

# Analytical Study of Enrichment of Low Content Platinum in Natural Minerals by using Polymeric Sorbent

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## Abstract

In order to enrich low content platinum (Pt), polystyrene-azo-thiazan-dithion-2.4(PSTDT) has been selected from several polymeric sorbents that able to create with it a chelate complex. We studied physical-chemical characteristics of sorbent and their complexes with platinum. Analytical parameters of condition for platinum concentration are determined. The platinum sorption process with sorbents having thiazan-dithion groups runs with detaching of two protons from FAG. In the complex these results allow to suggest the obvious, structure of chelate fragments. We define that in the optimal conditions for platinum sorption  $[H^+]$ , sorption all time and temperature. A new rapid and reliable method of concentration and derivation of quantitative of (Pt) natural minerals objects by polymeric FAG thiazan-dithion groups is proposed.

**Keywords:** platinum standard solution; polystyrene-azo-thiazan-dithion-2.4; chelate complex; natural rock.

## 1. Introduction

The polymeric sorbents have strong inter molecular bonds which are insoluble in water, acids, bases and organic solvents.

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The molecule of these polymers has functional analytical group (FAG) such as  $-\text{NH}_2$ ,  $-\text{NO}_2$ ,  $-\text{COOH}$ ,  $-\text{OH}$ ,  $-\text{SO}_3$ ,  $-\text{HSO}_3$ ,  $=\text{S}$ ,  $=\text{NH}$ , which include chemical communication through these atoms, creating metal ions chelating [1-5]. Basargin and his colleagues used the polystyrene-azo-thiazandithion-2.4 (PSTDT) polymer, to determine the low-content gold in silicates, quartz, and sulfide ores [6], by atomic absorption spectroscopy (AAS) and used to determine the Hg(II) in natural water by sorption spectrophotometric method [7].

The approaching of methodological and chemical techniques in platinum determination using polymer adsorbents to creating chelate complex with platinum ion [8-12].

Solvent extraction of precious metals is widely employed in chemistry and industry for many years. This technique has been used for separation of platinum metals [13-15].

Functional Analytic Group(FAG) is placed in the structure of polymeric sorbent. This FAG has ability to create chelate complex with metal ion. S, N containing FAGs are the most selective toward noble metals [16-24].

We aimed to develop a rapid physical-chemical method for precise determination and concentration of low content ( $10^{-5}$ - $10^{-7}\%$ ) platinum from raw materials by pure chemical methods. Low content platinum concentration from raw minerals by formation of chelate complex compound and a method derivation for their separation from other elements. In order to achieve this purpose we selected the polymer agents with platinum sorption quality based on their chemical properties. The analytical parameters of theoretical basis of agent selective FAG of polymer is determined and the adsorption mechanism of platinum by using polymer is explained in this work.

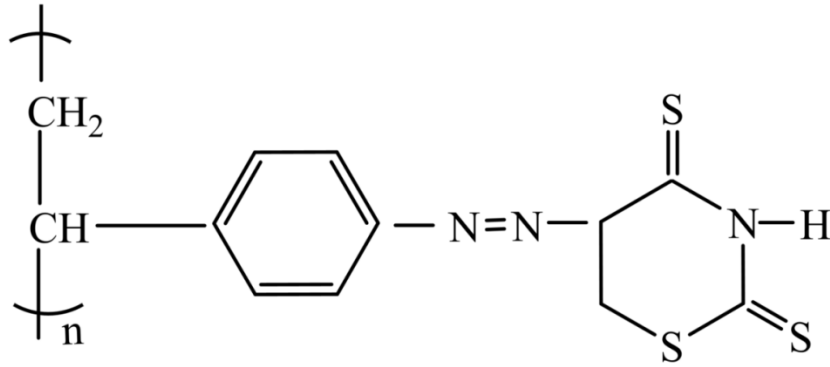
## **2. Material and Methods**

### **2.1. Materials**

Polystyrene-azo-thiazondithion-2.4 (Astralabor, Russia) was used to determine the platinum content in standard solution(ACROS Organics) and samples.

The PSTDT polymer (Fig.1) 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. Rozovskiii and his colleagues firstly synthesized polystyrene-azo-thiazan-dithion-2.4 on the basis of polystyrene-azo compound at the Central Chemical Laboratory of the Institute of the Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry (IGEM, Russia) [25].

Certified reference material(SRM) and samples were used SARM 7, OREAS 13b and serpentine ore /rokcs/ Govi-Altai province Khantaishir (Western Mongolia) - sample1, Umnugovi province Toromkhon (South Mongolia) - sample2, Bulgan province Khyalganat ( Northern Mongolia) - sample3, waste copper- sample4, copper ore - sample5 and copper concentrate - sample 6 of Erdenet Mining Corporation respectively.



**Figure 1:** Representation of molecular structure of PSTDT adsorbent.

## 2.2. Methods

### 2.2.1. Optimum condition for platinum adsorption

In order to define the optimum condition as temperature (20 °C, 50 °C and 80 °C), time (20–120 minutes) and HCl (0.1- 1.0N) affecting to the platinum adsorption, 25 mg PSTDT with 500 ppb platinum solution were taken for 100 ml solution and stirred on the magnetic mixer. Platinum contents in the solution were measured by spectrophotometry (MAPADA V-1600PC) to form the color complex with rodasol-XC. Adsorption efficiency of the gold was calculated as following equation:

$$R = \frac{q_a - q_f}{q_a} \times 100\% \quad (\text{Eq. 1})$$

Where,  $R$ ,  $q_a$ , and  $q_f$  are the adsorption efficiency (%), concentrations (ppb) of the gold in the standard solution and filtrate solution, respectively.

### 2.2.2. Sorption capacity of sorbent (SCS)

The solutions of platinum with concentrations of 200, 400, 600, 800, 1000, 1200 and 1400 ppb were prepared from the standard solution to determine the maximum amount of platinum per adsorbent. 50 mg PSTDT added into each solutions at optimum condition then filtrate solutions were analyzed to adsorption efficiency.

Sorption capacity of sorbent is calculated following equation:

$$SCS_{Pt} = \frac{(C_0 - C) * V}{m} \quad (\text{Eq. 2})$$

Where,  $C_0$ ,  $C$  -gold concentration in initial and remained solution, respectively,  $V$  -50 ml standard solution,  $m$ - 50 mg sorbent

### 2.2.3. Determination of proton number detaching from PSTDT FAG

The proton number detached from the agent FAG during the platinum adsorption defined by graphical and calculation methods in relation with “pH” environment [26].

### 2.2.4. Frontier-Transform Infrared (FT-IR) spectroscopy

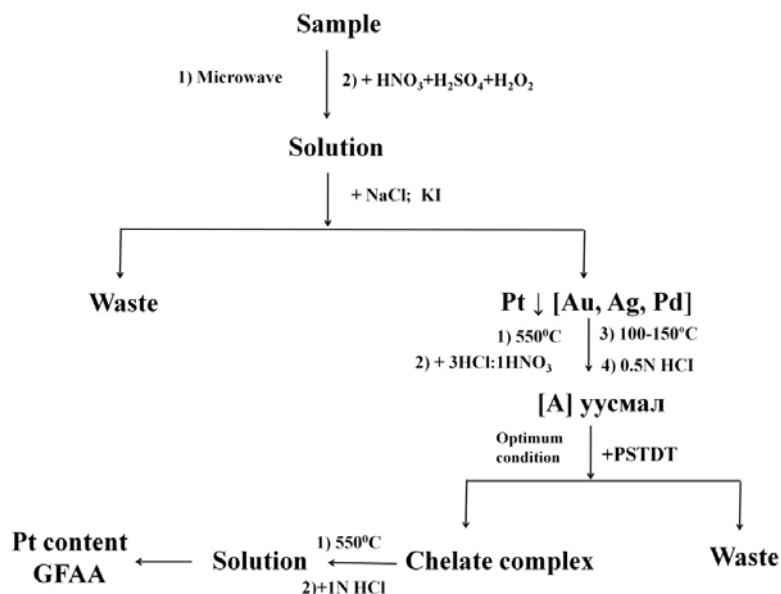
The chemical bond frequencies of functional groups of polymer before and after treatment of sample were analyzed by using Frontier-Transform Infrared (FT-IR) spectrophotometer (IRPrestige-21, Shimadzu, Tokyo, Japan). The powdered samples were mixed with KBr and made the pellets. The FT-IR spectra were obtained with frequency range of 4000 – 400  $\text{cm}^{-1}$ .

### 2.2.5. Determination of platinum content in samples

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 0.5 g, respectively which were dissolved on  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}_2$  in each solutions then the samples were put in microwave during 1 hour. Then was added NaCl and KI with concentration of 10 % to separate the gold, platinum, silver and palladium. This procedure was repeated twice. The precipitate was filtered and calcinated at 600 °C. The precipitate was dissolved in “Aqua regia” solution and evaporated then dissolved in 0.5 N hydrochloric acid. (A solution)

*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.

### 3. Results and discussion

#### 3.1. Optimum condition for adsorption

**Figure 3:** Adsorption efficiency dependence on the pH (a), time and temperature (b), and concentration of platinum using 25 mg PSTDT (c).

Figure 3a shows the platinum extraction versus solution  $[H^+]$  plots for the PSTDT. It can be seen that PSTDT successfully extracted platinum with the value of adsorption efficiency was 98 % at the solution HCl from 0.5N. Figure 3b graphically illustrated the effect of the phase-contact time ( $\tau$ ) at the solution temperature (T) on the adsorption efficiency of platinum by PSTDT. The adsorption efficiencies at different temperatures increased until contact time of 60 min, then they were stabilized. The adsorption efficiency at 80 °C of platinum by PSTDT was greater than other temperatures as 20 °C and 50 °C. Figure 3c shows the adsorption efficiency versus the concentration of platinum. 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.

#### 3.2. Determination of proton number detaching from PSTDT FAG

Numbers of detached protons (n) during the platinum sorption were determined according to the  $[H^+]$  influence on the degree of sorption using graphical and computational data. The  $>C=S$ ,  $>NH$  groups in the polymer have electrons with higher movement and they are protonated and deprotonated at the first. This property depends on energy bounds of atoms.

Sorption chemical mechanism were defined considering number of detached protons, structure and nature of the FAG that input into the sorbent's structure. Firstly, the hydrogen (H) of the NH is substituted then form the coordination bonds by C=S because the order of energy value of bonds is  $NH(132 \text{ kkal/mol}) > C=S(103 \text{ kkal/mol})$ .

Experimental results shows that polymer by FAG groups connect with metal ion to form chelate ring by

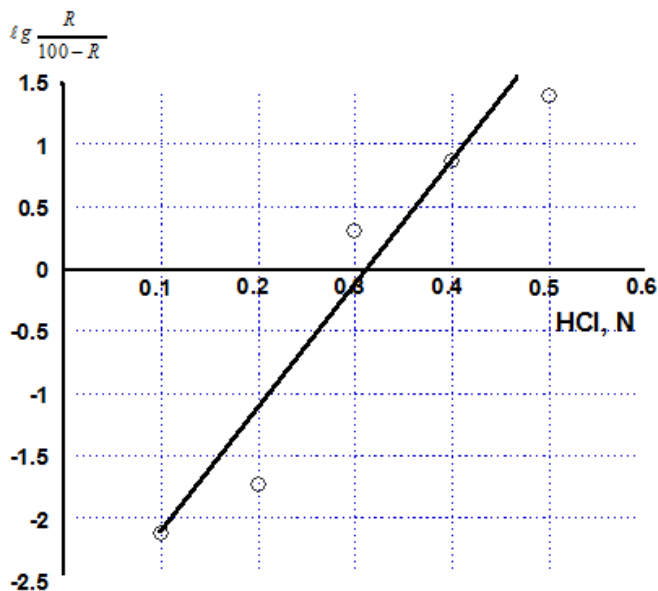
substituting the proton and proton number was determined by using graphical method. We defined the platinum sorption mechanism of agent has the following form:



Substituted proton number was calculated by complex numerical dependence for various [H<sup>+</sup>] environment. Substituted proton number (n) is determined by Astohov method [26]. The adsorption coefficient by percent (R) depend on the concentration of hydrochloric acid is shown in Table 1.

**Table 1:** Adsorption percent of platinum.

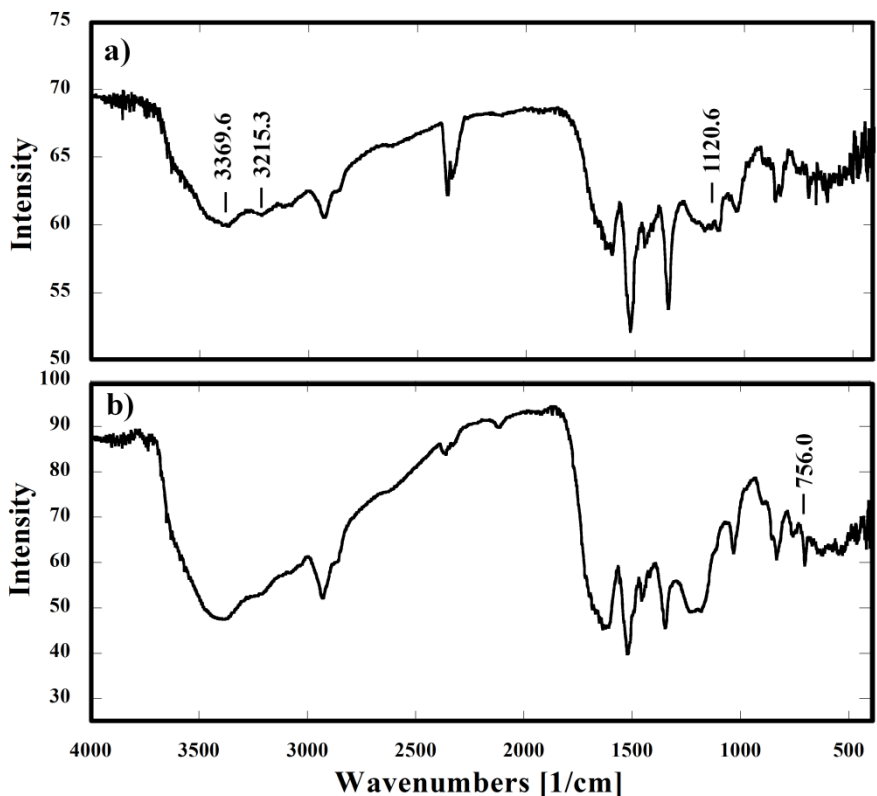
N <sub>o</sub>	HCl[N]	R[%]	$\frac{R}{100-R}$	$\lg \frac{R}{100-R}$
1	0.1	38.0	0.6129	-2.125
2	0.2	49.0	0.9607	-1.728
3	0.3	67.0	2.0303	0.307
4	0.4	88.0	7.3333	0.865
5	0.5	96.0	24.000	1.380



**Figure 4:** Graph of R depend on the concentration of hydrochloric acid.

Fig. 5 shows that the R depend on the concentration of hydrochloric acid. From this graph, the tangent of the curve was  $\tan\alpha=1.92$  (correlation coefficient is 0.96), therefore the substitution proton was  $n=2$ .

**3.3. Frontier-Transform Infrared (FT-IR) spectroscopy**



**Figure 5:** FT-IR spectra of PSTDT polymer before (a) and after (b) treatment of platinum sample

The functional groups of PSTDT polymer before and after treatment of gold samples were identified using FT-IR experiment and the spectrum is shown in Fig. 5. In Fig. 5, the observable IR signals for PSTDT polymer were 3215 and 3370  $\text{cm}^{-1}$  for N-H, 1121  $\text{cm}^{-1}$  for  $\text{-C=S}$ . The intensities at these wave numbers were decreased after the treatment of PSTDT to serpentine samples. The differences of the intensities of  $\text{-NH}$  group are shown in the figure which means that the platinum was adsorbed onto PSTDT polymer. The  $\text{-CS}$  group shows the important for the sorption of the metal [27] The IR signals were similar with the group frequencies vice versa the frequencies do not shown for PSTDT polymer after treatments of the platinum sample. It shows that the platinum atom substituted the hydrogen atom of imine group and connected with sulfur atom by coordination.

### 3.4. Sample analyse

*Sample decomposition stage*





Enrichment stage;

**Table 2:** The metal contents in A solution (ISP-OES)

Solution	Content, ppm								
	Fe	Co	Cr	Mg	Cu	Au	Ag	Pt	Pd
Sample 1	39	30	10	112	25	1.2	2.0	1.3	2.1
Sample 2	12	5	9	130	18	0.78	21	1.9	3.7
Sample 3	18	5	16	125	26	1.8	33	2.7	4.1
SARM7 (3.74 ppm)	67	38	0.02	100	12	0.403	0.324	4.14	1.89
Sample 4	15	6	15	34	0	32	67	2.1	4.6
Sample 5	5	23	18	25	0	0,971	39	1.5	1.9
Sample 6	8	18	8	19	0	1,680	10	0.79	2.1
OREAS13b	8	25	31	11	0	0.187	0.587	0.21	0.42
Wavelength, nm	260	228.6	284	279.6	325	242.2	328.1	265.9	340.5

**Table 2:** The ratio of metal and platinum contents to delay the analysis of platinum content by using PSTDT polymer

Metal	The ratio of metal and platinum content Me/Pt		
	1M HCl	2M HCl	5M HCl
Fe(II)	$4 \cdot 10^6$	$5 \cdot 10^5$	$2 \cdot 10^5$
Fe(III)	$3 \cdot 10^6$	$8 \cdot 10^5$	$2 \cdot 10^5$
Ca	$5 \cdot 10^6$	$5 \cdot 10^6$	$5 \cdot 10^6$
Co(II)	$6 \cdot 10^5$	$4 \cdot 10^5$	$2 \cdot 10^5$
Cu(II)	$2 \cdot 10^5$	$3 \cdot 10^4$	$3 \cdot 10^4$
Mo(VI)	$1 \cdot 10^6$	$7 \cdot 10^5$	$4 \cdot 10^5$
Ni	$8 \cdot 10^5$	$1 \cdot 10^5$	$2 \cdot 10^5$
Au(I)	$5 \cdot 10^2$	$1 \cdot 10^2$	$3 \cdot 10^2$
Cr(VI)	$6 \cdot 10^6$	$5 \cdot 10^5$	$4 \cdot 10^5$
Mg	$4 \cdot 10^6$	$3 \cdot 10^6$	$4 \cdot 10^6$



**Table 3:** Comparison of platinum contents traditional and chemical enrichment methods.

№	Sample	Pt content, ppm	
		Assaying analysis	Chemical analysis
1	Sample 1	0.470	0.477
2	Sample 2	0.220	0.233
3	Sample 3	0.090	0.112
4	SARM7 (3.74 ppm)	3.72	3.75
5	Sample 4	0.090	0.085
6	Sample 5	0.112	0.106
7	Sample 6	0.361	0.359
8	OREAS13b(0.197 ppm)	0.195	0.198

The contents of platinum of SRM and samples are shown in Table 3 by using assaying analysis and using traditional method. It shows that our chemical enrichment method is suitable for these samples because the maximum concentration of platinum is 1000 ppb can be adsorbed using 25 mg PSTDT. The averaged platinum content in SARM7 and OREAS13b by chemical enrichment method using PSTDT was 3.75 and 0.198 ppm which is in good agreement with using assaying analysis (Table 3) to use our enrichment method is suitable for rocks. In this work, the solution A was prepared from samples by decomposition stage then the platinum in solution A was adsorbed by enrichment stage at optimum conditions of the  $[H^+]$ , time and temperature which established as ~0.5N HCl, 60 min and 80 °C, respectively and to analyze the platinum content by analysis stage using graphite furnace atomic absorption (GFAA) spectroscopy. Table 3 shows the averaged platinum contents in solution A (Fig. 2) as prepared from Samples. The platinum contents in samples by using our chemical enrichment is higher efficiency than by using assaying analysis.

#### 4. Conclusion

The low content platinum determination in samples of serpentine rocks was clearly examined using GFAA. The platinum enrichment optimum condition as the  $[H^+]$ , time and temperature were determined which were 0.5N HCl, 60 min and 80 °C, respectively and the substituted proton number was ~2.

These analytical parameters are basis to develop the new methodology to enrich the low content ( $10^{-6}$ - $10^{-9}$ %) platinum in minerals. Low content platinum determination in serpentine rocks and copper samples are suitable using chemical enrichment method by using PSTDT and this method is selective, simple, functional, rapidly, power consumption compared to the assaying analysis.

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