Analysis of Platinum Group Elements (PGEs) in road dust using the Agilent 8900 Triple Quadrupole ICP-MS in MS/MS mode

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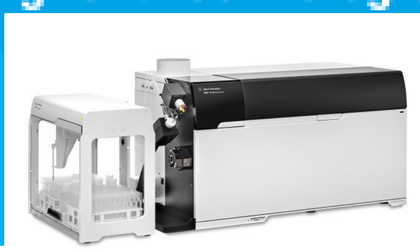

Introduction

The monitoring of Platinum Group Elements (PGEs: Ru, Rh, Pd, Os, Ir and Pt), Au and Ag has become of great interest in the environmental field as the presence of these elements in the environment has increased since the introduction of automobile catalytic converters. Thanks to its high sensitivity and multi-element capability, ICP-MS is widely used for quantification of the PGEs. However, the analysis of PGEs in soil and dust samples is challenging for conventional quadrupole ICP-MS due to the low concentrations of the elements, and the presence of several severe polyatomic interferences derived from the matrix. Examples include NiAr and NiCl on Ru-101, CuAr on Rh-103 and Pd-105, ZrO on Ag-107, and TaO on Au-197.

To remove the multiple, complex and variable interferences on the PGEs, and still be able to measure concentrations in the ng/L range in the digested samples, the Agilent 8900 Triple Quadrupole ICP-MS (ICP-QQQ) was used in MS/MS mode, with ammonia as the reaction gas. To evaluate the quantification capabilities of the ICP-QQQ method, a certified reference material of road dust (BCR 723) was analyzed following acid digestion.

The high sensitivity, low background and unique interference removal capability offered by tandem mass spectrometry allowed the quantification of PGEs at ng/L level in a complex matrix.

Experimental

Measurement were performed on an Agilent 8900 using a standard quartz introduction system. Nickel plated nickel sampler cone and a nickel skimmer cone were used for all the experiments.

Standard plasma conditions were used (CeO^+/Ce^+ of 1.0 %).

Typical tuning of the instrument is shown in the following table:

Parameter	Value
RF Power (W)	1550
Sample Depth (mm)	10
Carrier Gas (L/min)	1.05
He flowrate (mL/min) When He mode activated	5
NH_3 flowrate (mL/min) When NH_3 mode activated	2 – 3 or 5

Sample preparation for road dust samples is performed using microwave digestion. 2 mL of HNO_3 and 6 mL of HCl are added to 0.5 to 1 g of samples and after complete digestion the volume is adjusted to 50 mL by adding ultra-pure water.

Samples were then manually diluted 2 times in 2% HCl and 1% HNO_3 before being measured. Internal standards (In and Bi) were added online. Both peristaltic pump tubing for the sample and the internal standard solution were 0.76 mm id.

Calibration was prepared from 0 to 0.500 µg/kg for all target elements : Ru, Rh, Pd, Ag, Ir, Pt and Au.

Rinse solutions consisted of one basic rinse (NH_4OH), one containing 0.5% H_2SO_4 and 2% HCl and a final rinse containing 3% HCl and 2% HNO_3. The use of H_2SO_4 allows a better rinsing of Au.

A Certified Reference Material (BCR 723) was prepared along with 4 unknown road dust samples.

In addition to the quantification of PGEs in those samples, an interference removal study was performed with synthetic interference solution to compare between No Gas and He mode, that can be used on a single quadrupole instrument, and NH_3 mode using MS/MS with different gas flowrates.

Detection limits for the Platinum Group Elements

Mass Pair	LD (ng/kg)	BEC (ng/kg)	Mass Pair	LD (ng/kg)	BEC (ng/kg)
99-99Ru	0.661	0.596	109-109Ag	0.336	0.322
101-101Ru	0.151	0.075	191-206Ir	28.770	13.880
103-103Rh	0.138	0.184	195-195Pt	1.934	0.821
105-105Pd	0.243	0.091	198-198Pt	7.001	2.173
107-107Ag	0.261	0.534	197-231Au	0.738	1.583

- Excellent sensitivity and low background in NH_3 mode
- Detection limits are below 1 µg/kg for all elements except Ir and Pt in the ng/kg range

Interference removal study in synthetic solutions

Synthetic solution containing 10 ppm of Cu, Zn, Sr, Rb, Ni, Mo, Pb, Hg, REE, Sc, Y, Ta, Hf, W separately or all together were prepared and measured in the analytical conditions previously described. The following table showcases the interference removal capabilities between No gas, He and NH_3 modes for Ru, Ag, Ir and Au.

- NH_3 mode provides the best interference removal where He in single quadrupole mode is limited.

Element	Ruthenium			Silver			Iridium			Gold		
Isotope	101			107			191			197		
Gas Mode	No Gas	He	NH_3-M	No Gas	He	NH_3-H	No Gas	He	NH_3-M	No Gas	He	NH_3-H
NH3 flowrate in mL/min	0	0	3.0	0	0	5.0	0	0	3.0	0	0	5.0
Method	on-mass	on-mass	on-mass	on-mass	on-mass	on-mass	on-mass	on-mass	mass-shift	on-mass	on-mass	mass-shift
Mass Pair	101-101	101-101	101-101	107-107	107-107	107-107	191-191	191-191	191-206	197-197	197-197	197-231
10 ppm Cu Zn	0.010	0.000	0.000	0.009	0.002	0.001	0.000	0.000	0.000	0.003	0.003	0.002
10 ppm Sr Rb	0.029	0.000	0.001	0.009	0.002	0.002	0.000	0.000	0.000	0.002	0.002	0.002
10 ppm Ni	0.005	0.000	0.000	0.001	0.001	0.001	0.000	0.000	0.000	0.002	0.002	0.001
10 ppm Mo	0.012	0.004	0.000	0.002	0.001	0.001	0.000	0.000	0.003	0.002	0.002	0.001
10 ppm Pb, 1 ppm Hg	0.001	0.000	0.000	0.012	0.012	0.012	0.000	0.000	0.021	0.001	0.001	0.001
10 ppm Zr Nb	0.001	0.000	0.000	15.854	0.555	0.005	0.000	0.000	0.003	0.021	0.008	0.001
10 ppm REE, Sc, Y	0.025	0.002	0.002	0.154	0.019	0.016	87.943	16.824	0.077	0.216	0.009	0.002
10 ppm Ta	0.001	0.000	0.000	0.001	0.001	0.000	0.000	0.000	0.004	143.909	44.466	0.000
10 ppm Hf	0.000	0.000	0.000	0.002	0.001	0.001	0.171	0.043	0.054	9.127	1.434	0.000
10 ppm W	0.001	0.001	0.000	0.001	0.001	0.001	0.000	0.000	0.012	0.244	0.107	0.000
10 ppm all, 1 ppm Hg	0.092	0.008	0.003	14.598	0.644	0.035	83.652	15.910	0.125	165.475	43.460	0.003

Rh, Pd and Pt recovery for the BCR 723 CRM

Mass Pair	103-103 Rh			105-105 Pd			198-198 Pt		
Gas Mode	NoGas	He	NH_3	NoGas	He	NH_3	NoGas	He	NH_3
Gas Flowrate (mL/min)	0	5	5	0	5	5	0	5	5
Certified Value (µg/kg)	12.8 ± 1.3			6.1 ± 1.9			81.3 ± 2.5		
Measured Conc (µg/kg)	0.19	0.296	0.063	1.107	0.049	0.037	8.492	3.067	0.395
Final Conc (µg/kg)	39.09	60.73	12.97	227.22	10.09	7.65	1743.59	629.72	81.01
Recovery (%)	305.38	474.48	101.30	3724.95	165.39	125.34	2144.63	774.57	99.64

- Overestimation of the Rh, Pd and Pt content when measuring in No Gas and He mode
- Recovery for the 3 certified elements is within the acceptance limits when measuring in NH_3 mode using MS/MS with very good recoveries for Rh and Pt

Measurement of PGEs in the unknown samples

Element	99 -> 99 Ru	101 -> 101 Ru	103 -> 103 Rh	105 -> 105 Pd	107 -> 107 Ag	109 -> 109 Ag	191 -> 206 Ir	197 -> 231 Au	198 -> 198 Pt
Gas Mode	NH3-M	NH3-M	NH3-H	NH3-H	NH3-H	NH3-H	NH3-M	NH3-H	NH3-H
Sample Name / Total Dil.	Conc. [ug/kg]	Conc. [ug/kg]	Conc. [ug/kg]	Conc. [ug/kg]	Conc. [ug/kg]	Conc. [ug/kg]	Conc. [ug/kg]	Conc. [ug/kg]	Conc. [ug/kg]
BCR 723 / 205.330	0.876	0.904	12.967	7.646	200.271	201.517	3.020	2.567	81.010
CH 1998 / 122.299	0.900	0.845	3.493	7.633	534.160	540.702	0.041	12.901	83.579
CH 2005 / 186.137	0.804	0.771	5.819	26.282	334.112	333.766	< LD	8.527	257.234
CH 2009 / 200.244	1.020	1.135	10.644	37.163	566.126	556.859	0.833	14.662	583.962
CH 2016 / 179.093	0.910	0.950	10.002	33.486	510.368	502.330	1.396	10.764	136.558

- PGEs were quantified in the unknown samples in the optimum NH_3 mode to be certain to measure interference free

Conclusions

Using Agilent 8900 ICP-MS/MS:

- Excellent detection limits were obtained
- Excellent interference removal was achieved using the unique MS/MS capability with NH_3 gas mode
- Successful measurement of PGEs in road dust samples was performed

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