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Analytical chemistry

DETERMINING OF ZIRCONIUM(IV) WITH 2,3,4-TRIHIDROXY-4'- SULPHOAZOBENZOL AND CATIONIC SURFACE-ACTIVE SUBSTANCES IN ALLOYS AND IN QUARTZ DIORITIN CONSISTING OF PYRITE

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The complex formation of zirconium(IV) with 2,3,4-trihydroxy-4'-sulphoazobenzene in presence of cationic surface-active substances (SAS) – setylpyridin bromide, setylpyridin chloride and setylmethylammonium bromide was investigated by photometric method. It was determined that, the mixed ligand complexes are formed with the ratio of Zr:R:SAS components as 1:2:2 when pH is 1,0-1,5. In this work was been researched the ligand-ligand interaction of reagent with SAS in the optimal condition of complex formation and determined that are forming ion associates, which have a high resistance. The comparison of chemical-analytical characteristics of associates and mixed ligand complexes showed that, by increasing the stability constants of associates will increase the stability constant, molar absorptivity and contrast of reaction of formation differentligand complexes will increase. Has been developed the more selective methods to photometric determination of microquantities of zirconium in quartz dioritin consisting of pyrite and in the alloys on the base of copper and aluminium.

Keywords: *spectrophotometric determination, zirconium, pyroghallol, surface-active substances*

For photometric determination of zirconium(IV) widely used o-hidroxyazocompounds. Previously, by us showing that, azocompounds on the base of pyroghallol are valuable analytic reagents to photometric determination rows of inorganic ions, including zirconium(IV). Well known, that cationic surface-active substances strongly influence to acidity properties of polidentant chromophoric reagents and essentially improve their chemical-analytical characteristics.

In article has been searched the complex formation of zirconium(IV) with 2,3,4-trihydroxy-4'-sulphoazobenzene in presence of cationic surface-active substances and has been developed the more selective methods to photometric determination of microquantities of zirconium in quartz dioritin consisting of pyrite and in the alloys on the base of copper and aluminium.

Experimental part

Standard $1 \cdot 10^{-1}$ M solution of zirconium (IV) has been prepared by solving calculated hitch of metallic zirconium in H_2SO_4 by technique. Work solutions $5 \cdot 10^{-4}$ M was received by dilution of previous solution by distilled water. $1 \cdot 10^{-3}$ M so-

lution of 2,3,4-trihydroxy-4'-sulphoazobenzene (R) and $1 \cdot 10^{-2}$ M cationic surface-active substances (SAS) – setylpyridin chloride (SPCl), setylpyridin bromide (SPBr) and setylmethylammonium bromide (SMABr) was preparing by solving of concerning hitches in water. For making of necessary acidifying were used buffer solutions of acetate-ammonia (pH=3-11) and fiksanal HCl (pH=0-2). All of used reagents had qualification no lower than n.f.a.

Acidity of solutions was controlled on the ionomer İ-130 with glass electrode customized by standart bufer solutions. Optical density of solutions was measured at the spectrophotometer Lambda-40 (Perkin Elmer) and photoelectrocolorimeter AE-30F in the cuvette with the thickness of layer 1sm. The specific conductivity of solutions was measured at the conductometer CEL-1M2.

Results and discussions

The coloured complex compound is formed in the reaction of Zr (IV) with the reagent with the maximum of light absorption at 460 nm. The maximum output is observed at

pH=2,0-2,3. In this environment reagent absorbs at 379 nm. In the presence of surface-active substance (SAS) mixed ligand complexes of Zr(IV)-R-SAS are formed. Herewith, the bathochromic shift compared to the spectrum of the binary complex is observed and maximum output shifts to more acid environment.

Light absorption of Zr (IV)-R-CPBr, Zr (IV)-R-CPCl and Zr(IV)-RCPMABr complexes are maximum at 471, 469 and 466 nm respectively. Studying of dependence of optical density on pH have shown that all mixed ligand complexes of Zr(IV) are formed at pH=0-6,5 and maximal output of these complexes is observed at pH=1,0-1,5. The color of reagent and complexes depends on pH of environment. Therefore absorption spectrums of complexes are shot against the background of control experiment (R+SAS), which was prepared in the same conditions, and it was found that the light absorption of mix-ligand complexes is maximum at 470 nm.

Further, in order to find the optimal conditions of mixed ligand complexes formation, the influence of concentration of reactive components, temperature and time were studied. It was found that the output of all mixed ligand complexes are maximal at the concentration value $6,0 \cdot 10^{-5}$ M and $1,0 \cdot 10^{-4}$ M for R and SAS respectively. The value of optical density of mix-ligand complex solutions stays constant in 3,0-10,0 and 5,0-14,0 excess of R and SAS respectively. Binary and all mix-ligand com-

plexes of Zr(IV) are immediately formed after mixing component solutions, which are stable. So that if binary complex is stable during 2 hours and by heating till 60°C, then mix-ligand complexes are stable more than one day and by heating till 80°C.

The ratio of reactive components in the structure of coloured compounds was found using the methods of isomolar series, relative yield of Starick-Barbanel and the method of balance shifting [12]. The results of all methods have shown that the ratio of components in binary complex is 1:2, and mixed ligand complexes - Zr(IV):R:SAS=1:2:2. The amount of H^+ ions which were displaced during complexation was determined by Astakhov's method, which also proved the shown ratio of components in complex [13].

The stability constants of binary and mixed ligand complexes of Zr(IV) were calculated. The method of intersection of curves was used for calculation of the stability constants of complex Zr(IV)-R and it was found that $\lg \beta = 9,92 \pm 0,17$. Considering the molar ratio of components in mixed ligand complexes their stability constants were calculated. It is found that in the presence of SAS the stability of complexes rises more than two times: $\lg \beta$ (Zr-R-CPBr) = $13,08 \pm 0,11$; $\lg \beta$ (Zr-R-CPCl) = $12,90 \pm 0,18$; $\lg \beta$ (Zr-R-CPMABr) = $12,74 \pm 0,20$. The molar ratio of light absorptions are shown in the table 1. It's seen that in the presence of SAS the molar ratio of light absorption increases.

Table 1

Chemical-analytical characteristics of complexes of Zr(IV) with 2,3,4-trihydroxy-4'-sulfoazobenzene in the presence of cationic SAS

Complexes	pH _{opt}	$\lambda_{\max}$, nm	$\Delta\lambda$, nm	Components ratio	$\varepsilon \cdot 10^{-4}$	Linearity interval of calibration graph, mg/ml	$\lg \beta$
Zr(IV)-R	2,0-2,3	460	81	1:2	$3,30 \pm 0,12$	0,18-2,18	$9,92 \pm 0,17$
Zr(IV)-R-CPBr	1,0-1,5	471	92	1:2:2	$4,40 \pm 0,15$	0,09-2,92	$13,08 \pm 0,11$
Zr(IV)-R-CPCl	1,0-1,5	469	90	1:2:2	$4,20 \pm 0,16$	0,09-2,92	$12,90 \pm 0,18$
Zr(IV)-R-CPMABr	1,0-1,5	466	87	1:2:2	$3,95 \pm 0,10$	0,15-2,18	$12,74 \pm 0,20$

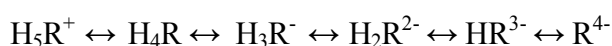
Table 2

The characteristics of R-SAS system at pH=1 ($\lambda_R=379$ nm, R:SAS=1:1, pH=1,0-2,0)

SAS	λ_{R-SAS} , nm	lgK
CPBr	429	7,14±0,08
CPCl	425	6,68±0,14
CPMABr	421	5,93±0,13

The ligand-ligand cooperation is investigated to study the influence of SAS to complexation in R-SAS system. For this purpose the absorption spectrum of the reagent was shot in the presence of SAS at pH=1,0-2,0, in the wide range of wavelength. It's found that in the presence of SAS in the absorption spectrum of the reagent the bathochromic shift and hyperchromic effect are observed. It is known that [9], cationic SAS exists in acid environment in protonated form and electrostatically cooperates with reagent, which owns acid properties, to form ionic associates. Stoichiometry and stability constant of the associates are determined with the method of intersection of curves (table 2).

2,3,4-Trihydroxy-4'-sulfoazobenzene is the four main acid and in addition to the acidity of environment could exist in protonated (H_5R^+ - at pH≤0), molecular (H_4R , H_3R^- - at pH=0-7,2) and anionic (H_2R^{2-} - at pH=7,2-8,3, HR^{3-} - at pH=8,3-9,5 and R^{4-} - at pH≥9,5) forms [14]. By increasing the value of pH the pointed forms of reagent move into the following forms:



The transition of the H_4R form into H_3R^- form is characterized with cleavage of hydrogen in the structure of sulfo-group of reagent. This transition doesn't have any analytical effect. Therefore we can accept both forms as molecular ones. Molecular forms of reagents form ionic associates with ratio of components R:SAS=1:1 at pH=1,0-2,0 for its electrostatic cooperation with the sulfo-group of SAS. Maximal delocalization of π -electronic system of reagent leads to the bathochromic shift of absorption band of formulated associate, which is also connected with the increasing of negative induction effect of sulfo group under the pressure of SAS. As it's seen

from table 2, the stability constant and contrast of the reaction of formation of associates are decreasing in a following row:



The comparison of chemical-analytical characteristics of associates and mix-ligand complexes shows that increasing of stability constant of associates leads to growth of the stability constant, molar ratio of light absorption and contrast of the reaction of mix-ligand complexes formation.

In order to work out a method of photometric definition of Zr(IV) with the reagent in the presence of SAS was found an interval of concentration of obeying to Ber's law and studied the influence of foreign ions and masking agents to complexation. Binary complex of zirconium(IV)-R is subordinate to the Ber's law in the interval of concentration 0,18-0,28 mg/ml, mixed ligand complexes Zr(IV)-R-SPBr and Zr(IV)-R-SPCl - 0,09-2,92 mg/ml and Zr(IV)-R-SPMABr - 0,15-2,18 mg/ml respectively. As we show from the table 3 in the presence of SAS selection of the reaction was considerably increasing. Have been developed the photometric determination of zirconium (IV) in form of mixed ligand complexes with 2,3,4-trihydroxy-4'-sulphoazobenzene and cationic surface-active substances and have been applied the determination of microquantities of zirconium in quartz diorite consisting of pyrite and in the alloys on the base of copper and aluminium.

Determination of zirconium in diorite

Have been analysed three samples of diorite. Hatched diorite 2 g in graphite crucible are solved in mixture of 8 ml HF+3 ml HCl +1 ml HNO₃. Received paste was worked up by 3-4 ml HNO₃ at 50-70 °C to full distillation of HF.

Received precipitation was solved in distilled water, transferred in measuring bottle with capacity 100 ml. For reducing Fe(III) to Fe(II) introduce 0,3 g of metallic zinc, well shuffled and diluted to marker. An aliquot part of this solution was transferred in measuring bottle with capacity 25 ml, introduce 1,5 ml $1 \cdot 10^{-3}$ M solution of R, 2,5 ml $1 \cdot 10^{-3}$ M SPBr and diluted to

marker with 0,1 ml HCl. Optical density of solution is measured in photoelectrocolorimeter AE-30F in 470 nm. Comparatively to control experiment (R+SPBr) in ditch with thickness of the layer 1,0 cm. Maintenance of zirconium is found by calibration graphic. Received results are shown in table 4.

Table 3

Influence of accompanying ions to results of determination of zirconium (IV) (introduce 1,82 mkg/ml zirconium, mistake is $\pm 5\%$)

Accompanying ions(AI)	Admissible weight surplus of AI			
	R	R-SPBr	R-SPCl	R-SPMABr
Alkali metals	4000	7500	7200	6600
Ca(II)	2640	6200	6000	6000
Mg(II)	3700	6100	5900	5800
Ba(II)	2000	5200	5200	5200
Cu(II)	430	600	600	600
Co(II)	900	1100	1000	1000
Ni(II)	810	1100	1000	900
Mn(II)	850	1050	1000	900
Zn(II)	440	1000	1000	900
Cd(II)	750	1600	1500	1350
Pb(II)	0,5	150	120	100
Sn(II)	13	150	130	100
Al(III)	180	580	500	420
Ga(III)	1,0	210	180	150
In(III)	80	1000	1000	890
Fe(II)	243	1582	1320	1000
Fe(III)	0,6	130	120	100
Cr(III)	200	1000	1000	1000
Bi(III)	4,0	160	145	140
Ti(IV)	3,2	64	50	50
Hf(IV)	0,5	5,0	5,0	3,6
Th(IV)	255	1100	1100	905
Mo(VI)	2,1	5,2	4,0	3,6
W(VI)	10	45	30	30
V(VI)	1230	2100	2100	2000
F ⁻	0,8	42	38	35
C ₂ O ₄ ²⁻	27	50	50	50
HPO ₄ ²⁻	3,0	315	300	280
Trilon B	28	750	700	700

Table 4

Results of determination of zirconium in dioritin (n=5, P=0,95)

Sample of pyrite	Was found Zr, %		Sr	
	R+SPBr	Alizarine S	R+SPBr	Alizarine S
I	0.183 $\pm$ 0.010	0.180 $\pm$ 0.032	0.022	0.069
II	0.135 $\pm$ 0.012	0.140 $\pm$ 0.020	0.035	0.054
III	0.618 $\pm$ 0.026	0.611 $\pm$ 0.044	0.016	0.028

Table 5

Results of determination of zirconium in alloys (n=5, P=0,95)

Mark of sample	Quantity of Zr by passport, %	Was found			Sr		
		R-SPCI	R-SPBr	R-STMABr	R-SPCI	SPBr	R-STMABr
M 172-1	0.15	0.139±0.016	0.155±0.014	0.143±0.019	0.045	0.035	0.052
M 272-2	0.09	0.086±0.008	0.093±0.008	0.085±0.009	0.036	0.033	0.041
M 145-5	0.07	0.067±0.009	0.072±0.005	0.074±0.008	0.052	0.027	0.042
M 295-3	0.15	0.143±0.017	0.156±0.008	0.145±0.013	0.046	0.020	0.035

Determination of zirconium in alloys

It's been analysed copper alloys from mark M 145-5 and M 295-3 and aluminium alloys from mark M 172-1 and M 272-2. Hitch of sample with mass 0,5 g in heating solved in 25 ml czar's vodka, adding 10 ml H₂SO₄ (1:1) and received solution are evaporate to humid salts. Residuum are solved in heating in distilled water, transferred in measuring bottle with capacity 100 ml, delivered to mark with water and well shuffle. An aliquot part of this solution has been introduced in bottle with capacity 25 ml and analysis carry out as seems higher. The results of determination are shown in table 5.

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ƏRİNTİLƏRDƏ VƏ KVARSA SAXLAYAN DİORİTDƏ SİRKOİNİUMUN 2,3,4-TRİHİDROKSİ-4'-SULFOAZOBENZOL VƏ KATİON TİP SƏTHİ-AKTİV MADDƏLƏRLƏ TƏYİNİ

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Kation tip səthi-aktiv maddələr (SAM) – setilpiridin xlorid, setilpiridin bromid, setiltrimetilammonium bromid iştirakında sirkoniumun(IV) 2,3,4-trihidroksi-4'-sulfoazobenzolla kompleks əmələ gətirməsi fotometrik metodla tədqiq edilmişdir. Müəyyən edilmişdir ki, pH 1,0-1,5 turşuluqlu mühitdə komponentləri nisbəti Zr:R:SAM=1:2:2 olan müxtəlifliqandlı komplekslər əmələ gəlir. Reaktivlə SAM arasında lıqand-lıqand qarşılıqlı təsir də tədqiq edilmiş və yüksək davamlılığa malik ion assosiatlarının əmələ gəldiyi müəyyən edilmişdir. Assosiat və müxtəlifliqandlı komplekslərin kimyəvi-analitik xarakteristikalarının müqayisəsi assosiatın davamlılıq sabitinin artması ilə müxtəlifliqandlı komplekslərin davamlılıq sabiti, molyar udma əmsalının və kompleks əmələgəlmə reaksiyalarının kontrastlığının artdığını göstərmişdir. Kvars saxlayan dioritdə və mis və alüminium əsaslı ərintilərdə sirkoniumun mikromiqdarının yüksək seçiciliyə malik fotometrik təyini metodikası işlənilmişdir.

Açar sözlər: spektrofotometrik təyinat, sirkonium, piroqallol, səthi-aktiv maddə

**ОПРЕДЕЛЕНИЕ ЦИРКОНИЯ С 2,3,4-ТРИГИДРОКСИ-4'-СУЛЬФОАЗОБЕНЗОЛОМ
И КАТИОННЫХ ПОВЕРХНОСТНО-АКТИВНЫХ ВЕЩЕСТВ В СПЛАВАХ
И В ПИРИТСОДЕРЖАЮЩЕМ КВАРЦЕВОМ ДИОРИТЕ**

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Фотометрическим методом исследовано комплексообразование циркония(IV) с 2,3,4-тригидрокси-4'-сульфоазобензолом в присутствии катионных поверхностно-активных веществ (ПАВ) - хлорида цетилпиридиния, бромид цетилпиридиния, бромид цетилтриметиламмония. Установлено, что при pH 1,0-1,5 образуются разнолигандные комплексы с соотношением компонентов $Zr:R:PAV=1:2:2$. Также исследовано лиганд-лигандное взаимодействие реагента с ПАВ в оптимальной среде комплексообразования и установлено, что образуются ионные ассоциаты, отличающиеся высокой устойчивостью. Сравнение химико-аналитических характеристик ассоциатов и разнолигандных комплексов показало, что с повышением констант устойчивости ассоциатов увеличивается константа устойчивости, молярный коэффициент светопоглощения и контрастность реакции образования разнолигандных комплексов. Разработана высокоселективная методика фотометрического определения микроколичеств циркония в пиритсодержащем кварцевом диорите и в сплавах на медной и алюминиевой основе.

Ключевые слова: *спектрофотометрическое определение, цирконий, пирогаллол, поверхностно-активные вещества*