uncertainties in the analysis method as only one replicate was used, in addition to the common nature of the non-PGMs which makes them easily influenced by contamination of the sample solutions.

4.2.1.2 Differences in adsorption from fresh versus stored solutions

The time in which the solution has been stored is an important factor in the distribution of complexes of the PGMs in the solution. This is particularly important for Rh in low acidity conditions, where kinetically inert hydrated species become prevalent [25]. To investigate this effect, a fresh solution of 5 µg mL^{-1} PGMs and 0.15 M HCl was made and applied to a SAX cartridge by the same method as previously described. The adsorbed amount of PGMs from the fresh solution was compared to the adsorbed amount in the 3 months old 0.15 M HCl solution mentioned in the last section and the compared result can be seen in Figure 8.

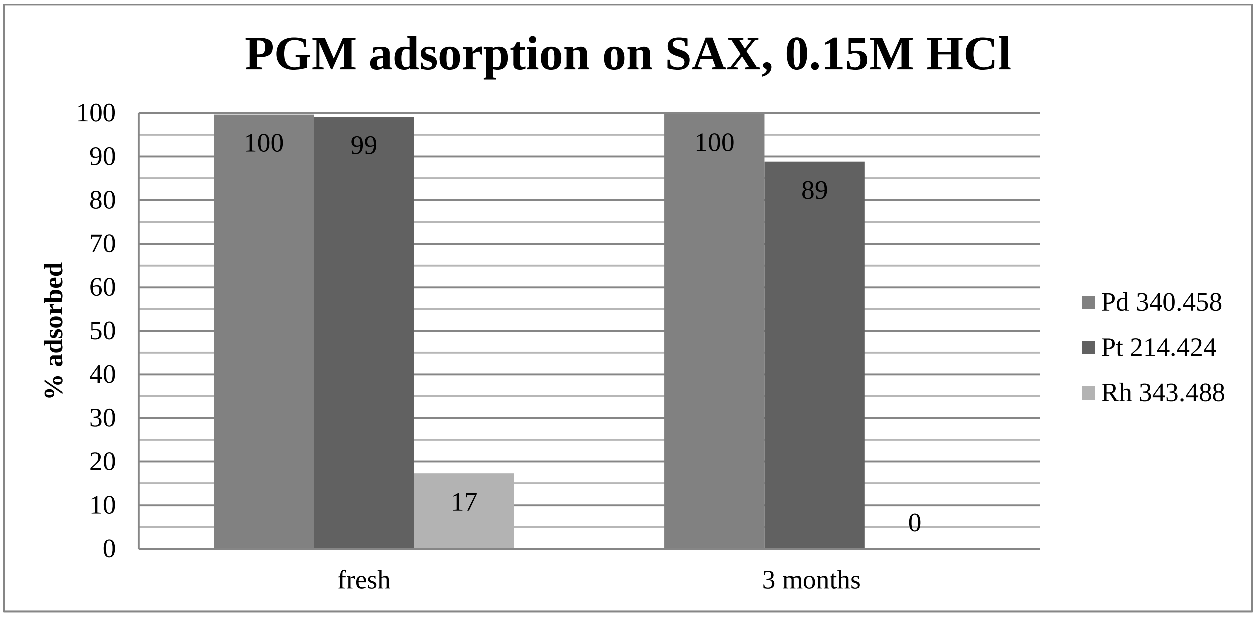

Figure 8 Differences in the adsorption of the PGMs between a fresh solution and a solution that had been stored over 3 months in ambient temperature (one replicate).

As seen in the figure, rhodium and platinum shows differences in adsorption depending on how long the solution has been stored. Platinum is completely retained in the fresh solution whereas approximately 10 % was found in the effluent from application of the aged solution. This may indicate an increased amount of hydrated platinum complexes over time, as these are more inert and therefore less readily adsorbed [7]. Rhodium shows a significant amount of retention in the fresh solution but not in the aged solution. This is also likely an indication that neutral chloro-aquo complexes of Rh form over time, while initially some $[RhCl_6]^{3-}$ may be present [25]. Palladium adsorption seems to be unaffected by the three months of storage when 0.15 M HCl is used as the matrix. This was also confirmed later in the separation scheme (see section 4.7).

4.2.2 Recovery

Several solutions were tested as eluents in order to check for specific desorption of the analytes. The eluent solutions tested consisted of HCl, HNO_3, H_2SO_4 and thiourea + HCl in different concentrations. The different solutions used and their concentrations can be seen in Table 13. Recovery percentage was calculated as described in the appendix, section 7.3. Figure 9 shows the recovery percentages for the different eluents. The amount of eluent was 10 mL unless otherwise stated and all samples were analysed by ICP-OES.

Table 13 The different eluent solutions tested to elute Pt and Pd from the SAX sorbent

Solution	Concentrations tested
HCl	0.5, 1, 3 and 6 M solutions. 1 M was tried with both 10 and 20 mL
HNO_3	0.5, 1, 3 and 6 M solutions.
H_2SO_4	Only 1 M was tested
TU + HCl	0.1 M TU + 1 M HCl, 3x5 mL, successively

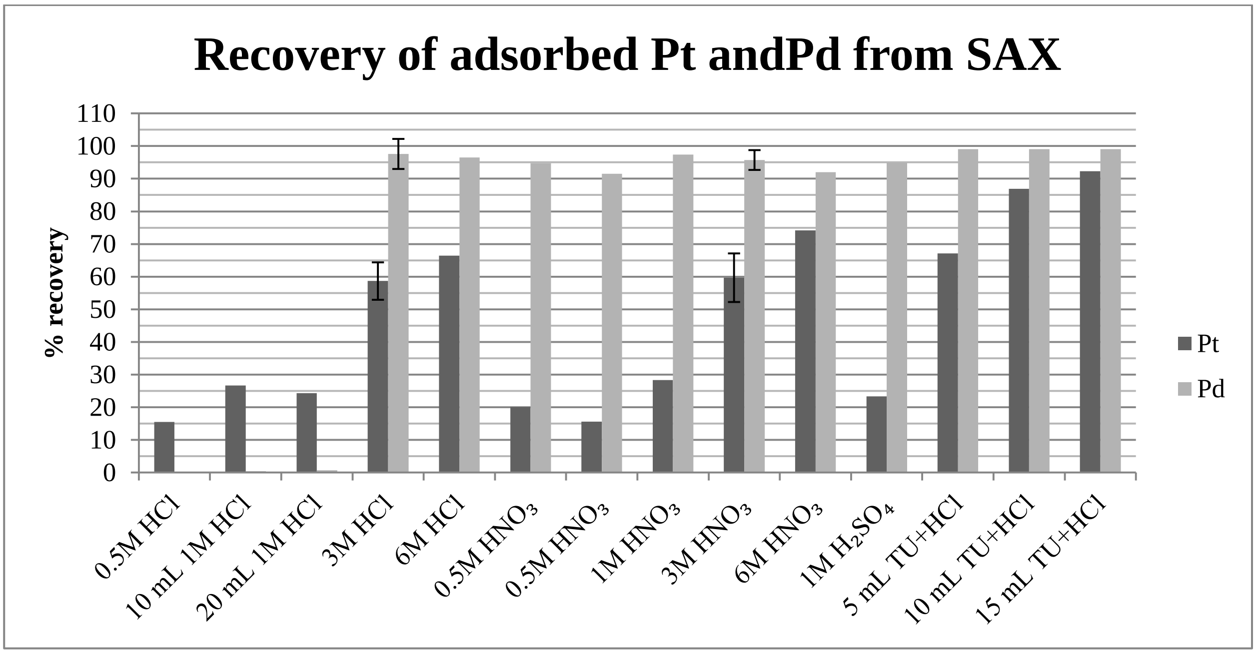

Figure 9 Recovery percentage of Pt and Pd on SAX with different eluents, relative to the amount adsorbed on the sorbent. The error bars in the 3 M solutions indicate the standard deviation for three replicates, while the rest of the results had one replicate each. 10 mL of eluent solution was used unless otherwise stated.

As can be seen, palladium was over 90 % recovered by all eluents except when using HCl concentration of 1 M or lower. This is in accordance with the results showing that Pd is quantitatively retained when using a feed solution of 1 M HCl. Platinum was recovered by various degrees in all solutions. In order to check if 10 mL was a sufficient volume to elute the retained Pt, 20 mL of 1 M HCl was tested as well. No practical difference in elution was seen for these two samples, which indicates that the eluted Pt is a specific species which is easier eluted than the rest of the adsorbed Pt. For the thiourea containing eluent, 3 x 5 mL of eluent was applied and collected successively and the cumulative recovery is shown by the 5, 10 and 15 mL bars. As thiourea is complex forming, it is likely that a slower flow rate could give increased recovery of Pt with a smaller volume of eluent solution. A higher concentration of thiourea in the eluent could also be of advantage. All the retained Pd was recovered in the first 5 mL of the thiourea-containing eluent, which can be likely explained by steric effects of the chlorocomplexes. As the Pt(II) complexes are square planar, their ligands are more easily exchanged than the ligands in the octahedral Pt(IV) complexes and thus more readily extracted by thiourea [29].

Additional tests were performed to try to quantitatively recover the retained Pt. Four different solutions of thiourea + HCl were tested as eluents, using combinations of 0.1 M and 0.5 M thiourea with 0.5 M HCl and 0.9 M HCl. The reason for choosing 0.9 M HCl instead of 1.0 M was because of easier pipetting of the concentrated HCl. After loading the cartridge with Pt, 3 x 5 mL of eluent was successively applied and collected and the recovered percentage can be seen in Figure 10. The samples were analysed on ICP-MS and diluted prior to analysis in order to get the theoretical maximum concentration of analytes down to an amount appropriate for the calibration solutions for the ICP-MS. This also assured that the TDS (of thiourea) was below the 0.2 % appropriate for introducing into the ICP-MS. The figure also shows the cumulative recovery for the three eluent fractions as the “total” bars.

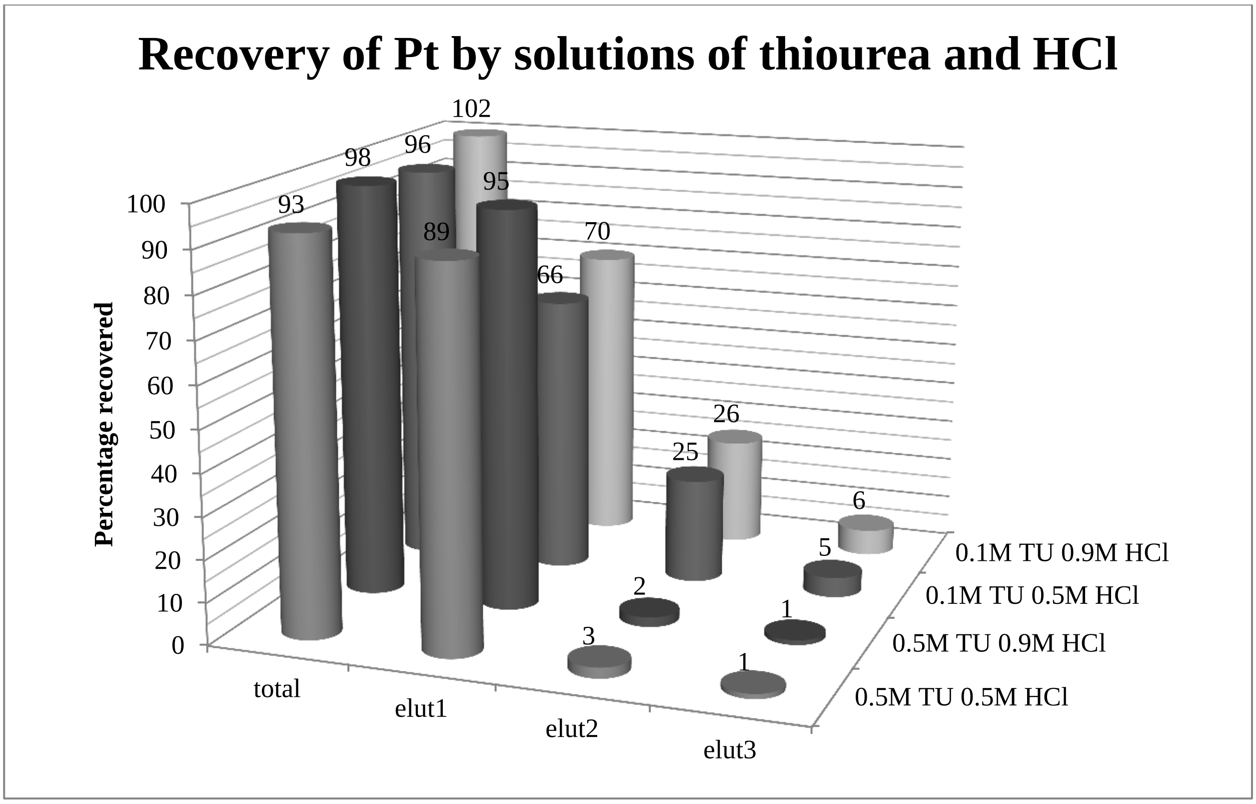

Figure 10 The recovery percentage of Pt adsobed to SAX sorbent, by solutions containing different amounts of thiourea (TU) and HCl. Each of the elution steps consisted of 5 mL of the eluent and the total shows the cumulative recovery for the 15 mL of eluent. One replicate was used for each thiourea solution.

As the figure shows, an increased amount of thiourea in the solution leads to a higher recovery of platinum in the first 5 mL fraction of the elution. The HCl concentration appears to be less important, although the total recovery seems to be slightly higher where the higher HCl concentration was used. This may well be within the experimental error, as only one sample replicate was made for each eluent solution.

4.2.3 Breakthrough

The breakthrough capacity is defined as the amount of metal ion that can be adsorbed per unit mass of solid before being detected in the outlet of the column. The breakthrough point is often set as when the effluent are showing 5 % of the initial concentration of elements, as it can be hard to detect very low concentrations. The breakthrough capacity is specific to the conditions used in the setup including, but not limited to, temperature, acidity of the solution, flow rate and presence of other ions in the sample [6, 25].

Breakthrough of a SAX cartridge was estimated by using 80 mL of a 50 µg mL^{-1} solution of Pd with 0.15 M HCl matrix. This feed solution was continuously applied to the SAX cartridge with a flow rate of 1 mL min^{-1}. Effluent samples were collected in 10 or 5 min fractions, corresponding to 10 or 5 mL of feed solution, respectively and collected in 25 or 10 mL volumetric flasks. The first samples were analysed directly on the ICP-OES, after only adding HCl to matrix match with the calibration solutions and dilution to the volume indicated by the volumetric flask. Extra diluted samples were made for the last four samples, in case the nondiluted samples had analyte concentrations which exceeded the calibration range (100 % recovery corresponds to 25 µg mL^{-1} concentration of analytes in the undiluted final sample when 5 mL was collected on 10 mL flasks). The molar amount of Pd applied to the cartridge was calculated and Figure 11 shows the amount of Pd found in the effluent samples, relative to the initial feed concentration.

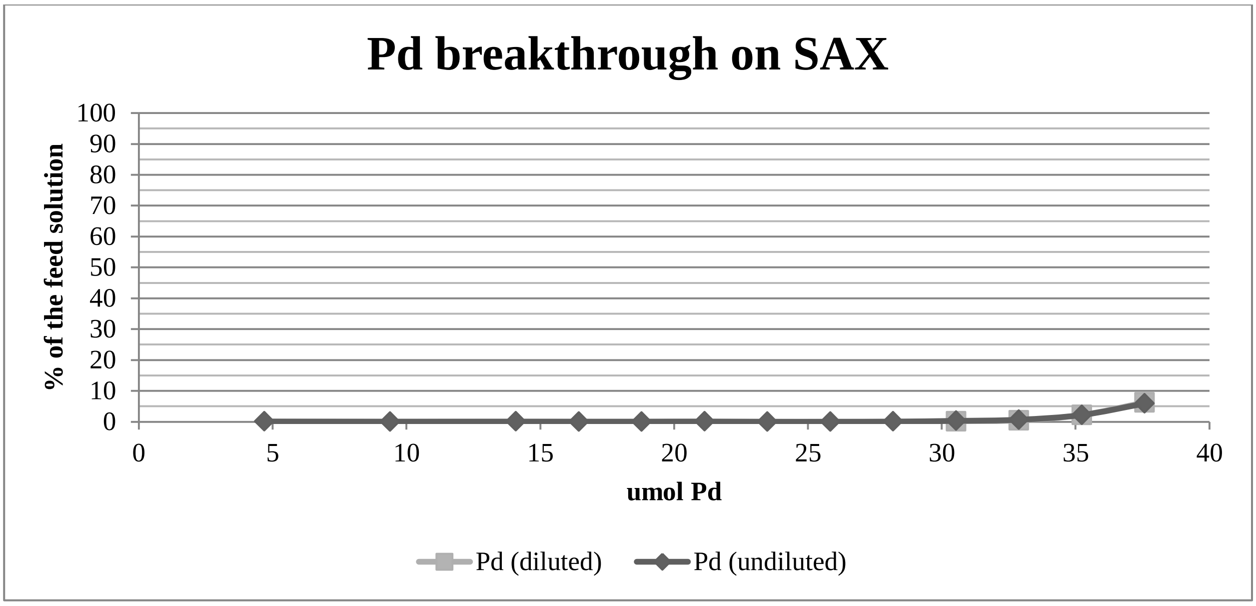

Figure 11 The relative concentration of Pd found in the effluent from a SAX cartridge. The samples marked as undiluted were analysed directly. Additionally, dilutions of the last four samples (10 times diluted) was made in case the undiluted samples had Pd concentrations above the calibration range of the ICP-OES.

Only palladium was tested for breakthrough on the SAX resin as the purpose of this experiment was to ensure that the resin is not overloaded with sample. Palladium is lighter and has a higher molarity per weight unit in the sample than platinum. Pd is also less retained than Pt by the SAX resin [25] and both are reasons for choosing Pd over Pt for the breakthrough test. The figure shows that approximately 35 µmol Pd can be applied to the cartridge without reaching 5 % breakthrough in the given conditions. This corresponds to 75 mL of a sample solution with Pd concentration of 50 μg mL^{-1} or a total of 70 μmol applied Pd per gram resin. Assuming the retained Pd is present as $[PdCl_4]^{2-}$, this is equivalent to a breakthrough capacity of 0.35 meq g^{-1} compared to the given total capacity of 0.7 – 0.9 meq g^{-1} of the SAX.

4.3 Strong cation exchange (SCX)

Cation exchange has been used for group separation in order to separate matrix elements and interferences from PGM solution containing HCl. The anionic PGM chloro complexes will flow freely through the cation exchanger while most contaminant metals are present as cations and will be adsorbed to the resin. This type of group separation will remove many of the potential interferences for the ICP-OES and ICP-MS. The adsorption efficiency is dependent on the amount of HCl in the solution. Too low concentration will limit the formation of PGM chloro complexes and too high concentration will limit the adsorption of the matrix elements. Several studies have used an HCl concentration of approximately 0.5 M HCl [38, 42, 43, 48].

4.3.1 Adsorption

The adsorption of of elements on SCX was investigated using five 5 μg mL^{-1} multielement feed solutions of differing age and HCl concentration. 10 mL of the feed solutions was applied to the SCX syringe barrels while collecting the effluent. The same amount of H_2O was then applied as a wash step and collected in order to remove any residual elements. Reference samples were also collected from each feed solution and all samples were finally analysed by ICP-OES. The amount of analytes in the effluent and in the wash step were added up and used as the $[M]_{effluent}$ from the equations seen in the appendix (7.3). The adsorbed percentage of each of the elements can be seen in Figure 12 and instrumental standard deviations are noted by the error bars. There were a few notable differences between the analyte compositions of the different feed solutions. The 216 days old feed solution did not contain Zn, as this element was not included in the first multielement trial experiments in which the feed solution was initially prepared for. The fresh
1 M HCl solution did not contain PGMs due to analyst error. However, since the PGMs are not adsorbed on the cation exchange resin in lower acidic samples it is not likely that it would adsorb in a solution with a higher HCl concentration.

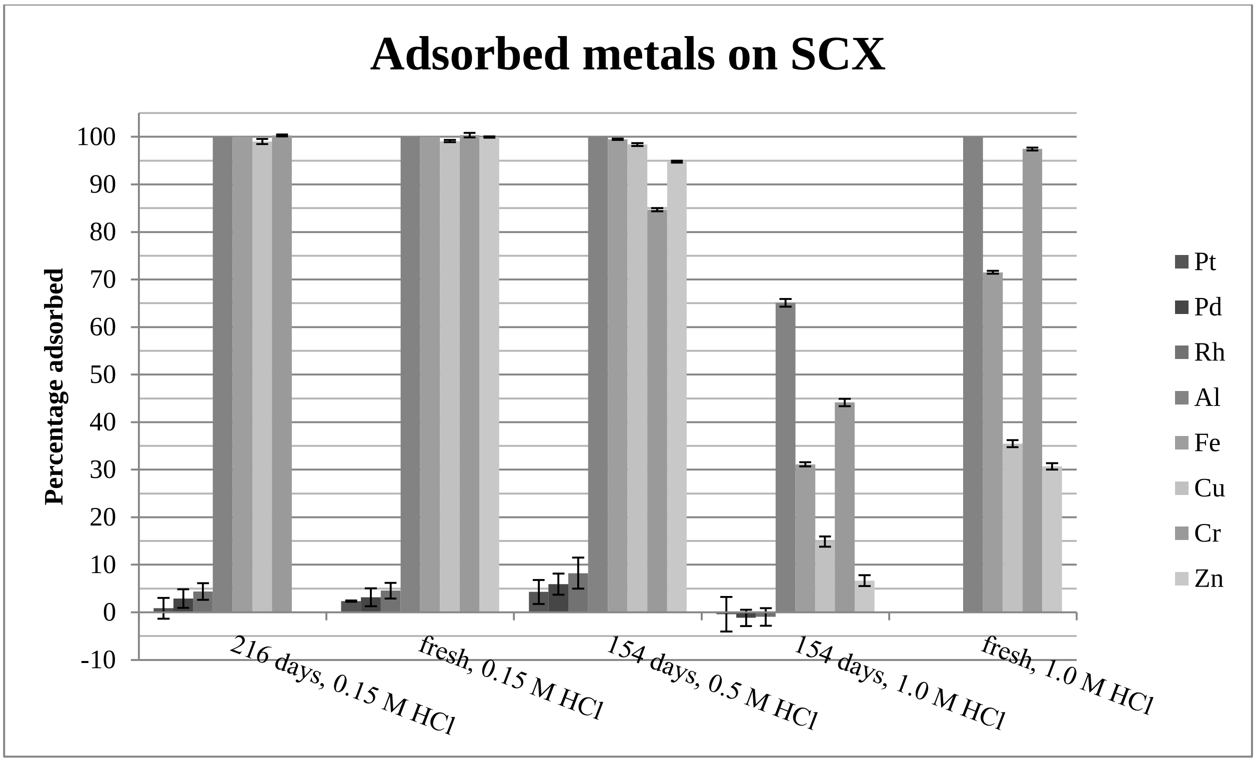

Figure 12 Adsorbed percentage of the metals on a cation exchange resin. The different feed solutions vary both by age and HCl concentration and each result is found after analyzing the effluent and the wash solution. The error bars show the instrumental standard deviation (three instrumental replicates).

As seen in the figure, a small amount of PGMs appears to be adsorbed to the SCX sorbent when using ≤ 0.5 M HCl in the feed solution. The fresh solution and the 216 days old solution show that age is insignificant for SCX adsorption when this low HCl concentration is used. Only one replicate was used for each feed solution, so the small adsorption of PGMs may be within the analytical uncertainty, which is further indicated by the error bars showing the instrumental uncertainty. The figure does, however, show that the effect of acidity and age on the adsorption of base metals is important. With higher acidity in the feed solution, less matrix elements are adsorbed, which is consistent with the increased elution strength of the solution. This effect can be seen for Cr and Zn on the 0.5 M HCl feed solution while Al, Fe and Cu are still practically quantitatively adsorbed. For the 1 M HCl solutions however, adsorption is supressed by the additional ions in solution. For this acid strength, the ageing effect is also obvious and much less base metals are adsorbed from the old solution than the fresh one. In order to ensure quantitative adsorption of the base metals, 0.15 M HCl was used as the standard solution matrix, although the literature shows that acidic solutions up to 0.6 M HCl have been successfully used for adsorption of base metals on SCX [48].

4.3.2 Recovery

The base metals can be easily eluted from the SCX cartridge by high concentration of HCl. As indicated by the reduced amount of base metals adsorbed by the SCX cartridge when using 1 M HCl as the feed solution, a large amount of the metals should be eluted even by 1 M HCl. In order to quantitatively elute and clean the sorbent for reuse, 100 – 300 mL of 4 – 6 M HCl have been used in the literature, although a higher amount of sorbent (3.5 g) was also used in one of these cases [38, 48]. Figure 13 shows the recovered amount of base metals from the SCX resin, using 10 mL of 1 M HCl for elution. Although the previous section showed that a good portion of the base metals is adsorbed to the resin when 1 M HCl is used as the feed solution matrix, most of the elements are practically quantitatively eluted by the 10 mL of 1 M HCl eluent solution. Elution recovery of Fe and Cu was later shown to be quantitative when using 5 mL 3 M HCl (see section 4.8).

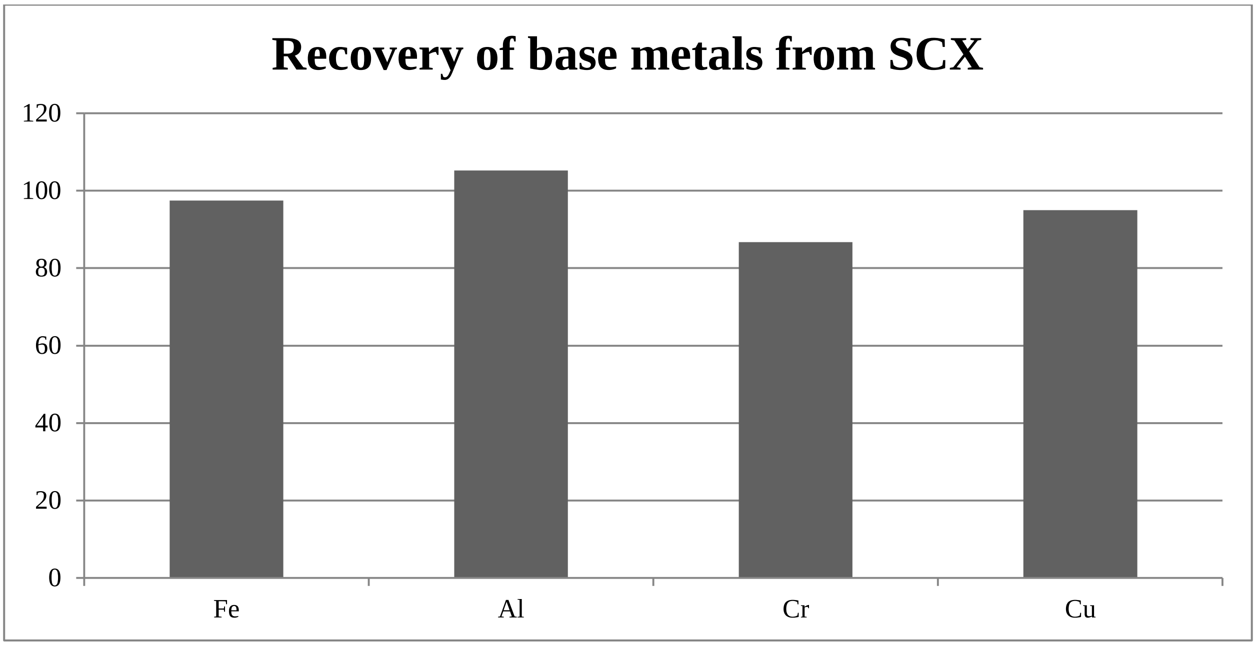

Figure 13 Recovery of base metals from SCX resin, using 10 mL of 1 M HCl for elution. Only one replicate was used and the sample was analysed on ICP-OES.

4.3.3 Breakthrough

4.3.3.1 Multielement

The breakthrough capacity of the SCX cartridges was initially investigated by continuously applying a multielement solution containing Fe, Al, Cu, Cr and Zn (20 µg mL^{-1} of each element, in 0.15 M HCl) onto a SCX cartridge using 1 mL min^{-1} flow rate and collecting every 5 mL of the effluent in volumetric flasks with the help of a stop watch. After matrix matching and dilution to the volume indicated by the volumetric flasks, the samples were analysed by ICP-OES. The breakthrough curves for the elements is seen in Figure 14. As can be seen, there is a breakthrough around 25 mL of introduced sample (2.5 mg total metals).

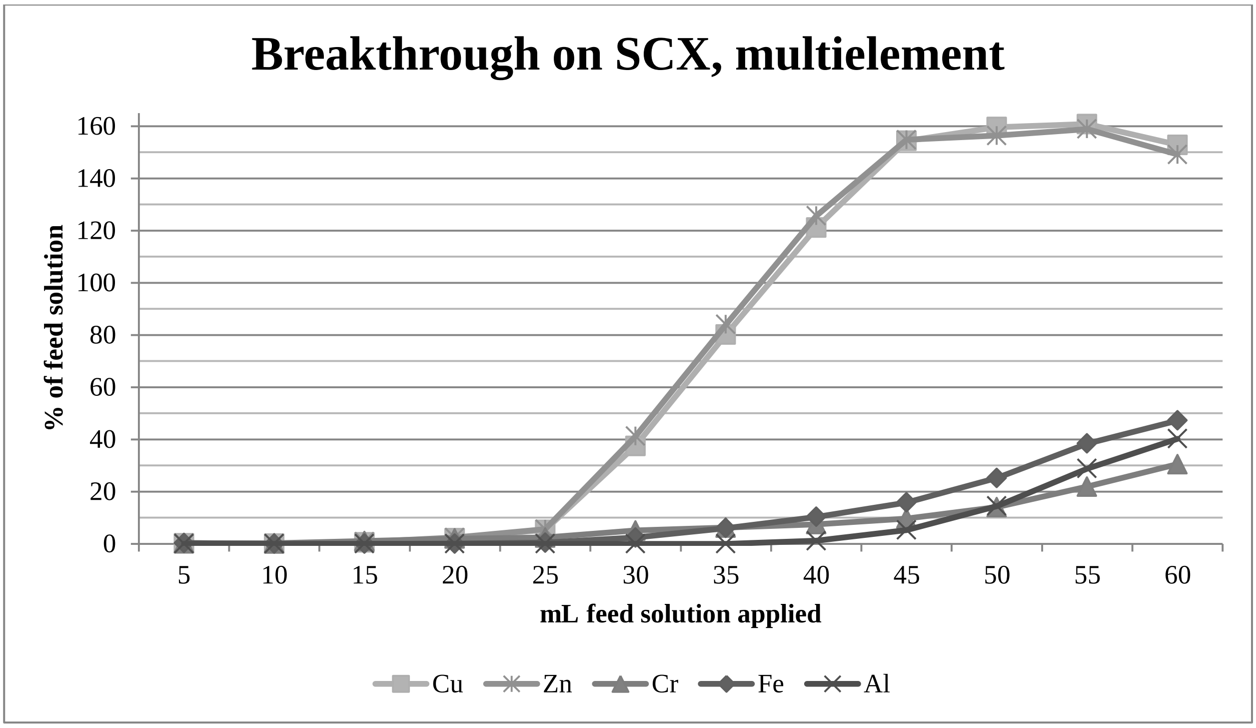

Figure 14 Multielement breakthrough curves of the base metals on 500 SCX sorbent, showing the percentage of elements found in the effluent compared to the feed solution composition.

For the samples 40 mL – 60 mL, the recovery of Cu and Zn is above 100 %. This means that a higher concentration of the elements was found in the effluent than in the feed solution. These two elements are most commonly found as divalent ions while Cr, Fe and Al are commonly trivalent, and as the affinity of an ion towards an ion exchange resin generally increase with its charge [52], it is likely that previously retained Cu and Zn are exchanged with the trivalent ions of higher resin affinity. This means that the adsorbed ions are eluted while a constant amount of elements is still applied on the SPE, resulting in a recovery above 100 %. An estimation of the breakthrough capacity was made using the assumption that Cu and Zn are divalent while Cr, Fe and Al are trivalent. The calculated capacity of the SCX cartridge was then found to be 0.28 meq g^{-1}. The amount of elements adsorbed to the cartridge at 25 mL is approximately 53 µmol.

4.3.3.2 Aluminium

For further investigation on the breakthrough capacity, a solution containing 50 µg mL^{-1} aluminum in 0.15 M HCl was made and applied to a new SCX cartridge using the same method as previously described. Every 5 mL was collected and analysed by ICP-OES. Figure 15 shows the relative amount of aluminium in the effluent, compared to the feed concentration. The breakthrough point seems to be around 1.5 mg Al, which corresponds to approximately 55 µmol applied Al. The molar amount is comparable to what was found around the breakthrough point of the multielement solution. The calculated capacity from 55 µmol aluminium is 0.33 meq g^{-1} and the total capacity given for the SCX cartridge is 1 meq g^{-1}. The total capacity is a measure of the number of ion exchange sites in the resin, but in practice, the analytes will start to bleed through before the resin is fully loaded. This is due to the lower number of active sites available as more of the active sites are occupied by the analytes.

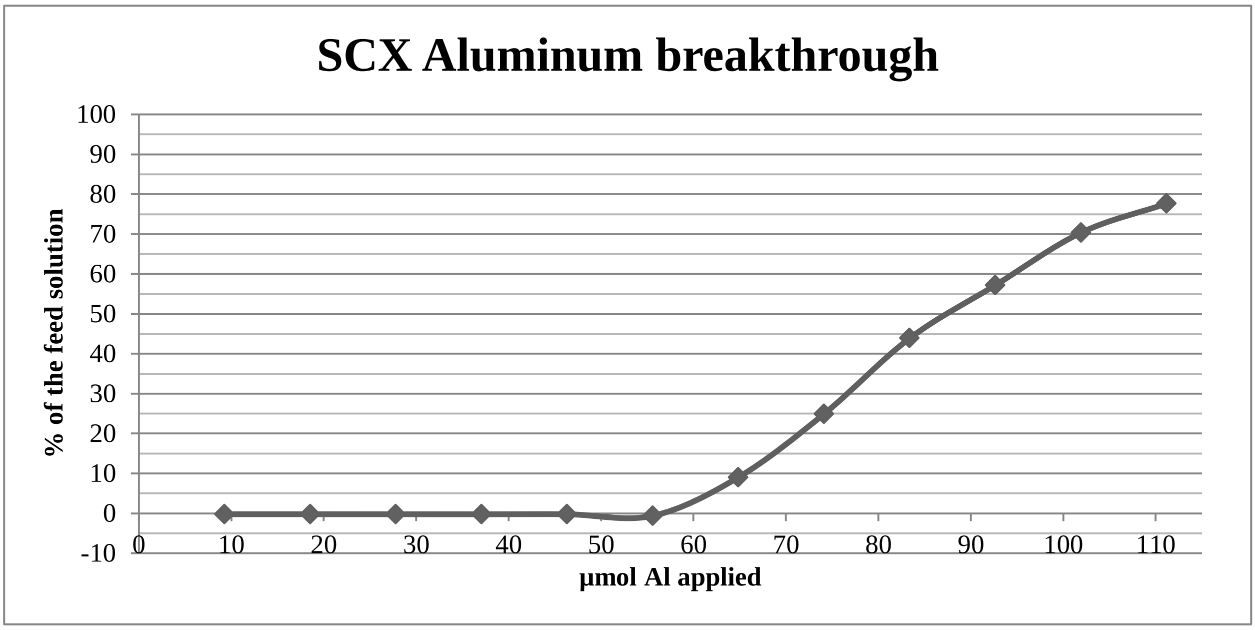

Figure 15 Breakthrough curve of Al on a 500 mg SCX cartridge, showing the percentage of Al in effluent compared to the feed solution.

4.4 Cyano (CN) sorbent

The commercially available CN SPE has recently been shown to be able to selectively adsorb Pd and Au from hydrochloric solutions. This was explained by the hard and soft acids and bases theory [53]. Both Pd(II) and Au(III) have a low oxidation state and belong to the “soft acids” which has a strong affinity towards “soft base” donor atoms, including both C and N. While Au is readily adsorbed to the CN resin even from highly acidic media (up to 5 M HCl), Pd was only shown to be quantitatively adsorbed when the hydrochloric acid concentration is less than 0.15 M [29].

4.4.1 Adsorption

Adsorption was investigated by applying 5 mL of a 5 µg mL^{-1} multielement feed solution (with 0.15 M HCl) on a conditioned CN cartridge with a flow rate of 1 mL min^{-1}. The effluent was collected on volumetric flasks before 5 mL of water was applied as a wash fraction and collected separately. A reference sample was also made, in order to calculate the relative amount of analytes adsorbed to the resin. The experiment was done in triplicate and the obtained samples were analysed by ICP-OES. Figure 16 shows the relative amount of elements adsorbed to the sorbent before and after the wash step.

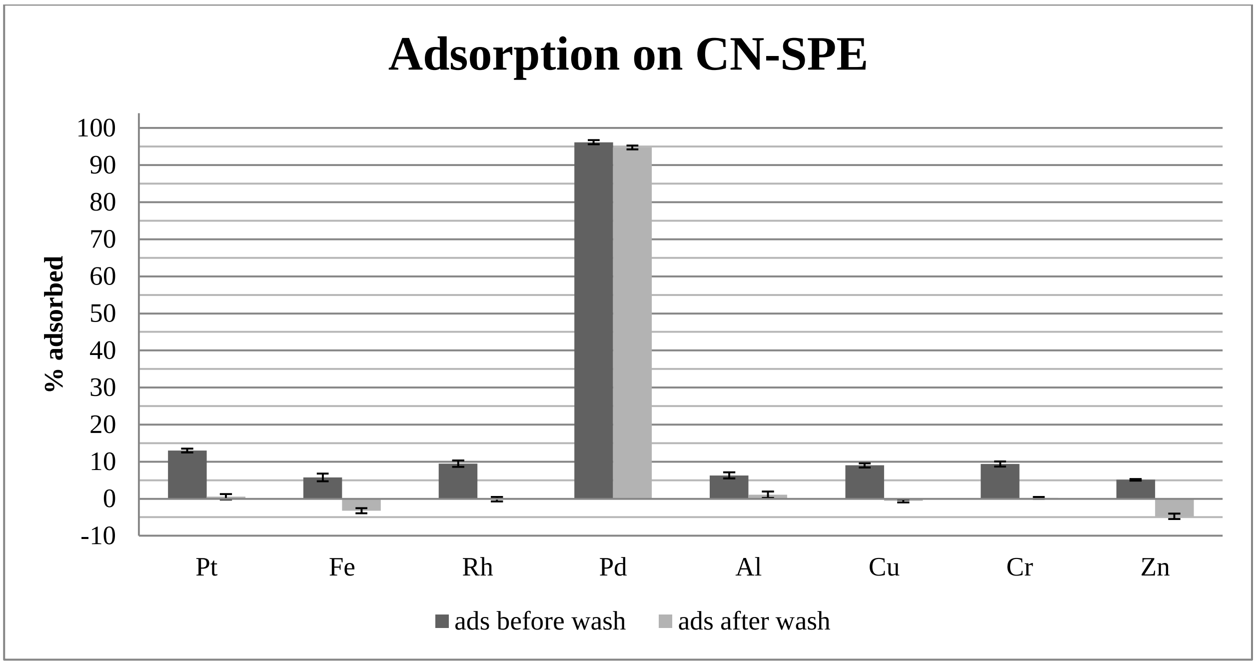

Figure 16 The adsorbed percentage of the analytes on 500 mg CN resin from a 0.15 M HCl multielement solution, before and after a 5 mL wash with H_2O. The error bars shows the standard deviation for 3 sample replicates.

The figure shows that palladium is the only analyte adsorbed by the CN SPE after the 5 mL wash step. Although Pd is not quantitatively retained (approximately 5 % was found in the effluent), this was consistent with previous findings. A lower flow rate has been found to be advantageous for obtaining a quantitative adsorption of Pd on this type of sorbent [29]. A small part (5 – 10 %) of the other elements is adsorbed on the cartridge after the initial sample application. This is likely due to some sample being retained in the pore volumes of the resin and shows the importance of including a wash step in the SPE procedure. The wash solution will flush out the remaining part of the initial feed solution from the cartridge and remove the last traces of the matrix elements without sorbent interaction.

4.4.2 Recovery

For the elution study, three CN cartridges loaded with Pd (from the previous section) was treated with three different eluent solutions. The solutions consisted of 3 and 6 M HCl in addition to a solution of 1 M HCl + 0.1 M thiourea. Only 5 mL of the HCl solutions were used for elution of Pd, in order to avoid having samples with a higher HCl concentration than the calibration solutions. The recommended elution volume for these silica based CN sorbents is 6 mL (8 bed volumes) so 5 mL of eluent solution should therefore be a large enough volume for complete desorption [54]. For the thiourea containing solution, 10 mL was used as the eluent in order to ensure as good an elution as possible. The recovered amount of palladium by the three elution solutions can be seen in Figure 17. All three eluents elute over 85 % of the adsorbed Pd although only the thiourea containing solution gave a quantitative elution. A lower flow rate or the use of larger volumes of eluent may give a more quantitative recovery.

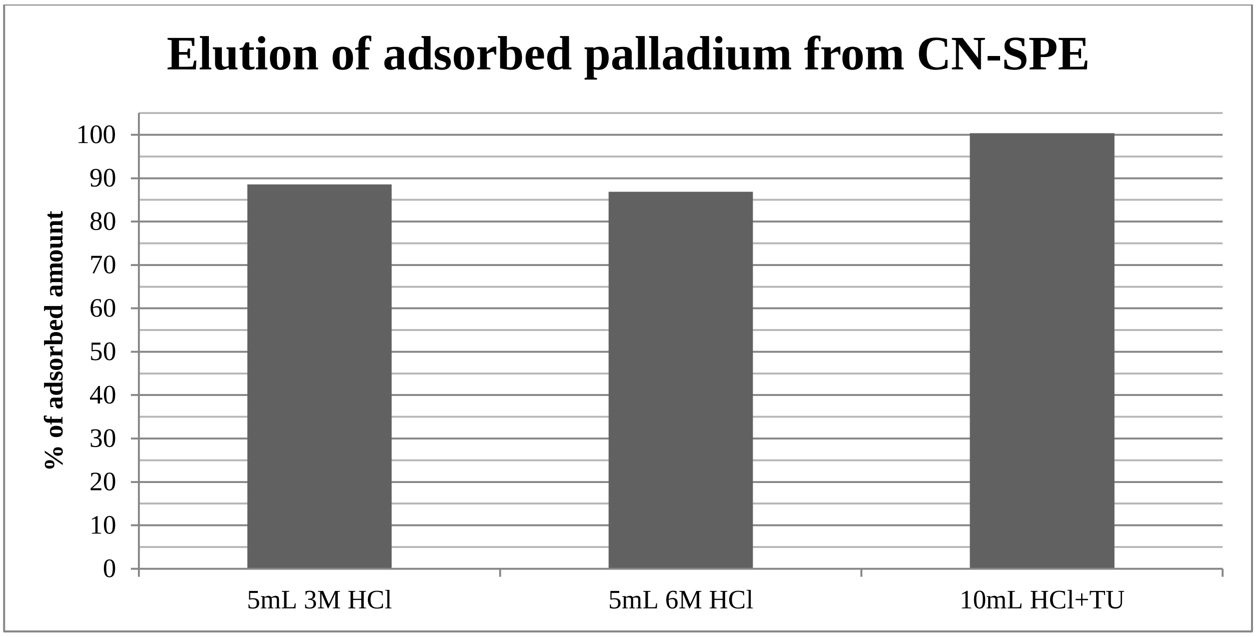

Figure 17 Recovery of adsorbed Pd from 500 mg CN sorbent, using 3 M HCl, 6 M HCl and 1 M HCl + 0.1 M thiourea as eluents (one replicate each).

4.4.3 Breakthrough

Breakthrough of palladium on the CN cartridges was tested several times with different conditions. Initially, it was tested whether the cartridge had a higher capacity if it was conditioned with methanol instead of water. After conditioning with approximately 10 mL of either methanol or water, volumes of 5 mL feed solution consisting of 2 µg mL^{-1} Pd in 0.15 M HCl was successively applied to the cartridges and collected on volumetric flasks at a flow rate of 1 mL min^{-1}. After adding appropriate amount of HCl and diluting to the mark indicated by the volumetric flask, the samples were analysed on the ICP-OES. These two sample collections can be seen as the “methanol-cond.” and “water-cond. 1” curves in Figure 18. In case the use of non-continuous sample application caused Pd to elute early, a continuous sample application was also tested (with water as conditioning), using the same concentration of feed solution and flow rate. These samples were collected by changing the collecting volumetric flask every 5 min, before dilution and being analysed as previously described. The results from this experiment can be seen as the “water-cond. 2” curve. In all the three experiments, the amount of Pd in the effluent reached 20 – 40 % of feed solution within the first 10 mL of applied feed solution. One last experiment was then done, collecting each 2 mL fraction. These samples were analysed on the ICP-MS due to their low maximum Pd concentration. Results from this can be seen as the “water-cond. ICP-MS” curve.

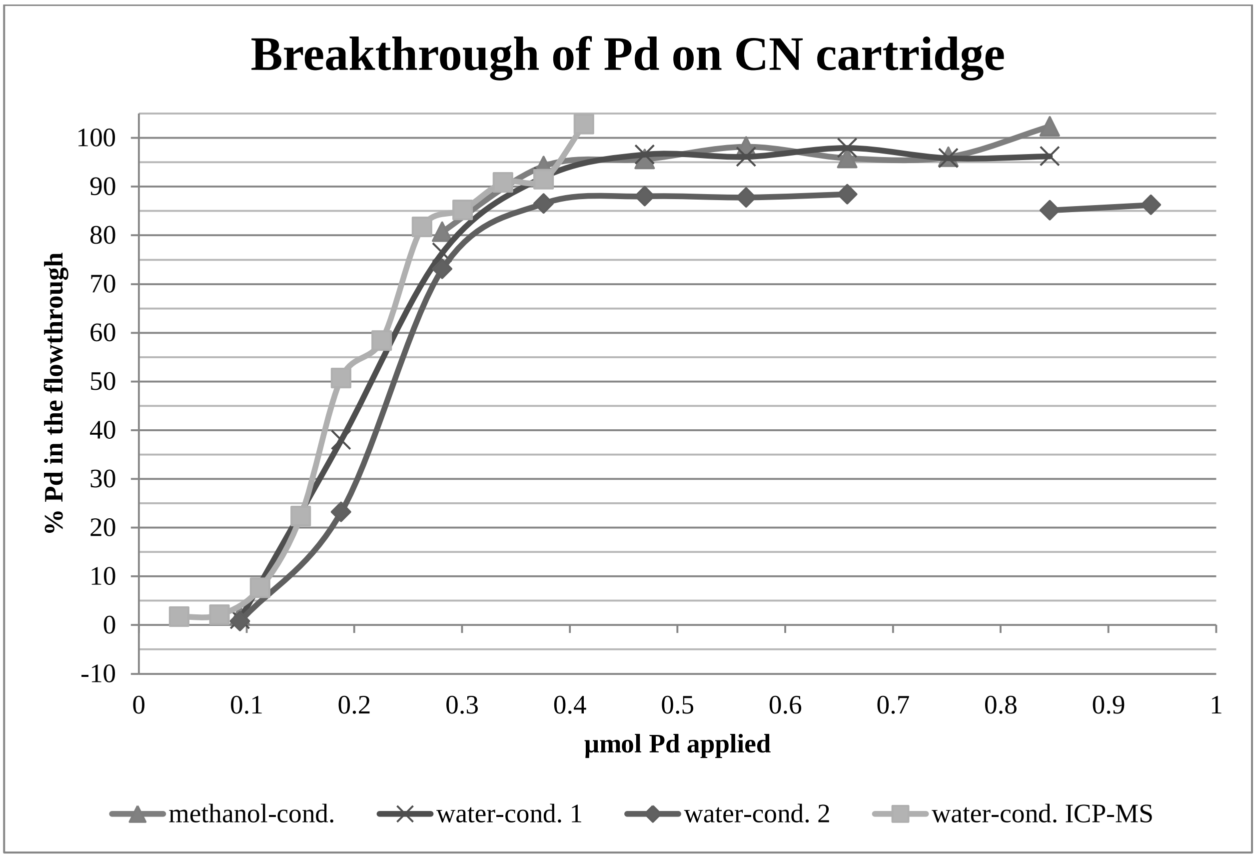

Figure 18 Breakthrough curves of Pd on 500 mg CN resin. Four different experiments was done, all using a flow rate of 1 mL min^{-1} and a feed solution of 2 µg mL^{-1} Pd. Samples were analysed by ICP-OES or ICP-MS.

One point of the “water-cond. 2” curve has been removed due to it showing a lower relative concentration of Pd (~70 %) than the previous and later sample. The lower amount of Pd was likely due to a mishap with the timer as it got turned off by accident and an educated guess had to be taken as to when to stop the collection and move on to the next sample.

For the methanol-conditioned sample and the first water-conditioned sample, the percentage of recovery was calculated using reference solutions from their respective feed solutions. For the last two sample collections, a reference solution was not made, and the relative recovery was calculated by using the theoretical concentration of the feed solution. This may be a reason for why the “water-cond. 2” curve flattens off at 90 % recovery instead of 100 %, as the feed solution may have a slightly lower concentration than the theoretical concentration. This is not unlikely, as it was prepared using only 200 µL of a 1000 µg mL^{-1} stock solution.

The “water-cond. ICP-MS” curve is uneven, which can likely be explained by the low effluent volume collected in each sample, as small inaccuracies in the timing of collection will have a larger influence on the final concentration.

The four experiments show that CN resin does not seem to have a large capacity for Pd when using large volumes of sample application. This indicates that this resin is not suited for preconcentration of Pd from large volumes containing a low concentration of Pd. Higher capacity has, however, been found with the use of a higher concentration of Pd in the feed solution so although the resin seems to be unsuitable for preconcentration, it may be of use for isolating Pd from other PGMs in an industrial scale [29].

4.5 Dioctyl sulphide (DOS) impregnated reverse phase (RP)

Dioctyl sulphide and other thioethers have previously been used to extract Pd from hydrochloric solutions. DOS is a coordination extractant, as it only has one sulphur atom that can form complexes with the metal. Previously, it has been used in LLE, to extract Pd from an aqueous phase to an organic phase in the form of $[PdCl_{2(}R_2S)_2]$ where the rate limiting step is the reaction of $PdCl_3(H_2O)^-$ with R_2S [55]. In this work, DOS have been immobilized on a reverse phase sorbent as described in section 2.2 and is based on work by a previous master student in our group [34].

4.5.1 Adsorption

For the adsorption studies, 5 mL of a 5 μg mL^{-1} multielement feed solution (in 0.15 M HCl) was applied to the modified resin while collecting the effluent as samples. 10 mL water was then applied to the cartridges and the effluent was collected separately as “wash”. This was done in triplicate and analysed on the ICP-OES. A reference solution was made from the feed solution, and the concentration of elements in this solution was used as the $[M]_{feed}$ to calculate the relative amount of elements found in the effluent and wash fractions. In addition to the three replicates mentioned, a fourth replicate was collected at a later time (for the elution studies). Figure 19 shows the relative amount of elements adsorbed to the resin after the sample application and after the wash step. The error bars indicate the standard deviation of the four replicates, except for Zn, where one of the replicates was removed due to it being an outlier according to Grubb's test for outliers [51]. Calculation of G the statistics can be seen in the appendix, section 7.4.3.2.

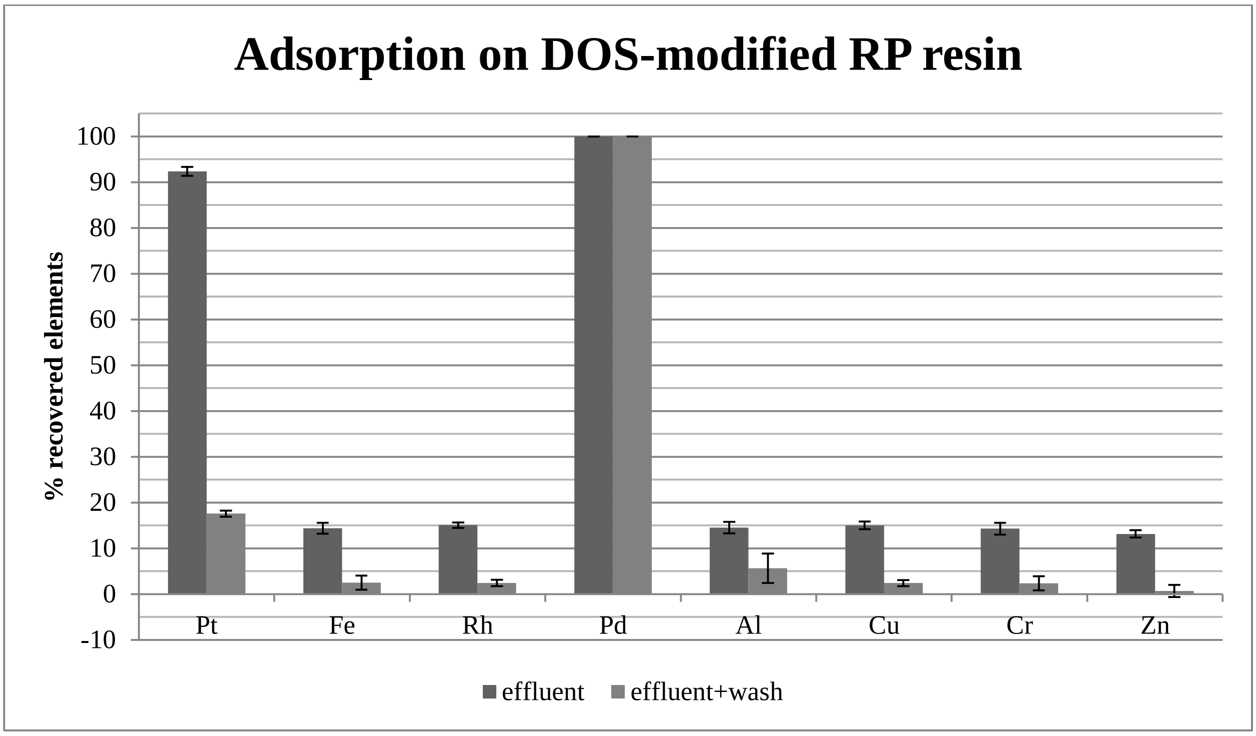

Figure 19 The relative amount of elements adsorbed on a RP resin modified with 0.65 mmol DOS before and after a wash step. The error bars show the standard deviation for four replicates, except for Zn which uses three replicates due to an outlier having been removed.

It can be seen from the figure that palladium is completely retained on the resin and the measured amount of Pd in the effluent samples was below the LOD of the method. Platinum is over 90 % retained during the sample application although the adsorbed amount is eluted to a large degree by water in the wash step. Approximately 18% of Pt is still adsorbed to the cartridge after the wash step. The adsorbed Pt and Pd may be in the form of square planar $[MCl_4]^{2-}$ complexes. These will undergo ligand substitution easier than the octahedral $[MCl_6]^{2-}$ which has more sterical hindrance [13]. Additionally, Pt(IV) has less affinity for the sulphur atom as it not as soft as Pt(II) according to the hard and soft acids and bases theory [44]. It is also known that interaction of the PGM chlorocomplexes with complexing sorbents is kinetically hindered at room temperature, with the exception of Pd(II) complexes [21]. More Pt could possibly be adsorbed if the flow rate was decreased, as the Pt chlorocomplexes would have more time to interact with the sorbent. The rest of the analytes are less than 6 % retained on the resin after the wash step.

4.5.2 Recovery

For recovery of the adsorbed palladium, six different eluents was tested. This was 99.8% methanol, 6 M HCl, 1 M HCl + 0.1 M thiourea, 1, 3 and 5 % NH_3. The methanol was tested because it has high elution strength for reverse phase sorbents. The idea was that it might elute the $[PdCl_{4-n}(R_2S)_n]$ complexes adsorbed to the RP resin. 6 M HCl was tested because it has a high elution strength for ion exchange sorbents, in addition to the complexing abilities of the Cl^- ions towards the PGMs. The thiourea containing solution was tested due to thiourea being a very good complexing agent for the PGMs, as previously described. Finally, NH_3 was tested in three different concentrations, as ammonia has been used in the industry to remove Pd from n-alkyl sulphides in liquid-liquid extraction [35].

After loading the cartridges with the feed solution as described in the adsorption study, 5 mL (10 mL for HCl + TU) eluent solution was applied to the cartridge and effluent was collected in volumetric flasks. When 5 mL eluent was used, another 5 mL of water was applied and collected together with the eluted fraction in order to ensure that all possible elements were eluted. This was done because 5 mL is the practical minimum elution volume for 500 mg polymer based sorbents [54].

The relative recovered amount of Pt and Pd can be seen in Figure 20. The Pt elution is the recovery relative to the adsorbed amount, while the Pt tot recovery shows the total amount of Pt accounted for in the effluent, wash and eluent step, relative to the amount in the feed solution. As Pd was quantitatively adsorbed, only the relative elution is shown. Only one replicate was collected for each eluent, which were applied to the loaded SPE syringe barrels used in the adsorption study.

It seems as the thiourea solution is most efficient in eluting both Pt and Pd from the modified RP resin. Ethanol and 6 M HCl does not elute any Pd and the recovered amount in the samples was < LOD of the ICP-OES when using these two eluents. Ammonia elutes up to approximately 45 % of the retained Pd. Both thiourea and ammonia contain “soft base” donor atoms (S and N, respectively), which can form complexes with Pd(II) and Pt(II). The affinity for the sulphur atom is higher than for nitrogen, which can explain the higher elution percentage by using the thiourea-containing solution compared to ammonia. A lower flow rate and higher concentration of complexing agent in the eluent may cause increased recovery. The similar result of 3 % and 5 % NH_3 on Pd seems to indicate that recovery is not very dependent on the NH_3 concentration.

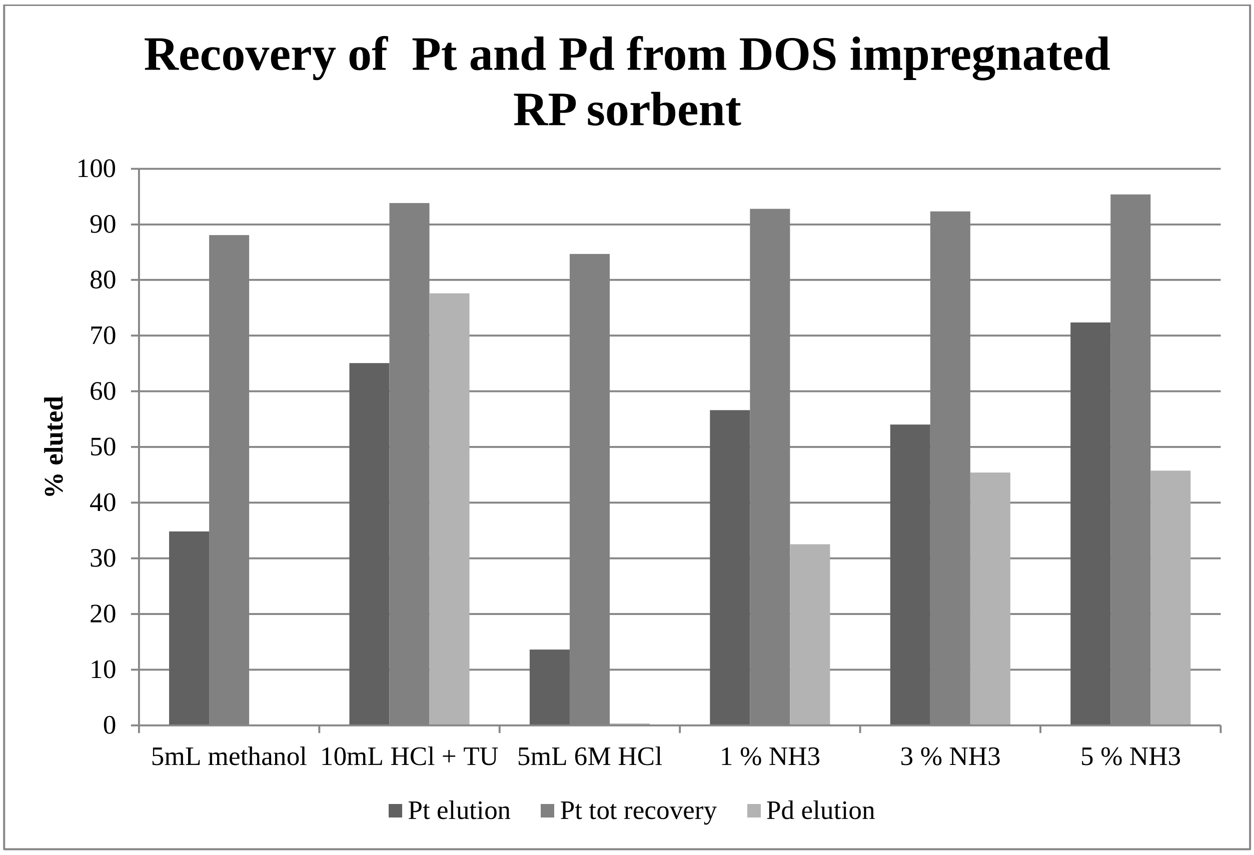

Figure 20 Recovery of Pt and Pd from DOS impregnated RP sorbent by different eluent solutions. Pt total recovery accounts for the Pt recovered in the effluent and wash solutions in addition to the eluted amount. Pd total recovery was not included as this would be identical to the Pd elution. One replicate was made for each eluent solution.

4.5.3 Breakthrough

4.5.3.1 Multielement

The first experiment on the breakthrough of a DOS-modified RP SPE used the same feed solution as in the adsorption study; 5 µg mL^{-1} multielement standard of all analytes in 0.15 M HCl. 5 mL equivalents of the 5 µg mL^{-1} feed solution was applied successively until a total of 40 mL had been applied and each 5 mL effluent was collected in volumetric flasks and analysed using ICP-OES after matrix matching with concentrated HCl and dilution to the indicated volume. A reference sample was also obtained from the feed solution. Figure 21 shows the relative amount of elements recovered in each sample solution. It is seen that palladium has no breakthrough within the 40 mL applied. This corresponds to 200 µg (or approximately 2 µmol) Pd having been applied. Platinum seems to have some interaction with the modified SPE, although quantitative retention is not obtained. The rest of the elements are not retained by the modified resin.

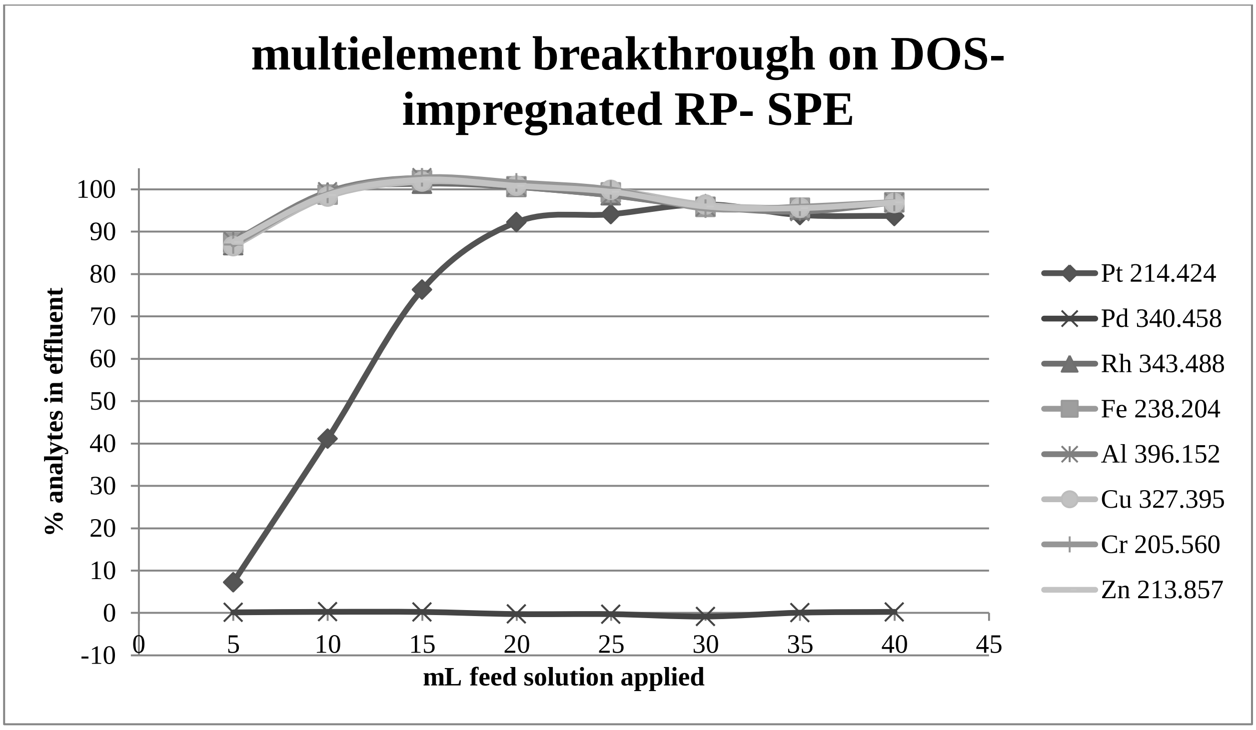

Figure 21 Breakthrough curves of a multielement solution on a RP resin modified with 0.65 mmol DOS. Samples were analyzed on ICP-OES and the wavelengths can be seen in the legend.

4.5.3.2 Palladium

The breakthrough was also tested using a single element solution containing 50 µg mL^{-1} Pd (Replicate 1) and a solution containing 100 µg mL^{-1} Pd (Replicate 2), both in 0.15 M HCl. The feed solutions were applied and collected as described for the multielement solution and reference samples was collected from both feed solutions to obtain the relative amount of Pd in the effluent. Figure 22 shows the breakthrough curves found from the two replicates.

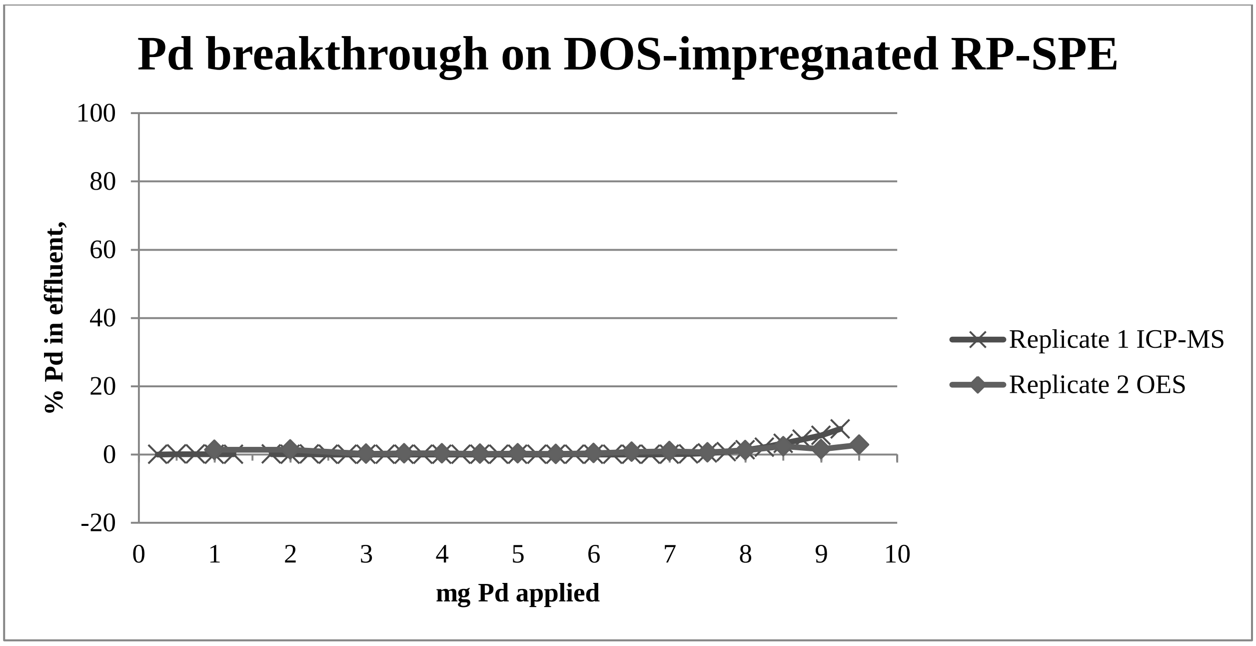

Figure 22 Breakthrough curves of two solutions of different Pd concentration on a RP resin modified with 0.65 mmol DOS. One of the sample groups were analyzed on the ICP-OES and the other on ICP-MS.

For Replicate 1, most of the samples were measured without additional dilution, as the amount of Pd found in the samples was within the 0 – 100 ng mL^{-1} calibration curve of the ICP-MS (100 % recovery would give a Pd concentration of 25 µg mL^{-1}). When it was seen that the Pd concentration started to rise, the last samples was diluted in order to keep the concentration within the calibration range.

For Replicate 2, the undiluted samples were measured by ICP-OES. They showed a higher concentration of Pd in the effluent than the samples from Replicate 1 (> 100 ng mL^{-1}) which is likely due to the feed solution having a higher concentration while the flow rate was kept constant. As the figure shows, the relative amount of Pd in the samples of the two replicates are quite consistent and the modified SPE seems to have a quite high capacity for Pd. Breakthrough are not seen until at least 9 mg Pd have been applied. This corresponds to approximately 85 µmol Pd applied on 500 mg resin modified with 0.65 mmol DOS.

4.6 Chromatography (LC-ICP-MS)

In order to see if an on-line separation of the PGMs could be accomplished, it was tried using a SAX analytical column coupled to the ICP-MS as described in the method development section. Initially a mobile phase gradient of 0 – 1 M HCl was used in order to compare the results with what had been previously done in our group [34]. A measurement of the base metals showed that with increasing HCl concentration, relatively large amounts of these elements was introduced into the ICP-MS while the PGMs did not seem to be eluted. As the system was not converted to an inert system at that time, the experiment was put on hold until the inert system was implemented.

After the inert system was in place, the method described in the method development (section 1.3.3) was tested, using a maximum concentration of 2 M HCl in the mobile phase. The flow rate was set to 0.5 mL min^{-1} after experiencing problems with one of the couplings inside the autosampler due to high pressure when using 1 mL min^{-1}. The 0.5 mL min^{-1} flow rate also corresponds better with the normal flow rate of the ICP-MS in which the instrument is optimized with in the daily performance. During the pump program, the MP was left at 2 M HCl for 18 minutes in order to minimize memory effects from retained PGMs.

10 µL of a blank sample consisting of 0.15 M HCl was introduced via the autosampler in three separate runs and it could be seen that the background of Pt decreased for each time. Even after the three runs which amount to approximately one hour of rinsing with 2 M HCl, there still seemed to be Pt eluted in wide peaks as the background. This can likely be explained by the fact that the column was used by the previous master student, who introduced relatively large amounts of PGMs (10 µg mL^{-1} solution) into the column while using a gradient elution of 0.01 – 1 M HCl, seemingly without obtaining any elution peaks [34]. Rh and Pd also showed a reduction of the background over the runs of the three blank samples.

Despite the apparent problems with the column, it was decided to see what would happen when introducing 10 µL of a 80 ng mL^{-1} PGM sample using the mentioned pump program. As with the blank samples, this was done three times in order check if any elution peaks would be reproducible. For Pt and Pd, the only peaks found were also present when introducing the blank solution as a sample. For Rh, however, there seems to be a few distinctive peaks that are not present when introducing the blank sample. A chromatogram showing the signals from all the PGMs in the last of the three sample introductions is seen in Figure 23 and Figure 24 shows the chromatogram comparing the Rh signal from the last of the three introduced blanks and samples.

The peak positions in the chromatograms are quite reproducible, as can be seen by the chromatogram in Figure 25. This shows the signals from the three sample introductions of Rh. The rest of the chromatograms can be seen in the appendix, section 7.5.

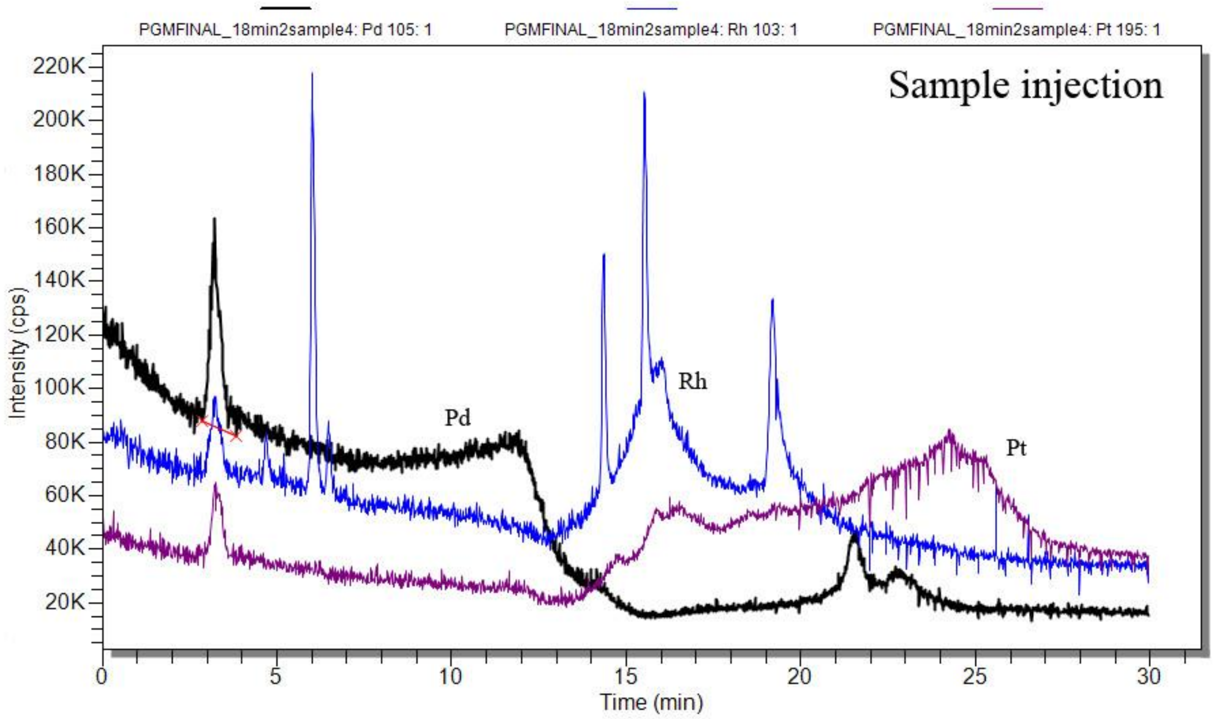

Figure 23 Chromatogram showing the signals from Pd, Rh and Pt over the 30 min run using the gradient and step pump program described in the method development section, with MP composition ranging from 0.1 M HCl to 2.0 M HCl.

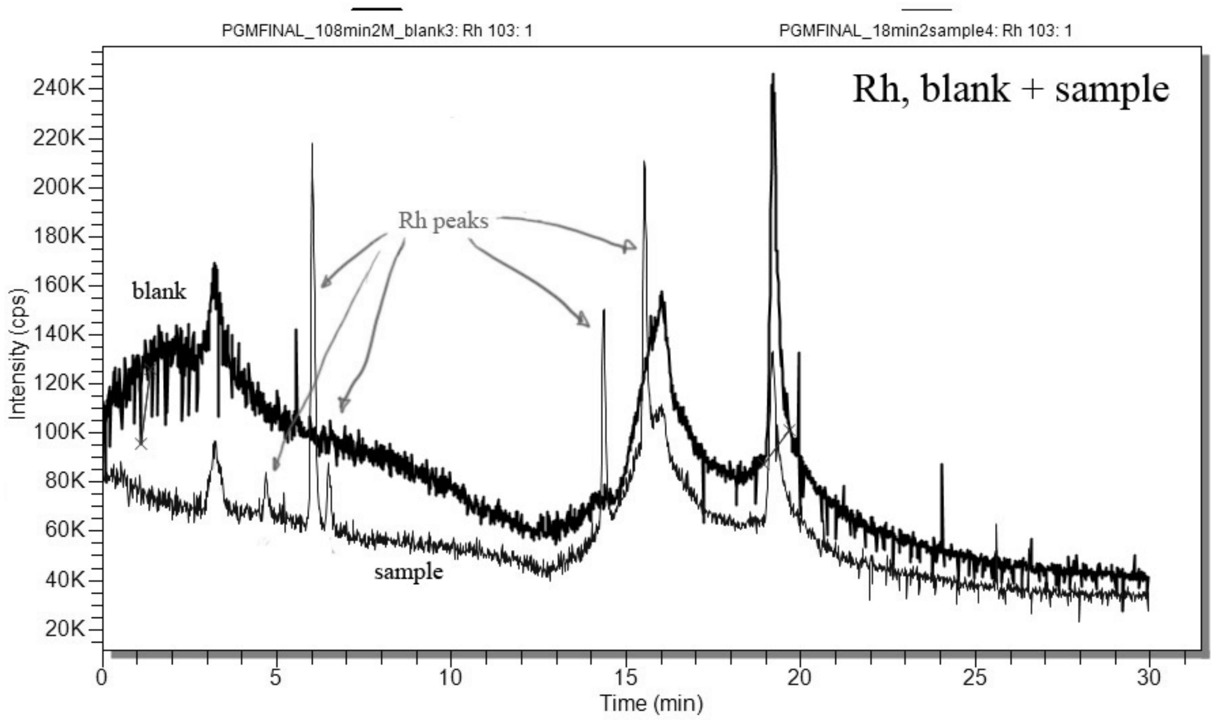

Figure 24 Chromatogram showing the Rh signals from the introduction of 10 µL of a blank sample and a PGM-containing (80 ng mL^{-1}) sample over the 30 min run using the gradient and step pump program described in the method development section, with MP composition ranging from 0.1 M HCl to 2.0 M HCl.

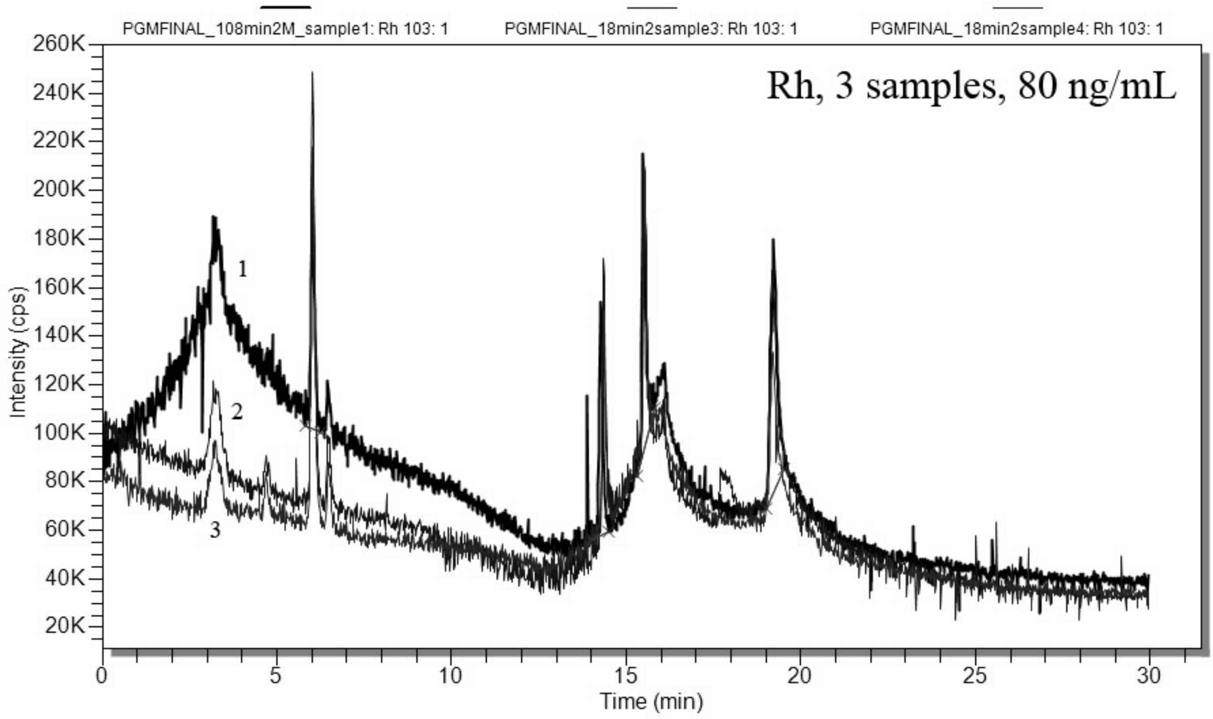

Figure 25 Chromatogram showing the Rh signal from introduction of three replicates (10 µL) of the PGM sample (80 ng mL^{-1}) over the 30 min run using MP composition ranging from 0.1 M HCl to 2.0 M HCl, as described in the method development section.

4.7 Separation scheme

On the basis of the findings from the adsorption and elution on the SCX and SAX SPE, a separation scheme was proposed. This can be seen in Figure 26.

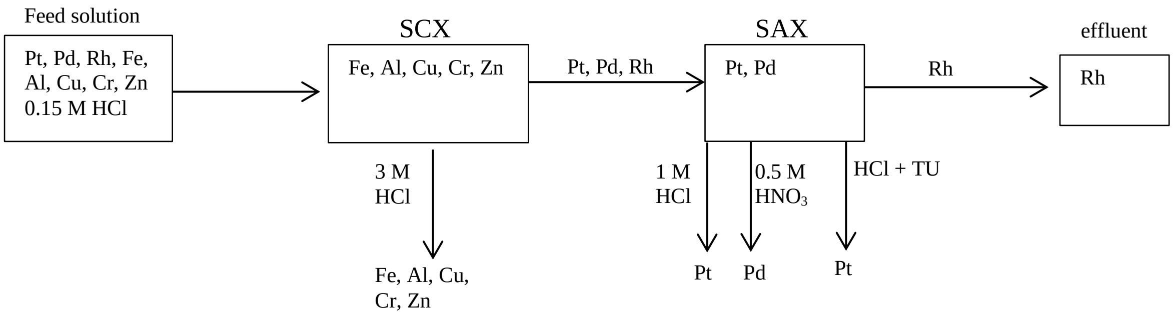

Figure 26 Proposed separation scheme for a solution containing the PGMs in addition to selected base metals. The horizontal arrows indicate the effluent from the different SPE cartridges and the vertical arrows indicate elution by different eluents. Results from this separation scheme can be found in Table 14 and Figure 27.

Two feed solutions containing 5 µg mL^{-1} analytes and 0.15 M HCl were tested in triplicates. One of these was prepared from a one year old 100 µg mL^{-1} multielement solution which included all of the elements shown in Figure 26. The other was freshly prepared from 1000 µg mL^{-1} single element stock solutions, and contained the PGMs in addition to Fe. A flow rate of 1 mL min^{-1} was always used. As the SAX is a cartridge type SPE, it was connected directly to the male luer tip of the SCX syringe barrel. The resins were conditioned with water before 15 mL feed solution was applied while collecting the effluent. 10 mL H_2O was then applied as a wash step. The two SPE's were then disconnected and the SAX cartridge was connected to an empty syringe which functioned as an eluent reservoir. 2 x 5 mL of 1 M HCl was then applied and collected as two samples. Then, 10 mL of water was applied and collected as another rinse step. This was repeated with 2 x 5 mL HNO_3 before another rinse step and finally 2 x 5 mL of a solution containing 0.5 M HCl and 0.5 M thiourea.

The collected samples were diluted before analysis in order to get the maximum theoretical concentration in the samples within the 0 – 100 ng mL^{-1} calibration range of the ICP-MS. This also ensured that the total dissolved solids in the samples were below the 0.2 % required for ICP-MS. As the water samples and the second 5 mL fraction of HNO_3 and HCl elution contained elements below the LOD, the undiluted samples of these fractions were analysed as well. Where possible, the results from the undiluted samples were used for the results. Finally, the effluent from the solution prepared from the single element standards (containing the PGMs in addition to Fe) was directly analysed on the ICP-OES in order to measure for any traces of Fe. It was found that Fe was 99.9 ± 0.09 % adsorbed. Although only Fe was measured for complete adsorption, the previous results from the SCX studies indicate that all the other base metals are equally quantitatively adsorbed.

Three of the samples had a deviating replicate. Two of these were outliers according to Grubb’s test for outliers [51], while the third could not be discarded. The calculation of the G statistics can be seen in the appendix, section 7.4.3.1. Figure 27 shows a visual representation of the average relative recovery of Pt, Pd and Rh for all sample fractions and Table 14 shows the relative recovery including standard deviations for the three sample replicates. The standard deviation is not included where one replicate was discarded. Raw data and statistics of the separation scheme can be seen in Table A9, Table A10 and Table A11 in the appendix (section 7.6.1).

The total recovery shows that the PGMs are not always quantitatively accounted for. This is especially true for Pt in the fresh solution, where approximately 20 % is unaccounted for. Some of this may be adsorbed to the SCX resin, which has been shown to be the case from the previous SCX studies. Additionally, there may still be Pt left on the SAX resin. There are also distinct differences of the adsorption and elution of elements between the fresh and the aged solutions. The most notable differences are that Pt is not quantitatively adsorbed to the SAX in the aged solution as opposed to the quantitative adsorption from the fresh solution, and that Rh is partly adsorbed to the SAX in the fresh solution (~ 25 %) while only to a small degree (~ 3 %) from the aged solution.

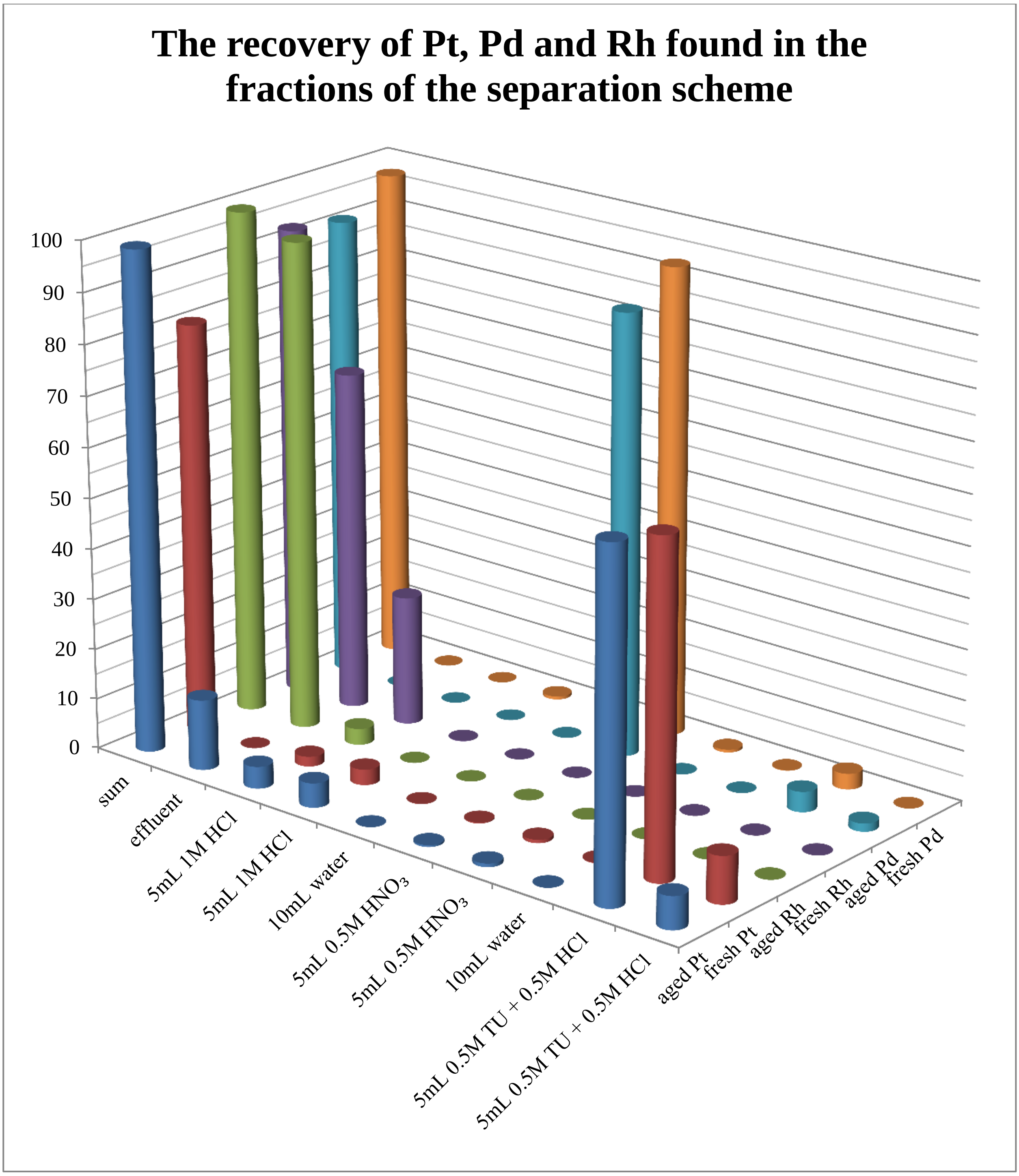

Figure 27 The recovery of Pt, Pd and Rh found in each fraction of the separation scheme, using a fresh and an aged solution of PGMs in 0.15 M HCl. The results are averages of 3 replicates, except for Rh and Pt in the effluent of aged solution, where two replicates were used due to the third being outliers according to Grubb's test. The percentage values can be seen in Table 14.

Table 14, Recovery percentage of the elements eluted in each fraction of the separation scheme, including the standard deviation for three replicates. Measurements were done either by ICP-OES or ICP-MS

Fraction	Pt aged	Pt fresh	Rh aged	Rh fresh	Pd aged	Pd fresh
flowthrough	14*	< LOD	96**	67 ± 7.4	< LOD	< LOD
5mL 1M HCl	4.4 ± 0.35	2.0 ± 0.41	3.2 ± 0.27	25.6 ± 0.83	< LOD	< LOD
5mL 1M HCl	4.9 ± 0.31	3.1 ± 0.19	< LOD	0.10 ± 0.018	< LOD	0.6 ± 0.68
10mL water	< LOD	0.1 ± 0.0042	< LOD	< LOD	< LOD	0.3 ± 0.30
5mL 0.5M HNO_3	< LOQ	< LOQ	< LOD	< LOD	87 ± 1.3	93 ± 4.6
5mL 0.5M HNO_3	0.71 ± 0.066	0.7 ± 0.12	< LOD	0.006 ± 0.0016	< LOD	0.5 ± 0.35
10mL water	< LOD	0.1 ± 0.034	< LOD	< LOD	< LOD	0.10 ± 0.05
5mL 0.5M TU + 0.5M HCl	68 ± 1.6	65.7 ± 16***	< LOD	< LOD	4 ± 1.9	3 ± 1.8
5mL 0.5M TU + 0.5M HCl	6.5 ± 0.42	9.4 ± 0.37	< LOD	< LOD	< LOQ	< LOD
TOTAL recovery	99%	81%	100%	93%	91%	98%

* Replicate values: 23.86, 13.92 and 14.12 (of a max theoretical amount of 100 ng mL^{-1})

** Replicate values: 168.71, 95.68 and 97.2 (of a max theoretical amount 100 ng mL^{-1})

*** Replicate values: 56.83, 56.34 and 83.89 (of max 100 ng mL^{-1})

4.8 Real sample

The solution containing a 5 mg mL^{-1} digest of real converter sample in 10 % aqua regia was diluted in order to obtain 200 µg mL^{-1} of total converter sample in 0.15 M HCl. 10 mL of this feed solution was then applied to a SCX cartridge with a flow rate of 1 mL min^{-1} before 6 mL H_2O was applied as a wash step. The effluents from both steps were collected in the same 50 mL volumetric flask. In order to elute the adsorbed elements from the SCX resin, 5 mL of 3 M HCl was applied to the resin and this effluent was collected in a separate 50 mL volumetric flask. Lastly, 10 mL of the feed solution was pipetted into another 50 mL volumetric flask in order to serve as a reference solution. All the samples were matrix matched to the ICP-OES calibration solutions with appropriate amounts of HCl before diluting to the mark with water. The theoretical concentration of each of the analytes in the final samples was then calculated and can be seen in Table 15.

Table 15 The theoretical concentration of each element (µg mL^{-1}) for the diluted real converter sample.

Fe	Ni	Cu	Pt	Pd	Rh	Slag
27.6	2.88	0.18	1.44	0.8	0.334	6.7

As Ni was not present in the ready-made calibration solutions for the ICP-OES, this was omitted from the analysis. As mentioned in the method development, an additional 2.0 µg mL^{-1} multielement calibration standard was made especially for analysis of these samples in order to increase the linear range. The reference solution was analysed and the results compared to the theoretical amount in the solution. Figure 28 shows the relative amount of elements found in the reference solution compared to the theoretical amount found from the specifications. The effluent sample and the sample eluted with 3 M HCl were then analysed. These values were compared to the amount found in the reference solution and the recovery percentage in the effluent and eluted solutions can be seen in Figure 29.

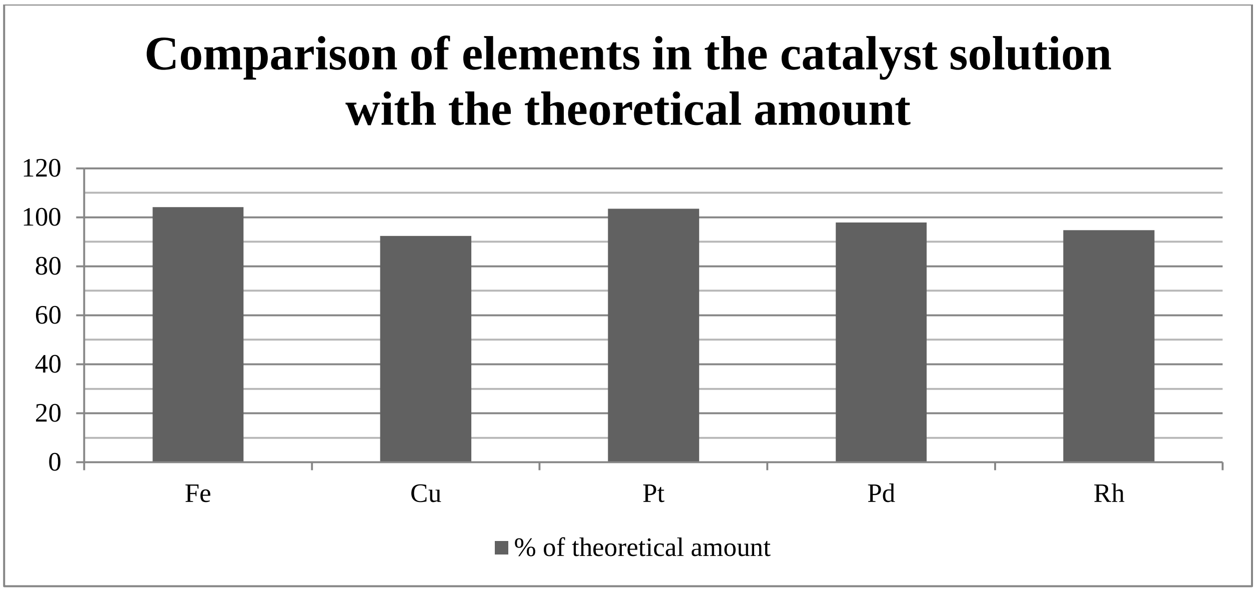

Figure 28 The amount of elements found in the reference sample of the real converter digest, relative to the theoretical amount calculated from the specifications. Only one replicate was used.

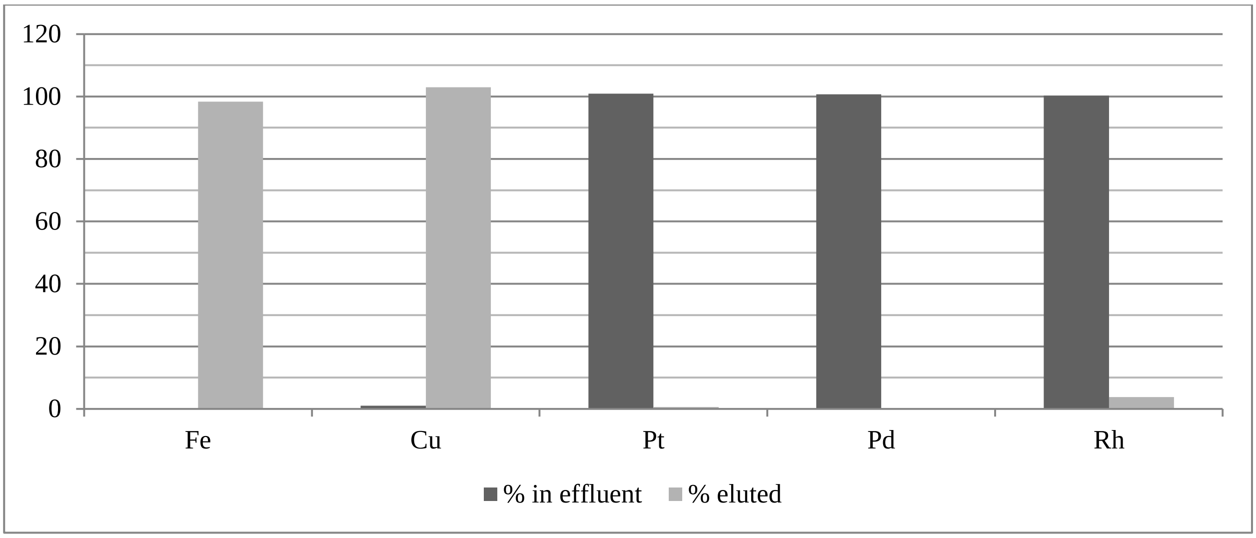

Figure 29 The amount of elements recovered in the effluent of a SCX SPE application and after using 5 mL 3 M HCl to elute the adsorbed elements from the SPE. Relative to the amount found in the reference solution and with one replicate.

It is seen that good correlation is found between the concentration of analytes in the reference solution and the theoretical amount. As the theoretical amount of Fe was approximately 15 times higher than the calibration solution with highest concentration, the calibration curve for Fe was extrapolated in order to get an estimate of the concentration in the sample. This is generally advised against, although for an estimate it gave a very good fit with the theoretical amount. The result was therefore kept, but it must be stressed that this is only an estimate. The rest of the elements had theoretical and measured concentrations covered by the calibration curves.

The effluent sample showed that Fe and Cu were retained quantitatively on the SCX while Pt, Pd and Rh were not retained. The adsorbed Fe and Cu were then quantitatively eluted in the 5 mL of applied 3 M HCl. The results show that even with high concentrations of base metals compared to the PGMs in solution, SCX can be used to adsorb the base metals while the PGM are passed through unretained. This can likely be up-scaled for industrial clean-up of base metals from PGM solutions in weakly acidic solutions.

5 Concluding remarks

In this study, the adsorption and subsequent recovery of PGMs and selected base metals in HCl solutions has been investigated using SAX, SCX, CN and DOS modified RP resins in solid phase extraction. It was found that a concentration of 0.15 M HCl was ideal for quantitative adsorption of Pt and Pd on SAX as well as for the base metals on SCX. As Pt and Pd is likely present as $[PtCl_6]^{2-}$ and $[PdCl_4]^{2-}$, respectively, these are retained on anion exchange resins while the anions of the base metals flow freely though the resin. For the cation exchange, the anionic base metal ions are retained while the PGM chlorocomplexes have no interaction with the resin. It was also found that the use of solutions which had been stored over time resulted in a decrease in Pt adsorption on SAX resins. This is presumably due to formation of some neutral aqua-chloro complexes over time. Rh was not retained on any of the resins tested and is likely present as the neutral aqua-chloro complexes $[RhCl_3(H_2O)_3]$. There was an exception when using freshly made PGM solutions, where about 15 % of Rh was retained on SAX. This is presumably due to presence of $[RhCl_6]^{3-}$ and the equilibrium having not yet been reached. While Pd could easily be recovered from the SAX resin using 0.5 M HNO_3 or 3 M HCl, Pt showed a strong adsorption and could only be quantitatively recovered with the use of thiourea. SCX was found to be very effective as a matrix separation tools, as it can adsorb large amounts of base metals.

The CN and the DOS-modified RP resins have complexation abilities due to the presence of N and S, and these were found to selectively retain Pd. For CN, the retention is weak and the capacity is low when using low concentration of Pd in the solutions. Most of the retained Pd was recovered using 3 M HCl. For the DOS modified resin, however, the use of 6 M HCl did not elute any of the adsorbed Pd and quantitative recovery was only found when using thiourea in the eluent.

With the results obtained from the SPE trials, a separation scheme was proposed using SCX to remove the base metals and SCX to adsorb Pt and Pd while Rh was collected in the effluent. Pd and Pt were then recovered using 0.5 M HNO_3 and a thiourea containing solution, respectively. Although a good separation was obtained, the need for thiourea to elute Pt is a drawback of the method. It should also be possible to use the Pd selective resins in a separation scheme, although SAX would still be needed to separate Pt and Rh.

ICP-OES was found to be a good instrument for analysing samples containing both the PGMs and the base metals, and the LOD was found to be 10 – 15 ng mL^{-1} for the PGMs and 1 – 6 ng mL^{-1} for the selected base metals. While providing superior LOD for the PGMs, in the range of 0.1 – 0.9 ng mL^{-1}, there were problems using the ICP-MS for analysis of the base metals and good calibration curves was not found. One explanation of this is the common nature of the base metals, as samples are easily affected by contamination. Another explanation is the presence of spectral interference from polyatomic ions. For further work, it would be of interest to use a dynamic reaction cell in order to remove some of the polyatomic interferences and more accurately determine the base metals.

The use of LC-ICP-MS for on-line separation of the PGMs was only investigated using a SAX column, and a MP containing up to 2 M HCl only seemed to efficiently elute Rh. A high background of Pt and Pd was also seen, presumably due to high amounts of PGMs having been previously applied to the column. Modifying the MP with $NaClO_4$ or thiourea could help elute the PGMs, although then a more complicated sample introduction system would have to be implemented, to reduce the % TDS introduced into the ICP-MS. The late implementation of an inert pump system restricted the time available for testing other columns. It would be interesting to test a SCX and a CN column, to see if a better separation of the analytes can be achieved. Additionally, it could be of interest to try the HPLC method on a new SAX column, in case elution peaks was masked by the high background. It seems, however, that SPE could be implemented on an industrial scale without a need for a continuous column separation.

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7 Appendix

7.1 Method Development ICP-OES

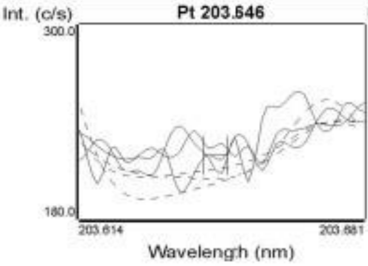
In the method development 4 wavelengths (5 for Al) were initially monitored for each element. These can be seen in Table A1. These were narrowed down to two wavelengths for each element, which were monitored for all the samples analysed. The signal data from the blank, calibration solution 1 and calibration solution 4 can be seen on the following pages, in addition to the calibration curves for all the 16 wavelengths monitored (2 for each element). Calibration statistics are included for the wavelengths selected for the final results.

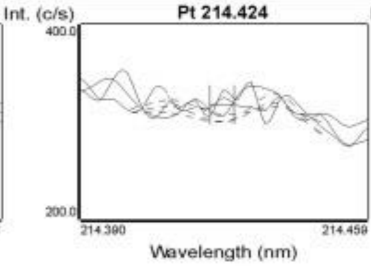
7.1.1 Wavelengths initially monitored

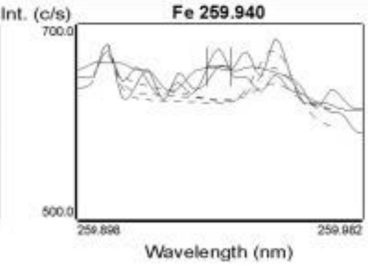
Table A1 Wavelengths initially monitored for each element in the ICP-OES method development, in order to select the best wavelength for the analysis.

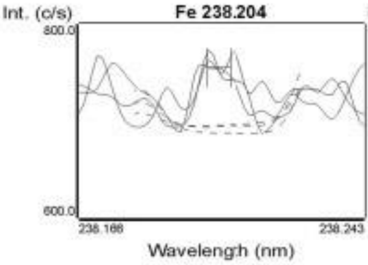
	1	**2**	**3**	**4**	**5**
Al	167.019	396.152	237.312	208.215	394.401
Cr	268.716	205.560	206.158	206.550	
Cu	327.396	324.754	213.598	224.700	
Fe	238.204	259.940	234.350	239.563	
Pd	340.458	229.651	360.955	342.122	
Pt	214.424	203.646	177.648	217.468	
Rh	343.488	396.236	249.078	233.477	

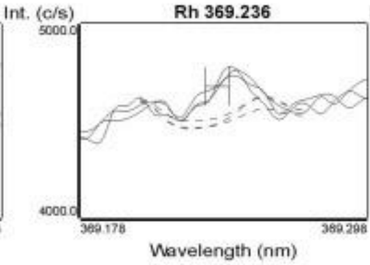
7.1.2 Signal data for the blank

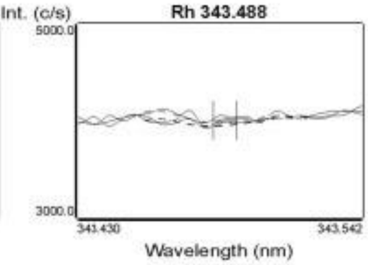


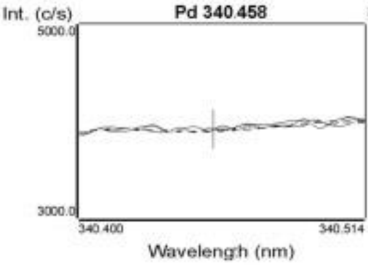


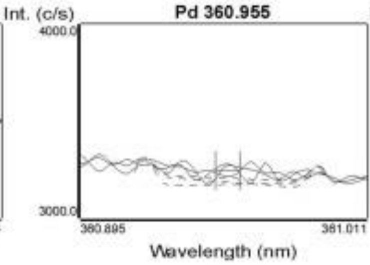


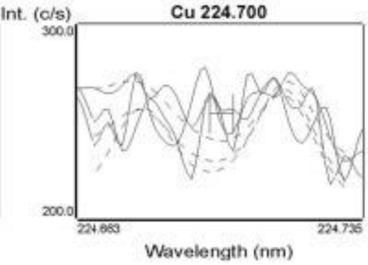


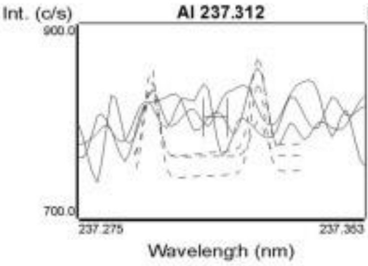


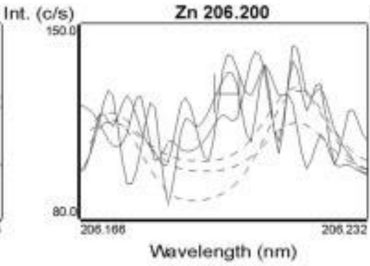


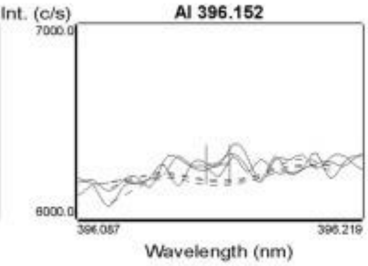


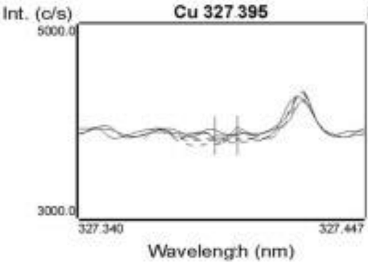


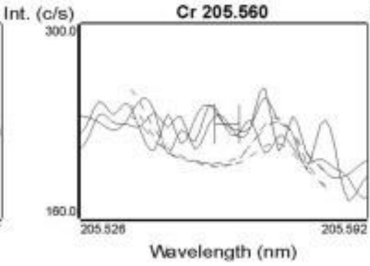


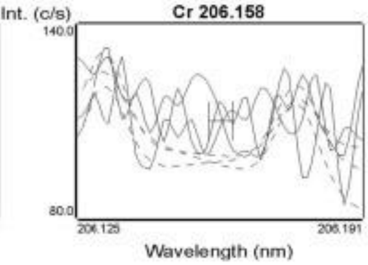


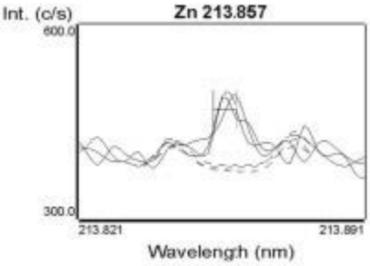




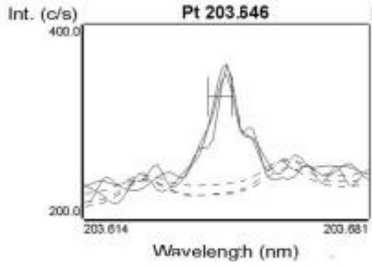


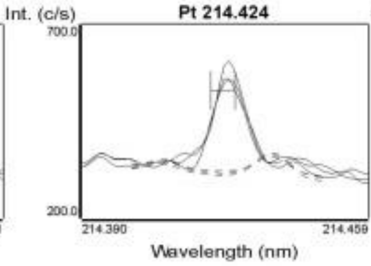


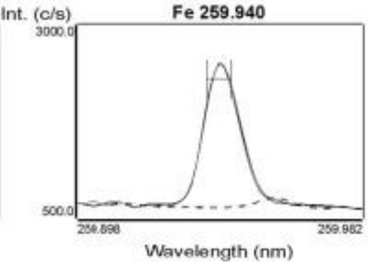


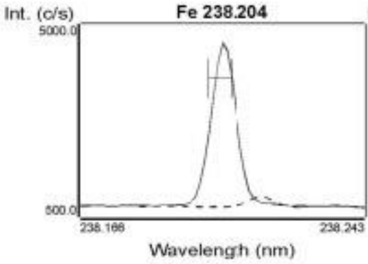


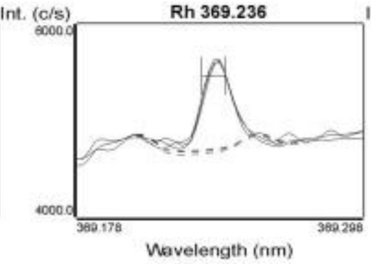
7.1.3 Signal data for Standard 1 (0.2 µg mL^{-1})

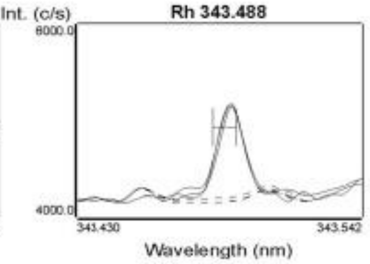

Pt 203.546

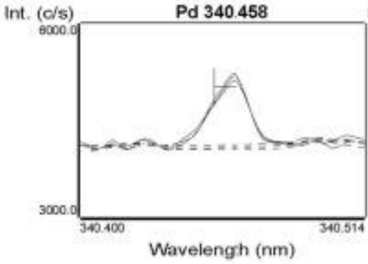

Pt 214.424

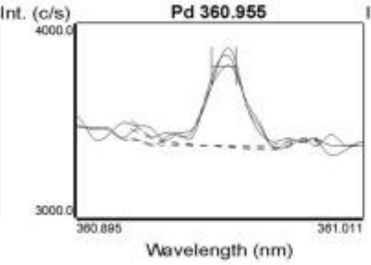

Fe 259.940

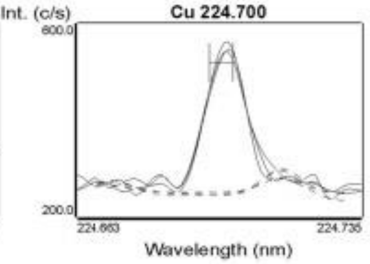

Fe 238.204

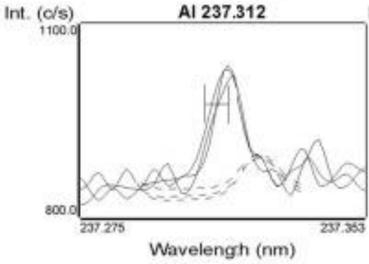

Rh 369.236

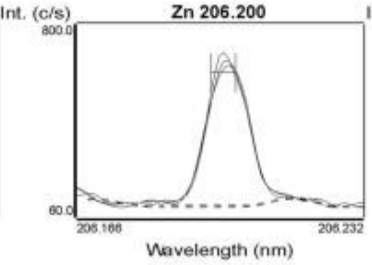

Rh 343.488

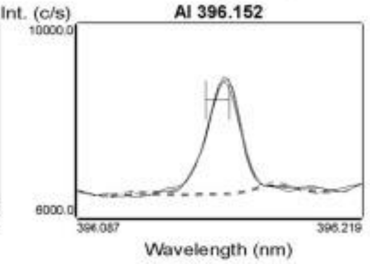

Pd 340.458

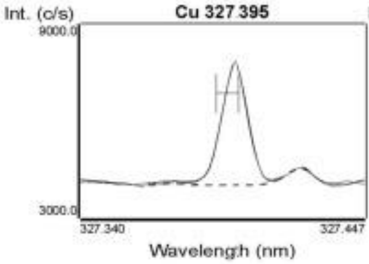

Pd 360.955

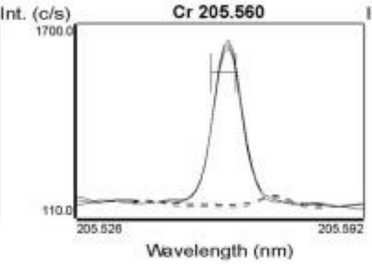

Cu 224.700

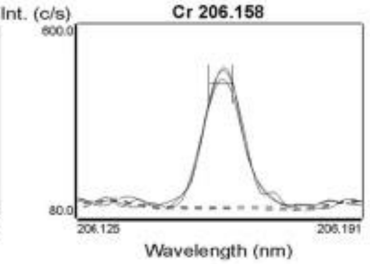

Al 237.312

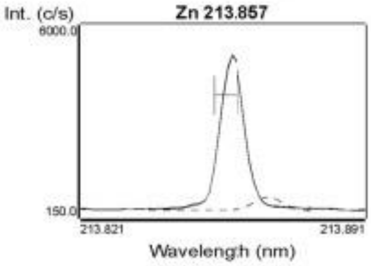

Zn 206.200


Al 396.152

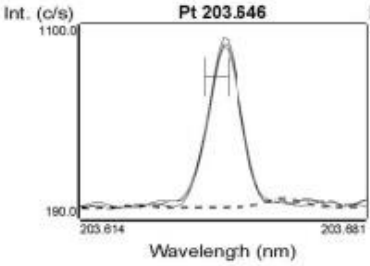

Cu 327.395

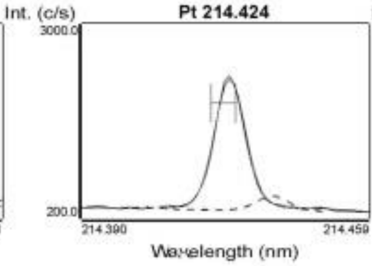

Cr 205.560

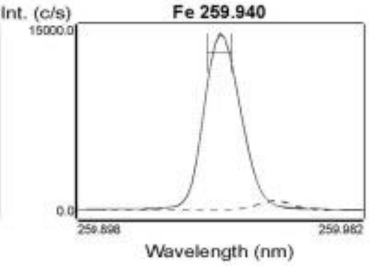

Cr 206.158

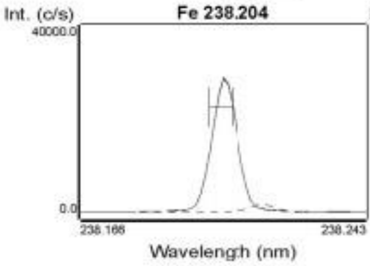

Zn 213.857

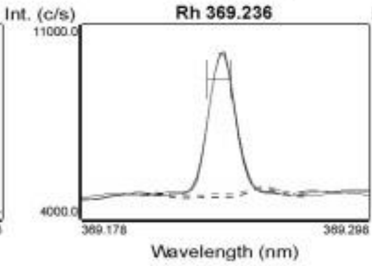
7.1.4 Signal data for Standard 4 (1.5 µg mL^{-1})

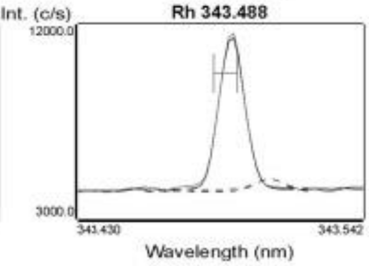


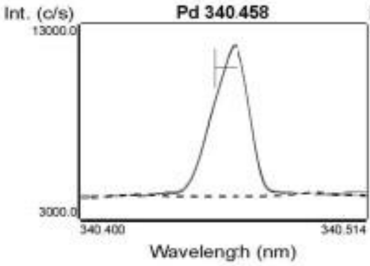


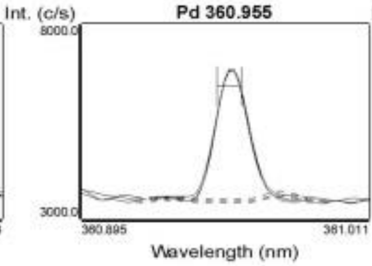


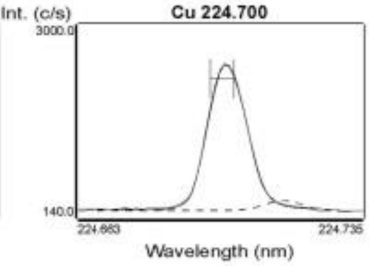


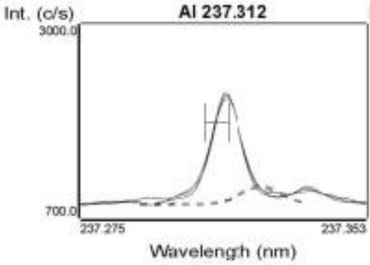


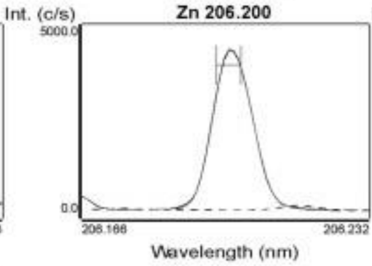


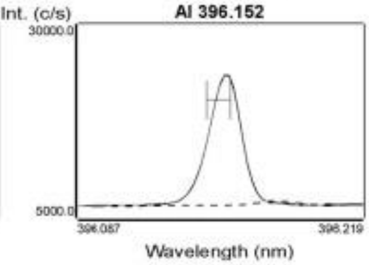


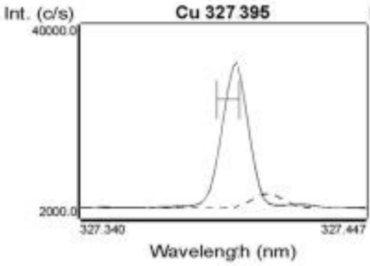


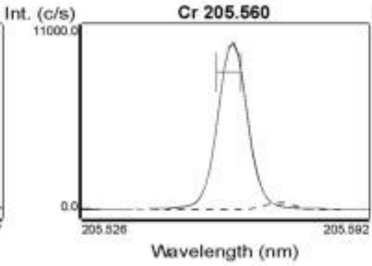


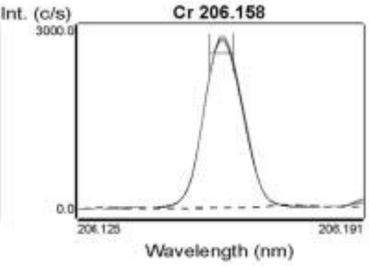


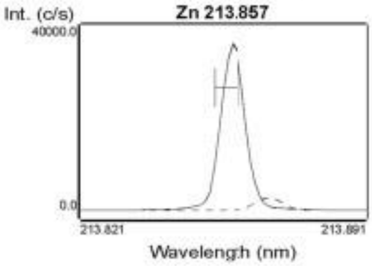




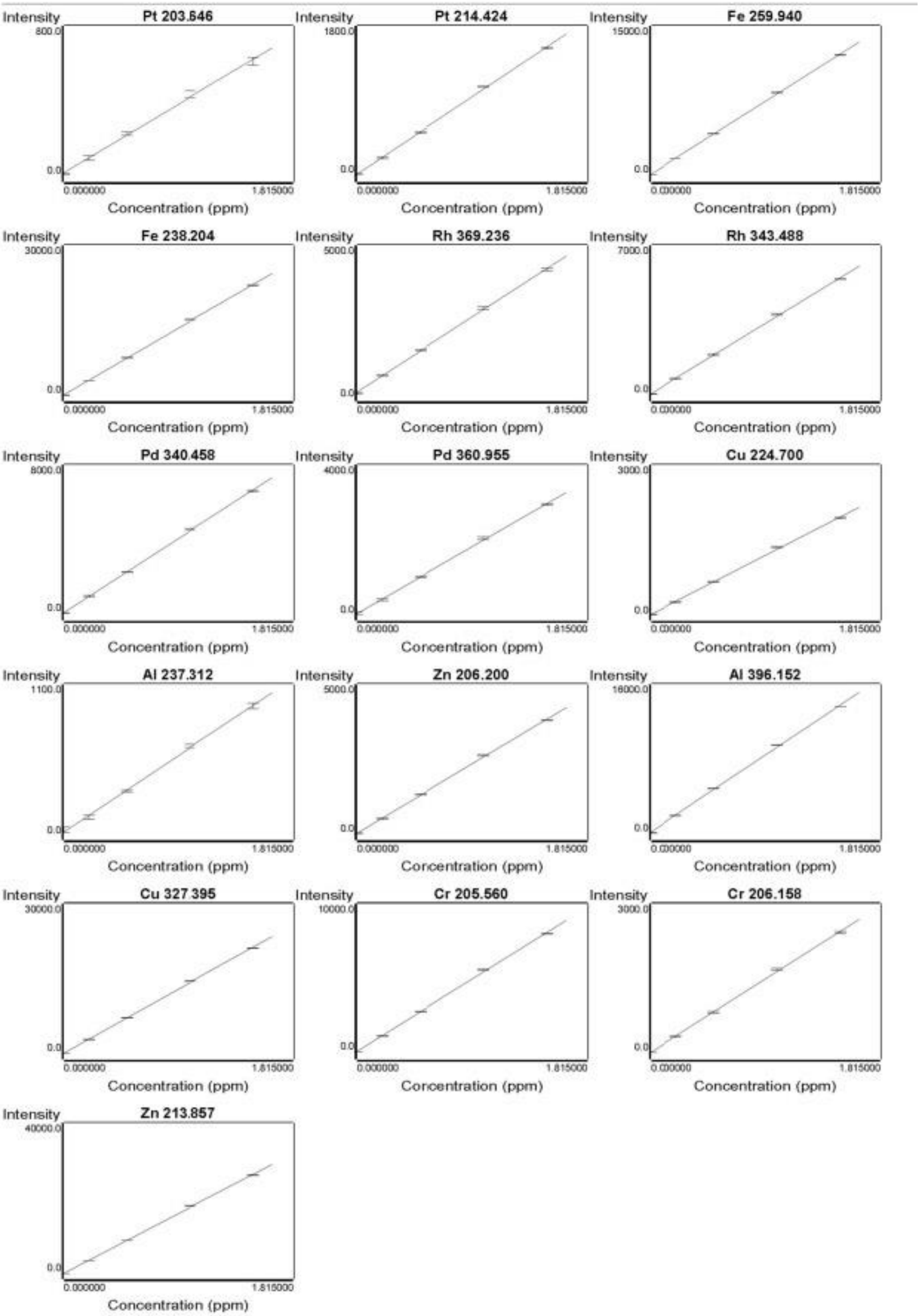




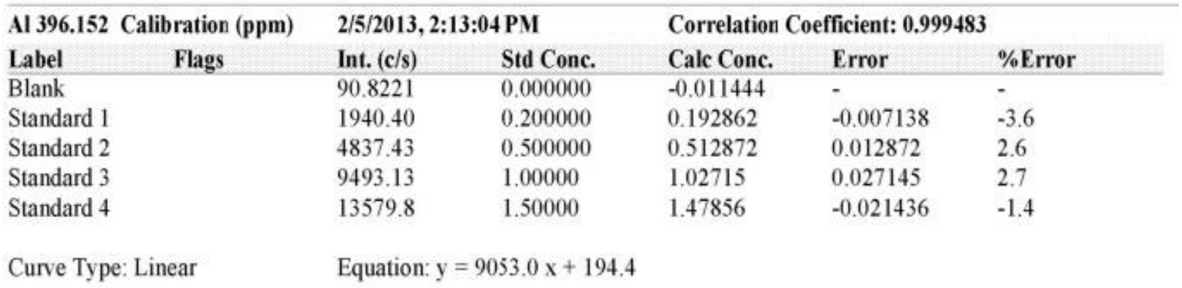




7.1.5 The calibration curves



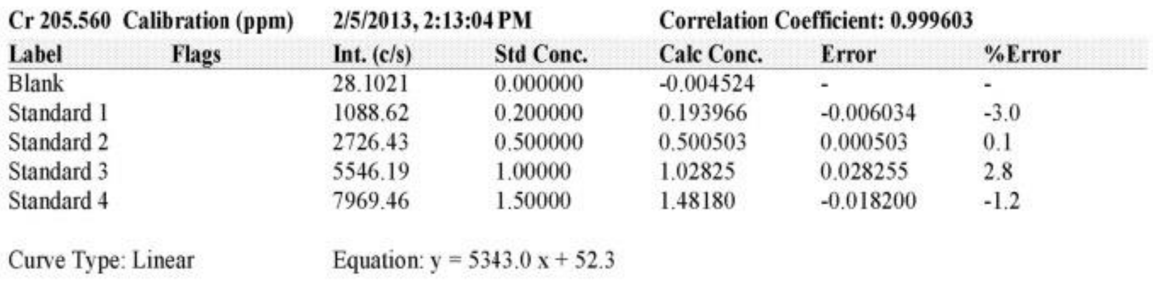
7.1.6 Calibration statistics for the analytical wavelengths



Al 396.152 Calibration (ppm) **2/5/2013, 2:13:04 PM** **Correlation Coefficient: 0.999483**

Label	Flags	Int. (c/s)	Std Conc.	Calc Conc.	Error	%Error
Blank		90.8221	0.000000	-0.011444	-	-
Standard 1		1940.40	0.200000	0.192862	-0.007138	-3.6
Standard 2		4837.43	0.500000	0.512872	0.012872	2.6
Standard 3		9493.13	1.00000	1.02715	0.027145	2.7
Standard 4		13579.8	1.50000	1.47856	-0.021436	-1.4

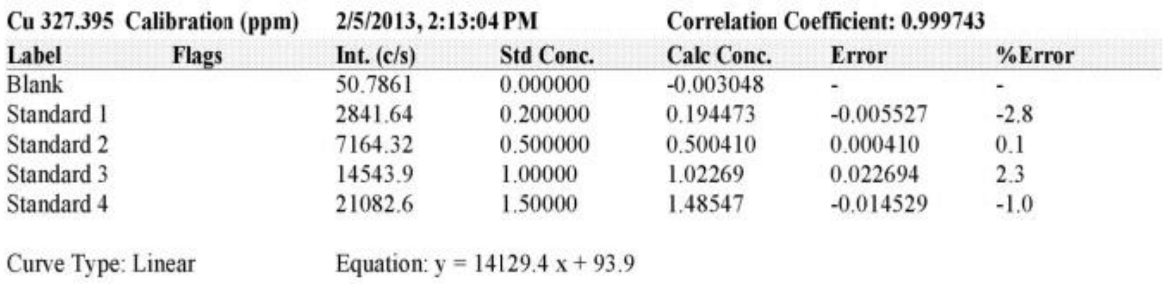
Curve Type: Linear Equation: y = 9053.0 x + 194.4



Cr 205.560 Calibration (ppm) **2/5/2013, 2:13:04 PM** **Correlation Coefficient: 0.999603**

Label	Flags	Int. (c/s)	Std Conc.	Calc Conc.	Error	%Error
Blank		28.1021	0.000000	-0.004524	-	-
Standard 1		1088.62	0.200000	0.193966	-0.006034	-3.0
Standard 2		2726.43	0.500000	0.500503	0.000503	0.1
Standard 3		5546.19	1.00000	1.02825	0.028255	2.8
Standard 4		7969.46	1.50000	1.48180	-0.018200	-1.2

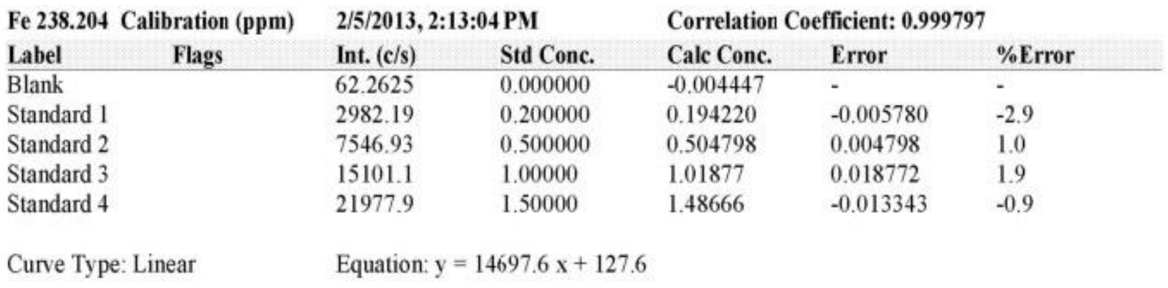
Curve Type: Linear Equation: y = 5343.0 x + 52.3



Cu 327.395 Calibration (ppm) **2/5/2013, 2:13:04 PM** **Correlation Coefficient: 0.999743**

Label	Flags	Int. (c/s)	Std Conc.	Calc Conc.	Error	%Error
Blank		50.7861	0.000000	-0.003048	-	-
Standard 1		2841.64	0.200000	0.194473	-0.005527	-2.8
Standard 2		7164.32	0.500000	0.500410	0.000410	0.1
Standard 3		14543.9	1.00000	1.02269	0.022694	2.3
Standard 4		21082.6	1.50000	1.48547	-0.014529	-1.0

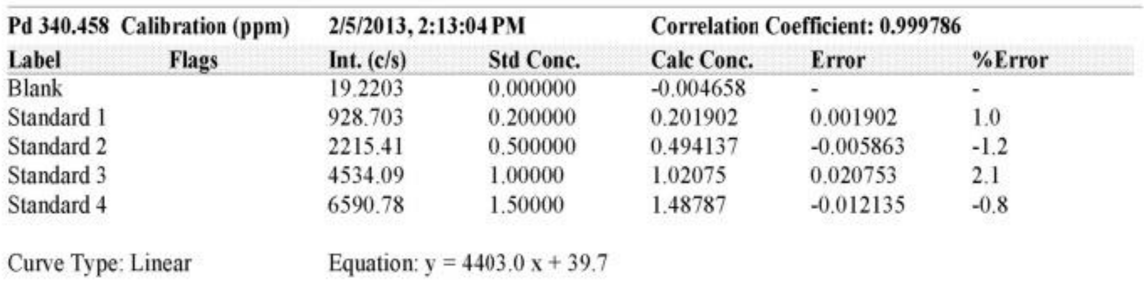
Curve Type: Linear Equation: y = 14129.4 x + 93.9



Fe 238.204 Calibration (ppm) **2/5/2013, 2:13:04 PM** **Correlation Coefficient: 0.999797**

Label	Flags	Int. (c/s)	Std Conc.	Calc Conc.	Error	%Error
Blank		62.2625	0.000000	-0.004447	-	-
Standard 1		2982.19	0.200000	0.194220	-0.005780	-2.9
Standard 2		7546.93	0.500000	0.504798	0.004798	1.0
Standard 3		15101.1	1.00000	1.01877	0.018772	1.9
Standard 4		21977.9	1.50000	1.48666	-0.013343	-0.9

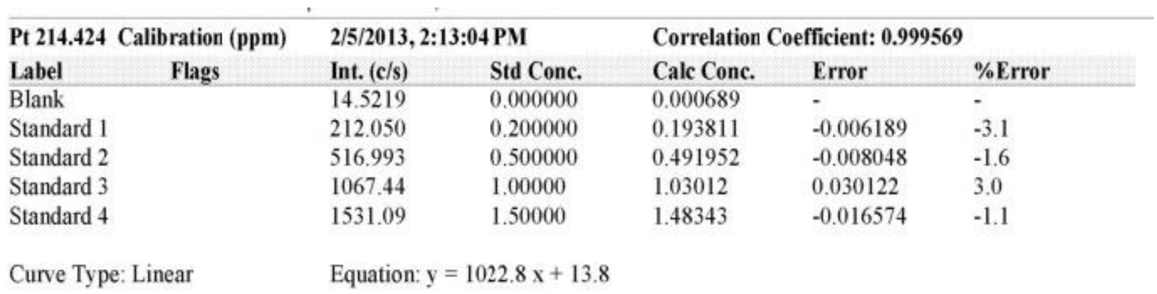
Curve Type: Linear Equation: y = 14697.6 x + 127.6



Pd 340.458 Calibration (ppm) **2/5/2013, 2:13:04 PM** **Correlation Coefficient: 0.999786**

Label	Flags	Int. (c/s)	Std Conc.	Calc Conc.	Error	%Error
Blank		19.2203	0.000000	-0.004658	-	-
Standard 1		928.703	0.200000	0.201902	0.001902	1.0
Standard 2		2215.41	0.500000	0.494137	-0.005863	-1.2
Standard 3		4534.09	1.00000	1.02075	0.020753	2.1
Standard 4		6590.78	1.50000	1.48787	-0.012135	-0.8

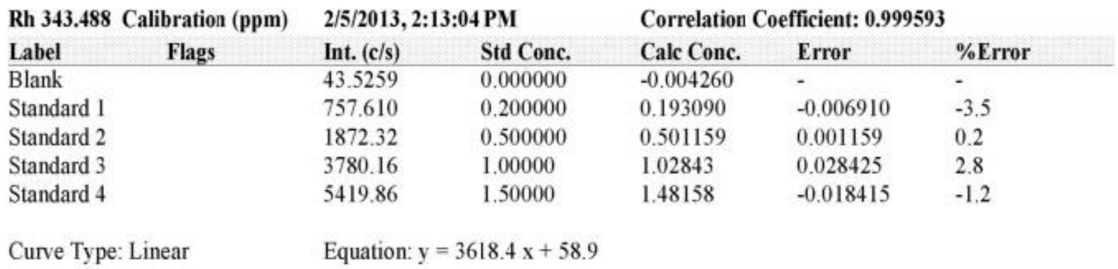
Curve Type: Linear Equation: $y = 4403.0\ x + 39.7$



Pt 214.424 Calibration (ppm) **2/5/2013, 2:13:04 PM** **Correlation Coefficient: 0.999569**

Label	Flags	Int. (c/s)	Std Conc.	Calc Conc.	Error	%Error
Blank		14.5219	0.000000	0.000689	-	-
Standard 1		212.050	0.200000	0.193811	-0.006189	-3.1
Standard 2		516.993	0.500000	0.491952	-0.008048	-1.6
Standard 3		1067.44	1.00000	1.03012	0.030122	3.0
Standard 4		1531.09	1.50000	1.48343	-0.016574	-1.1

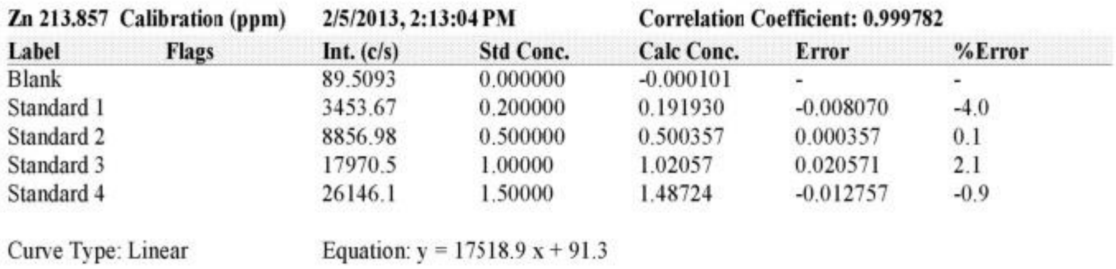
Curve Type: Linear Equation: $y = 1022.8\ x + 13.8$



Rh 343.488 Calibration (ppm) **2/5/2013, 2:13:04 PM** **Correlation Coefficient: 0.999593**

Label	Flags	Int. (c/s)	Std Conc.	Calc Conc.	Error	%Error
Blank		43.5259	0.000000	-0.004260	-	-
Standard 1		757.610	0.200000	0.193090	-0.006910	-3.5
Standard 2		1872.32	0.500000	0.501159	0.001159	0.2
Standard 3		3780.16	1.00000	1.02843	0.028425	2.8
Standard 4		5419.86	1.50000	1.48158	-0.018415	-1.2

Curve Type: Linear Equation: $y = 3618.4\ x + 58.9$

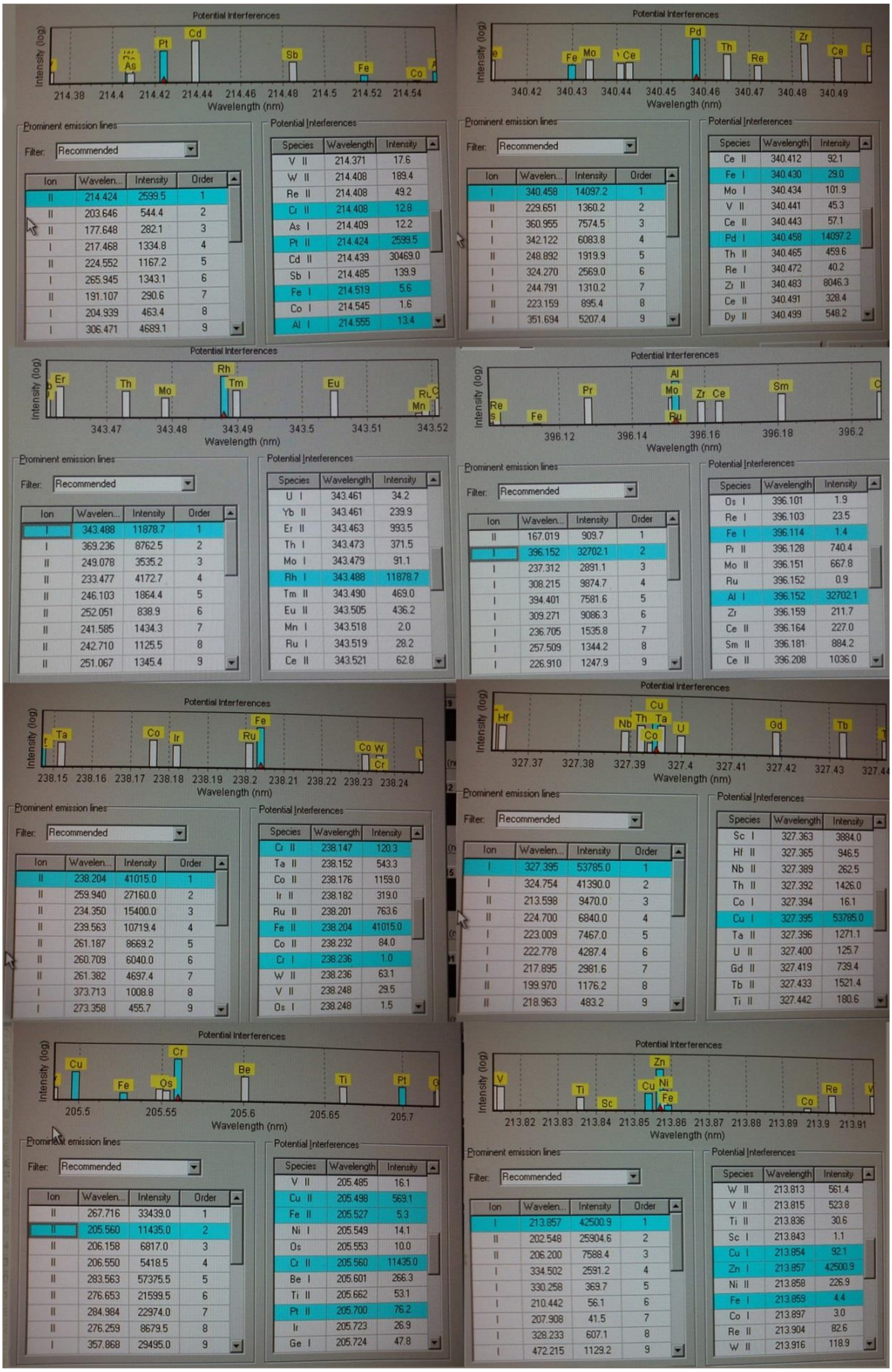


Zn 213.857 Calibration (ppm) **2/5/2013, 2:13:04 PM** **Correlation Coefficient: 0.999782**

Label	Flags	Int. (c/s)	Std Conc.	Calc Conc.	Error	%Error
Blank		89.5093	0.000000	-0.000101	-	-
Standard 1		3453.67	0.200000	0.191930	-0.008070	-4.0
Standard 2		8856.98	0.500000	0.500357	0.000357	0.1
Standard 3		17970.5	1.00000	1.02057	0.020571	2.1
Standard 4		26146.1	1.50000	1.48724	-0.012757	-0.9

Curve Type: Linear Equation: $y = 17518.9\ x + 91.3$

7.1.7 Possible interferences on the analytical lines for the ICP-OES



Prominent emission lines

Filter: Recommended

Ion	Wavelen...	Intensity	Order
II	214.424	2599.5	1
II	203.646	544.4	2
II	177.648	282.1	3
I	217.468	1334.8	4
II	224.552	1167.2	5
I	265.945	1343.1	6
II	191.107	290.6	7
I	204.939	463.4	8
I	306.471	4689.1	9

Potential Interferences

Species	Wavelength	Intensity
V II	214.371	17.6
W II	214.408	189.4
Re II	214.408	49.2
Cr II	214.408	12.8
As I	214.409	12.2
Pt II	214.424	2599.5
Cd II	214.439	30469.0
Sb I	214.485	139.9
Fe I	214.519	5.6
Co I	214.545	1.6
Al I	214.555	13.4

Prominent emission lines

Filter: Recommended

Ion	Wavelen...	Intensity	Order
I	340.458	14097.2	1
II	229.651	1360.2	2
I	360.955	7574.5	3
I	342.122	6083.8	4
II	248.892	1919.9	5
I	324.270	2569.0	6
I	244.791	1310.2	7
II	223.159	895.4	8
I	351.694	5207.4	9

Potential Interferences

Species	Wavelength	Intensity
Ce II	340.412	92.1
Fe I	340.430	29.0
Mo I	340.434	101.9
V II	340.441	45.3
Ce II	340.443	57.1
Pd I	340.458	14097.2
Th II	340.465	459.6
Re I	340.472	40.2
Zr II	340.483	8046.3
Ce II	340.491	328.4
Dy II	340.499	548.2

Prominent emission lines

Filter: Recommended

Ion	Wavelen...	Intensity	Order
I	343.488	11878.7	1
I	369.236	8762.5	2
II	249.078	3535.2	3
II	233.477	4172.7	4
II	246.103	1864.4	5
II	252.051	838.9	6
II	241.585	1434.3	7
II	242.710	1125.5	8
II	251.067	1345.4	9

Potential Interferences

Species	Wavelength	Intensity
U I	343.461	34.2
Yb II	343.461	239.9
Er II	343.463	993.5
Th I	343.473	371.5
Mo I	343.479	91.1
Rh I	343.488	11878.7
Tm II	343.490	469.0
Eu II	343.505	436.2
Mn I	343.518	2.0
Ru I	343.519	28.2
Ce II	343.521	62.8

Prominent emission lines

Filter: Recommended

Ion	Wavelen...	Intensity	Order
II	167.019	909.7	1
I	396.152	32702.1	2
I	237.312	2891.1	3
I	308.215	9874.7	4
I	394.401	7581.6	5
I	309.271	9086.3	6
I	236.705	1535.8	7
I	257.509	1344.2	8
I	226.910	1247.9	9

Potential Interferences

Species	Wavelength	Intensity
Os I	396.101	1.9
Re I	396.103	23.5
Fe I	396.114	1.4
Pr II	396.128	740.4
Mo II	396.151	667.8
Ru	396.152	0.9
Al I	396.152	32702.1
Zr	396.159	211.7
Ce II	396.164	227.0
Sm II	396.181	884.2
Ce II	396.208	1036.0

Prominent emission lines

Filter: Recommended

Ion	Wavelen...	Intensity	Order
II	238.204	41015.0	1
II	259.940	27160.0	2
II	234.350	15400.0	3
II	239.563	10719.4	4
II	261.187	8669.2	5
II	260.709	6040.0	6
II	261.382	4697.4	7
I	373.713	1008.8	8
I	273.358	455.7	9

Potential Interferences

Species	Wavelength	Intensity
Cr II	238.147	120.3
Ta II	238.152	543.3
Co II	238.176	1159.0
Ir II	238.182	319.0
Ru II	238.201	763.6
Fe II	238.204	41015.0
Co II	238.232	84.0
Cr I	238.236	1.0
W II	238.236	63.1
V II	238.248	29.5
Os I	238.248	1.5

Prominent emission lines

Filter: Recommended

Ion	Wavelen...	Intensity	Order
I	327.395	53785.0	1
I	324.754	41390.0	2
II	213.598	9470.0	3
II	224.700	6840.0	4
I	223.009	7467.0	5
I	222.778	4287.4	6
I	217.895	2981.6	7
II	199.970	1176.2	8
II	218.963	483.2	9

Potential Interferences

Species	Wavelength	Intensity
Sc I	327.363	3884.0
Hf II	327.365	946.5
Nb II	327.389	262.5
Th II	327.392	1426.0
Co I	327.394	16.1
Cu I	327.395	53785.0
Ta II	327.396	1271.1
U II	327.400	125.7
Gd II	327.419	739.4
Tb II	327.433	1521.4
Ti II	327.442	180.6

Prominent emission lines

Filter: Recommended

Ion	Wavelen...	Intensity	Order
II	267.716	33439.0	1
II	205.560	11435.0	2
II	206.158	6817.0	3
II	206.550	5418.5	4
II	283.563	57375.5	5
II	276.653	21599.5	6
II	284.984	22974.0	7
II	276.259	8679.5	8
I	357.868	29495.0	9

Potential Interferences

Species	Wavelength	Intensity
V II	205.485	16.1
Cu II	205.498	569.1
Fe II	205.527	5.3
Ni I	205.549	14.1
Os	205.553	10.0
Cr II	205.560	11435.0
Be I	205.601	266.3
Ti II	205.662	53.1
Pt II	205.700	76.2
Ir	205.723	26.9
Ge I	205.724	47.8

Prominent emission lines

Filter: Recommended

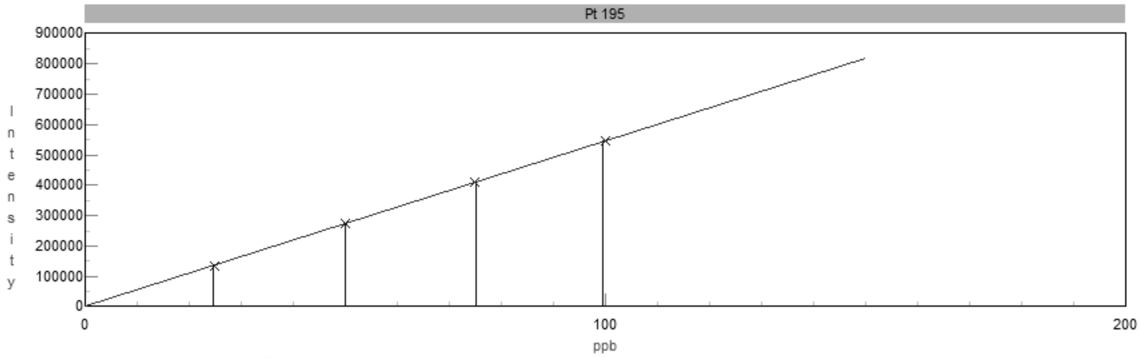
Ion	Wavelen...	Intensity	Order
I	213.857	42500.9	1
II	202.548	25904.6	2
II	206.200	7588.4	3
I	334.502	2591.2	4
I	330.258	369.7	5
I	210.442	56.1	6
I	207.908	41.5	7
I	328.233	607.1	8
I	472.215	1129.2	9

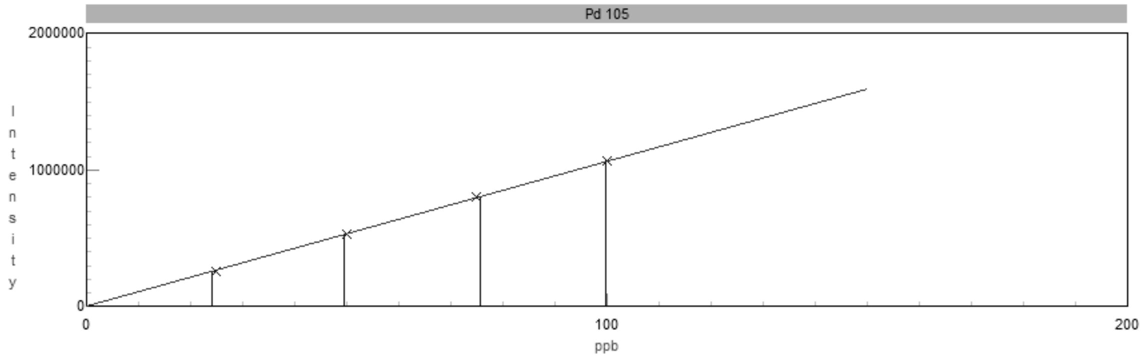
Potential Interferences

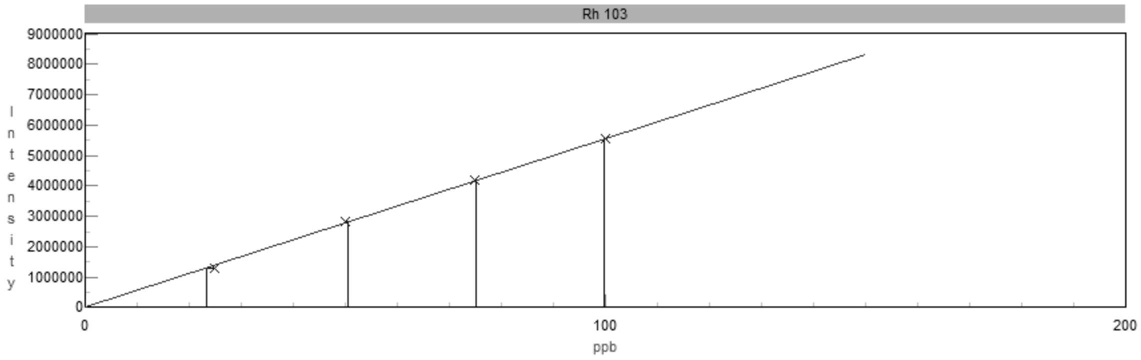
Species	Wavelength	Intensity
W II	213.813	561.4
V II	213.815	523.8
Ti II	213.836	30.6
Sc I	213.843	1.1
Cu I	213.854	92.1
Zn I	213.857	42500.9
Ni II	213.858	226.9
Fe I	213.859	4.4
Co I	213.897	3.0
Re II	213.904	82.6
W II	213.916	118.9

7.2 Method development ICP-MS

7.2.1 Calibration curves and statistics for Pt, Pd and Rh







The calibration curve statistics for the calibration curves of Pt, Pd and Rh in ICP-MS can be seen in Table A2.

Table A2 Calibration statistics for the calibration curves of Pt, Rh and Pd for the ICP-MS.

A	Mass	Curve Type	Slope	Intercept	Corr.Coeff	1	2	3	4	Unit
Pt	195	Linear Thru Zero	5468.038	0	0.999993	25	50	75	100	ppb
Rh	103	Linear Thru Zero	55499.61	0	0.999907	25	50	75	100	ppb
Pd	105	Linear Thru Zero	10647.79	0	0.999965	25	50	75	100	ppb

7.3 Calculation of retained and recovered percentage

The amount of elements adsorbed on the SPE cartridges, $[M]_{adsorbed}$ was calculated from the concentration of elements found in the effluent $[M]_{effluent}$ and the concentration of metals in the feed solution $[M]_{feed}$ using equation 1. Where available, the $[M]_{feed}$ was found by analysing a reference solution of the feed solution, in case the actual concentration differed from the theoretical value. The theoretical value was used when a reference solution was not available.

$$[M]_{adsorbed} = [M]_{feed} - [M]_{effluent} \tag{1}$$

The percentage of element found in the effluent, compared to the feed solution, was found by using equation 2. This is the equation used for the breakthrough curves.

$$\%\, in\, effuent = \frac{[M]_{effluent}}{[M]_{feed}} * 100\% \tag{2}$$

The percentage of elements adsorbed was calculated from the $[M]_{adsorbed}$ and the $[M]_{feed}$ using equation 3.

$$\%\, adsorbed = \frac{[M]_{adsorbed}}{[M]_{feed}} * 100\% \tag{3}$$

Finally, the percentage recovered was calculated from the concentration of elements recovered in the eluent step, $[M]_{recovered}$ and the $[M]_{adsorbed}$ using equation 4.

$$\%\, recovered = \frac{[M]_{recovered}}{[M]_{adsorbed}} * 100\% \tag{4}$$

7.4 Statistics

7.4.1 LOD and LOQ for ICP-OES

The ICP-OES has an implemented way of saying the result is under the limit of detection. The instrument LOD was still checked by analysing 10 replicates of the calibration blank. The Raw data obtained from the ten replicates is seen in Table A3 and the statistics (including LOD and LOQ) obtained from these replicates is seen in Table A4. The calibration curve used multielement standard solutions ranging from blank to 1.5 µg mL^{-1} for each element.

Table A3 The raw data (ng mL^{-1}) obtained from 10 measurements of the calibration blank on the ICP-OES

	LOD1	LOD2	LOD3	LOD4	LOD5	LOD6	LOD7	LOD8	LOD9	LOD10
Pt 214.424	-9.7	-7.7	-1.7	-13.3	-10.1	-8.1	-15.0	-5.5	1.4	-7.3
Fe 238.204	-5.4	-5.4	-5.8	-5.3	-5.3	-5.7	-6.6	-6.4	-6.2	-6.4
Rh 343.488	2.6	2.0	3.2	12.9	6.0	10.3	-2.3	6.2	9.7	-1.7
Pd 340.458	-1.8	-2.7	2.1	-1.5	-8.4	-3.9	-3.4	-6.4	3.4	-0.7
Al 396.152	-2.8	-8.4	-5.3	-6.9	-6.0	-7.0	-6.4	-5.8	-7.2	-7.0
Cu 327.395	-3.1	-3.4	-2.7	-3.4	-3.2	-1.8	-2.0	-1.0	-2.7	-3.7
Cr 205.560	-3.4	-4.1	-1.4	-2.1	-0.3	-6.4	-3.8	-5.6	-4.5	-5.4
Zn 213.857	-1.0	-0.8	-1.1	-1.2	-1.3	-2.0	-1.8	-2.0	-1.8	-1.6

Table A4 The statistics from the ten measurements of the calibration blank on the ICP-OES, in addition to the LOD and the LOQ. Values in ng mL^{-1}.

	average	St.Dev	LOD 3 x St.Dev	LOQ 10 x St.Dev
Pt 214.424	-7.7	4.9	14.8	49.4
Fe 238.204	-5.9	0.5	1.5	5.1
Rh 343.488	4.9	5.1	15.2	50.6
Pd 340.458	-2.3	3.5	10.6	35.4
Al 396.152	-6.3	1.5	4.5	15.2
Cu 327.395	-2.7	0.8	2.5	8.3
Cr 205.560	-3.7	2.0	5.9	19.6
Zn 213.857	-1.5	0.4	1.3	4.3

7.4.2 LOD and LOQ for ICP-MS

The raw data output for ten readings of a blank solution in the ICP-MS can be seen in Table A5. This was done over an 80 minute run on the ICP-MS, using a “linear through zero” calibration curve ranging from blank to 100 ng mL^{-1} of the elements. Recalibration was done between replicate five and six. The two first replicates of Pd were much higher than the last eight. This is likely due to memory effects from the high-concentration calibration solution analysed previous to the two blank replicates. The two measurements is included in the calculation of the LOD and LOQ in order to more accurately account for the actual conditions used in the analyses of the samples. Standard deviation was calculated using the MS Excel function for standard deviation. The LOD and LOQ values can be seen in Table A6.

Table A5 The raw data from 10 measurements of the blank solution measured in ICP-MS. Values in ng mL^{-1}.

	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Pt 195	-0.04	-0.05	-0.13	-0.03	-0.03	0	0	0.02	0	0
Rh 103	-0.04	-0.05	-0.07	-0.01	-0.01	0.01	0	0	0	0
Pd 105	0.76	0.75	-0.05	-0.01	-0.01	0.04	0.01	0.02	0	0

Table A6 Statistics from the 10 measurements of the blank solution. Values in ng mL^{-1}.

	Average	**St.Dev**	**LOD 3xSt.Dev**	**LOQ 10xSt.Dev**
Pt 195	-0.025	0.044	0.13	0.44
Rh 103	-0.018	0.026	0.08	0.26
Pd 105	0.166	0.312	0.94	3.12

If the first two Pd measurements are omitted, the LOD is reduced to 0.12 and the LOQ is reduced to 0.39 ng mL^{-1}. This corresponds better with the values obtained for Pt and Rh.

7.4.3 Grubb’s test for outliers

Grubbs’ test is the ISO recommended test for outliers. It can be used for sample population down to 3. The null hypothesis H_0 is used, which tests that all samples are from the same population. The G statistic is calculated using the $\bar{x}$ and s with the suspected value included and can be seen in equation (5)

$$G = \frac{|suspect\ value - \bar{x}|}{s} \tag{5}$$

The critical value for the G statistic for a two-sided test with P = 0.05 is 1.155 for n = 3 and 1.481 for n = 4. If the calculated G statistic is larger than the critical value, the sample can be rejected [51].

7.4.3.1 Separation scheme

The replicates of Pt and Rh in the effluent of the aged solutions from the separation scheme (section 4.7) can be seen in Table A7. The calculation of the G statistics is seen below.

Table A7 Replicate values from the separation scheme data sets, containing suspected outliers. Values in ng mL^{-1}.

	1 Pt aged (flowthrough)	2 Rh aged (flowthrough)	3 Pt fresh (TU+HCl first 5mL)
Rep 1	23.86	168.71	56.83
Rep 2	13.92	95.68	56.34
Rep 3	14.12	97.2	83.89
Average	17.30	120.53	65.69
St.dev	5.68	41.73	15.77

$$G_1 = \frac{|34.86 - 17.30|}{5.68} = 1.155$$

$$G_2 = \frac{|168.71 - 120.53|}{41.73} = 1.155$$

$$G_3 = \frac{|83.89 - 65.69|}{15.77} = 1.154$$

The critical value for 3 replicates is 1.155 so the suspected outliers from G_1 and G_2 are rejected while the suspected outlier from G_3 is not rejected.

7.4.3.2 Effluent and wash of Zn from DOS-impregnated RP-SPE

The replicate values of Zn in the effluent and H_2O wash of the adsorption of analytes on DOS-impregnated RP SPE (section 4.5.1) can be seen in Table A8.

Table A8 Replicate values from the data sets of DOS-impregnated SPE, containing suspected outliers. Values in µg mL^{-1}.

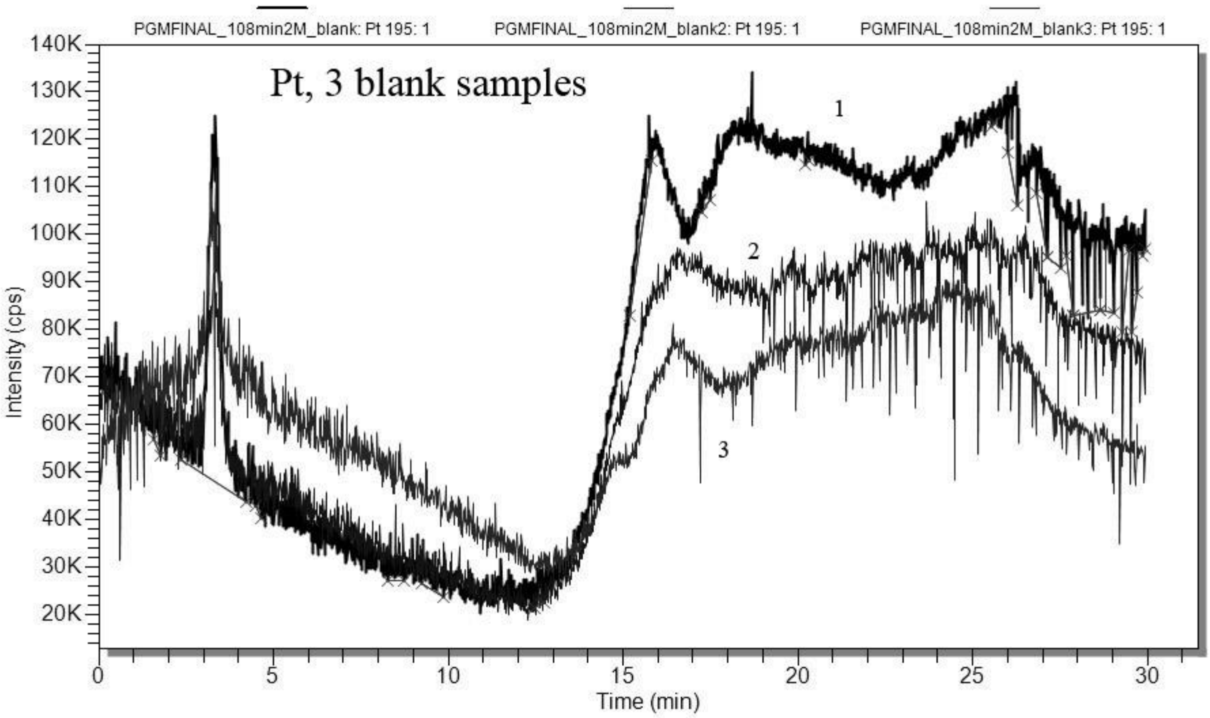
	4 **Effluent**	**5** **H_2O wash**
Rep 1	0.851	0.124
Rep 2	1.067	0.261
Rep 3	0.854	0.116
Rep 4	0.865	0.128
Average	0.909	0.157
St.dev	0.105	0.069

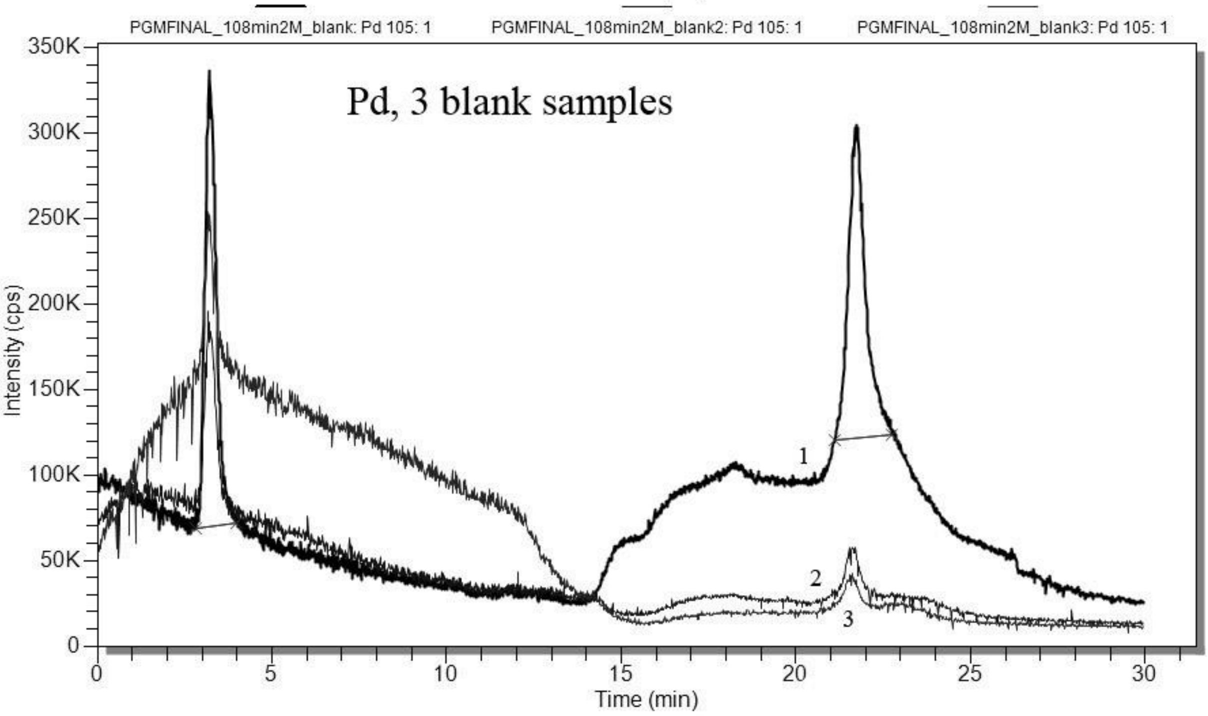
$$G_4 = \frac{|1.067 - 0.909|}{0.105} = 1.504$$

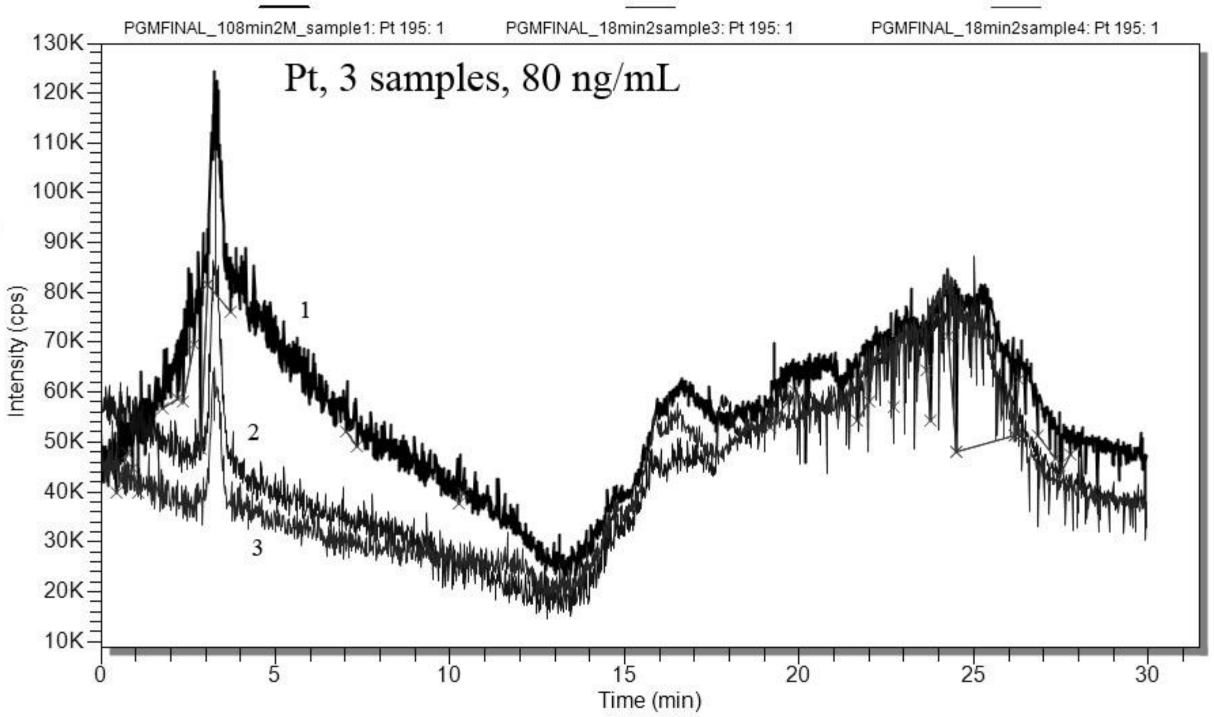
$$G_5 = \frac{|0.261 - 0.157|}{0.069} = 1.507$$

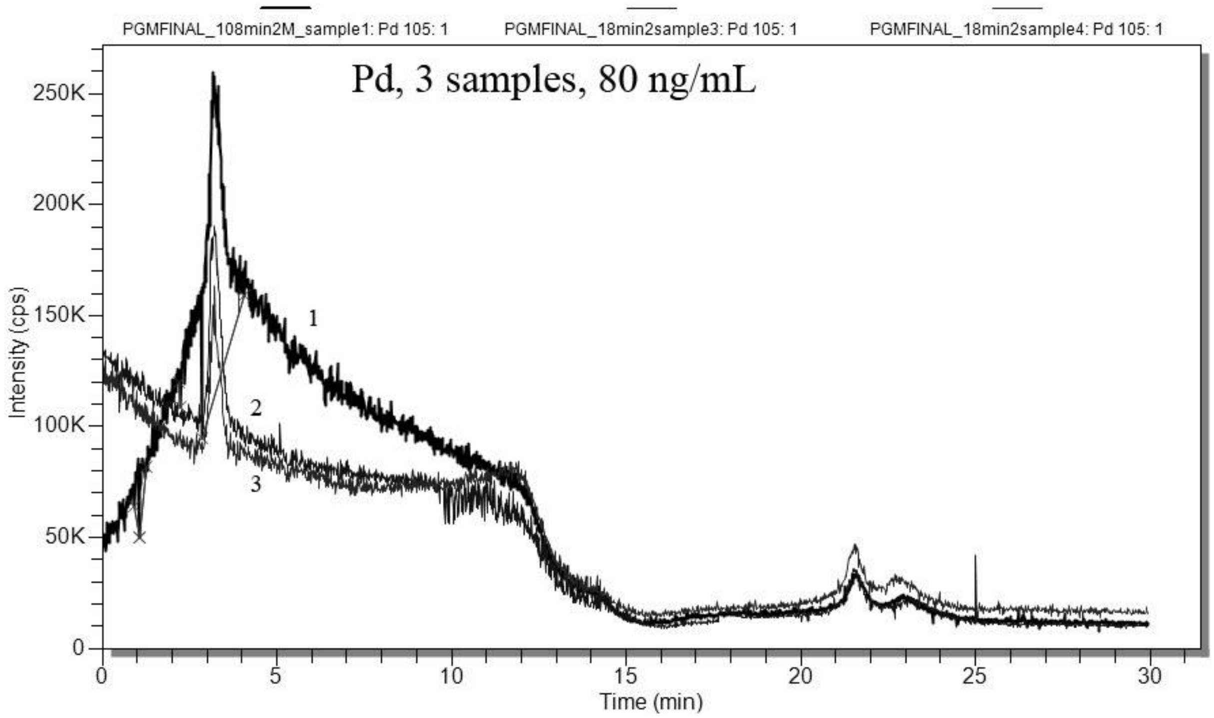
Both G_4 and G_5 is higher than the critical value of 1.481 (for four replicates) and both suspected outliers are rejected.

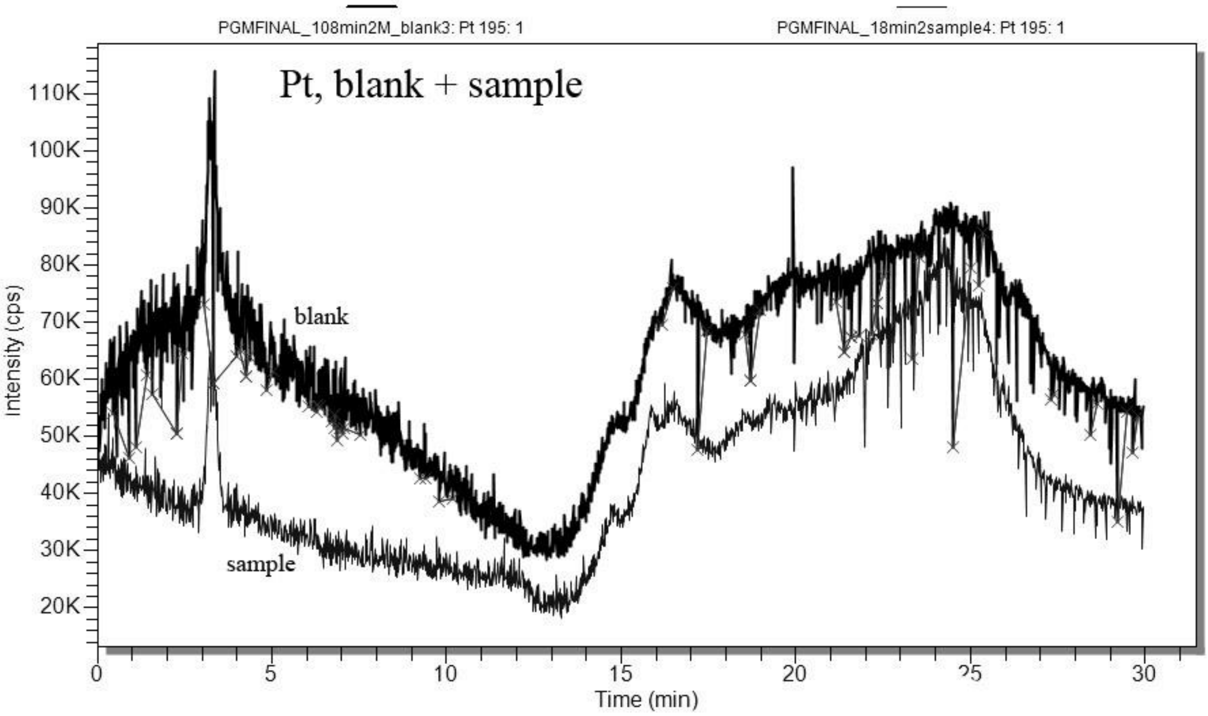
7.5 LC-ICP-MS chromatograms

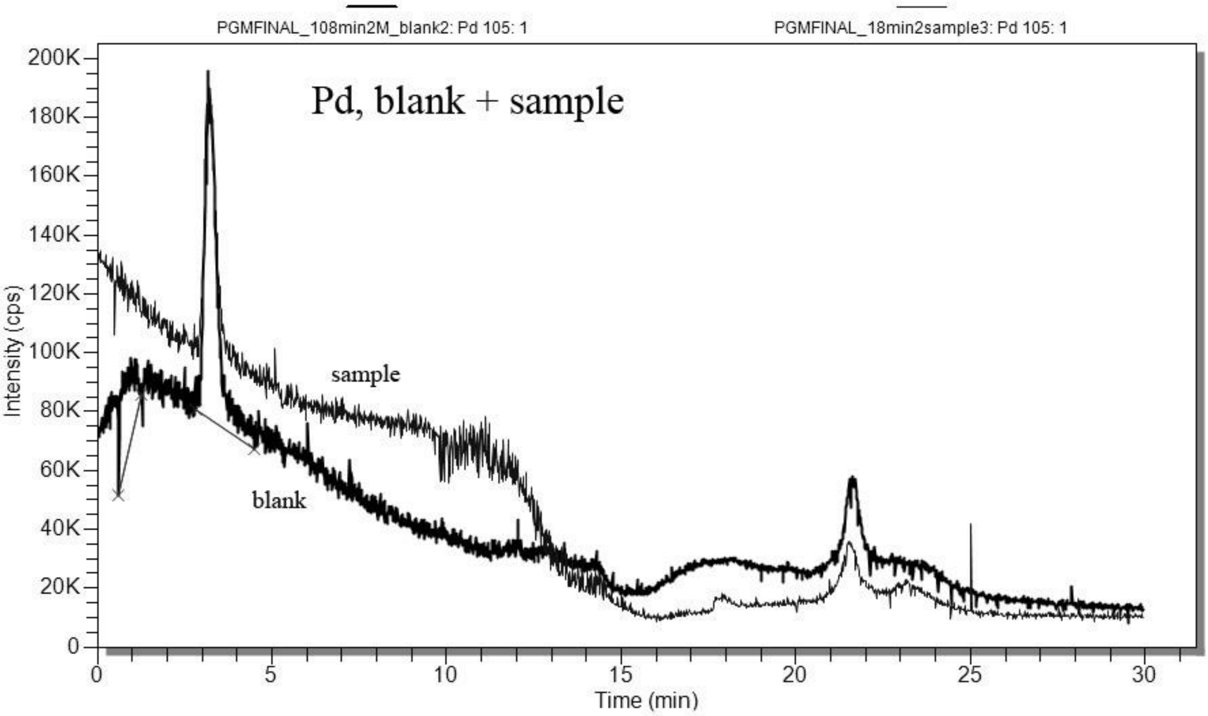


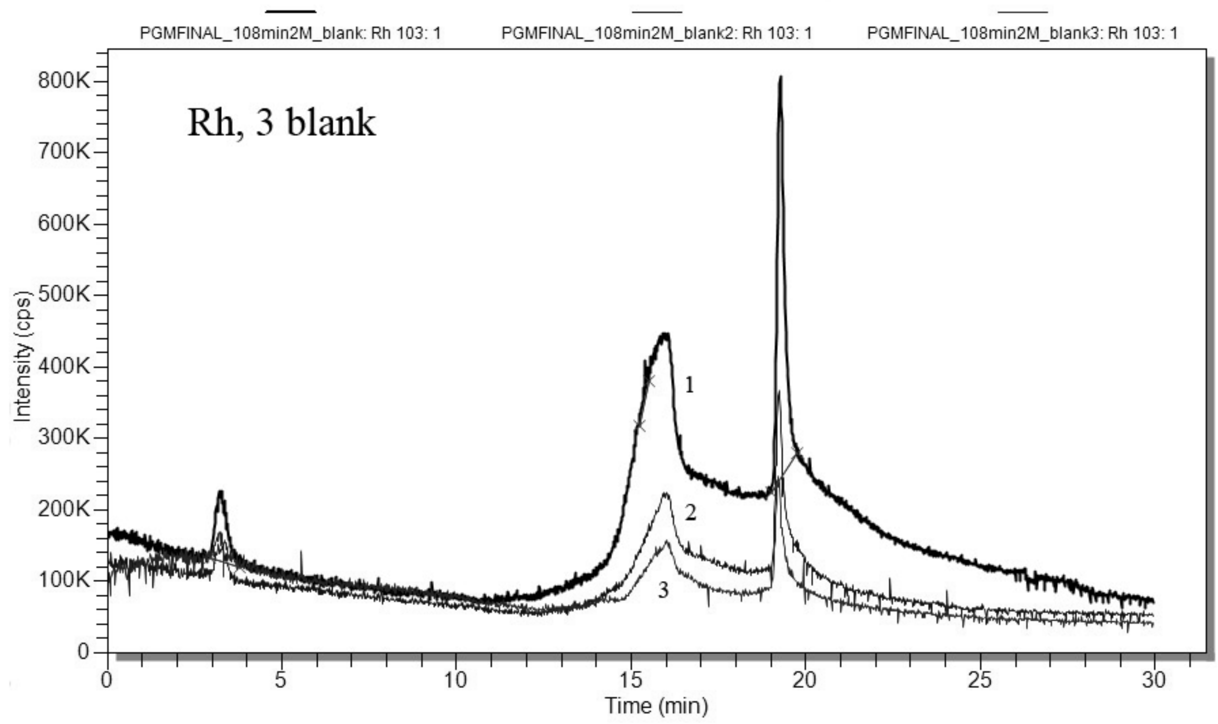



PGMFINAL_108min2M_sample1: Pt 195: 1
PGMFINAL_18min2sample3: Pt 195: 1
PGMFINAL_18min2sample4: Pt 195: 1
Pt, 3 samples, 80 ng/mL
Intensity (cps)
130K
120K
110K
100K
90K
80K
70K
60K
50K
40K
30K
20K
10K
0
5
10
15
20
25
30
Time (min)
1
2
3


PGMFINAL_108min2M_sample1: Pd 105: 1
PGMFINAL_18min2sample3: Pd 105: 1
PGMFINAL_18min2sample4: Pd 105: 1
Pd, 3 samples, 80 ng/mL
Intensity (cps)
250K
200K
150K
100K
50K
0
5
10
15
20
25
30
Time (min)
1
2
3


PGMFINAL_108min2M_blank3: Pt 195: 1
PGMFINAL_18min2sample4: Pt 195: 1
Pt, blank + sample
blank
sample
Intensity (cps)
110K
100K
90K
80K
70K
60K
50K
40K
30K
20K
0
5
10
15
20
25
30
Time (min)


PGMFINAL_108min2M_blank2: Pd 105: 1
PGMFINAL_18min2sample3: Pd 105: 1
Pd, blank + sample
sample
blank
Intensity (cps)
200K
180K
160K
140K
120K
100K
80K
60K
40K
20K
0
0
5
10
15
20
25
30
Time (min)



7.6 Selected Raw Data

7.6.1 Raw data from the separation scheme

The raw data results from the separation scheme can be seen in the tables A9, A10 and A11.

Table A9 Results and statistics of the content of Pt in the different samples from the separation scheme. Flowthrough and the sum of Pt aged has 2 replicates while the rest have 3. Values are in ng mL^{-1}.

		Pt aged (%)	±	stdev	RSD (%)	Pt fresh	±	stdev	RSD (%)
1	**flowthrough**	14.0	±	0.14	1	<LOD			
2	**5mL 1M HCl**	4.4	±	0.35	8	2.0	±	0.41	21
3	**5mL 1M HCl**	4.9	±	0.31	6	3.1	±	0.19	6
4	**10mL water**	<LOD				0.059	±	0.0042	7
5	**5mL 0.5M HNO_3**	<LOQ				<LOQ			
6	**5mL 0.5M HNO_3**	0.71	±	0.066	9	0.7	±	0.12	18
7	**10mL water**	<LOD				0.13	±	0.034	25
8	**5mL 0.5M TU + 0.5M HCl**	68	±	1.6	2	66	±	16	24
9	**5mL 0.5M TU + 0.5M HCl**	6.5	±	0.42	6	9.4	±	0.37	4
	sum	98.8	±	0.5	0.5	81.0	±	15.9	19.7

Table A10 Results and statistics of the content of Rh in the different samples from the separation scheme. Flowthrough and the sum of Rh aged has 2 replicates while the rest have 3. Values are in ng mL^{-1}.

		Rh aged (%)	±	stdev	RSD (%)	Rh fresh	±	stdev	RSD (%)
1	flowthrough	96	±	1.1	1	67	±	7.4	11
2	5mL 1M HCl	3.2	±	0.27	8	25.64	±	0.83	3
3	5mL 1M HCl	<LOD				0.10	±	0.018	19
4	10mL water	<LOD				<LOD (ud)			
5	5mL 0.5M HNO_3	<LOD				<LOD			
6	5mL 0.5M HNO_3	<LOD				0.006	±	0.0016	26
7	10mL water	<LOD				<LOD(ud)			
8	5mL 0.5M TU + 0.5M HCl	<LOD				<LOD			
9	5mL 0.5M TU + 0.5M HCl	<LOD				<LOD			
	sum	99.7	±	1.3	1.3	92.9	±	8.1	8.7

Table A11 Results and statistics of the content of Pd in the different samples from the separation scheme. All results have got 3 replicates. Values are in ng mL^{-1}.

		Pd aged (%)	±	stdev	RSD (%)	Pd fresh	±	stdev	RSD (%)
1	flowthrough	<LOD				<LOD			
2	5mL 1M HCl	<LOD				<LOD			
3	5mL 1M HCl	<LOD				0.6	±	0.68	115
4	10mL water	<LOD				0.3	±	0.30	91
5	5mL 0.5M HNO_3	87	±	1.3	2	93	±	4.6	5
6	5mL 0.5M HNO_3	<LOD				0.5	±	0.35	66
7	10mL water	<LOD				0.10	±	0.048	49
8	5mL 0.5M TU + 0.5M HCl	4	±	1.9	47	3	±	1.8	56
9	5mL 0.5M TU + 0.5M HCl	<LOQ				<LOD			
	sum	91.5	±	1.0	1.1	97.7	±	5.2	5.3

7.7 Raw data ID's from all the figures containing data

Adsorption effects by sample solution acidity, Figure 7

0 M	TB-008
0.15 M	TB-024
0.5 M	TB-009
1 M	TB-010

Adsorption effects from storage over time, Figure 8

Fresh	TB-029
3 months	TB-024

Recovery of adsorbed Pt and Pd from SAX, Figure 9

0.5 M HCl	TB-029
10 mL 1 M HCl	TB-001
20 mL 1 M HCl	TB-007
3 M HCl	TB-008, TB-009, TB-010
6 M HCl	TB-008
0.5 M HNO_3	TB-004
0.5 M HNO_3	TB-005
3 M HNO_3	TB-008, TB-009, TB-010
6 M HNO_3	TB-008
1 M H_2SO_4	TB-006
5, 10 and 15 mL TU + HCl	TB-030

Adsorption on SCX, Figure 12

216 days, 0.15 M HCl	TB-011
Fresh, 0.15 M HCl	TB-012
154 days, 0.5 M HCl	TB-014
154 days, 1.0 M HCl	TB-013
Fresh, 1.0 M HCl	TB-028

Elution on CN, Figure 17

5 mL 6 M HCl	TB-034
5 mL 3 M HCl	TB-036
10 mL 1 M HCl + 0.1 M TU	TB-035

Breakthrough Pd on CN, Figure 18

Methanol-cond.	TB-043
Water-cond.1	TB-044
Water-cond.2	TB-047
Water-cond. ICP-MS	TB-048

Recovery of Pt and Pd from DOS-impregnated sorbent, Figure 20

5 mL methanol	TB-031
10 mL HCl + TU	TB-032
5 mL 6M HCl	TB-033
1 % NH_3, 3 % NH_3, 5 % NH_3	TB-040

Pd breakthrough on DOS-impregnated RP, Figure 22

Replicate 1	TB-045
Replicate 2	TB-046

Separation scheme, Figure 27

Aged solution	TB-052, TB-053, TB-054
Fresh solution	TB-056, TB-057, TB-058

Other

SAX elution. TU solutions, Figure 10	TB-051
SAX breakthrough, Figure 11	TB-049
SCX elution, Figure 13	TB-003
SCX breakthrough, multielement, Figure 14	TB-016
SCX breakthrough, Al, Figure 15	TB-050
CN adsorption, Figure 16	TB-034, TB-035, TB-036
DOS-mod RP adsorption, Figure 19	TB-031, TB-032, TB-033, TB-040
DOS-mod breakthrough, multi, Figure 21	TB-038