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DEVELOPMENT OF SORPTION-SPECTROPHOTOMETRIC DETERMINATION OF COBALT IONS IN ENVIRONMENTAL OBJECTS

Abstract. The complexation of cobalt(II) ions with immobilized 4-((2-hydroxy-3-nitroso-1-naphthyl)azo)benzenesulfonic acid (HNNBSA) on a synthesized polyacrylonitrile sorbent (PPD). Optimal conditions for immobilization of the reagent and complexation with cobalt ions have been established. The analytical properties of the immobilized reagent were studied by spectrophotometric, spectroscopic, X-ray fluorescence and scanning electron microscopy methods. It is established that the analytical procedure based on the HNNBSA–PPD system is characterized by high selectivity, accuracy and reproducibility. The maximum spectral signals of the immobilized reagent and its complex with cobalt(II) ions are observed at 475 and 575 nm, respectively. The detection limit of cobalt is 0.02 µg/mL. The developed method is characterized by simplicity of sorbent regeneration and high expressiveness and can be used to determine cobalt ions in environmental objects.

Keywords: cobalt(II), 4-((2-hydroxy-3-nitroso-1-naphthyl)azo)benzenesulfonic acid, immobilization, polyacrylonitrile sorbent, complex formation, sorption-spectrophotometric method, spectrophotometry.



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Introduction. Cobalt belongs to the heavy metals, the content of which in the environment is gradually increasing owing to the development of the metallurgical and chemical industries, as well as the active production of lithium-ion batteries. At the same time, cobalt is necessary for the body in small quantities, since it is a part of vitamin B₁₂. However, elevated concentrations of cobalt can have toxic effects. In addition, the International Agency for Research on Cancer classifies metallic cobalt and soluble Co(II) compounds as group 2A, substances likely to be carcinogenic to humans [1]. Therefore, the presence of cobalt in industrial wastewater and soils located near industrial facilities is an environmental problem that requires the development of effective methods for its sensitive and selective determination. Various instrumental methods have been used to determine cobalt in environmental objects. One of the most accessible and widely used is the spectrophotometric method, which is characterized by relatively simple equipment

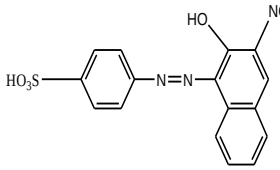
and ease of analysis [2]. However, when analyzing natural and wastewater, direct spectrophotometric determination of cobalt may not be effective enough. This is primarily due to the low metal content and the presence of a large number of other components that can affect the results of the analysis. Therefore, prior extraction and concentration of cobalt is often required before determination. For this purpose, sorption methods based on the extraction of cobalt complexes using various sorbents, such as inorganic ion-exchange materials and synthetic polymers, are used. Nitrosonaphtholic azo compounds are of particular interest for the determination of cobalt. These reagents can form stable colored complexes with Co(II) ions, which makes it possible to use them for the photometric determination of metals [3-4]. A promising direction is the fixation of such reagents on the surface of polymeric materials, such as polyacrylonitrile fibers. In this case, the complexation and concentration of cobalt occur directly on the sorbent, which simplifies the analysis procedure, increases its sensitivity and selectivity, and also provides the possibility of reuse of the sorption material [5]. The effectiveness of this approach is confirmed by studies in which magnetic sorbents modified with azo compounds are used to concentrate cobalt and other metals. Magnetic solid-phase extraction methods make it possible to quickly separate the sorbent from the analyzed solution and ensure efficient extraction of target components even from complex matrices [6]. Such sorption systems can be used in the analysis of various objects, including natural and wastewater, soils, and foodstuffs, which makes them promising for environmental and analytical control.

Materials and methods In the studies, cobalt(II) ions were determined using the reagent 4-((2-hydroxy-3-nitroso-1-naphthyl)azo)benzenesulfonic acid immobilized on PPD-1 fibers.

Table 1 presents the structural formula of the reagent HNNBSA used in this study.

Table 1

The structural formula of the organic reagent

№	Name	Molecular formula and molar mass	Structural formula
1	HNNBSA 4-((2-Hydroxy-3-nitroso-1-naphthyl)azo)benzenesulfonic acid	$C_{18}H_{11}N_3O_5S$, $M_r = 381$ g/mol	

The physicochemical properties of the reagent immobilized on PPD-1, synthesized at the Department of Polymer Chemistry of the National University of Uzbekistan, were studied. The optimal conditions for immobilization of the reagent on various supports are presented in Table 2.

Table 2

Optimal conditions for immobilization of 4-((2-hydroxy-3-nitroso-1-naphthyl)azo)benzenesulfonic acid ($m = 0.2000$ g)

Reagent	Support	pH	Volume of buffer solution, mL	Absorption maximum, nm	Time, min
HNNBSA	PPD-1	2-3	2	485	30

The results of quantum-chemical calculations of the HNNBSA reagent and its interaction with cobalt(II) ions immobilized on PPD-1 were evaluated based on such analytical criteria as rapidity and selectivity. The optimal conditions for the immobilization of the organic reagent and its complex formation with cobalt(II) ions were established, as well as the dependence of the analytical response on wavelength, time, temperature, and reagent concentration. According to the Sidgwick rule, the bond between a metal ion and oxygen is weaker than that between the metal ion and a nitrogen atom. Therefore, considering the high probability of forming a stable complex between cobalt ions and nitrogen-containing organic reagents, HNNBSA was selected, with coordination occurring through nitrogen atoms. Quantum-chemical calculations were performed to predict the processes of reagent immobilization and the formation of coordination compounds with the selected polymeric support and metal ions. According to these calculations, protonation of the reagent in an acidic medium results in coordination through electrostatic attraction involving an electron pair. The reagent selected for immobilization contains several potential coordination centers with a high electrostatic affinity for metal ions.

Research results and discussion The electron density (ED) of the sulfonic group in the reagent is the highest; therefore, the immobilization process on the fiber occurs in this region. The next-highest ED values are associated with the $-N=N-$ bonds (azo group), as well as the $=CH-N=$ and $C-O-$ bonds, which participate in forming coordination bonds with the metal ion.

The electrostatic potential (ESP) of a reagent is used in molecular modeling to understand and predict molecular behavior and interactions with other molecules. ESP is also an important indicator for identifying reactive sites, as it reveals nucleophilic and electrophilic centers in a molecule. The red spherical points in Figure 2 represent electron-rich regions and correspond to minima on the molecular surface. The blue spherical points represent electron-deficient regions and correspond to the maximum values on the molecular surface. The oxygen atom of the sulfonic group can act as an electron donor in intermolecular interactions.

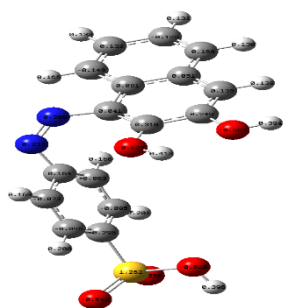


Fig. 1. Electron density distribution of HNNBSA

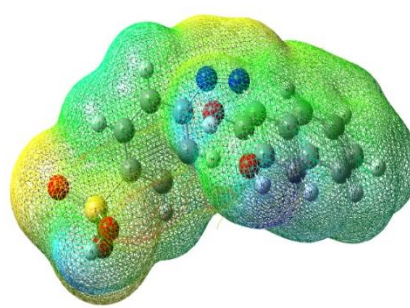


Fig. 2. Electrostatic potential (ESP) distribution

Table 3

Electron density values for HNNBSA determined using the Gaussian-09 program

$-SO_3H$	$-N=N-$	$=CH-N=$	$C-O-$	$-SO_3H$
0.549 / 0.520 / 0.550	0.209 / 0.233	0.543	0.623	0.549 / 0.520 / 0.550

The values presented in the table indicate that the sulfonic group has the highest electron density in the reagent, suggesting that the immobilization process on the fiber occurs in this region. The next highest values are associated with the --N=N-- bonds (azo group), as well as the =CH--N= and C--O-- bonds, which were found to participate in coordination bonding with the metal ion.

The analyses performed showed that the presence of an analytically active group (AAG) increases the selectivity and sensitivity of the synthesized reagents toward cobalt ions.

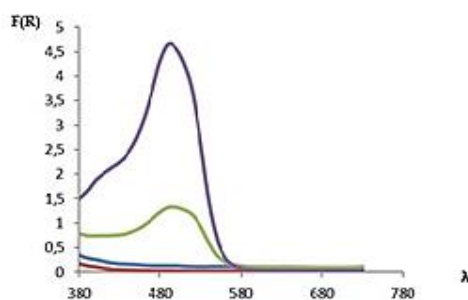


Fig. 3. Diffuse reflectance spectra in terms of the Kubelka–Munk function for the results of immobilization of the HNNBSA reagent on PPA, PPD, and SMA-3 fibers

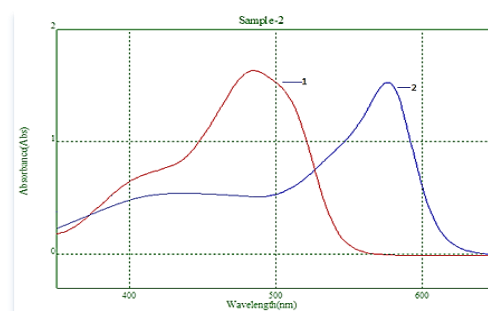


Fig. 4. Absorption spectra of the HNNBSA reagent (1) and its complex with Co(II) ions (2)

The results show that the maximum analytical signal of HNNBSA with Co(II) occurs at 575 nm. To confirm the results, we compared the absorption spectrum with the diffuse reflectance spectrum. The maximum light absorption corresponds to a minimum in the reflectance spectrum. When the reflectance spectrum is transformed using the Kubelka–Munk function, the minimum becomes a maximum, and the observed absorption spectrum coincides with the maximum of the Kubelka–Munk function. For the complex formation of Co(II) at 50 mg/mL with the HNNBSA reagent, the optimum pH was 2.5. All subsequent experiments were therefore performed at this pH.

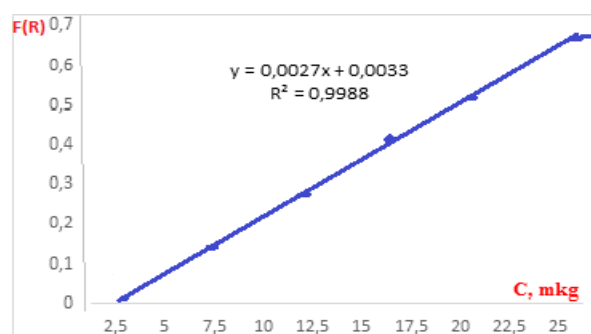


Fig. 5. Calibration curve demonstrating compliance with the Beer–Lambert law

Table 4

Spectral characteristics of the cobalt complex with immobilized reagents

Metal	Complex color	pH	λ_{MeR} , nm	λ_{HR} , nm	$\Delta\lambda$, nm	$C_{Me^{2+}}$, μg	Sensitivity according to Sendel, $\mu g/cm^2$
Co(II)	Brown-violet	3	575	475	100	50	0.0029

The data presented in Table 4 show that the spectral characteristics of the cobalt complex with the immobilized reagent are sufficiently well contrasted ($\Delta\lambda = 100\text{ nm}$), while the Sandell sensitivity value indicates the sensitivity of the method for cobalt determination. The composition and molar ratio of the resulting coordination compounds were determined by the method of continuous variations. It was established that the molar ratio of cobalt(II) to the immobilized HNNBSA in the complex is 1:1. To confirm the formation of the complex, the Tolmachev method was used, and the equilibrium constants and true molar absorption coefficient were calculated. Based on the calculated values of ϵ_{true} and K_{eq} for cobalt(II), it was established that the developed method is highly sensitive and that the resulting coordination compound has sufficient stability. The molar extinction coefficient for Co(II) ions was calculated to be $3,42 \cdot 10^{-5}$.

The results of the calculations showed that the detection limit for cobalt is $0.02\text{ }\mu g/mL$. FT-IR (Fourier transform infrared), X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy (SEM) analyses were performed, and the spectra obtained before and after immobilization of the HNNBSA reagent on the support were analyzed. The results of the IR spectroscopic analysis of the PPD-1 support and the HNNBSA reagent immobilized on it in the $1500\text{--}1700\text{ cm}^{-1}$ region further confirmed that immobilization occurs through the sulfonic group of the reagent, which acts as an analytically active group (AAG), and that the results of the quantum-chemical calculations are consistent with the experimental data. The sorption of cobalt ions by HNNBSA immobilized on PPD fibers was analyzed using an X-ray fluorescence spectrometer, model 9825 Spectrum Drive, Austin, Texas 78717, USA.

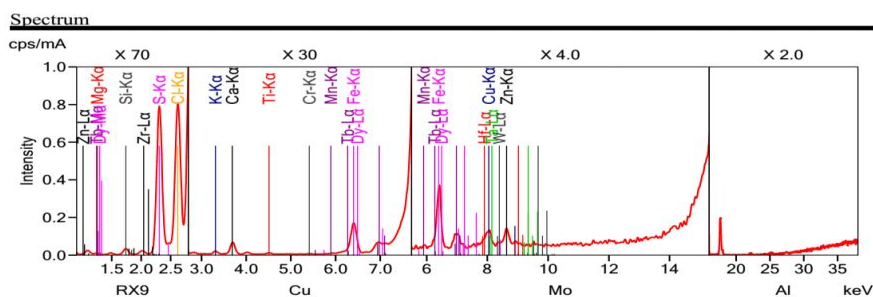


Fig. 6. X-ray fluorescence spectra of immobilized HNNBSA

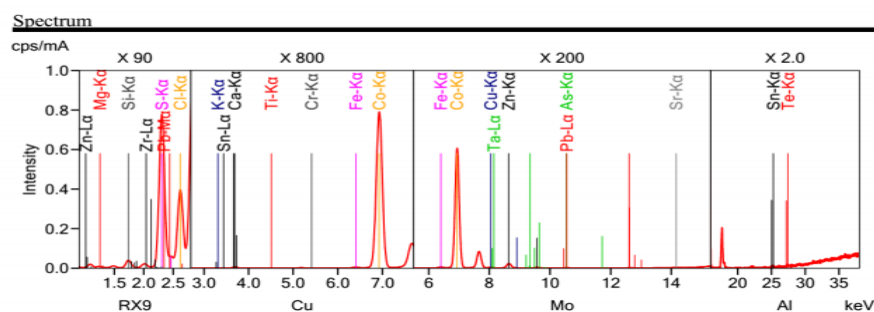


Fig. 7. X-ray fluorescence spectra of cobalt complexes with immobilized HNNBSA

Table 5

Results of the X-ray fluorescence analysis of cobalt ion sorption by immobilized HNNBSA

Components	Cl, wt%	S, wt%	Co ²⁺ , wt%
IF + R	17.3	33.1	0.0
IF + R + Co	10.9	41.9	43.2

According to the results of the X-ray fluorescence analysis of the spectra of 4-((2-hydroxy-3-nitroso-1-naphthyl)azo)benzoic acid immobilized on PPD fibers and its *Co(II)* complex (Figs. 6 and 7), the reagent contains a sulfonic group involved in the immobilization process, as evidenced by the appearance of a high-intensity sulfur peak. The formation of a new coordination compound between the reagent and the metal ion is indicated by the appearance of a characteristic high-intensity peak corresponding to cobalt. When examining the morphology of the silk fibroin fiber modified with *HCl*, it was observed that the chlorine content decreased after immobilization of the organic HNNBSA reagent (Fig. 6 and Table 5). This may be attributed to the replacement of the sulfur-containing groups of the *SO₃H* functional analytical group of HNNBSA during the immobilization process. Examination of the complexes formed by *Co(II)* ions with the reagent immobilized on the support (Fig. 7) revealed a high-intensity peak corresponding to *Co*²⁺, which accounted for 43.2 wt%. The formation of the *Co(II)* complex with HNNBSA immobilized on PPD fibers can be explained by the appearance of a signal characteristic of cobalt ions, which is observed in the X-ray fluorescence spectra (Fig. 7).

The formation of the *Co(II)* complex with HNNBSA immobilized on PPD fibers can be explained by the appearance of a signal characteristic of cobalt ions, which is observed in the SEM diffractograms.

Table 6

Results of scanning electron microscopy of *Co(II)* complexes with organic reagents immobilized on the support (n = 3, P = 0.95)

Sample	C, wt%	N, wt%	Cl, wt%	O, wt%	S, wt%	P, wt%	Co, wt%
IF + R + Me	37.16 ± 0.01	14.13 ± 0.02	16.21 ± 0.02	18.05 ± 0.04	2.36 ± 0.02	0.97 ± 0.01	19.00 ± 0.01

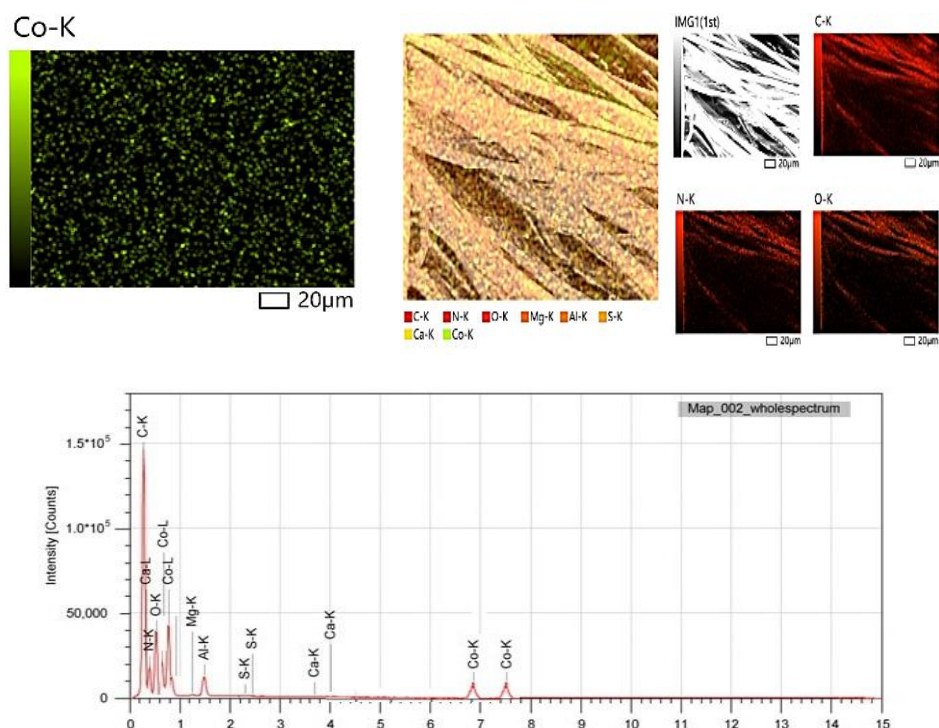


Fig. 8. SEM image of the immobilized silk fibroin fiber

According to the analysis results, HNNBSA immobilized on the silk fibroin fiber forms a complex with $Co(II)$ ions, with the elemental cobalt content in the sample reaching 19%, confirming the validity of the developed method. The effect of interfering ions on the determination of $Co(II)$ ions was studied. In a strongly acidic medium, Cu^{2+} , Fe^{2+} , Fe^{3+} , In^{3+} , Ga^{3+} , Bi^{3+} , and $EDTA$ interfere with the determination. However, after formation of the cobalt complex, $EDTA$ does not interfere with the determination at any proportion, allowing interfering ions to be removed by washing with an $EDTA$ solution. The interfering ions were eliminated using masking reagents, and the results obtained from the analysis of synthetic mixtures were used to determine the cobalt content.

Table 7

Results of the determination of cobalt(II) ions in binary, ternary, and more complex mixtures using the HNNBSA reagent [$\lambda = 580$ nm, pH = 3; P = 0.95; n = 3]

Composition of the analyzed mixture, μg	Found Co^{2+} , μg , $\bar{X} \pm \Delta\bar{X}$	S	S_r
Co(10) + Ni(2.0)	10.28 ± 0.22	0.198	0.019
Co(10) + Cu(5.0) + Cr(15.0)	9.91 ± 0.17	0.141	0.014
Co(20) + Fe(50.0) + Ni(50.0)	19.77 ± 0.26	0.246	0.012
Co(20) + Cd(30.0) + Pb(5.0) + Cu(10.0)	19.79 ± 0.23	0.185	0.009
Co(30) + Cu(20.0) + Mn(10.0) + Fe(15.0)	29.91 ± 0.18	0.166	0.006
Co(40) + Cr(50.0) + Pb(1.0) + Cd(30.0)	39.94 ± 0.25	0.210	0.005
Co(40) + Ni(30.0) + Cu(0.5) + Zn(10.0) + Cd(5.0)	39.93 ± 0.24	0.177	0.004

The data in the table indicate that the developed method for determining the studied ions does not require additional procedures to improve sensitivity and

selectivity. The relative standard deviation for all results does not exceed 0.33, confirming the method's accuracy and reproducibility for determining the analyte ions. Based on the ICP-MS analysis of wastewater from the Navoi Region, the cobalt ion content was determined. According to the analysis results, the wastewater from Navoiyazot JSC contains 43 elements, while the concentration of the studied cobalt ions in the wastewater is 115 mg/L. Cobalt(II) ions were also determined in these wastewater samples using the developed sorption-spectrophotometric method; the results were consistent with those obtained by ICP-MS analysis.

Water and wastewater from the Zarafshan River in the Navoi Region were analyzed. Table 8 presents the results.

Table 8

Results of the determination of cobalt(II) ions in various samples by the “added–found” method

No.	Added, mg/L	Optical density after desorption, mg/L, A	Found, mg/L	$\bar{X} \pm \Delta\bar{X}$	S	S _r
Drinking water						
1	1.0	0.267	0.985	0.994 ± 0.012	0.004	0.004
		0.272	0.998			
		0.263	1.000			
Zarafshan River water						
2	1.0	0.298	1.011	1.027 ± 0.015	0.019	0.019
		0.301	1.000			
		0.297	1.007			
Konimex Canal water						
3	1.0	0.378	1.000	1.005 ± 0.0017	0.004	0.004
		0.377	1.008			
		0.374	1.006			

The developed method for the preconcentration of metal ions on PPD-1 fibers with the immobilized reagent was found to be effective and accurate based on the analytical results presented in Table 9.

Table 9

Application of the developed method to soil analysis

Soil composition, µg/kg	Masking reagent	Added, µg/mL	Found, µg/mL	S	S _r
Determination of cobalt					
Cu (7.413), Ni (4.7), Si (0.297), Fe (1.386), Al (7.100), sulfates (740.7), Co (3.2), Ca (2.8)	Ascorbic acid, thiourea, sodium fluoride	5	3.67	0.012	0.03

Based on the analysis results in Table 9, the cobalt ion content determined using the developed method in the soil exceeds the maximum permissible concentration (MPC). The developed sorption-spectrophotometric method for determining cobalt ions was applied to water from the Zarafshan River in the Navoi Region. The results showed a relative standard deviation of no more than 10%, indicating the method's accuracy.

Conclusion. 4-((2-Hydroxy-3-nitroso-1-naphthyl)azo)benzoic acid immobilized on the PPD-1 support is proposed as an analytical reagent for the determination of cobalt ions.

The optimal conditions for the immobilization and complex formation of cobalt ions with immobilized 4-((2-hydroxy-3-nitroso-1-naphthyl)azo)benzoic acid were established. The composition of the complex was determined using the method of continuous variations (Job's method), the Asmus method, and the Babko dilution method, giving a molar ratio of Me:R = 1:1. The Co²⁺ system obeys the Beer-Lambert law in the concentration range of 10–100 µg.

The developed method was compared with the results of spectrophotometric determination. The low content of interfering substances, rapidity, complex stability, and possibility of repeated sorbent use offer advantages over other methods; the method is recommended for determining cobalt ions.

The analytical parameters and monitoring of cobalt ions in Zarafshan River water were evaluated using the developed method.

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ҚОРШАҒАН ОРТА ОБЪЕКТІЛЕРІНДЕ КОБАЛЬТ ИОНДАРЫНЫҢ СОРБЦИЯЛЫҚ-СПЕКТРОФОТОМЕТРИЯЛЫҚ АНЫҚТАМАСЫН ӘЗІРЛЕУ

Аңдатпа. Бұл зерттеу мақаласында кобальт(II) иондарының синтезделген полиакрилонитрилді сорбентке (PPD) иммобилизацияланған 4-((2-гидрокси-3-нитрозо-1-нафтил)азо)бензолсульфон қышқылымен (HNNBSA) комплекстүзуі зерттелді. Реагентті иммобилизациялау және оның кобальт иондарымен комплекстүзуінің оңтайлы жағдайлары анықталды. Иммобилизацияланған

реагенттің аналитикалық қасиеттері спектрофотометриялық, спектроскопиялық, рентген-флуоресценттік талдау және сканерлеуші электрондық микроскопия әдістерімен зерттелді. HNNBSA–PPD жүйесіне негізделген аналитикалық әдістің жоғары селективтілікпен, дәлдікпен және қайталанғыштықпен сипатталатыны анықталды. Иммобилизацияланған реагенттің және оның кобальт(II) иондарымен түзілген кешенінің спектрлік сигналдарының максимумдары сәйкесінше 475 және 575 нм-де байқалады. Кобальтты анықтау шегі 0,02 мкг/мл құрайды. Зерттеу нәтижесінде әдіс сорбентті регенерациялаудың қарапайымдылығымен және жоғары жеделдігімен сипатталады және қоршаған орта объектілеріндегі кобальт иондарын анықтау үшін қолданылуы мүмкін.

Тірек сөздер: кобальт(II), 4-((2-гидрокси-3-нитрозо-1-нафтил)азо)бензолсульфон қышқылы, иммобилизация, полиакрилонитрилді сорбент, комплекстүзу, сорбциялық-спектрофотометриялық әдіс, спектрофотометрия.

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РАЗРАБОТКА СОРБЦИОННО-СПЕКТРОФОТОМЕТРИЧЕСКОГО ОПРЕДЕЛЕНИЯ ИОНОВ КОБАЛЬТА В ОБЪЕКТАХ ОКРУЖАЮЩЕЙ СРЕДЫ

Аннотация. Исследовано комплексообразование ионов кобальта(II) с иммобилизованной 4-((2-гидрокси-3-нитрозо-1-нафтил)азо)бензолсульфоновой кислотой (ГННАБСА) на синтезированном полиакрилонитрильном сорбенте (ППД). Установлены оптимальные условия иммобилизации реагента и комплексообразования с ионами кобальта. Аналитические свойства иммобилизованного реагента изучены спектрофотометрическим, спектроскопическим, рентгенофлуоресцентным методами и методом сканирующей электронной микроскопии. Установлено, что аналитическая метод с использованием системы ГННАБСА–ППД характеризуется высокой селективностью, точностью и воспроизводимостью. Максимумы спектральных сигналов иммобилизованного реагента и его комплекса с ионами кобальта(II) наблюдаются при 475 и 575 нм соответственно. Предел обнаружения кобальта составляет 0,02 мкг/мл. Разработанный метод характеризуется простотой регенерации сорбента и высокой экспрессностью и может быть использован для определения ионов кобальта в объектах окружающей среды.

Ключевые слова: кобальт(II), 4-((2-гидрокси-3-нитрозо-1-нафтил)азо)бензолсульфоновая кислота, иммобилизация, полиакрилонитрильный сорбент, комплексообразование, сорбционно-спектрофотометрический метод, спектрофотометрия.