

DETERMINATION OF PLANTINUM IN ROCKS BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY AFTER SEPARATION ON SORBENT

Samgain Odonchimeg^{1*}, Jamba Oyun², Namsrai Javkhlantugs³

¹Engineer, Quality Control Department, Central Laboratory of Chemistry/ Erdenet Mining Corporation, Mongolia

²Professor, Chemistry Department/ Ulaanbaatar State University, Mongolia

³Professor, School of Engineering and Applied Sciences/ National University of Mongolia, Mongolia

-----***-----

Abstract - This paper describes the potential of graphite furnace atomic absorption spectrometry(GFAAS) for determination of platinum after separation and concentration by polysterene-azo-thia-zan-dition-2.4(PSTDT) polymer S, N-containing sorbent. The method of samples were digested by aqua regia and hydrogen fluoride in microwave, precious metals precipitated completely after the analyte element was separated on the polysterene-azo-thiazandition-2.4(PSTDT) sorbent and determination of analytes by GFAAS. The PSTDT sorbent enables the selective separation of platinum. The most suitable analytical methods for the platinum determination at a such low concentration level are graphite furnace atomic absorption spectrometry (GFAAS). To control the accuracy of platinum in sorption concentrates by GFAAS method, it was appropriate to conduct an inter-method comparative experiment. The researches on the application of concentrate assaying analyse GFAAS and inductively coupled plasma(ICP-OES) as a comparative method were conducted. In addition, the trueness control of the obtained results is confirmed by added-found method. Therefore content of platinum existed in samples from serpentine rocks was clearly examined using GFAAS, and it was in the range of 0.005–0.1 ppm for a range of spiked natural rocks.

Key Words: Platinum standard solution, Polystyrene-azo-thiazan-dithion-2.4, chelate complex, natural rock, graphite furnace atomic absorption spectrometry.

1. INTRODUCTION

Problems of man-induced and secondary metal-containing raw materials are of global nature in the modern world. This problem attained the paramount importance and scales in Mongolia- the country with huge raw material resources, developed metallurgy industry, large-scale production of metal-containing products for such socially important and strategic industries as aviation, railway and

motor transport, construction and not less large-scale consumption. The important aspect is that the secondary metal-containing raw materials are the most important source of non-ferrous, rare and precious metals. The content of valuable components in it exceeds mineral raw materials multiply.

The content of platinum-group metals is controlled by different analytical methods, which are imposed by high requirements to precision, expression, traceability, and comprehensiveness. Usually, the quantitative determination of determined components is preceded by a general survey X-ray fluorescence analysis providing a general indication about complete chemical composition of an assay [1-3].

There are many different methods of chemical sample preparation in open and closed systems by example of separation sorption sorbent samples for further determination of platinum (Pt) by different methods.

A lot of advanced techniques, namely graphite furnace atomic absorption spectrometry (GFAAS) [4,5] and inductively coupled plasma mass spectrometry (ICP-MS) [6-8], stopped-flow injection spectrophotometric determination [9], flow injection analysis (FIA) [10], flame atomic absorption spectrometry (FAAS) [11], electro thermal vaporization inductively coupled plasma mass spectrometry (EVI-CP-MS) [12], electro thermal atomization-laser induced fluorescence ion chromatography [13], polarography [14], have been developed for the determination of trace amount of platinum and palladium in various complex matrices such as ores, alloys, seawater, biological samples and autocatalytic exhaust samples.

However, most of chemical sample preparation methods studied in the literature do not allow conducting direct determination of Pt in by GFAAS method due to high mineralization of samples and influence of matrix components on results of GFAAS analysis. In such cases, separation and concentration methods are used [15-17]. In our study, we examined the method to enrich the platinum in serpentine rocks by using PSTDT.

2. MATERIAL AND METHODS

2.1. Instrumentation.

This experiment was implemented on Perkin Elmer AAnalyst 800 Graphite Furnace Atomic Absorption spectroscopy (GFAAS) excites a enrichment liquid sample in a small graphite tube allowing a very low range analysis of platinum in solution, in the parts per billion (ppb) ranges. Visimax cathode lamp for platinum was used. Pyrolytically coated graphite tubes were used for all measurements. All glassware were cleaned by soaking in 20% nitric acid (48 h) and then rinsed with water. This GFAAS analyzes platinum at a time, on 265.9 nm wavelength only. PerkinElmer's WinLab32 software guides users through calibration and sample file setup and provides a visual representation of the calibration curve and each individual emission being analyzed. For decomposition of samples in Microwave MARS6. Over SP-D systems, samples are heated sequentially, one sample at a time, automatically. Once the samples are loaded and the methods selected, the robotic arm will grab a sample, move it to a small microwave cavity, run the appropriate method, and report the result, while it moves on to the next loaded sample.

2.2. Standard solutions, sample and sorbent

In order to create a calibration curve, standard solutions were prepared for every element to be determined by consecutive dissolution of source standard solutions from a stock concentration of 1 mg/ml (ACROS Organics). The calibration solutions were prepared by consecutive dissolution of the stock solution with the addition of 0.1N hydrochloric acid. The general problems in the determination of platinum group elements, irrespective of the analytical method used, are the low concentrations and the lack of certified reference materials for quality control. In this research work, we are used SARM7 and three different serpentine ore samples. Certified reference material of SARM7 (MINTEK, Republic of South Africa) is selected because it is a similar rock as our samples. Serpentine ore and rocks of Khantaishir (Sample 1) in Govi-Altai province (Western Mongolia), Toromkhon (Sample 2) in Umnugobi province (South Mongolia), Khyalganat (Sample 3) in Bulgan (Northern Mongolia) province were selected. Polystyrene-azo-thia-zandition-2.4 (Astralabor, Russia) was used to determine the platinum content in serpentine ores and rocks. The PSTDT polymer (Fig. 1a) is not dissolve in water, acid, base and organic solvents, alcohol and brown, red colored pellets 0.25–1 mm in sizes, dry reagent that includes functional group imine and thione in ortho position which forms a stable chelate complex with platinum. Basargina et al. firstly synthesized polystyrene-azo-thiazan-dition-2.4 on the basis of polystyrene-azocompound at the Central Chemical Laboratory of the Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM, Russia) [19]. The sorbent structure is shown below.

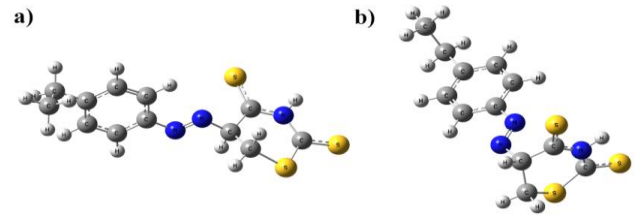


Figure 1: Representation of molecular structure of PSTDT sorbent.

It was studied [18] that complete extraction of analytes takes place under the following conditions of sorption: acidity of chemical environment – 0.5 N HCl; adsorption efficiency at 80°C; sorption time- 60 minutes. Capacity of the sorbent is 4 mg/g for Pt. It is seen that the maximum concentration as 1000 ppb of platinum can be adsorbed using 25 mg PSTDT adsorbent. Maximum concentration was converted per gram adsorbent which was 4 mg/g using 100 ml platinum solution. The sorbent capacity was calculated experimentally by saturation of applied sorbent prior to the termination of sorption. Extraction value of analytes is 98 % for Pt [18]. Thus, the sorbent has high sorption capacity, resistant to dilute acids and high selectivity.

2.3. Procedures

Experimental procedures were applied to platinum determination can be broadly divided into three stages as the sample decomposition, enrichment and analysis stages which were summarized as a scheme in Figure 2.

Sample decomposition stage: It is known that strong acids are effective in dissociating complexes and releasing free metal ions. SARM7 or each samples were weighed 0.1g or 1g, respectively which were dissolved on 10 ml HCl:HNO₃ (3:1) solution and added 2 ml conc. HF in each solutions then the samples were put in microwave during 1 hour. Then a solution added 5 ml NaCl (10 % w/v) and 1 ml KI (10 % w/v) until precious metals precipitated completely. The precipitation were calcined at 650 °C and dissolved in 10 ml HCl:HNO₃ (3:1) solution and 10 ml ascorbic acid (10 % w/v) to reduce the oxidation number of platinum which can be produced the chelate complex between platinum (II) and PSTDT then vaporized the solution to form dry powder. Dried powders dissolved in 50 ml HCl (0.5 N) which is defined "solution A" in Figure 2.

Enrichment stage: 25 mg adsorbent reagent PSTDT were added into "solution A" to enrich the platinum in the optimum condition by mixing. After the formation of chelate complex, the solids were filtered and were calcined at 550 °C then dissolved in 100 ml hydrochloric acid (1 N).

Analysis stage: The platinum were analyzed on wavelength of 265.9 nm using graphite furnace atomic absorption (GFAAS) spectroscopy (Perkin Elmer AAnalyst 800).

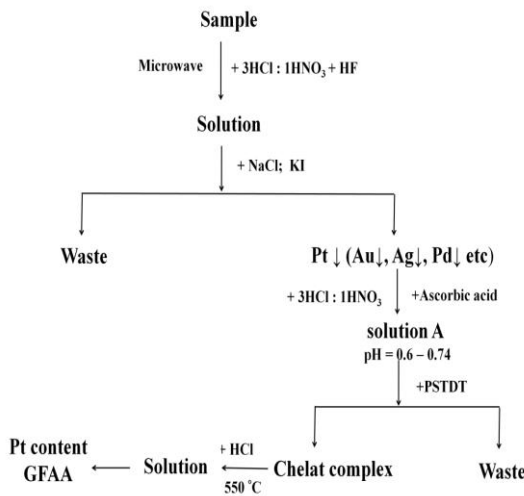


Figure 2: Scheme of chemical enrichment procedure of platinum in serpentine rocks.

2.4. Interferences sorption element

We tested 300 ppb 0.1; 0.5; 1N solution of hydrochloric acid environment gold standard on a number of metals (based on the chemistry of the samples selected), adding a certain amount of gold, PSTDT by conditions set by the quality of absorption (50 mg PSTDT, t ° C = 80, T = 60 minutes) [18].

3. Results and Discussion

Research dried in selected samples of 105 ± 5 ° C, crushing and shredding into the cheek until 3.35 mm and prepared thinly and grinding until the vibrating mill 0.074 mm chemical analysis. Sample chemical composition, and inductively coupled plasma (methods, such as ICP-OES), rebound X-ray fluorescence (XRF) is defined by, respectively.

Table1

Table1: The chemical content of samples

Sample	ICP-OES, ppb			XRF, %						
	Au	Pd	Pt	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	MnO
1	275	120	458	35.2	0.60	6.75	0.06	1.50	40.90	0.15
2	210	190	217	35.4	0.70	8.50	0.05	0.40	37.60	0.10
3	125	87	93	40.0	0.50	3.15	0.04	0.80	43.51	0.10

The chemical composition of samples Table 1 shows the basic elements constituting rocks are Mg and Si.

Sample decomposition. Ores, rock samples, glass and other inorganic materials can be dissolved rapidly in Parr Acid Digestion Vessels using strong mineral acids: HF, HCl, H₂SO₄, HNO₃, Aqua regia and others. Using reaction temperatures well above normal boiling points, samples can be dissolved or digested rapidly for all types of chemical analyses, particularly for AAS and ICP spectroscopy, and for other instrumental methods in which trace elements must be identified.[20]

It is known that strong acids are effective in dissociating complexes and releasing free metal ions. For this purpose, 1HNO₃+3HCl mixture and hydrofluoric acid at different concentrations was examined in microwave MARS6.

Table 2: Working conditions for microwave oven

step	Reagent	Volume	Temperature	Pressure	Time
1	3HCl+1HNO ₃	10	250°C	120psi	30 minut
2	HF	2			

Quantitative relationship is, we cannot prevent a number of elements that might inhibit the quality of the sample chemical composition of the Pt removals selected pilot serving with sorbent (PSTDT) determined. Table 3.

Table 3: The solution via PSTDT affect ratios to absorb choose platinum

Metal	Interferencessorption metal Me/Pt		
	1M HCl	2M HCl	5M HCl
Fe(II)	4 · 10 ⁶	5 · 10 ⁵	2 · 10 ⁵
Fe(III)	3 · 10 ⁶	8 · 10 ⁵	2 · 10 ⁵
Ca	5 · 10 ⁶	5 · 10 ⁶	5 · 10 ⁶
Co(II)	6 · 10 ⁵	4 · 10 ⁵	2 · 10 ⁵
Cu(II)	2 · 10 ⁵	3 · 10 ⁴	3 · 10 ⁴
Mo(VI)	1 · 10 ⁶	7 · 10 ⁵	4 · 10 ⁵
Ni	8 · 10 ⁵	1 · 10 ⁵	2 · 10 ⁵
Au(I)	5 · 10 ²	1 · 10 ²	3 · 10 ²
Cr(VI)	6 · 10 ⁶	5 · 10 ⁵	4 · 10 ⁵
Mg	4 · 10 ⁶	3 · 10 ⁶	4 · 10 ⁶

A solution determined by the second, GFAAS macro elements content of additives content by ICP-OES, precious metals, shows Rolled Table 4. Table 4 results, we can conclude that sedimentation of samples was carried out in complete breakdown and precious metals.

Table 4: A solution elements content (ICP-OES, X_d±Δ, n=3, P=0.95)

Solution A	content, ppm							
	Fe	Co	Cr	Mg	Cu	Au	Pd	Pt
SARM7	6.70	3.80	20	100.0	12.0	3.74	1.53	0.31
Sample 1	39.0	30.0	10.0	112.0	25.0	0.270	0.123	0.449
Sample 2	12.0	5.0	9.0	130.0	18.0	0.203	0.180	0.220
Sample 3	18.0	5.0	16.0	125.0	26.0	0.120	0.082	0.089

Calibration schedules of platinum and thresholds of detection.

Determination of elements in a sample is carried out by means of calibration schedules of dependence of absorption signal from concentration. For creation of calibration schedules of the determined elements, standard solutions of platinum with concentration 0.0008; 0.0025; 0.05; 0.10; 0.20; 0.30; 0.40; 0.50; 1µ/mL have been prepared. Mainly calibration schedules of all studied elements with concentration more than 1µ/mL stopped being linear. Limits of detection of elements were calculated as triple standard deviation of 10 parallel measurements of "blank" sample (1N of HCl). Limits of determination were calculated as triple standard deviation for 10 parallel measurements of the model solution, which was prepared by means of standard solutions

Direct atomic absorption determination of platinum. The weighted portion of sample weighing 0.1; 1 g was

transferred to solution by above methods, the aliquot part of solution was diluted if necessary 5–10 times and carried out determination of Pt in solution by GFAAS. Calculation of the determined concentration was carried out on calibration dependence. The temperature programs are the most important part in the GFAAS. The instrumental conditions of the determination are established in Table 5.

Table 5: Instrumental conditions for GFAAS determination of platinum

Step	Temperature (°C)	Ramp (s)	Hold (s)	Argon flow (ml min ⁻¹)
Drying 1	110	1	20	250
Drying 2	130	5	30	250
Ashing	1300	10	20	250
Atomization	2300	0	5	0
Cleaning	2400	1	5	250

Table 5 shows the heating program used for Pt measurements.

Sample analysis. Trueness of the analysis was controlled by comparison with results received by independent methods. Results enrichment by PSTDT have been compared with results by assaying analysis. The results of comparison of the analysis of samples received by GFAAS are given in table 6. The table shows that results are comparable.

Table 6: Results obtained after enrichment PSTDT by mean GFAAS.

№	Sample	Mass, g	Pt content, ppb	
			Solution after assaying analysis	Solution after enrichment by PSTDT
1	Sample 1	1	470	477
2	Sample 2	1	220	233
3	Sample 3	1	90	112
4	SARM7 (3.74 ppm)	0.1	372	375

Conclusion

The low-content platinum determination in samples of serpentine rocks was clearly examined using GFAAS. Selected solutions are going, digest and refining, was provided instrumental precision of Pt. Low content platinum determination in serpentine ore is suitable using chemical enrichment method by PSTDT and this method is selective, simple, functional, timing and power consumption compared to the assaying analysis.

ACKNOWLEDGEMENT

One of the authors thanks (N. J) for part of calculations to High Level Research Foundation of National University of Mongolia, #26 (2015-2016). We also wish to thank Professor N. N. Basargin for carrying out the synthesis of PSTDT.

REFERENCES

[1] V. I. Bukin, M. S. Igumnov, V. V. Safonov, Recycling of industrial wastes and secondary raw materials containing rare, precious and non-ferrous metals, The publishing house "Business Capital", Moscow, 2002.

- [2] A. Bashilov, "Microwave sample preparation for elemental analysis - yesterday, today and tomorrow," *Analytica*, vol. 1, pp. 6-15, 2011.
- [3] C. H. Kim, S. I. Woo, S. H. Jeon, "Recovery of Platinum-Group Metals from Recycled Automotive Catalytic Converters by Carbochlorination," *Industrial & Engineering Chemistry Research*, vol. 39, pp. 1185-1192, 2000. DOI: 10.1021/ie9905355
- [4] B. Godlewska-Zylkiewicz, "Biosorption of platinum and palladium for their separation/preconcentration prior to graphite furnace atomic absorption spectrometric determination", *Spectrochim. Acta Part B: Atomic Spectro*, vol. 58(8), pp. 1531-1540, Aug. 2003.
- [5] P. S. Hooda, A. Miller and A. C. Edwards, "The distribution of automobile catalysts-cast platinum, palladium and rhodium in soils adjacent to roads and their uptake by grass," *Sci. Total Environ*, vol. 384(1-3), pp. 384-392, Oct. 2007.
- [6] P. Petrova, S. Velichkov, N. Velitchkova, I. Havezov and N. Daskalova, "Problems, possibilities and limitations of inductively coupled plasma atomic emission spectrometry in the determination of platinum, palladium and rhodium in samples with different matrix composition," *Spectrochim. Acta Part B: Atomic Spectro*, vol. 65(2), pp. 130-136, Feb. 2010.
- [7] C. Colombo and A. John monhemius, "Platinum, palladium and rhodium release from vehicle exhaust catalysts and road dust exposed to simulated lung fluids," *Ecotoxi. Environ. Safety*, vol. 71(3), pp. 722-730, Nov. 2008.
- [8] C. Colombo, A. John monhemius and A. Plant Jane, "The estimation of the bioavailabilities of platinum, palladium and rhodium in vehicle exhaust catalysts and road dusts using a physiologically based extraction test," *Sci. Total Environ*, vol. 389(1), pp.46-51 Jan. 2008.
- [9] N. Anthemidis Aristidis, G. Themelis Demetrius and A. Stratis John, "Selective stopped-flow injection spectrophotometric determination of palladium(II) in hydrogenation and automobile exhaust gas converter catalysts," *Anal. Chim. Acta*, vol. 412(1-2), pp. 161-167, May 2000.
- [10] R. K. Klaus and D. Auer, "Determination of platinum and palladium in strongly acid solution by means of flow injection analysis," *Talanta*, vol. 40(12), pp. 1975-1980, 1993.
- [11] I. A. Kovalev, L. V. Bogacheva, G. I. Tsysin, A. A. Formanovsky and Yu. A. Zolotov, "FIA-FAAS system including on-line solid phase extraction for the determination of palladium, platinum and rhodium in alloys and ores," *Talanta*, vol. 52(1), pp. 39-50, May. 2000.
- [12] S. Woinska and B. Godlewska-Zylkiewicz, "Determination of platinum and palladium in road dust after their separation on immobilized fungus by electrothermal atomic absorption spectrometry," *Spectrochim. Acta Part B: Atomic Spectro*, vol. 66(7), pp. 522-528, July. 2011.

- [13] E. Maserà, P. Mauchien and Y. Lera, "Electrothermoatomization-laser induced fluorescence determination of iridium, rhodium, palladium, platinum and gold at the ng/l level in pure water," *Spectrochim. Acta Part B: Atomic Spectroscopy*, vol. 51(5), pp.543-548, 1996.
- [14] J. G. M. Van Der Linden and A. H. Dix, "Electrochemical redox behaviour of dithiocarbamates and diselenocarbamates of nickel, palladium and platinum," *Inorg. Chim. Acta*, vol. 35, pp. 65-71, 1979.
- [15] M. Paraskevas, F. Tsopelas, M. Ochsenkühn-Petropoulou, "Determination of Pt and Pd in particles emitted from automobile exhaust catalysts using ion-exchange matrix separation and voltammetric detection," *Microchimica Acta*, vol. 176, pp. 235-242, 2012.
- [16] O. A. Dalnova, Sorption-atomic absorption analysis of secondary and man-made materials for determination of platinum metals: Ph.D. thesis in Engineering Science – Moscow, 2009.
- [17] B. Rajua, J. R. Kumarb, J.-Y. Leeb, H.-S. Kwoncc, M. L. Kantama, B. R. Reddya, "Separation of platinum and rhodium from chloride solutions containing aluminum, magnesium and iron using solvent extraction and precipitation methods," *Journal of Hazardous Materials*, vol. 180, pp. 253-258. 2012. Doi:10.1016/j.jhazmat.05.025
- [18] S. Odonchimeg, J. Oyun, "Study using polymer chelate solvent in rocks," *AN, ICCT*, vol. 2, pp. 30-33, 2015./in Mongolia/
- [19] N. N. Basargin, Rozovsky, U.G., Volchenkova, V.A. et al., *Органические реагенты и хелатные сорбенты в анализе минеральных объектов* М. Nauka (M. Science), 1980, pp. 82-116. /in Russia/
- [20] Altundag H, Tuzen M. Comparison of dry, wet and microwave digestion methods for the multi-element determination in some dried fruit samples by ICP-OES. *Food Chem Toxicol.* 2011;49:2800e2807.