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Palladium(II)'nin Selat Oluşturan Sorbentlerle Önderiştirilmesi ve 2,2',3,4-Tetrahidro-3'-Sülfo-5'-Klorazobenzol İle Fotometrik Tayini

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Özet: Paladyum (II)'nin 2,2 '3,4-tetrahidroksi-3′-sülfo-5 ′-klorazobenzol ile kompleks oluşumu incelendi. Bileşenlerinin 1 : 2 mol oranı ile homojen bir kompleks oluşturduğu gözlendi, kompleksin maksimum ışık absorbsiyonu 474 nm'de görülmekte olup, molar soğurma katsayısı $(2.00 \pm 0.02) .10^4$'dir. Karboksil grubu içeren yeni bir sorbent üretildi. Ve K^+ iyonları üzerine statik soğurma kapasitesi incelendi ve iyonojen grupların iyonizasyon sabitleri potansiyometrik titrasyon vasıtasıyla belirlendi. Bu sorbentce paladyum'un soğurma izotermi yapıldı ve konsantrasyon durumu incelendi. Optimum koşullarda Pd(II) iyonlarının ekstraksiyon derecesi 96% fazladır. Algılama sınırları (3 σ, n=20) 14.2 ng/ml'dir. Bu teknik standart bizmut-polimetalik örneğinde paladyum belirlemek için kullanılır.

Anahtar kelimeler: paladyum, sorbent, fotometrik, complexformation, soğurma kapasitesi

Preconcentration of Palladium (II) by Chelateforming Sorbent and Its Photometric Determination With 2,2',3,4-Tetrahydro-3′-Sulpho-5′-Chlorazobenzol.

Abstract: The complex formation of palladium(II) with 2,2',3,4-tetraxydroxy-3′-sulpho-5′-chlorazobenzol was studied. Homogenous complex with 1:2 molar ratio of components there was formed, maximum light absorption of complex was observed at 474 nm, molar coefficient of absorption is $(2.00\pm0.02)\cdot10^4$. It was produced a new sorbent containing carboxyl group. A static sorption capacity on K^+ ions was studied and the constants of ionization of ionogenic groups were determined by potentiometric titration. It was made an izoterm of sorption of palladium with that sorbent and there were investigated a condition of concentration. The degree of extraction of Pd (II) ions at optimal conditions is more than 96%. Limits of detection (3σ, n=20) are 14.2 ng/ml. The technique is used to determine palladium in standard bismuth-polymetallic sample.

Key Words: palladium, photometric determination, complexformation, sorption capacity.

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Introduction

Palladium is an important element. It is important for industry and biological systems as well (W. Bauer, W. Beck, and W. Ponikwar 2000), (G. Patrick, and P. Michel. 2003). Many sensitive instruments, such as spectrofluorimetry, X-ray fluorescence spectrometry, neutron activation analysis, atomic absorption spectrometry, chemiluminescence, and the like, have widely been applied to the determination of palladium. We have investigated the complexformation of Pd(II) with 2,2',3,4-tetraxydroxy-3′-sulpho-5′-chlorazobenzol. It was worked out a technique of sorption-photometric determination of Pd (II) in trade water.

For determination and extraction of palladium from natural and industrial objects by concentration they often use natural and synthetic sorbents. Nowadays they use chelateforming sorbents as a synthetic sorbent for concentration and determination of palladium (II). Efficiency, simplicity and selectivity of this technique provide its consumer use in analytical chemistry. Receipt of sorbents had better properties with regard to palladium (II) is always an actual problem. Sorption properties of polymer sorbents depend on nature, position in the link, quantity of functional analytical groups, contained in polymer and also depend on physical-chemical properties of polymer matrix. The main aim in the represented work is to investigate of sorption of palladium (II) with chelateforming sorbent, containing carboxyl group.

Experımental Part

Reagents

2,2',3,4-tetraxydroxy-3′-sulpho-5′-chlorazobenzol was obtained by azocombination of diazotated amine with piragollole in low acid medium on recommended technig and its composition and structure was established. In this work we applied a new polymer chelateforming sorbent with fragments of 2-amino-4-nitro-6-sulphofenol acid. Sorbent is synthesized on technique (Aliyeva et al 2006). This sorbent was dried at 50-60°C.

A solution of palladium (II) with a concentration of were prepared from $PdCl_2$ salt as described in (Korostelev 1964), the concentration of metal established gravimetrically using dimethylglyoxime.

Work solutions of Pd (II) were prepared by dissolving of an initial solution with distillated water. For making of needed acidity we used phycsanal HCl (pH 1-2) and ammonium-acetate buffer solution (pH 3-11). To create a constant ionic force we used KCl.

Apparuts

pH of solutions we measured by ionometr I-130 with glass electrod. Optical density of solutions we measured by using of photocolorimetr KFK-2 (l=1 sm). For photometric determination of palladium we used 2,2',3,4-tetraxydroxy-3′-sulpho-5′-chlorazobenzol as a reagent. Concentration of Pd (II) was calculated by using of calibration curve and the result were worked up by math statistic methods. The investigation of sorption was made in static and dynamic conditions.

In dynamic conditions all solutions were passed through glass minicolumn (inner diametr is 0.5 sm, length is 5 sm), filled of polymer chelateforming sorbent (100 mg).

Result and Discussion.

Characteristics of palladium (II) - TSXAB complex

The study of depending of complexformation on pH showed that the yield of homogeneous complex of Pd(II) with TSXAB is maximal at pH 3 (λ_{max}=474 nm), the reagent has a maximal light absorption at 383 nm. The complex is formed right away after the mixing of components. The rutio of reactants in the complexes was established by methods of relative output of Starik-Barbanel, shift of equilibrium and izomolar series **(**Bulatov and Kalinkin 1972). Molar coefficients of absorption of complexes were calculated from curves of saturation. The intervals of concentrations of obeying to Beer′s low were established (Tabl.1)

Tabl. 1**.** Some analytical characteristics of complex of Pd(II) with TSXAB.

pH_{opt}	λ_{max}, nm	$\varepsilon_{max} \cdot 10^4$	Composition of complex	Interval of obeying to Beer′s low, μg/ml
3	474	2,00±0,02	1:2	0,42-5,09

For determination of microamounts of ions of Pd (II) we investigated the conditions of prior concentration of Pd (II) by using of a new chelateforming sorbent on the basic of sopolymer of malehine anhydride-styrol, by following determination of ions of Pd (II) on aforesaid photometric technique. The optimal conditions of concentration of Pd(II) ions by polymer sorbent were established.

Acid-base constants of ionization of polymer sorbents are one of the basic properties. To determine the constant of ionization of sorbent we studied its total static sorption capasity

on K^+ ions (SSC_{K^+} = 5.46 mmol/g) and the potentiometric titration was done on known

technique (Basargin and Isayev 1986).

On the base of results of potentiometric titration we made a differential curve of titration

between $\frac{\Delta pH}{\Delta V}$ - f (V_{KOH}) (Fig.1)

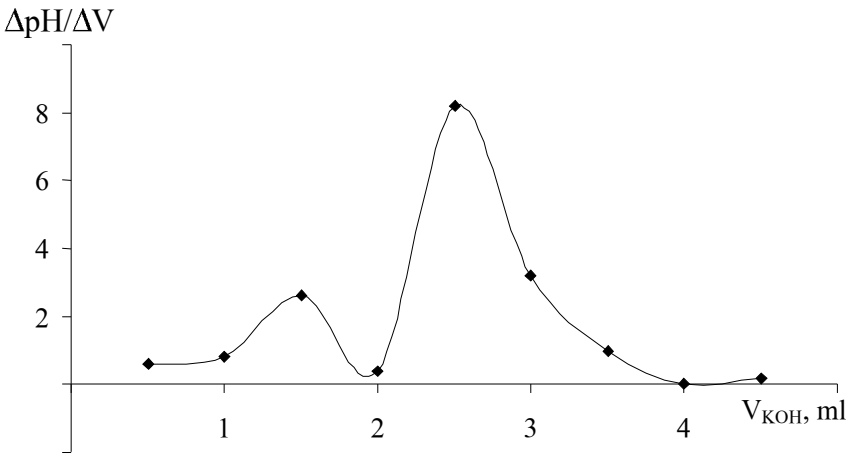

Fig.1. Differential curve of titration of sorbent.

At fig.1. we can see that the sorbent contains 2 different ionogenic groups. So the ionization of the sorbent goes on in 2 stages:

$$H_2R \Leftrightarrow HR^- + H^+$$

$$HR^- \Leftrightarrow R^{2-} + H^+$$

To determine the contains of ionization of the sorbent we can use data of differential curve of titration. The results are shown in tablo 2.

Tabl.2. Results for calculating of the constants of ionization of the sorbent. (C_{KOH}=0.1M, m_{sorb}=100 мg, $\overline{pK_1}$ =3.24; $\overline{pK_2}$ =7.91).

α	$\frac{\alpha}{1-\alpha}$	$\lg\frac{\alpha}{1-\alpha}$	V_{KOH}, ml	pH	pK_1	α	$\frac{\alpha}{1-\alpha}$	$\lg\frac{\alpha}{1-\alpha}$	V_{KOH}, ml	pH	pK_2
0.1	0.(1)	-0.954	0.2	2.4	3.07	0.1	0.(1)	-0.954	2.2	5.8	5.99
0.2	0.25	-0.602	0.4	2.6	3.02	0.2	0.25	-0.602	2.4	6.6	6.72
0.3	0.43	-0.368	0.6	2.8	3.06	0.3	0.43	-0.368	2.6	7.8	7.87
0.4	0.(6)	-0.176	0.8	2.9	3.01	0.4	0.(6)	-0.176	2.8	8.0	8.04
0.5	1.0	0.000	1.0	3.1	3.10	0.5	1.00	0.000	3.0	8.2	8.20
0.6	1.5	0.176	1.2	3.3	3.18	0.6	1.50	0.176	3.2	8.4	8.37
0.7	2.(3)	0.368	1.4	3.6	3.34	0.7	2.(3)	0.368	3.4	8.6	8.53
0.8	4.0	0.602	1.6	4.2	3.78	0.8	4.00	0.602	3.6	8.8	8.68
0.9	9.0	0.954	1.8	4.3	3.63	0.9	9.00	0.954	3.8	9.0	8.81

The constant of ionization of the sorbent is calculated on modified Handerson-Hasselbach equation.

After the measuring of pH values of solutions under the sorbent for each value of α, we showed the dependence of pH = f ($\lg\frac{\alpha}{1-\alpha}$). There were calculated the parameters m ($tg\alpha$ = m) on the value of tangent of the straight′s inclination′s angle.

Graphic determination of the ionization constants of the sorbent is shown in figure 2.

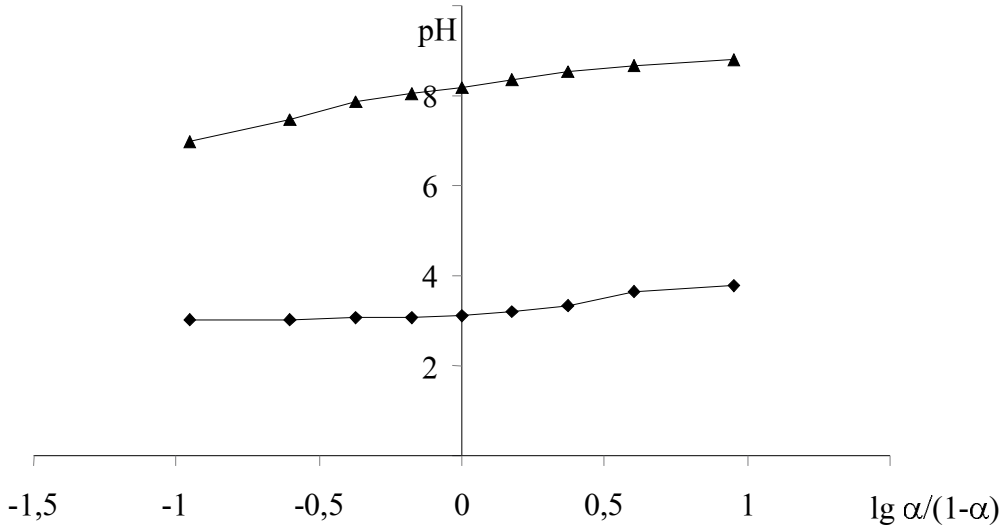

Fig.2. Graphic determination of the ionization constants of the sorbent: $pK_{1(graph)}$=3.24, $pK_{2(graph)}$=7.91 , m_1=0.700; m_2=0.194;

To determine the optimal conditions of sorption of Pd (II) with this sorbent we made an izoterm of sorption (Fig 3).

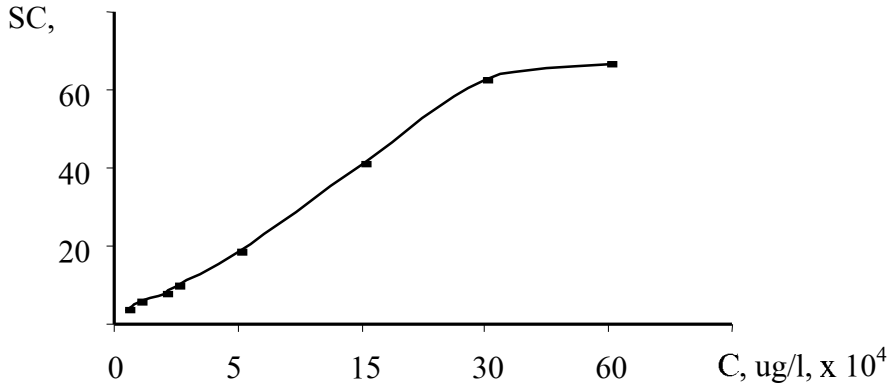

Fig 3. Isoterm of sorption of Pd(II) with the

The sorption capacity is maximal at pH 5. The sorption capacity of the sorbent increases with increasing of concentration of palladium ions in solution and the sorption capacity is maximal when concentration of palladium ions equals to 100mq/l (pH = 5, $C_{Pd^{2+}}$ = 100 mq/l, $V_{vol.}$ = 20 ml, $m_{sorb.}$ = 0.05 g, SC = 362 mg/g).

The influence of ionic force on the sorption was studied. Increasing of ionic force till 0.8 mol/l does not influence so much. The following increasing leads to considerable decrcusing of sorption. It happen because with the increasing of ionic surroundings of functional groups the complexformation of Pd (II) decreases. The dependence of sorption on time also was investigated. Complete sorption of Pd(II) goes on after 2 hours at static conditions.

The influence of some mineral acids and their concentrations on desorbtion of Pd (II) from the sorbent was studied. The experiment shows that the maximal desorbtion of Pd (II) goes on in sulphuric acid.

The investigation was made also at dynamic conditions. The dependence of the sorption on the rate of introduction of sample′s solutions.

The desorbtion also was investigated at dynamic conditions: the rate of introduction of an acid and the influence of the concentration. The optimal conditions of concentration of Pd (II) ions by polymer sorbent were established. The investigation showed that at optimal conditions the concentration of Pd (II) ions quantitatively absorbs and desorbs (R > 96%) (Tabl 3).

Tabl.3**.** Optimal conditions of concentration of palladium(II) ions by polymer sorbent

$pH_{opt.}$	Rate of introduction of sample, ml/min	Rate of introduction of eluent, ml/min	Concentration H_2SO_4 mol/l
5	1.0	1.0	1.5

Method of determination of

Palladium in the bismuth-polymetallic sample.

Method supplements analyzed bismuth-polymetallic ore №616-75, as part of which contains,%: 1.32 Cu, 3,88 Pb, 2,02 Zn, 1,06 As, 0,51 Bi, 0,009 Cd, 3,18 Mn, 0,071 Sb, other-SiO_2 (Arncutov 1978).

Weighed sample weighing 2.0 grams in a graphite crucible was dissolved with heating in a mixture of 16 ml HF 5 ml HNO_3 5 ml HCl. The resulting paste was treated with 8 ml of HNO_3 at 50-60°C to complete distillation of the HF. The resulting precipitate was dissolved in distilled water and the undissolved part was separated by filtration. To the resulting solution was poured 5 ml of 1 • 10-3 M standard solution of palladium (II), transferred to a flask with a capacity of 100 ml, adjusted to the

desired pH value by adding HNO_3 and passed through the column at a flow rate of 1.5 ml/min. Sorbed metal ions were eluted with 5 ml of 1M $HClO_4$, at a rate of elution 2.5 ml/min. In the eluate concentration of Pd(II) was determined by photometric method.

The results, calculated on the assumption 100% aqueous extract determined by the ion are given in tab 4.

Tabl 4. Results of the analysis of ore samples (sample volume 100 ml, volume of eluent 5 ml; msorb .= 100 mg, P = 0,95; n = 5)

Sample	Determined element	Introduction, ug / l	Found, ug / l
bismuth-polymetallic cally ores	Pd(II)	-	5,2±0,2
		10	15,1±0,3
		15	20,1±0,4
		20	25,2±0,4

References

Aliyeva RA, Veliyev VN, Qamidov SZ, Chiraqov FM 2006. *J Chemical problems*., № 3, 496 p.

Arnautov NV. Standard samples of chemical composition of natural minerals:Method. recommendations. *Novosibirsk*: IGiGSO ANSSSR.1987, 204 p.

Basargin NN, Isayev EI 1986. Corellation and forecasting of analytical properties of organic reagents and chelate sorbents. *M Science*, 199 p.

Bauer W, Beck W, Ponikwar W.2000. Zeitschrift fur Naturforschung, 55: 946-952

Bulatov MI, Kalinkin IP 1972. Practical book on photometric and spectrometric methods of analysis. *L Chemistry*, 407 p.

Korostelev PP 1964. Preparing of solutions for chemical-analytical works. *M Science*, 261p.

Patrick G, Michel P 2003. Platinum Metals review. 47: 60-72


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