Atomic Spectroscopy

Article

An Alumina-based Method for the Preconcentration of Pd, Pt, and Au Determined by Flow Injection-ICPMS: A Fast and Accessible Approach

Madison Langley, Sarah Meston, and Diane Beauchemin*

Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, ON K7L 3N6, Canada

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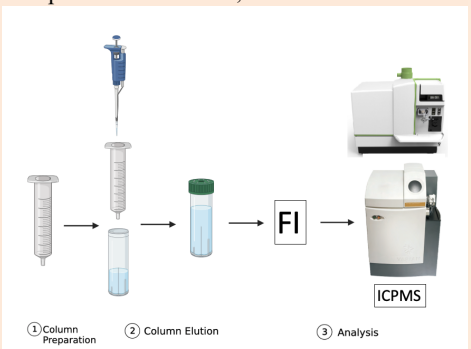
ABSTRACT: A method for the preconcentration and determination of Pd, Pt, and Au in ore was developed. A basic alumina sorbent with an 0.01 M HCl conditioning wash was used for the retention of chloro-complexed noble metals, which were then eluted with a 3% thiourea and a 10% aqua regia mixture. Flow injection was used for introduction of eluates into inductively coupled plasma mass spectrometry to effectively mitigate signal drift typically caused by thiourea with direct nebulization. Using this method, complete recovery (i.e. a 25-fold preconcentration) was achieved for Pd and Pt with an 8-fold recovery for Au and effective removal of matrix interferences. The method was validated using CDN-PGMS-29 ore reference material: agreement with certified concentrations of Pd, Pt and Au was achieved based on a Student's t-test at the 95% confidence level. This simple, low-cost method enables efficient preconcentration of Pd, Pt and Au, making it well suited for trace determination of Pt, Pd and Au for geological applications.



INTRODUCTION

Palladium, platinum, and gold are noble metals located within the fifth and sixth rows of the periodic table. They are valued for their distinct chemical and physical properties such as high ability for corrosion resistance, high melting points, and catalytic properties that make them crucial to various industrial applications.[1] Due to the increasing global demand for these metals, the development of efficient and accessible methods for determination in geological samples becomes increasingly urgent, as the analysis of geological samples for noble metals presents significant challenges in current analytical methods.

The determination of Pd, Pt, and Au is often hindered due to their occurrence in ore deposits with complex matrices and at low concentrations (from low μg kg^{-1} level to mg kg^{-1} level).[2] Indeed, although inductively coupled plasma mass spectrometry (ICPMS) is the preferred technique for ultra-trace analysis, challenges arise from spectroscopic interferences.[3] Matrix elements, such as Cu, Zn, Sr, Y, Zr, Ta, Yb, and Hf, can form polyatomic species that interfere with Pd, Pt, and Au isotopes (Table S1).[4] Those interferences may be reduced by using double-focusing mass spectrometry in high resolution mode or by using a collision-reaction cell (CRC) or collision-reaction interface (CRI), but at the expense of sensitivity. The many laboratories that are not equipped with these specialized instrument features may use another analyte isotope free from significant interferences if available, again with a concurrent sacrifice in sensitivity as the alternative isotope is usually less abundant, or apply a correction equation, introducing a source of error in the process.[5]

Using preconcentration techniques prior to ICPMS analysis can address such analytical challenges. Among many preconcentration techniques, solid phase extraction (SPE) is promising due to its efficiency, simplicity, and the potential to simultaneously remove matrix interferents while improving detection limits.[6] However, many current SPE methods are selective to one or two analytes, require custom or expensive sorbents, or involve extensive sample

preparation steps and are then prone to contamination.[7]

A previous method by Asfaw *et al*. involved the selective adsorption of chloro-complexes of noble metals on activated alumina (Al_2O_3) and their recovery with 2 M HCl as the eluent.[8] Using Al_2O_3 as a sorbent presents a highly effective and practical solution for the preconcentration of noble metals. Compared to other commercial resins and sorbents, it is relatively inexpensive (less than $100 per 100 g) and is commercially available. It has a large surface area (50-300 m^2/g) and amphoteric properties that allow it to act as a cation or anion exchanger depending on the surface pH.[9] In the acidic form, alumina can selectively retain anionic chloro-complexes of noble metals via electrostatic interactions with the surface while allowing matrix cations to pass through the column. Unfortunately, the above-mentioned alumina-based method required two different sample preparation procedures and used different eluents to recover different elements. Notably, Au could not be determined using this method, requiring evaporation of HNO_3 and elution with thiourea. The authors mentioned that 0.01 M HNO_3/3% thiourea as eluent showed potential for the recovery of Au, Ag, Pt, and Pd but had to be abandoned because this eluent caused significant signal drift when continuously nebulized.

However, signal drift can be alleviated by using flow injection (FI) coupled to ICPMS, where a discrete sample volume is injected into an unsegmented carrier stream, resulting in a transient signal. With FI, short and discrete sample slugs containing thiourea eluent would be immediately washed out by the carrier solution thereby reducing signal drift and carbon deposition on the cones. Other benefits of using FI are high precision, minimal sample consumption and a high sampling rate.[5] Thus, the objective of this work was to develop a simple and unified method for the preconcentration and determination of Pd, Pt and Au using activated alumina and FI-ICPMS. Analytes were adsorbed onto the sorbent as chloro-complexes and subsequently eluted with thiourea-containing eluents. Various parameters, including pH, eluent composition, and column conditioning, were optimized to enable the simultaneous recovery of Pd, Pt and Au in a single elution step so that the method may easily be implemented by commercial laboratories.

EXPERIMENTAL

Instrumentation. To test if the approach suitably separated the analytes from interferents, measurements were conducted using a Varian 820MS quadrupole-based ICPMS instrument (Varian, Mulgrave, Victoria, Australia) without using its CRI. The samples were introduced using a Scott double-pass spray chamber, a MicroMist glass concentric nebulizer (Glass expansion, MA, USA), and a three-channel peristaltic pump. The optimization of the torch alignment was performed daily using a 5 µg L^{-1} tuning solution containing Be, Mg, Co, In, Ce, Pb, and Ba in 1% HNO_3. Alternatively, measurements were conducted using a NexION 2000B (PerkinElmer, Waltham, MA, USA) quadrupole-based ICPMS instrument, without using its CRC. The samples were introduced using a Meinhard glass concentric nebulizer, a glass cyclonic spray chamber and a three-channel peristaltic pump. The optimization of daily operating conditions was conducted using a tuning solution of 1 µg/L Be, Ce, Fe, In, Li, Mg, and Pb. All optimized ICPMS operating conditions are summarized in Table 1. After measurements, the instrument was flushed with 2% HNO_3 for 5 min with the plasma on for daily cleaning.

Table 1. Varian 820MS and NexION 2000B ICPMS optimized operating conditions

Parameter	Value	
	Varian 820 MS	NexION 2000B
Ar plasma gas flow rate (L min^{-1})	18.0	18.0
Ar auxiliary gas flow rate (L min^{-1})	1.75	1.20
Ar nebulizer gas flow rate (L min^{-1})	0.90	1.00
Ar sheath gas flow rate (L min^{-1})	0.04	0.99
Plasma RF power (kW)	1.40	1.60
Spray chamber temperature (°C)	3	N/A
Sample uptake rate (µL min^{-1})	300	300
Dwell time (ms)	10	20
Sampling position [a]	6.0	0
Monitored analytes (m/z)	$^{105}Pd^+$, $^{197}Au^+$	$^{115}In^+$, $^{195}Pt^+$,

[a]: distance between the load coil and the interface for Varian 820 MS, mm, distance on the z axis for NexION 2000B.

Flow injection manifold. A manual Cheminert 6-port valve FI manifold (Valco Instruments Co. Inc., Brockville, ON, Canada) was fitted with a 50 µL sample loop and used doubly deionized water (DDW) as the carrier. The valve was positioned as closely as possible to the nebulizer to minimize dispersion (Fig. 1a).

Reagents. Doubly deionized water (DDW) for the preparation of sample solutions came from an Arium Pro UV/DI (Sartorius Stedim Biotech, Göttingen, Germany) water purification system. The water was purified to a resistivity of 18 MΩ cm. All the polypropylene bottles and graduated cylinders were soaked in 10% (v/v) HCl overnight prior to use. They were rinsed thoroughly with DDW prior to use. Two different sorbents were tested: activated acidic alumina (Brockmann Activity I, standard grade, 80 – 200 mesh particle size, 58 Å pore size, pH 4.5 ± 0.5, Sigma Aldrich, Canada) and activated basic alumina (Brockmann Activity I, standard grade, 80 – 200 mesh particle size, 58 Å pore size, pH 9.5 ± 0.5, Acros Organics, Canada). For the eluents, sub-boiled HCl and HNO_3 (ACS grade; Fisher Scientific, Canada), purified using a DST-1000 sub-boiling distillation system (Savillex, Minnetonka, MN, USA), and reagent grade thiourea (Sigma Aldrich ≥99.9%, India) were used. Argon (99.996% purity, liquid in Dewar, MEGS Specialty Gases, Ottawa, ON, Canada) served for the plasma, auxiliary, bypass, and carrier gases during ICPMS analysis.

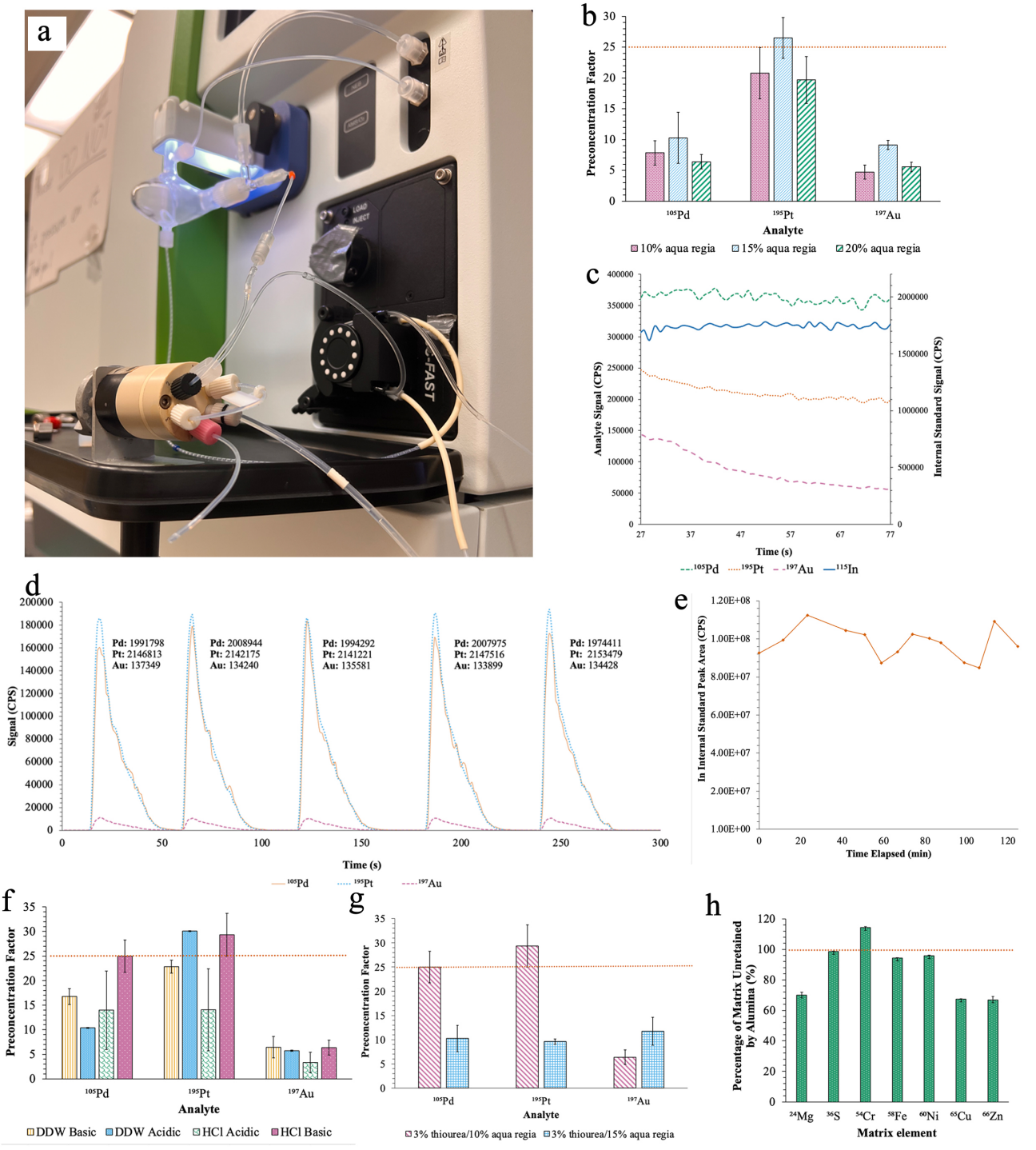


Fig. 1 (a) Example of FI sample introduction setup (with NexION 2000B); (b) Preconcentration factor using various concentrations of aqua regia with 3% thiourea as an eluent on an acidic alumina sorbent washed with 10 mL of DDW (n=5) (Varian 820MS); (c) Direct Nebulization of a 3% thiourea eluent solution (NexION 2000B); (d) Temporal profile of five replications FI peak injections using a 3% thiourea eluent (NexION 2000B); (e) Internal standard (In) peak area measured in eluates over time with a 3% thiourea eluent; (f) Preconcentration factor of noble metals on acidic and basic alumina washed with 10 mL of DDW or 0.01 M HCl (n=2) and eluted with 3% thiourea/10% aqua regia (NexION 2000B); (g) Preconcentration factor of noble metals on basic alumina washed with 0.01 M HCl and eluted with 3% thiourea/10% aqua regia (n=2) and on acidic alumina washed with DDW and eluted with 3% thiourea/15% aqua regia (n=3) (NexION 2000B); (g) Fraction of matrix elements passing through the column when the column is loaded with 1 mg L^{-1} of matrix elements (n=3) (NexION 2000B).

Standard solutions and certified reference material. A 10 mg L^{-1} multi-elemental stock solution was prepared by weight from 10,000 and 1,000 mg L^{-1} mono-elemental analytical grade standard solutions (SCP Science, Baie d'Urfé, QC, Canada). The stock solution when not in use, was stored in the fridge in a polypropylene bottle to prevent degradation. For method optimization, the stock solution was diluted to 1 µg L^{-1} in a matrix of 0.01 M sub-boiled HCl (ACS grade; Fisher Scientific, Ottawa, ON, Canada) and used as test solution. For method validation, a certified reference material (CRM) of ore containing noble metals, CDN-PGMS-29 sourced from the Bushveld mafic intrusive complex in northern South Africa, was subjected to a proprietary fire assay method by Activation Laboratories Ltd. with the resulting prill dissolved to give a 4.5-mL solution in 10% v/v HCl. Prior to preconcentration, 100 µL of the CRM solution provided by Activation Laboratories Ltd. was diluted to 100 mL, adjusting the final HCl concentration to 0.01 M HCl in the process.

Preconcentration procedure. Simple alumina columns were prepared by loading 2 g of activated alumina into 20-mL syringes (12-cm long, with an inner diameter of 3.4 cm) plugged with quartz wool so that the bed depth was 3 cm. Sieving was avoided while loading alumina in the columns as this produced the best recoveries with good reproducibility. Gravity sample feeding and elution were carried out. Each column was washed with 10 mL of DDW or 0.01 M HCl and then 100 mL of gravity-fed sample solution was loaded carefully so as not to disturb the alumina, resulting in a flow rate of approximately 7.5 mL min^{-1}. After all the sample solution had passed through the column, the column was dried with a stream of nitrogen gas for 2-3 min to remove interstitial solution. Plastic vials with a screwable cap were then placed under each column and 4 mL of the eluent were added, which passed through at a flow rate of approximately 2 mL min^{-1}. A 25-fold preconcentration thus resulted when 100 percent recovery was achieved. A constant stream of nitrogen gas was applied for 2-3 min until the column was adequately dried and all the eluate collected. Each eluate collection bottle was spiked with In to achieve 25 µg L^{-1} In in each eluate prior to analysis. For each eluent tested, two to five replicate columns were eluted to ensure that the results were reproducible and to correct for drift. Eluates were analyzed by FI-ICPMS using five replicate injections to ensure reproducibility of the results. Between the testing of each eluent, the FI manifold was rinsed with DDW to clean the sample loop and tubing.

Data processing. The results from the analysis procedure were exported to Microsoft Excel. Point-by-point internal standardization was conducted by dividing the analyte signal by that of the internal standard, ^{115}In. The resulting temporal profile was examined to determine the start and end points of each FI peak, which was then background-corrected using a blank before integrating the peak area. The peak areas of replicates were then averaged. The preconcentration factor was calculated by dividing the peak area of the preconcentrated eluate signal by the peak area of the signal resulting from FI of the non-preconcentrated sample solution.

RESULTS AND DISCUSSION

Thiourea/aqua regia eluent. In a ferrofluid-based sorbent method by Gotame *et al*., chloro-complexed noble metals were eluted using 3% thiourea/10% aqua regia.[10] Aqua regia is known for its ability to dissolve noble metals, which may help enhance desorption from alumina. It may also allow thiourea to gain a positive charge that would help facilitate thiourea-noble metal complex formation. Furthermore, combining aqua regia and thiourea may help to reduce signal drift resulting from thiourea complexing onto the walls of the peristaltic pump tubing and increase elution efficiency.[11]

The concentration of thiourea was first varied (3%, 4%, 5%, and 6% thiourea) in an eluent containing 5% aqua regia. However, a complete preconcentration was not achieved for any of the metals using these conditions. As the thiourea concentration increased, the relative standard deviation also became larger. Because 3% thiourea achieved the greatest preconcentration with good reproducibility, it was used for further optimization conducted while varying the concentration of aqua regia (10%, 15%, and 20%) in the eluent (Fig. 1b). A complete recovery of Pt was achieved with 3% thiourea/15% aqua regia as well as the highest preconcentration between the three eluents for Pd and Au.

Verification of FI for drift mitigation using a 3% thiourea-based eluent. Asfaw *et al*. observed that eluates containing 3% thiourea induced signal drift in the internal standard by more than 50% compared to thiourea-free eluates when directly aspirated, leading them to move away from a thiourea-based eluent.[8] Fig. 1c shows a downward signal trend for all analytes, most notably for Pt and Au, which is not present in the In internal standard signal, making In ineffective in correcting for the thiourea-induced drift. Through flow injection, signal drift can be mitigated using two operational principles of the technique. Noble metal-thiourea complexes tend to adhere to peristatic pump walls; however, with flow injection, the sample is introduced downstream of the peristaltic pump to minimize contact with peristaltic pump tubing.[11] Furthermore, thiourea can lead to carbon deposits on the ICP torch and the cones causing signal drift, which is minimized through continuous washing by the DDW carrier. Fig. 1d illustrates the advantages of using FI to reduce signal drift as shown in the temporal profile of five replicate injection peaks with a 3% thiourea/10% aqua regia eluent. The reproducibility of these peaks can be demonstrated by relative standard deviation values of 0.71%, 0.23%, and 1.0% for Pd, Pt, and Au respectively in Fig. 1d. To assess the signal stability over longer periods of time, the peak area of the internal standard (In) was plotted versus time in Fig. 1e.

Table 2. Sensitivity and instrumental detection limits of 0.01 M HCl conditioning wash with 2 g of basic alumina using a 3% thiourea/ 10% aqua regia eluent without (A) and with (B) preconcentration

Analyte	Sensitivity (counts L µg^{-1})		Improvement Factor (B/A)	Detection Limits (µg L^{-1})		Improvement Factor (A/B)
	Without (A)	With (B)		Without (A)	With (B)	
^{105}Pd	132000 ± 7000	1644000 ± 96000	12.5 ± 1.0	0.07	^{105}Pd	2
^{195}Pt	37000 ± 3400	1047000 ± 18000	28 ± 3	0.03	^{195}Pt	4
^{197}Au	82800 ± 1800	535000 ± 17000	6.5 ± 0.3	0.008	^{197}Au	4

As can be seen, the In peak area is relatively stable, with a relative standard deviation of 8.4% for the 14 samples with 5 replicate injections done over a 2-h period, without any indication of a downward drift. Furthermore, at the 95% confidence level, a Student's t-test did not indicate a significant difference in the In signal between the 0.01 M HCl and the eluate matrices. Hence, FI may be used for the reproducible sample introduction of thiourea-containing eluents and analyte signals in the sample and preconcentrated sample can be directly compared to calculate the preconcentration factor.

Sorbent pH and column conditioning. Alumina is commercially available in either basic (pH 9.5 ± 0.5) or acidic (pH 4.5 ± 0.5) form. So far in this work, only acidic alumina was used. At a pH below ~8.5, the alumina surface carries a net positive charge.[12] The noble metal chloro-complexes are negatively charged and are retained on the column while any matrix cations simply pass through. However, previously, basic alumina was used for the preconcentration of Pd chloro-complexes in a sample solution with pH of 1.0.[13] Another study also showed that, depending on the sorbent pH, some analytes were more strongly retained.[14] The effect of the pH of the column conditioning step on retention was thus evaluated. To avoid the use of a buffer solution, the column was simply conditioned with 10 mL of 0.01 M HCl prior to sample loading. This acidic conditioning wash was compared with the previous DDW wash and tested on both acidic and basic alumina sorbents. As shown in Fig. 1f, using the acidic wash on a basic column achieved complete recovery of Pd and Pt, highlighting the importance of the conditioning step and matching the column conditions to the sample matrix prior to loading. Compared to the previously optimized 3% thiourea /15% aqua regia eluent with a DDW conditioning of an acidic alumina column, there is a greater recovery with basic alumina, a 0.01 M HCl conditioning and 3% thiourea /10% aqua regia eluent for Pd and Pt (Fig. 1g). Only if Au is the only analyte of interest would the acidic alumina method with 3% thiourea/15% aqua regia eluent be advantageous.

Sensitivity and detection limits. For calibration, 100 mL of multi-element standard solutions (0, 0.1, 0.5, 1, 5 µg L^{-1}) containing noble metals in 0.01 M HCl were used. The calibration solutions were loaded onto the column and eluted. To enable a direct comparison of sensitivity and detection limits, an additional set of calibration standards was prepared in 0.01 M HCl without preconcentration. Linear calibration curves resulted ($R^2 > 0.991$) for all analytes. The sensitivity and detection limit were calculated as the slope of the calibration curve and ten times the standard deviation of the blank signal divided by sensitivity respectively. Sensitivity and instrumental detection limits with and without preconcentration using the proposed method are summarized in Table 2. The improvement in detection limits is less pronounced, reflecting differences in the signal-to-noise ratio of the two matrices. This comparison therefore provides a conservative improvement of method performance as geological samples typically possess more complex matrices under which the improvement of preconcentration is expected to be more pronounced.

Table 3. Measured analyte concentration with internal standard (I.S) (mean ± standard deviation, µg kg^{-1}) of Au (n=4), Pt (n=3), and Pd (n=3) by the proposed method and without I.S. compared to the certified concentration (mean ± standard deviation, µg kg^{-1}) in CDN-PGMS-29

Analyte	Measured (with I.S.)	Measured (without I.S.)	Certified
Pd	5.04 ± 0.37	8.14 ± 0.49	4.51 ± 0.36
Pt	4.26 ± 0.90	3.02 ± 0.95	3.67 ± 0.38
Au	0.62 ± 0.18	1.069 ± 0.065	0.587 ± 0.093

Method selectivity. Three replicates of a 100 mL sample solution containing 1 µg L^{-1} of the noble metals with 1 mg L^{-1} of matrix elements (Cr, Cu, Fe, Ni, Mg, S, and Zn) were passed through columns packed with 2 g of basic alumina and preconditioned with 10 mL of 0.01 M HCl. Fig. 1h demonstrates that 66 – 114% of the matrix elements passed through. Subsequently eluting analytes with 3% thiourea/10% aqua regia revealed that the matrix elements neither interfered with the preconcentration of the noble metals nor with their accurate determination.

Assessment of method accuracy. To verify method accuracy for geological applications, a certified ore reference material, CDN-PGMS-29 was used. A 100 µL aliquot of the pre-digested CRM provided by Activation Laboratories Ltd. was diluted to 100 mL with DDW. A column was packed with 2 g of basic alumina and conditioned with 10 mL of 0.01 M HCl. A 100-mL aliquot of the CRM sample solution was then passed through the column, dried with N_2 and then eluted with 4 mL of 3% thiourea/10% aqua regia. When using internal standardization with In, the resulting concentrations of Au, Pd, and Pt agreed with the certified values according to a Student's t-test at the 95% confidence level (Table 3). Analyte concentrations in CDN-PGMS-29 are smaller than those in CDN-PGMS-19 (used by Asfaw *et al.*[7]) by orders of magnitude

Table 4. Summary of SPE sorbents for noble metal preconcentration

Sorbent	Eluent	Analyte(s)	Method of Determination	Sample	Method Detection Limits for Pd, Pt & Au	Reference
Alumina Sorbents						
Basic alumina	3% thiourea/10% aqua regia	Pd, Pt, Au	FI-ICPMS	Ore reference material CDN-PGMS-29 (after dissolution)	Pd: 4 μg kg^{-1} Pt: 1 μg kg^{-1} Au: 0.3 μg kg^{-1}	This work
Acidic alumina	2 M HCl	Ag, Ir, Os, Pd, Pt, Re, Rh, Ru	ICPMS	Ore reference material CDN-PGMS-19 (after dissolution)	Pd: 1 μg kg^{-1} Pt: 0.1 μg kg^{-1}	[8]
Acidic alumina	0.01M HNO_3/3% thiourea	Au	ICPMS	Ore reference material CDN-PGMS-19 (after dissolution)	Au: 4 μg kg^{-1}	[8]
Acidic alumina	2 M NH_4OH	Pt	ICPMS	Natural waters, motor car exhaust and common analytical reagents	Pt: 4 ng L^{-1}	[15]
Basic alumina	KCN	Pd	ICPMS	Urban water samples	Pd: 1 ng L^{-1}	[13]
Commercial Resins/ Polymer Sorbents						
Cross-linked polystyrene	1 M HCl in ethanol	Ru, Pd, Pt, Au	FI-ICPMS	CRM of basic and ultrabasic rocks GPt-5 (chromitite), GPt-6 (peridotite) and SARM-7 (pyroxenite) (after dissolution)	Pd: 3.3 μg kg^{-1} Pt: 1.4 μg kg^{-1} Au: 4.0 μg kg^{-1}	[16]
PVBC-VP [a]	Thiourea-thiocyanate-HCl mixture	Pd, Ir, Pt, Au, Ru, Rh	FI-ICPMS	Geological CRMs SARM-7, GPt-6, and GPt-5 (after dissolution)	Pd: 14.7 μg kg^{-1} Pt: 6.5 μg kg^{-1} Au: 7.8 μg kg^{-1}	[17]
PSTH-cpg [b]	0.03% thiourea/ 3.2% HNO_3	Pt, Pd, Ir	ICPMS	CRM NIST-2557 autocatalyst (after dissolution)	Pd: 55.5 ng L^{-1} Pt: 78.5 ng L^{-1}	[18]
Metalfix Chelamine	KCN	Au, Ir, Pd, and Pt	ICPAES	Anodic sludge from the electrolytic rafination of silver	Pd: 0.8 μg L^{-1} Pt: 1 μg L^{-1} Au : 0.5 μg L^{-1}	[19]
YPA_4[c] **Micro-Columns**	2.5 % thiourea	Au, Ag, Pt, Pt	FI-ICPAES	Geological CRM GBW07293, a low-grade platinum palladium ore and sewage sludge	Pd: 0.45 μg L^{-1} Pt: 0.76 μg L^{-1} Au: 0.23 μg L^{-1}	[20]
Other sorbents						
Polyethylenimine ion-exchange polymer coated with alumina	0.5 M thiourea, 1.0 M HCl	Au	FAAS	River water, spring water, tap water, and alloy (after dissolution)	Au: 26.2 ng L^{-1}	[21]
Ferrofluid	3% thiourea/ 10% aqua regia	Pt, Pd, Au, Ag	ICPMS	Ore reference material CDN-PGMS-29 (after dissolution)	Pd: 6 μg kg^{-1} Pt: 6 μg kg^{-1} Au: 2 μg kg^{-1}	[10]

[a] linear poly(4-vinylbenzylchloride) with 4-vinylpyridine; [b] 1,5-bis (2-pyridyl)-3-sulphophenyl methylene thiocarbonohydrazide immobilized on aminopropyl-controlled pore glass; [c] chelating resin of aminoisopropylmercaptan type with a polythioether backbone.

(14-fold lower for Pt to 472-fold lower for Au). The use of CDN-PGMS-29 is thus a better test of the preconcentration and separation capabilities of the proposed method. The fact that results without internal standardization were not accurate indicates the requirement for internal standardization to compensate for residual matrix effects when analyzing a real sample. For instance, CDN-PGMS-20 contains 1.4% S and S-containing compounds are known to also be retained on alumina and then eluted.[8]

Comparison to previous methods. Table 4 compares the proposed method to previous methods that used commercial and novel sorbents for noble metal preconcentration. As can be seen, the proposed method achieves comparable or lower detection limits for Pd and Pt and a lower detection limit for Au than previously published methods that simultaneously determined these three analytes, including those with more complex and specialized sorbent materials. Furthermore, no previously published alumina-based method has successfully achieved a reliable preconcentration of Au along with other noble metals. This method offers competitive detection limits while minimizing

cost and keeping the procedure simple for routine multi-elemental analysis of geological samples.

CONCLUSION

A basic alumina sorbent combined with a 3% thiourea/10% aqua regia eluent can be used to simultaneously preconcentrate Pd, Pt, and Au. By utilizing a reduced sample preparation approach and a commercially available sorbent, this method offers a simple and accessible solution to mitigate interferences from the matrix while improving sensitivity and detection limits. This method eliminates the need for time-consuming preparation steps or costly reagents, which makes it well suited for the accurate analysis of geological samples by commercial laboratories. Incorporating flow injection as the sample introduction technique mitigates signal drift induced by thiourea. The reuse of alumina was not studied, as it would likely be dependent on sample matrix, which is largely unknown for samples received by commercial laboratories for analysis.

ASSOCIATED CONTENT

The supporting information (Tables S1) is available at https://www.at-spectrose.com.

AUTHOR INFORMATION

Diane Beauchemin received her Ph.D. in 1984 from l'Université de Montréal. She is a professor (Full) and Undergraduate Chair at Queen's University. Her research efforts are focused on inductively coupled plasma mass spectrometry (ICPMS) and ICP optical emission spectrometry (OES) from both fundamental and application perspectives, and expanding the range of application of ICPMS/OES to geochemical exploration, risk assessment of food safety, characterization of nanoparticles, and forensic analysis. She has been working as member of editorial board for Atomic Spectroscopy. Diane Beauchemin won the Alan Date Memorial Award (1988) from VG Elemental, the Distinguished Service Award (2001) from Spectroscopy Society of Canada, the Maxxam Award (2017) and Clara Benson Award (2019) from Canadian Society for Chemistry, the Gerhard Herzberg Award (2018) from the Canadian Society for Analytical Sciences and Spectroscopy, and the 2024 Environment Division Research and Development Dima Award from the Chemical Institute of Canada. She is author or coauthor of over 186 articles published in peer-reviewed scientific journals.

Corresponding Author

* D. Beauchemin

Email address: diane.beauchemin@queensu.ca

Notes

This work was presented as a poster in French at Spectr'Atom 2025 and received the third-place prize for the best student poster.

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