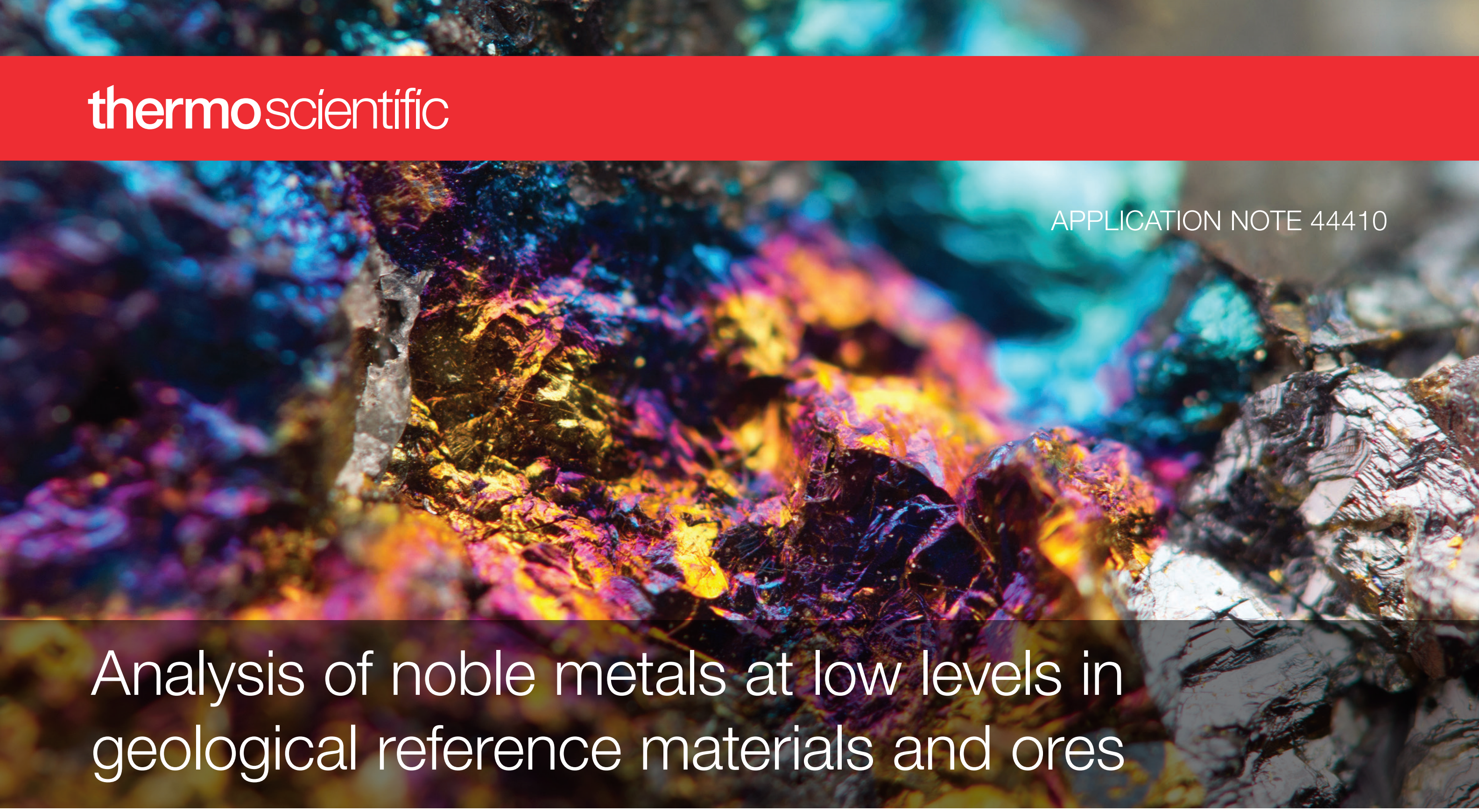

APPLICATION NOTE 44410

Analysis of noble metals at low levels in geological reference materials and ores

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Goal

To show the analysis of ultra-trace levels of different noble metals like Rh, Pd, Pt and Au in challenging sample matrices like rocks and ores.

Introduction

The so-called platinum group metals (PGM´s) strictly comprises six precious metals: ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir) and platinum (Pt). Another element of great interest is Gold (Au). All of the metals possess unique characteristics and are important for catalytic converters (both in the chemical industry as well as in cars), jewelry and electronic components. These elements are commonly used as catalysts in synthesis for core chemicals for polymerization, therefore they may also be found in consumer products made from silicone or other plastic ware. In cases where noble metals need to be accurately quantified at low levels, for example, to determine if their content in an ore deposit is high enough to economically justify mining and processing the ore, other elements may easily interfere and cause significant bias. For example, even trace amounts of hafnium and tantalum severely affect the detection of Pt and Au as a result of interference from HfO, HfOH and TaO and negatively impact analytical results. As another example, the detection of monoisotopic ^{103}Rh may be affected through $^{206}\mathrm{Pb}^{2+}$ or different polyatomic interferences such as $^{87}\mathrm{Sr}^{16}\mathrm{O}^{+}$ or $^{63}\mathrm{Cu}^{40}\mathrm{Ar}^{+}$. Especially when very low amounts need to be detected, kinetic energy discrimination (KED), the primary tool applied to remove polyatomic interferences in single quadrupole (SQ) ICP-MS, is not sufficiently effective to eliminate all interferences at the required level.

In contrast, triple quadrupole based ICP-MS can eliminate interferences in an alternative way, employing reactive gases and leveraging different reactivity of analyte and interfering ions. Through an additional quadrupole mass filter placed before the collision/reaction cell (CRC), potential side reactions of other elements present in the sample, are efficiently suppressed and full interference removal is achieved.

Method

Sample preparation

Two certified reference materials were prepared for analysis, GSP 2 (United States Geological Survey), a granodiorite, and AMIS 0416 (African Mineral Standards), a platinum ore. All samples were prepared externally following a previously published protocol[1].

Instrument configuration

All measurements were accomplished using a Thermo Scientific™ iCAP™ TQ ICP-MS system equipped with an autosampler (Teledyne Cetac Technologies ASX-560). The instrument was tuned using the autotune routines supplied with the operating software. The selection of analytes, appropriate analysis mode (single quad vs. triple quad, choice of reactive gas) was accomplished using the Reaction Finder method development assistant. Further analysis modes for particular isotopes were added manually for comparison. The mass selection in the first quadrupole was controlled using intelligent Mass Selection (iMS) in all cases. In order to compare the results obtained using different measurement modes, the iCAP TQ ICP-MS was configured to scan all samples in all measurement modes during one single aspiration of the sample solution. An overview of the instrument´s settings can be found in Table 1. After calibration using different multi-element standard solutions (concentration range between 50 and 1000 ng·L^{-1}, diluted in 3% hydrochloric acid and 1% nitric acid), an initial calibration verification (ICV) was performed (50 ng·L^{-1}). During analysis, repeated continuing calibration verification checks (CCV´s) were interspersed periodically at a concentration level of 500 ng·L^{-1}. In order to verify the accuracy and precision of the proposed method, GSP 2 was spiked with trace amounts of different noble metals (10 and 25 ng·L^{-1}) and analyzed as a quality control check repeatedly during analysis.

Table 1. Instrument configuration.

Parameter	Value		
Nebulizer	MicroMist Quartz nebulizer 0.4 mL·min^{-1}, pumped at 40 rpm		
Spraychamber	Quartz cyclonic spray chamber cooled at 2.7 ˚C		
Injector	2.5 mm i.d., Quartz		
Interface	High Matrix (3.5 mm) insert, Ni cones		
RF Power	1550 W		
Nebulizer Gas Flow	1.11 L·min^{-1}		
QCell Settings	**SQ-KED**	**TQ-O_2**	**TQ-NH_3**
Gas Flow	100% He, 4.5 mL·min^{-1}	100% O_2, 0.7 mL·min^{-1}	100% NH_3, 0.37 mL·min^{-1}
CR Bias	-21 V	- 7.5 V	- 7.5 V
Q3 Bias	-18 V	-12 V	-12 V
Scan Settings	0.1 s dwell time per analyte, 10 sweeps, 3 main runs		

General analytical conditions

In a first step, suitable measurement conditions involving different scan modes (SQ vs. TQ) and reactive gases (no gas, KED, O_2 or NH_3) were tested for the different PGMs and gold. To perform this study in a realistic sample matrix, containing typically interfering elements plus a considerable matrix load, the GSP 2 reference material provided by the United States Geological Survey (USGS) was chosen. This material represents a granodiorite rock collected in Silver Plume, CO (US). Most importantly for this study, GSP 2 does not contain significant amounts of any of the elements under scrutiny in this study, but plenty of interfering elements such as Hf (information value 14 ± 1 µg·g^{-1}, interfering on Pt), Lu and Yb (0.23 ± 0.03 and 1.6 ± 0.2 µg·g^{-1} respectively, interfering on Ir), Cu and Sr (43 ± 4 and 240 ± 10 µg·g^{-1} respectively, interfering on Rh), among others. The major components (and hence the sample matrix) consists of SiO_2 (66.6 ± 0.8 Wt%), Al_2O_3 (14.9 ± 0.2 Wt%), Fe_2O_3 (4.90 ± 0.16 Wt%) and K_2O (5.38 ± 0.14 Wt%). In the same analytical sequence, a second certified reference material, AMIS 0416 (provided by African Mineral Standards) was analyzed to validate the method. This material was derived from a platinum ore obtained in the Bushfeld complex in South Africa and is certified for its content of different noble metals. It´s main composition is slightly different from GSP 2, for example, containing much higher amounts of Fe_2O_3 (22.71 ± 0.26 Wt%), but also Cr_2O_3 (28.18 ± 0.42 Wt%).

Results

In order to eliminate the overlaps caused by the interfering elements and facilitate the detection of elements such as Rh, Pd, Ir, Pt and Au at ultra-trace levels, different measurement modes were applied. For example, Pt can be analyzed using two different reactive gases, O_2 and NH_3. Figure 1 highlights the reaction pathways in the CRC. As no reaction occurs between Pt and O_2, it will pass through the cell unaffected. In contrast, the interference, HfO, initially having the same m/z ratio, is converted into HfO_2 and hence eliminated in the analyzing quadrupole (Q3). At the same time, the first quadrupole (Q1) filters out all other ions with lower and higher mass, which could potentially react in a similar way, and hence create other interferences on the product ion mass. With ammonia, Pt undergoes a reaction forming different Pt-NH_3 clusters, the most abundant product ion being $Pt(NH_3)_2$, thus leading to a mass shift of 34 amu. Again, the HfO interferences will not react in the same way and will be eliminated in the analyzing quadrupole. Similar reaction schemes can also be applied for other PGM´s, such as Rh, Pd, Ir and also Au.

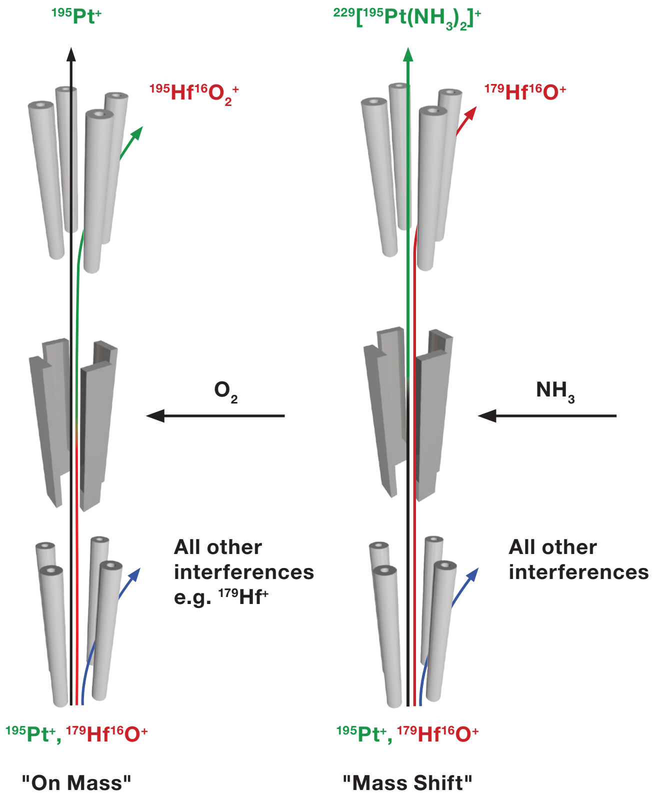

Figure 1. Schematic illustrating the analysis of platinum using triple quadrupole ICP-MS operated with oxygen and ammonia as reaction gas.

To prove the successful elimination of interferences and consistent quantification at ultra-trace levels, GSP 2 was analyzed directly, but also with low level spikes (10 and 25 ng·L^{-1}) of all elements under study. This allows determination of the blank equivalent concentration for each of the elements under study to assure complete interference removal, but also verification of the capability to accurately detect at these concentration levels. In total, GSP 2 and both spiked samples were analyzed six times in an 11 hour analysis. The results for ^{103}Rh and ^{195}Pt are summarized in Table 2. The signal observed in the unspiked solution of GSP 2 was consistently found to be around 5 ng·L^{-1}, so that probably a very low amount of Pt is indeed present in the material. Similar results were obtained for other elements (data not shown). Typical instrumental detection limits were observed to be between 0.1 and 2 ng·L^{-1} for all elements investigated in this study.

Table 2. Results for the analysis of the GSP 2 reference material, unspiked and spiked at different concentration levels.

	Sample	Result [ng·L^{-1}]		Recovery [%]	
		SQ-KED	TQ-O_2	SQ-KED	TQ-O_2
^{103}Rh	ICV (50 ng·L^{-1})	50.8	51.5	102	103
	CCV (100 ng·L^{-1})	-	-	97.6 ± 3.1	92.0 ± 8.3
	GSP unspiked	Not detected	Not detected	-	-
	GSP spiked 10 ng·L^{-1}	10.9 ± 0.6	10.6 ± 0.2	108	106
	GSP spiked 25 ng·L^{-1}	26.1 ± 1.8	23.3 ± 0.7	104	93

	Sample	Result [ng·L^{-1}]		Recovery [%]	
		TQ-O_2	TQ-NH_3	TQ-O_2	TQ-NH_3
^{195}Pt	ICV (50 ng·L^{-1})	45.2	53.0	90	106
	CCV (100 ng·L^{-1})	-	-	95.2 ± 3.6	95.0 ± 6.4
	GSP unspiked	4.6 ± 0.5	5.6 ± 1.3	-	-
	GSP spiked 10 ng·L^{-1}	16.0 ± 2.4	16.6 ± 2.4	114	110
	GSP spiked 25 ng·L^{-1}	29.9 ± 2.8	29.2 ± 4.7	101	95

As can be seen from the results obtained for the unspiked samples, triple quadrupole based modes allow complete removal of potential interferences. At the same time, all tested measurement modes accurately and precisely recovered the spiked amounts of both elements.

To further highlight the superior interference removal using triple quadrupole technology, different solutions containing elements potentially interfering on the noble metals under study were prepared and analyzed using kinetic energy discrimination (SQ-KED) and triple quadrupole modes using oxygen as reactive gas. The concentrations used for this experiment matched the concentrations found in the digested GSP 2 reference material. Table 3 gives an overview on the observed reduction of blank equivalent concentrations (BEC). Due to the complexity of the sample matrix, with potentially various interferences contributing for a given analyte, each interfering element was tested as in a separate solution. For all elements tested, a significant improvement in BEC was observed for the TQ modes versus the SQ mode.

Figure 2 shows the internal standard recovery for both internal standards in all measurement modes over the course of an 11 hour analytical sequence, containing in total more than 100 samples. As can be seen, the different sample matrices (QC checks, GSP 2 and AMIS 0416 reference materials) did not significantly affect the internal standard recovery over time, so that the analysis of a high number of samples is feasible without interruptions through failed QC´s or excessive signal suppression (± 30% as widely accepted in different regulatory guidelines).

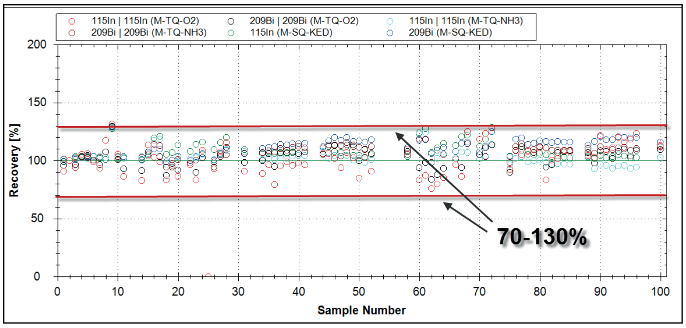

Figure 2. Internal standard recovery for ^{115}In and ^{209}Bi in three different measurement modes during an 11 hour analysis sequence (Rinse samples not containing the internal standard are removed).

The results obtained for the analysis of AMIS 0416 are displayed in Table 3. This table also contains all relevant information about the certified and provisional values as supplied by the certificate of analysis, as well as the method for collection (NiS vs. Pb collection), where applicable. Results are reported separately for the different measurement modes that were evaluated in this study. The given recoveries are either calculated for different measurement modes vs. available reference value when more than one result was available (e.g. ^{103}Rh), or relative to the reference values for different collection assays when more than one reference value was available (e.g. ^{108}Pd).

In all cases, the concentrations in the final measured solution were low (between 20 to 350 ng·L^{-1}), so that complete elimination of false positives was key to avoid large scaling errors when correcting for the dilution factor.

Table 3. Improvement of achievable blank equivalent concentrations for selected interferences on noble metals in triple quadrupole based analysis modes.

Interfered noble metal	Interferences	Approx. concentration in GSP 2 samples	Improvement factor BEC in TQ vs. SQ modes (x times)	Detection limit in TQ mode [ng·L^{-1}]
^{103}Rh	$^{206}Pb^{2+}$	5 µg·L^{-1} [Pb]	37	0.04
	$^{87}Sr^{16}O^{+}$	8 µg·L^{-1} [Sr]	70	
^{105}Pd	$^{88}Sr^{16}O^{1}H^{+}$	8 µg·L^{-1} [Sr]	66	0.23
^{191}Ir	$^{174}Yb^{16}O^{1}H^{+}$	1 µg·L^{-1} [Yb]	7*	0.09
^{195}Pt	$^{179}Hf^{16}O^{+}$, $^{178}Hf^{16}O^{1}H^{+}$	5 µg·L^{-1} [Hf]	26	0.08
^{197}Au	$^{181}Ta^{16}O^{+}$	1 µg·L^{-1} [Ta]	81	0. 12
	$^{180}Hf^{16}O^{1}H^{+}$	5 µg·L^{-1} [Hf]	≥ 200	

* Overall contribution to BEC was negligible.

As can be seen, the results for the platinum group elements Rh, Pd, Ir and Pt agree well with the certified values. However, only the result for Au falls short with respect to the reference value.

Most likely, as results obtained with GSP 2 indicate excellent recoveries, this is related to an unresolved issue during sample preparation or handling, which may lead to a loss of Au in the final analyzed samples. Gold is known to be ideally stabilized with higher concentrations of hydrochloric acid, typically above what was used as the acid diluent in this study.

Table 4. Results for the analysis of the AMIS 0416 reference material.

Element	Value [$g \cdot t^{-1}$]	Result [$g \cdot t^{-1}$]	Mode	Recovery [%]
Rh*	0.29 ± 0.04 (Prov.)	0.27 ± 0.03	^{103}Rh, TQ-O_2	93.1 ± 13*
		0.28 ± 0.02	^{103}Rh, SQ-KED	96.5 ± 7
Pd**	0.80± 0.06 (Cert., NiS Collection)	0.73 ± 0.05	^{108}Pd, TQ-O_2	91.3 ± 6.3
	0.75 ± 0.04 (Prov., Pb Collection)			97.3 ± 6.7
Ir	0.13 ± 0.02 (Prov., NiS Collection)	0.14 ± 0.02	^{191}Ir, TQ-O_2	107.6 ± 15.3
Pt	1.46 ± 0.18 (Pb Collection)	1.30 ± 0.15	^{195}Pt, TQ-NH_3	89.0 ± 10.3
		1.31 ± 0.19	^{195}Pt, TQ-O2	89.7 ± 13.0
Au***	0.14 ± 0.04 (Pb Collection)	0.073 ± 0.02	^{197}Au, TQ-NH_3	52.1 ± 14.3
				61.4 ± 21.4
	0.13 ± 0.02 (NiS Collection)	0.086 ± 0.03	^{197}Au, TQ-O_2	56.1 ± 15.8
				66.2 ± 23.0

* Recovery of different modes relative to the available reference value
** Recovery relative to reference values from the two different assays for collection
*** Recovery calculated for both results relative to all available reference values

Conclusion

This study reveals the potential of triple quadrupole ICP-MS for comprehensively eliminating interferences and subsequently allowing reliable quantification of noble metals at ultra-trace levels even in difficult matrices. The effective use of reactive gases for interference removal, complemented by mass filtration before the CRC enables full elimination of interferences of different nature (polyatomic, isobaric or doubly charged) and is therefore a significant improvement for challenging sample matrices such as rocks or ores. However, whereas controlling the analysis is one part of the story, a thorough and effective protocol for sample preparation and handling is equally important for successful ultra-trace analysis of noble metals given their similar, yet slightly different chemical behaviors.

Reference

1. Karandashev, V.K., Khvostikov, V. A., Nosenko, S. V., Burmii, Zh. P.; Inorganic Materials **53** (2017), 1432-1441

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