

## Determination of palladium by the method of concentration in various objects with the participation of synthetic sorbents

E. N. Hashimova <sup>1,\*</sup>, U. M. Abilova <sup>2</sup>, C. İ. Mirzai <sup>2</sup>, and F. M. Çıraçov <sup>2</sup>

<sup>1</sup> Azerbaijan State Oil and Industry University, Azadlig Avenue 30, AZ-1010, Azerbaijan

<sup>2</sup> Baku State University, AZ 1148 Bakı, Z.Xalilov str.23, Azerbaijan

**Abstract:** This work developed a method for determining palladium (II) in various objects. For this purpose, new polymer sorbents have been synthesized by chemical modification of a copolymer of styrene and maleic anhydride using formaldehyde and an amine fragment with various functional groups. The resulting polymer sorbents were identified by IR spectroscopy. The temperature stability of the synthesized sorbent with sulfodimezine (MS1) and the amino fragment of 1-aminophenol-2-hydroxy-4-sulfonic acid (MS2), was studied by thermogravimetric analysis. It has been established that sorbents based on a copolymer of maleic anhydride and styrene are unsuitable for use at temperatures above 120°C degrees. The resulting sorbent's sorption and desorption of Pd (II) ion was studied. The sorbent's sorption capacity increases when the density is too high, but the sorbents can be reused for 7-8 cycles. The developed methods make it possible to determine palladium (II) ions by condensation in natural and manufactured objects. Optimal sorption conditions were determined. It has been established that the sorption process must be carried out in an acidic environment. Concentrating palladium (II) ions in various objects using synthesized polymer sorbents has been studied. It has been shown that a more promising method for determining trace amounts of palladium (II) is the photometric method. To carry out photometric studies, it was first investigated with which reagent palladium forms a more stable complex compound. It has been established that palladium forms a more stable complex with 2,2,3-tetrahydroxy-3-sulfonic acid-5-chlorazobenzene. It has been shown that determination reactions based on the formation of various ligand complexes of these reagents have higher performance. It was established that palladium (II) forms stable complexes with reagents of functional groups containing donor atoms S, O, and N. Therefore, the photometric determination used reagents based on pyrogallol. It should be noted that the sorption capacities of complex bonds formed by reagents with donor atoms and palladium ions are high.

**Keywords:** Sulfodimezine; 1 amino phenol 2 hydroxy 4-sulfoacid; Nickel powder; Igneous rock; Palladium (II).

### 1. Introduction

In recent years, concentration and separation methods have been widely used to determine trace amounts of noble metals in various natural and technical objects. The low concentration of noble metals, their complex composition, and the presence of interfering ions make it challenging to obtain reliable results. Concentration and separation of trace elements are often used to increase the selectivity and sensitivity of several methods. Our studies have shown that the photometric method <sup>1</sup> is promising for determining trace amounts of palladium (II). To carry out photometric studies, we first selected a reagent with which palladium forms a more stable complex compound <sup>2</sup>. During the experiment, reagents based on pyrogallol were used. Pyrogallol-based azo compounds have wide practical applications

for the photometric determination of several metal ions. Determination reactions based on the formation of various ligand complexes of these reagents have higher performance. Therefore, it is essential for the photometric determination of specific metal ions. Palladium (II) forms stable complexes with reagents of functional groups containing donor atoms S, O, and N. Taking this into account, pyrogallol-based reagents were used for photometric determination. We used the reagent 2,3,4-trihydroxyphenylazo,5-sulfonaphthalene in our work. During hardening, chelating sorbents were used. It is known from the literature that chelate sorbents are widely used for the concentration of noble metals <sup>3</sup>. Concentration and separation using chelated polymer sorbents are often used as a preliminary step in determining elements by various chemical,

\*Corresponding author: E. N. Hashimova

Email address: [esmira.hashimova@mail.ru](mailto:esmira.hashimova@mail.ru)

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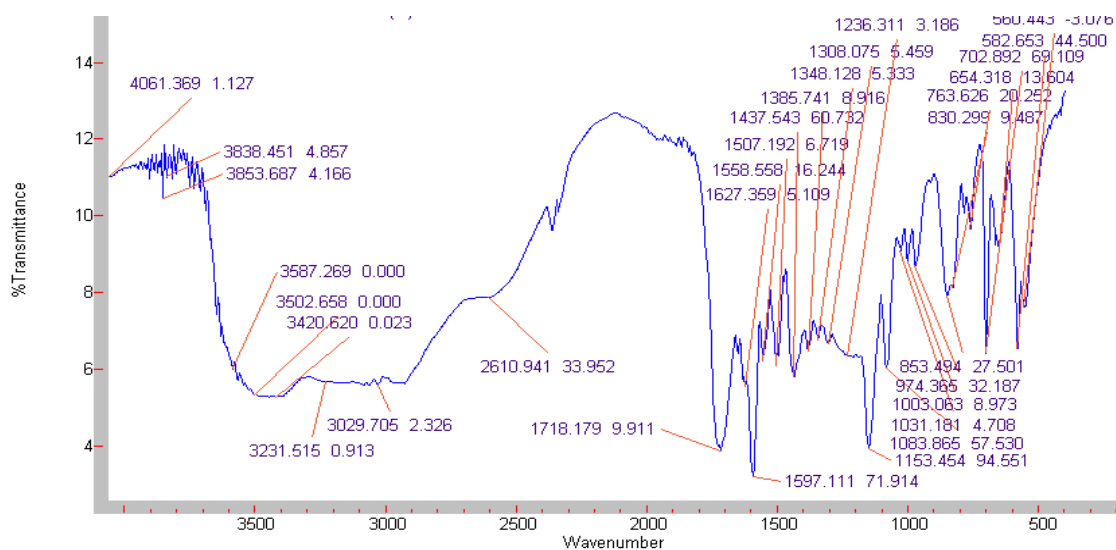
physicochemical, and physical methods. In this regard, in work for the determination of palladium (II) ion based on a copolymer of maleic anhydride and styrene in the presence of formaldehyde, new sorbents were synthesized by condensation using chemically modified sulfodimezine (MS1) and fragmented amine 1-aminophenol-2-hydroxy-4-sulfonic acid (MS2) <sup>4</sup>. The increasing demand for platinum group metals and the widespread use of palladium (II) in various industrial facilities and many catalysts indicate the importance of studying methods for concentrating and separating palladium (II) from multiple objects.

## 2. Experimental part

A solution of Pd (II) ion with a concentration of 1000 mg/l was prepared from the PdCl<sub>2</sub> salt to carry out the experiments. The density of the resulting solution was compared with standard ones (the density of the metal was determined by the gravimetric method using dimethylglyoxime) <sup>5</sup>. 37% HCl and 0.01 M HNO<sub>3</sub> were used to dissolve the sample taken. To maintain a stable pH of the medium, ammonium acetate buffer solution (pH 3–11) and fixanal HCl (pH 0–2) were used. A 0.1N KOH solution (20 ml of KOH solution was taken for the experiment) was prepared by dissolving the calculated mass of KOH in double-distilled water, and its

concentration was determined by titration with a standard HCl solution <sup>5</sup>. The pH of the solutions was controlled using a glass ionomer electrode pHS-25. The IR spectrum of the sorbent was studied on a Varian 3600 FI-IR device. A KFK-2 photo colorimeter and a Lambda-40 spectrophotometer (Perkin Elmer) were used to measure the optical density of solutions.

In this work, we synthesized new polymer sorbents and studied their adsorption properties. For this purpose, new chelate polymer sorbents with fragments of 1-amino-2-hydroxy-4-sulfonic acid and sulfodimezine were synthesized. To do this, a radical copolymerization of maleic anhydride (reagent grade) with styrene (reagent grade) was carried out in a benzene solution in a water bath (75–80°C, 120 min) according to the procedure given in the literature <sup>6</sup>. Benzoyl peroxide was used as an initiator. The resulting copolymer was dried in a vacuum at a temperature of 50°C. The calculated amount of formaldehyde and amines (3.54 g amine moiety, 20 mg formaldehyde, 3 g styrene, and maleic anhydride copolymer) was dissolved in alcohol and added to the resulting copolymer. The reaction was carried out in a water bath at a temperature of 65–70°C for 2 hours with continuous stirring. The resulting sorbent was washed with water and dried in a vacuum at a temperature of 50°C to constant weight..



**Figure 1.** IR spectra of the complex of palladium (II) ion with sulfodimezine (MS1) fragmented sorbent

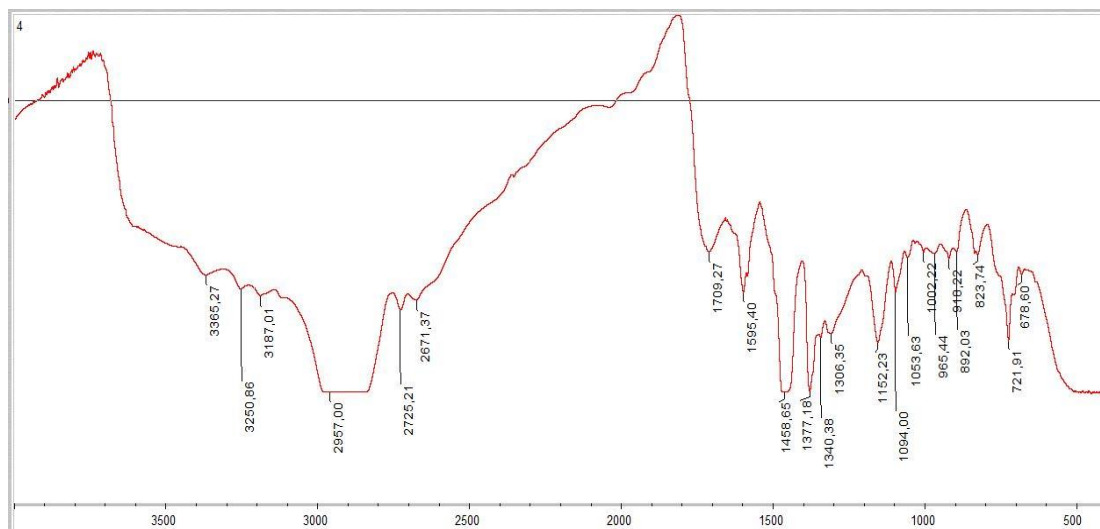
## 3. Results and discussions

We have studied the IR spectra of chelate complexes formed by palladium (II) ion with polymer sorbents, synthesized by adding the amine fragment MS1 (sulfodimezine) and MS2 (1-aminophenol-2-hydroxy-4-sulfonic acid) to a copolymer of maleic anhydride and styrene (Figs. 1 and 2). It has been established that shifts in the vibration frequencies of groups in the sorbent units are observed during the complexation process.

These shifts indicate the participation of analyte functional groups in complexation reactions with metal ions <sup>7</sup>. From Figs. 1 and 2, it is clear that in the IR spectra, there are bending vibrations of the C-H bond in the benzene ring (3029 cm<sup>-1</sup>), bending vibrations of the C-H bond in the CH and CH<sub>2</sub> groups (1437 cm<sup>-1</sup>), bending vibrations of the C-H bond C-H in the N-H bond (1570–1540 cm<sup>-1</sup>), stretching vibrations of the C=O group in acid (2610 cm<sup>-1</sup>), stretching vibrations of the C–O group in acid (1153 cm<sup>-1</sup>), stretching vibrations

of the C= group O ester ( $1031-1003\text{ cm}^{-1}$ ), stretching vibrations of the C–O group of the ester ( $1718\text{ cm}^{-1}$ ), stretching vibrations of the Car–N bond ( $1308\text{ cm}^{-1}$ ), stretching vibrations of the Ar–SO<sub>2</sub>–N bond ( $1348\text{ cm}^{-1}$ ), stretching vibrations of the –OH group in the carboxyl group ( $3600-3100\text{ cm}^{-1}$ ), stretching vibrations

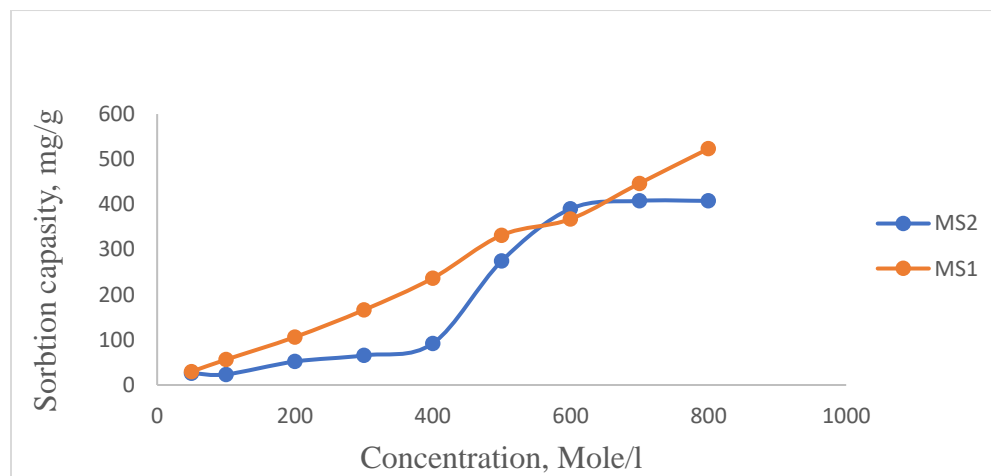
of the NH group ( $3400-3200\text{ cm}^{-1}$ ), stretching vibrations of the –C=O group in the carboxyl group ( $1780-1750\text{ cm}^{-1}$ ), C–C stretching vibrations in the benzene ring ( $1630-1500\text{ cm}^{-1}$ ). C–C bending vibrations ( $725-675\text{ cm}^{-1}$ ) are also observed in the benzene ring.



**Figure 2.** IR spectra of palladium (II) ion complex with 1- amino phenol 2-hydroxy 4-sulfo acid (MS2) fragmented sorbent

After identifying the sorbents using the sorption-photometric method, the amount of palladium (II) ion absorbed by the sorbent was determined <sup>8</sup>. We also calculated the sorption capacities of sorbents. It has

been established that the maximum light absorption of palladium (II) ion in the reactive background of the complex occurs at  $\lambda=490\text{ nm}$ . The sorption capacity reaches its maximum value (Fig. 3).



**Figure 3.** Dependence of the sorption capacity on the concentration of the metal in the process of sorption of MS1 and MS2 polymer sorbents with palladium (II) ions

The influence of several factors on the complexation reaction of palladium (II) ions with newly synthesized polymer sorbents was studied. One of these factors is the pH of the environment. The optimal pH value for palladium (II) ions sorption was 4-5. Based on the experiments, it was established that the value of the

distribution coefficient of Pd (II) ions in the system under study increases as it moves from an acidic environment to a weakly acidic and neutral environment. It can be said that polymer sorbents obtained in a practically neutral and slightly alkaline environment have better sorption capacity. The

influence of ionic strength on the sorption process was studied, and it was found that an ionic strength value of 0.8 mol/l does not seriously affect the sorption process<sup>9</sup>. Subsequently, an increase in ionic strength

leads to a decrease in the sorption rate. Table 1 shows the parameters of palladium (II) ion sorption on sorbents.

**Table 1.** Sorption indicators of palladium (II) ion on MS1 and MS2 sorbents.

Sorbent	Sorbition capacity, mg/g	Sorption degree, %	pH <sub>opt.</sub>	μ, mole/l	Time, hour	d, mm
MS1	523	98	5	0,8	1,0	0,14
MS2	521	98	4	0,6	1,0	0,14

After identifying the synthesized polymer sorbents, all factors influencing the sorption process and optimal sorption conditions were determined.

### 3.1. Determination of Pd(II) ions in nickel powder by curing on a sorbent based on sulfodimezine (MS1)

To prepare the collected sample for analysis, a sample weighing 2.0 g (0.028% Pt; Pd 0.071%; Rh 0.0018–0.0021%; Ir 10–4%; Ru 5 10–5%; Ni-base) heated in a glass, and then dissolved in 20 ml of gold. After

dissolving the sample, evaporation was performed to obtain a saturated solution. 20 ml of distilled water was added to the resulting residue and evaporated to obtain a dry residue. It was then dissolved by adding 10 ml of 0.01 M HNO<sub>3</sub> or HCl. The optimal sorption pH was established using 0.01 M HNO<sub>3</sub>. Finally, it is condensed and analyzed using MS1 sorbent. Based on the experiment results, it was established that the Pd(II) content in nickel powder is 1.39 mg/t.

**Table 2.** Results of concentration determination of Pd (II) ions in nickel powder (sample volume 1000 ml; eluent volume 5 ml; msorb.=100,000 mg; P=0.95; n=5).

Object	Sorbent	Pd (II) passport indicator mg/t	Pd (II) found, $\bar{x} \pm \frac{t_{pS}}{\sqrt{n}}$ mg/t
Nickel powder	MS1	1,42	1,39±0,001

### 3.2. Determination of palladium ion in standard igneous rock (MO-3) by the solidification method on a sorbent based on 1-aminophenol-2-hydroxy-4-sulfonic acid (MS2)

Based on the synthesized sorbent 1-aminophenol-2-hydroxy-4-sulfuric acid, a method for determining palladium (II) ion concentration in standard igneous rock (MO-3) was developed. Chemical compounds contained in the rock are indicated as percentages (the percentage of compounds is indicated according to passport indicators): CaO- 15.75%, Al<sub>2</sub>O<sub>3</sub> -13.67%, Fe<sub>2</sub>O<sub>3</sub> -8.48%, FeO-9.05%, MgO-8.66%, Na<sub>2</sub>O-0.72%,

K<sub>2</sub>O -0.204%, TiO<sub>2</sub> -1.46%, P<sub>2</sub>O<sub>5</sub> -2.15%, MnO -0.222%, S-0.124%, F-0.072, 0.05g/t Pd, 0.008 g/t Pt, the rest is SiO<sub>2</sub>. The experiments were carried out according to the specified method<sup>10,11</sup>. When dissolving, 1 ml of HCl, 2-3 drops of nitric acid, and 10 ml of distilled water are added to a sample weighing 0.01 g, taken from a standard object at a temperature of 50°C. The resulting mixture was dissolved. Optimal sorption conditions were created using HNO<sub>3</sub>, and the analysis was carried out by thickening with MS2 sorbent. The results are calculated considering 100% separation of the target ion and are presented in Table 3.

**Table 3.** Results of determination of palladium (II) ions concentration in MO-3 standard sample (%). (sample volume 100ml; msorb.=100mg, P=0.95; n=5).

Object	Sorbent	Pd (II) passport indicator mg/t	Pd (II) found, $\bar{x} \pm \frac{t_{pS}}{\sqrt{n}}$ q/t4
Igneous rock	MS2	0,05	0,049±0,001

Thus, methods have been developed for the sorption-

photometric determination of microquantities of palladium (II) ions in standard igneous rocks (MO-3) and nickel powder. Passport indicators and the additive method<sup>12</sup> mainly confirm the correctness of the newly developed methods. The developed methods make it possible to determine palladium (II) ions by condensation in natural and manufactured objects. These methods are rapid, characterized by high reproducibility, and allow the determination of low amounts of palladium in a sample.

#### 4. Conclusion

1. Two new chelate polymer sorbents were synthesized based on a modification of maleic anhydride-styrene copolymer with various amines for the selective concentration of palladium (II) ion.

2. The optimal conditions for the sorption of palladium (II) ions on the synthesized sorbents, namely pH, ionic strength, sorption time, and metal density, were studied. The sorption capacities of the sorbents were calculated, and based on the results obtained, it was found that MS1 has the greatest sorption capacity. With an increase in the number of donor atoms, namely N, S, and O, in the sorbent, the sorption capacity of the sorbent for palladium (II) ion increases.

3. It has been established that during the sorption of palladium (II) ion by the sorbent, the sorption capacity is maximum at a concentration of 800 mg/ml.

4. Methods have been developed for the sorption-photometric determination of microquantities of palladium (II) ions using MS1 sorbent in nickel powder and MS2 sorbent in standard igneous rock (MO-3).

5. The new determination method is more straightforward than other methods and generally has good reproducibility. The presented methods ensure the accuracy of the results when analyzing natural objects (the addition method and passport indicators confirm the accuracy).

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