



NOTE

Determination of Au, Pt and Pd in Biology Samples by ICP-MS

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The conditions of separation and enrichment for Au, Pt and Pd in geological samples were studied by 717 anion exchange resin. The exchange method was conducted under the optimized adsorption conditions (pH = 3.0). The effects of different enrich methods and different exchange procedures were compared. The present procedures are relatively simple and can be applied with high precision and reproducibility to the analysis of geological samples with wide ranges of concentrations. Finally, the application of our methods was verified by the analysis of geology reference materials.

Key Words: Geological samples, Platinum, Palladium, Gold.

Gold, platinum and palladium play an important role in aviation, industry, decoration and environment protection¹⁻⁶. Their distribution in the Earth contains important information about many fundamental geological processes, such as the differentiation of the core and mantle, the chemical evolution of the mantle controlled by melting and recycling processes, and the formation of ore deposits by igneous, metamorphic and hydrothermal processes. With the development of science and technology, the determination of Pd, Pt and Au in geological samples is of more considerable importance for the investigation of the mineral deposit not only for themselves, but also for other elements. Powerful and convenient analytical procedures are needed for the determination of these precious trace metals in geological samples. It requires a rapid method of analysis with sensitivity reaching the ng/g level and sometimes even sub ng/g level. 717 Anion exchanges have been used as inductively coupled plasma-mass spectrometry (ICP-MS) pretreatment methods, which offered the possibility of rapid analysis for Au, Pt and Pd, combined with excellent detection limits as is needed. This paper presents a convenient procedure for the determination of background levels of Pd, Pt and Au in geological samples based on ion-exchange and ICP-MS. Among the studied methods, our procedure performs a highly effective, economical, irreplaceable and simple.

The ICP-MS instrument used was the X series II (Thermal), the operation conditions are summarized in Table-1.

All vessels were cleaned by soaking in aqua acid 50 % before use and all the experiment progress was performed on a clean bench. Before use, all materials and chemical reagents

were checked for contamination to make sure they are Au, Pt and Pd free. Mixed acid (Au 100 ng/mL, Pt, 100 ng/mL, Pd, 1000 ng/mL) standard were made from 1 mg/mL single-element standards (Pt, Pd, Au) diluted by pure water and high-purity HCl and sub-boiled HNO₃ step by step. 717 anion exchange resin was soaked in 30 % HCl for 24 h for the transition. Then, the resin was washed with water for several times until the water is neutral.

TABLE-1
PARAMETERS FOR ICP-MS

Parameters	Values	Parameter	Values
RF power	1200 KW	Collector	-5.4 V
Outer gas	1.5 L/min	Lens 2	7.4 V
Nebulizer gas	0.73 L/min	Lens 3	3.7 V
Sampling uptake rate	0.16 mL/min	Dwell time	100 ms
Extraction	-369 V	Wash time	30 s

Weigh 10 g of the samples into the porcelain boat. The samples were roasted at 650 °C for 2 h. After roasting, transfer them into the breaker (250 mL). Add some water and shake. Then, 30 mL of HCl, 2 mL of H₂O₂, and 10 mL of HNO₃ were added. The beakers were closed and the samples were digested on the heating plate. After the heating the mixture to small volume, each fluid was diluted into 250 mL and shake well. The next morning, take 50 mL of the clear, supernatant solution into the glass beaker for further separation of Au, Pt and Pd. Wet resin 0.20 g was added into 50 mL sample solution. Set the pH as 3. Then, the mixture was shaken mechanically for 40 min at room temperature. After that, the phases were

separated by filtration and washed with 5 % HCl in order to determine the concentrations of Au, Pt and Pd in the solution. Take the resin out into the crucibles for dry ashing. After that, the ashes were dissolved in 50 % aqua acid. The solution was heated to small volume on a heating plate. The temperature was set at 120 °C. Finally, 10 mL of 1 % HCl was used to dissolve the ash in the colourimetric tubes. The solution was ready for the determination by ICP-MS.

Calibration: Standard series were performed by the standard additions procedure. The concentration of the new mixed acids would be 1, 10, 20 and 50 ng/mL of Pd, Pt and Au. These standard solutions were prepared freshly every day. All dilutions were performed the same enrichment procedure as the samples.

Digestion methods: Sample digestion is a critical step in methods for routine determination of chemical elements in geology samples. In this context, different mixtures of acids for the determination of blank samples were evaluated. The acids used for comparison were A (10 mL HNO₃, 30 mL HCl) and B (30 mL % 50 H₂SO₄). The test result of the digested solution indicated that our procedure was more effective at breaking down organic compounds than procedures A and B because our procedure solution was shown the smallest blank value.

Enrichment methods: The enrichment methods were also compared with C. The columns were packed with the same amounts of the wet 717 resin and used for the column adsorption. The resin was packed into the columns after being activated in 0.5 mol/L HCl aqueous medium for 24 h. The mixture solution containing Au, Pt and Pd was passed through the columns with 2 mL/min sample loading flow rate controlled by a peristaltic pump. The recovery rate was shown in Table-2.

TABLE-2
ANALYSIS RESULTS BY DIFFERENT
ENRICHMENT METHODS

	Recovery (ng/mL)			
Standard	1.00	10.00	20	50.00
C	1.09	9.55	21.24	46.19
Our method	0.94	9.47	18.55	47.12

It can be seen that there is no big difference between the two methods. However, our procedures were much simpler and cheaper. Thus our methods would be more promising the analysis in real application.

Interference analysis: The possible interference elements were studied in Table-3. For the rare earth element, Ta, Hf, Y and another element, W, the content of them in the samples were too low to interfere with the analysts of Au, Pt and Pd. The dissolve rate of Zr, Y and Mo was very small. After pretreated by 717 anion exchange resin enrichment, the concentration of the interferences become even lower. Therefore the interferences were completely separated.

Accuracy and detection limit: The instrument was set at 12 times the standard deviation of the signal for blank measu-

TABLE-3
INTERFERENCE ON ANALYZING 197 Au, 108 Pd AND 195 Pt

Analysis element	Interference elements	Interference correction
197 Au	181Ta16O, 180HfOH	Not Necessary
195 Pt	179Hf16O, 180HfOH, 180WO	Not Necessary
108 Pd	90ZrO, 89YOH, 98MoO	Separated

rements, respectively. The detection limits were calculated as the three-fold standard deviation of replicated measurements of blank values. All analyses were carried out under internal quality control conditions. The results obtained in the present work were 0.22, 0.19, 0.44 ng/mL for Pd, Pt and Au respectively. Then, the accuracy tests were operated by analyzing the reference material, GBW07288, Table-4. As can be seen in Table-4, the accuracy for Pd, Pt and Au are 8.9, 9.0 and 7.4 % respectively. So, the methods can be effectively applied in the geology sample analysis field.

TABLE-4
ACCURACY TEST

Element	ng/mL			RSD (%)
	Standard value	Measured value	Medium value	
Pd	0.26	0.29, 0.25, 0.24, 0.29, 0.31, 0.27, 0.24, 0.30, 0.29, 0.25, 0.27, 0.26	0.27	8.9
Pt	0.26	0.27, 0.25, 0.30, 0.29, 0.25, 0.28, 0.31, 0.23, 0.29, 0.25, 0.29, 0.26	0.27	9.0
Au	0.9	0.87, 0.92, 0.80, 0.84, 0.93, 1.0, 0.82, 1.0, 0.85, 0.87, 0.84, 0.86	0.88	7.4

Conclusion

We successfully developed a digestion method for Au, Pt and Pd in geology samples. As compared to method C, our 717 ions-exchanging procedures are ideal for Pd, Pt and Au determinations in geological samples for real application. This work has shown that ICP-MS can be used to successfully analyze geological samples by overcoming many of the difficulties presented by geological samples. The effects of interferences can be greatly reduced or completely eliminated.

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