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ARTICLES

Using Silica Modified by Poly(Hexamethylene Guanidine) and Nitroso-R-Salt for the Preconcentration and Determination of Cobalt

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Abstract—An adsorbent based on silica consecutively modified with poly(hexamethylene guanidine) and nitroso-R-salt is proposed for the adsorption preconcentration and photometric determination of cobalt. The approach gives adsorbents with the controlled surface concentration of the reagent. The adsorbent extracts cobalt(II) from solutions of pH 5–9 with partition coefficients of 5×10^3–1×10^4 cm^3/g. The specific features of the influence of Fe(II) and Fe(III) on the preconcentration and determination of cobalt are considered. The interference with Fe(II) is eliminated by its oxidation to Fe(III). It is shown that the performance characteristics of the procedures depend on the surface concentration of the reagent. The limit of detection for cobalt is 0.01 μg per 0.1 g of the adsorbent. The developed procedures were used for the determination of mobile cobalt species in soils.

Keywords: silica, poly(hexamethylene guanidine), nitroso-R-salt, cobalt
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Nitrosonaphthols have long been known as organic reagents in inorganic analysis. They have found the widest application to the photometric determination of cobalt [1]. In the complex formation of cobalt(II) with 1-nitroso-2-naphthol and its isomer, 2-nitroso-1-naphthol, cobalt(II) is oxidized to cobalt(III) [2]. The neutral CoL_3 compounds formed are extracted with nonpolar solvents [1, 3] or with hydrophobic adsorbents, for example, with C_{16} silica [4]; the last named adsorbents are used for the preconcentration and separation of cobalt from other metals followed by its photometric determination. The introduction of sulfo groups into 1-nitroso-2-naphthol with the formation of 1-nitroso-2-naphthol-3,6-disulfonic acid, nitroso-R-salt (NRS), offers a number of advantages, i.e., reduces the pK_a of the hydroxyl group in comparison to that of the not sulfonated analogue and enhances the solubility of the reagent and its complexes in water.

Procedures for the photometric determination of cobalt as its complex with nitroso-R-salt are sufficiently specific but not very sensitive, like the procedures using 1-nitroso-2-naphthol. To increase sensitivity, analysts use preconcentration, namely, coprecipitation [5] or extraction in the presence of quaternary ammonium bases [6, 7]. Two-phase aqueous extraction systems based on polyethylene glycols were proposed in [8] for the thermal lens determination of cobalt.

Adsorption preconcentration allows analysts to extract an analyte with a rather small portion of an adsorbent, to exclude the use of organic solvents, and is easy to perform. Adsorbents of different nature are widely used for the adsorption preconcentration and subsequent photometric determination of cobalt [9–15]. In determining cobalt in natural and process waters, it was extracted with a KB-4P-2 cation exchanger, treated with an NRS solution, and cobalt was determined by the color of its complex [9]. A QAE-Sephadex A-25 anion exchanger [10] and silica chemically modified with triphenylphosphonium groups [11] were used for the adsorption preconcentration of a cobalt(III) complex with NRS and its subsequent photometric determination. Adsorbents selective to cobalt were obtained by the immobilization of NRS on an Amberlite CG 400 [12] anion exchanger and gels based on chitosan [13] and gelatin [14, 15]. To attach NRS to a silica surface, we proposed the preliminary modification of silica with poly(hexamethylene guanidine) (PHMG) [16]. The adsorbent synthesis is simple and requires available reagents, which opens up a possibility of its wide application.

In this work we consider the use of silicas consecutively modified with poly(hexamethylene guanidine) and nitroso-R-salt for the preconcentration and determination of cobalt.

EXPERIMENTAL

Reagents. Stock solutions of metal salts with concentrations of 1 g/L were prepared by dissolving weighed portions of metal chlorides in 0.1 M HCl. Working solutions with lower concentrations were prepared by diluting stock solutions with deionized water. The required pH values were adjusted using solutions of HCl, NaOH of high-purity grade, and an acetate buffer solution. As a basis for the preparation of adsorbents we used silica Silochrome C-120 (fraction 0.1–0.2 mm, specific surface ~120 m^2/g, average pore diameter ~45 nm). A 7.5% solution of poly(hexamethylene guanidine) hydrochloride was prepared by dissolving a weighed portion of a BIOPAG-D preparation (Institute of Ecotechnologies, Moscow) in deionized water. A stock 1.35×10^{-3} M solution of NRS was prepared NRS by dissolving a weighed portion of a preparation in deionized water. Working solutions of the reagent with lower concentrations were prepared by diluting stock solutions with deionized water.

Equipment. Spectra of diffuse reflection (SDR) of the adsorbents in the region 380–720 nm were recorded on a Pulsar spectrocolorimeter (NPO Khimavtomatika, Russia). The spectra were presented on the coordinates Gurevich–Kubelka–Munk function $F(R) = (1-R)^2/2R$ vs. wavelength, nm. Electronic absorption spectra and the absorbance of solutions were recorded on a Cary 100 spectrophotometer (Varian, Australia).

The concentration of metal ions in solutions was determined by inductively coupled plasma atomic emission spectrometry on an Optima 5300 spectrometer (Perkin-Elmer, United States). A Seveneasy potentiometer with an ion-selective electrode (Mettler-Toledo, Spain) was used to measure the pH of solutions. To pump solutions through a microcolumn with an adsorbent, we used a Masterflex peristaltic pump (Cole-Parmer Instruments, United States).

Experimental procedure. *Synthesis of a SiO_2–PHMG–NRS adsorbent.* Silica (15 g) was allowed to stand in solution of pH 9 for 1 h to activate its surface and then washed with deionized water to pH 7. Next, 100 mL of a 7.5% PHMG solution was added to silica under continuous stirring at a rate of 1 mL/min. The adsorbent obtained (SiO_2–PHMG) was washed with deionized water to the disappearance of a positive reaction of wash water to PHMG and dried at 70°C. The concentration of PHMG in the water phase before adsorption was controlled by titration in a two-phase water–chloroform system using Bromophenol Blue in the presence of sodium dodecyl sulfate as an indicator.

Weighed portions of SiO_2–PHMG (0.1 g) were put into test tubes with ground-glass stoppers; 10 mL of an NRS solution of a required concentration was added; and the mixture was stirred for 5 min. The adsorbent obtained (SiO_2–PHMG–NRS) was separated from the solution by decantation. To determine the degree of desorption of the organic reagent, the SiO_2–PHMG–NRS adsorbent was treated with 1×10^{-3}–6 M HCl, HNO_3, or NaCl. The recovery and degree of NRS desorption were determined by analyzing the water phase by photometry using a characteristic band of reagent absorption with a maximum at 375 nm.

The adsorption of metal ions was studied in the batch and dynamic modes. In the study in the batch mode, a metal ion solution in 0.1 M HCl was placed in a graduated test tube with a ground-glass stopper; NaOH, an acetate buffer solution for the creation of the required pH, and water to a total amount of 10 mL were added. A 0.1-g portion of a SiO_2–PHMG–NRS adsorbent was introduced; the test tube was stopped; and its contents were stirred for 1–30 min. The solution was decanted; the adsorbent was transferred to a fluoroplastic cell; and the coefficient of diffuse reflection was measured in the region 380–720 nm. In the study of adsorption in the dynamic mode, solutions were pumped through a microcolumn (inner diameter 3 mm, height 10 cm) containing 0.1 g of an adsorbent using a peristaltic pump at a rate of 1 mL/min. The adsorbent height in the column was 3 cm. The concentration of metal ions in solution before adsorption was determined in the water phase using atomic emission spectrometry.

RESULTS AND DISCUSSION

Attachment of nitroso-R-salt to the SiO_2–PHMG surface. The maximum recovery of NRS with a SiO_2–PHMG adsorbent was attained in the pH range 2–8 (Fig. 1, curve *1*). On the adsorption of the reagent, the adsorbent became yellowish green. The SDR of the adsorbed reagent represented a broad band with a maximum at 420 nm. The color intensity of the adsorbent was constant in the pH range 3–8 (Fig. 1, curve *2*) and enhanced with increasing surface concentration of NRS.

The adsorption capacity of SiO_2–PHMG with respect to NRS was found from the horizontal section of the adsorption isotherm and comprised 42 μM/g (Fig. 2, curve *1*). In the Henry region of the adsorption isotherm, the recovery of NRS was quantitative (98–99%). This allowed us to adjust to any required surface concentration of NRS within the adsorption capacity of SiO_2–PHMG to the reagent. The SiO_2–PHMG adsorbent retained its adsorption properties to NRS within a long time. The adsorption capacity of SiO_2–PHMG to NRS did not change after storage for three years.

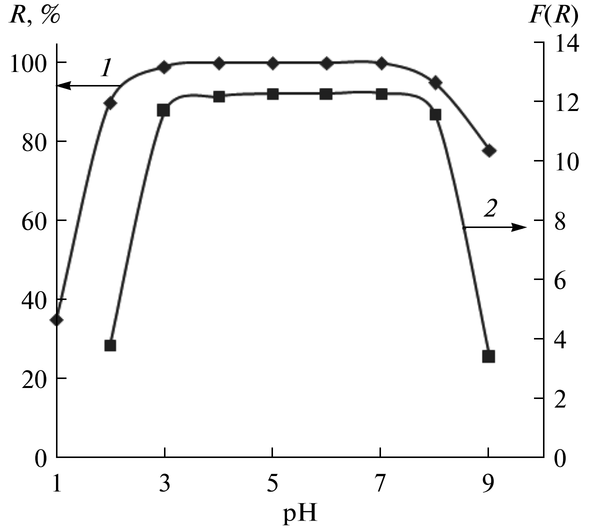

Fig. 1. pH dependences of (*1*) the recovery of NRS and (*2*) the intensity of diffuse reflection spectra of NRS at 420 nm on SiO_2–PHMG. c_{NRS}: *1*, 2.7 × 10^{-5} M; *2*, 2.7 μM/g; 0.1 g of adsorbent; *V* = 10 mL.

The consecutive treatment of the silica surface with PHMG and NRS gave a supramolecular ensemble, in which the reagents were bound to each other by electrostatic interactions and hydrogen bonds. The treatment of SiO_2–PHMG–NRS with HCl, HNO_3, or NaCl solutions resulted in the desorption of the reagent (Table 1). As the concentration of acid was increased, the degree of NRS desorption also increased. The desorption of NRS with acids was due to the protonation of the sulfo groups of the reagent ($pK_a < 1$ [17]). Treatment with acid solutions could lead not only to the break of bonds between the organic reagent and PHMG attached to the silica surface, but also of bonds between the PHMG and silanol groups of the silica. To assess the stability of PHMG attachment to the silica surface, we studied the adsorption of NRS before and after the treatment of SiO_2–PHMG with a hot (50°C) 6 M HCl solution. The isotherms of NRS adsorption on SiO_2–PHMG before (Fig. 2, curve *1*) and after treatment with 6 M HCl (Fig. 2, curve *2*) were almost identical, which was indicative of the strong attachment of PHMG to the silica surface and allowed us to repeatedly modify SiO_2–PHMG with the organic reagent in the case of its desorption. Nitroso-R-salt was not adsorbed on silica not modified with PHMG.

Adsorption preconcentration of cobalt(II) on SiO_2–PHMG–NRS. The time of attainment of an adsorption equilibrium in the adsorption of cobalt(II) on SiO_2–PHMG–NRS depended on the surface concentration of the reagent. As the surface concentration of the reagent was increased from 0.65 to 1.35 μM/g, the time of the attainment of an adsorption equilibrium decreased from 25 to 10 min. At the surface concentration of NRS ≥ 2.7 μM/g, the time of the attainment of an adsorption equilibrium did not exceed 5 min.

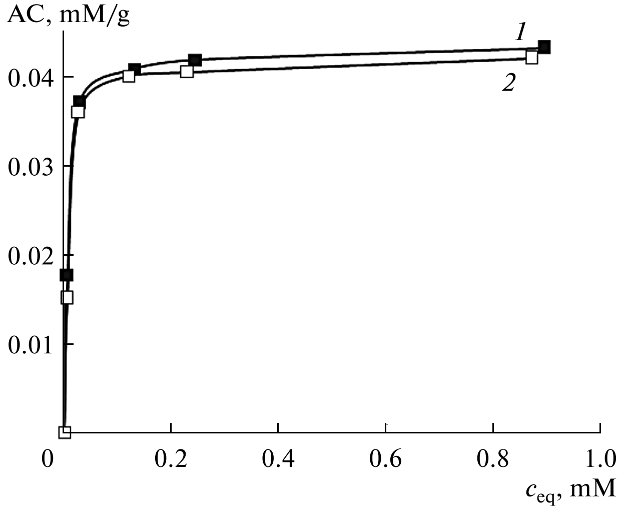

Fig. 2. Adsorption isotherms of NRS on (*1*) freshly prepared SiO_2–PHMG and (*2*) after its processing with 6 M HCl (AC is adsorption capacity).

As the concentration of NRS on the silica surface was increased, the pH range of the quantitative (≥98%) recovery of cobalt(II) shifted to the more acid region (Fig. 3). At the surface concentration of the reagent ≥22.7 μM/g, SiO_2–PHMG–NRS quantitatively extracted cobalt(II) from solutions in the pH range 6–8 (Fig. 3) with a partition coefficients of 5×10^3–1×10^4 cm^3/g. The region of the quantitative recovery of cobalt(II) by SiO_2–PHMG–NRS coincided with that of the formation of a cobalt(III)–NRS complex in solution [18]. Cobalt(II) was not extracted with a SiO_2–PHMG adsorbent in the wide range of acidities (2 M HCl to pH 8).

A comparison of the adsorption capacity of SiO_2–PHMG–NRS to cobalt(II) (Fig. 4) with the surface concentration of NRS allowed us to conclude that a complex of the composition Co : NRS = 1 : 3 formed irrespectively of the reagent concentration on the adsorbent surface. At higher concentrations of

Table 1. Degree of desorption of nitroso-R-salt from the surface of the SiO_2–PHMG–NRS adsorbent using HNO_3, HCl and NaCl solutions

c, M	HNO_3	HCl	NaCl
0.001	0.2	0.6	0.1
0.01	11	20	1
0.1	30	46	16
1	85	95	58
6	98	98	–

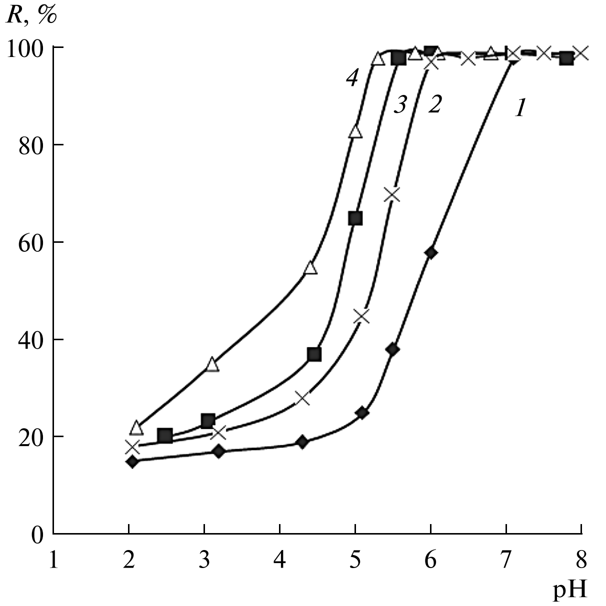

Fig. 3. Recovery of cobalt(II) with SiO_2–PHMG–NRS depending on acidity at different surface concentrations of the reagent, μM/g: *1*, 0.65; *2*, 2.7; *3*, 6.5; *4*, 27.

cobalt(II) in solution, a complex of the composition Co : NRS = 1 : 2 formed on the adsorbent surface.

In the adsorption of cobalt(II), the surface of the SiO_2–PHMG–NRS adsorbent colored in red. The SDR of the surface complex of cobalt(III) with NRS exhibited two bands with maxima at 420 and 510 nm (Fig. 5). The color intensity of the surface complex of cobalt(III) with NRS was the highest and constant in the pH ranges coinciding with the range of the quantitative recovery of cobalt(II) (Fig. 3) by adsorbents with the corresponding surface concentrations of the reagent. As the concentration of cobalt on the adsorbent surface was increased, the intensity of the band with the maximum at 510 nm proportionally increased.

In the adsorption of cobalt(II) by SiO_2–PHMG–NRS in the dynamic mode, we observed an intense red coloration of the upper adsorbent layer in the microcolumn, which was well distinguished against the yellowish green color of the reagent. The length of the red zone depended on the surface concentration of the reagent and linearly increased with the concentration of cobalt(II) in solution.

Desorption of cobalt from the surface of SiO_2–PHMG–NRS. As desorbing solutions we used 10-mL portions of 1, 4, and 6 M HCl. In the batch mode at the time of phase contact 10 min, the degree of cobalt desorption with 1 M HCl was no more than 3%. With 4 and 6 M HCl, the degree of cobalt desorption was 20 and 80%, respectively. Similar results were obtained with 4 and 6 M HNO_3.

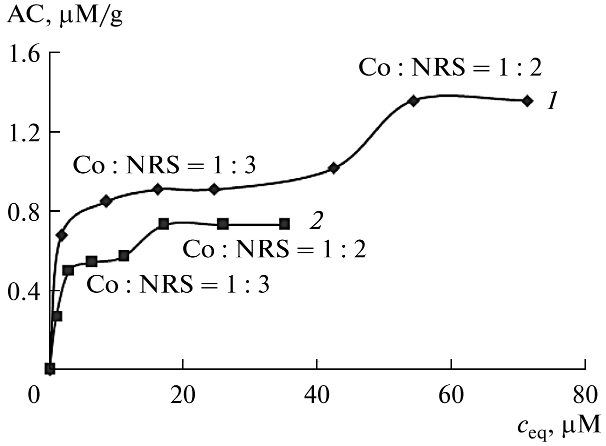

Fig. 4. Isotherms of cobalt(II) adsorption on SiO_2–PHMG–NRS. c_{NRS}, μM/g: *1*, 2.7; *2*, 1.35; 0.1 of adsorbent; $V = 10$ mL; time of phase contact 10 min; pH 6.

In treatment with dilute acid solutions, the desorption of the reagent was observed (Table 1), whereas the $[Co(NRS)_3]^{6-}$ complex, bearing a high negative charge, was retained on the adsorbent surface. To verify this assumption, we investigated the adsorption of the Co(III)–NRS complex from solutions on the SiO_2–PHMG adsorbent. It was found that the Co(III)–NRS complex was quantitatively extracted with SiO_2–PHMG from solutions of 0.1–1 M HCl, HNO_3, and NaCl.

In the dynamic mode on passing 1 M HCl through the adsorbent, the desorption of the reagent took

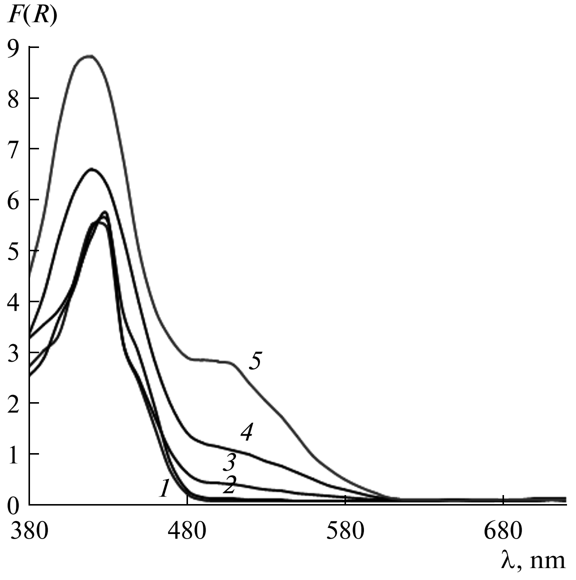

Fig. 5. Spectra of diffuse reflection of the cobalt(III) complex on the surface of SiO_2–PHMG–NRS. c_{Co}, μg: *1*, 0; *2*, 0.1; *3*, 0.5; *4*, 1; *5*, 2.5; 0.1 of adsorbent; c_{NRS} = 1.35 μM/g.

place, and the length of the red zone corresponding to the cobalt(III)–NRS complex did not change. When 4 M HCl was used, the reagent was desorbed and the length of the colored zone increases twofold. When 6 M HCl was used, the diffusion of the colored zone along the whole adsorbent layer in the microcolumn was observed together with a 50% desorption of the cobalt(III)–NRS complex, which colored the desorbing solution in red.

The quantitative desorption of cobalt from the SiO_2–PHMG–NRS surface could not be attained using acceptable (10 mL) volumes of even 6 M HCl; therefore, we next considered the possibility of its photometric determination as an intensely colored complex with NRS in the adsorbent phase.

Sorption–photometric determination of cobalt with SiO_2–PHMG–NRS. The effect of an increase in the intensity of the band in SDR with a maximum at 510 nm with an increase in the concentration of cobalt on the adsorbent surface (Fig. 5) was used for the development of a procedure for the sorption–photometric determination of cobalt.

Construction of calibration graphs. Portions of cobalt (from 0.01 to 10 μg) as its solution in 0.1 M HCl were put into three series of test tubes with ground-glass stoppers. A NaOH solution, an acetate buffer solution to attain the optimum pH value, and water to a total volume of 10 mL were added. Weighed portions of SiO_2–PHMG–NRS (0.1 g) with the surface concentration of the reagent 0.65 μM/g were put into test tubes of the first series; those with the reagent concentration 1.35 μM/g, into test tubes of the second series, and portions of adsorbent with the reagent concentration 2.7 μM/g, into test tubes of the third series. The use of adsorbents with higher surface concentrations of NRS for the determination of cobalt was inexpedient because of their intense colors. The test tubes are stopped and their contents were stirred for 25, 10 and 5 min, respectively, for adsorbents with corresponding surface concentrations of NRS. The solutions were decanted, adsorbents were transferred into fluoroplastic cells, and coefficients of diffuse reflection were measured at 510 nm.

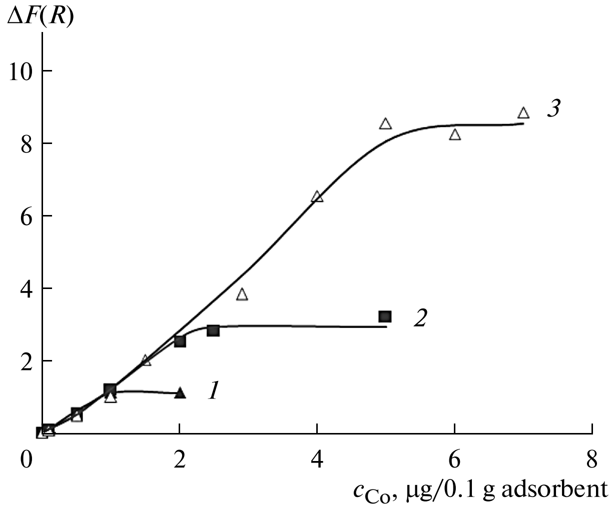

Fig. 6. Calibration graphs for the determination of cobalt(II) using SiO_2–PHMG–NRS adsorbents with different surface concentrations of the reagent. c_{NRS}, μM/g: *1*, 0.65; *2*, 1.35; *3*, 2.7; 0.1 of adsorbent.

Calibration graphs for determining cobalt(II) are shown in Fig. 6. It can be seen that the linearity range of the graphs widens with an increase in the surface concentration of NRS. A comparison of the amount of cobalt corresponding to the upper boundary of the analytical range with the surface concentration of the reagent indicates that the linearity of the calibration graphs was retained to the ratio Co : NRS = 1 : 3. The performance characteristics of the procedures for determining of cobalt are summarized in Table 2. The increase in the limit of detection for cobalt with an increase in the surface concentration of NRS is due to an increase in the intensity of the adsorbent color and, correspondingly, the value of the black experiment.

The sorption–photometric determination of cobalt(II) with SiO_2–PHMG–NRS was not affected by the following cations (in multiple amounts): Na^+, K^+, Sr^{2+}, Ca^{2+}, Mg^{2+}, Zn^{2+}, Pb^{2+}, and Cd^{2+} (10^3); Sn^{2+}, Cr^{3+}, Cr(VI) (10^2); Fe^{3+} (25). The determination of cobalt was affected by multiple amounts of Fe^{2+}, Cu^{2+},

Table 2. Performance characteristics of procedures for the sorption–photometric determination of cobalt using an adsorbent with different surface concentrations of NRS

Surface concentration of the reagent, μmol/g	Linearity range, μg/0.1 g	Limit of detection		RSD, %**
		μg/0.1 g	μg/mL*	
13.5	0.1–10	0.08	0.008	≤9
2.7	0.1–5	0.05	0.005	≤7
1.35	0.1–2.5	0.02	0.002	≤5
0.65	0.1–1	0.01	0.001	≤6

* Using 10 mL.

** In the determination of concentrations 10-fold higher than the limit of detection.

and Ni^{2+}, quantitatively extracted with the SiO_2–PHMG–NRS adsorbent from solutions of pH 6–8 and forming colored complexes on its surface.

Iron, copper, and nickel can be present in natural and industrial samples in amounts considerably exceeding the amounts of cobalt. This requires the elimination of the interference of the above elements.

When a solution containing Co(II) and Fe(II) was brought into contact with the adsorbent, the adsorbent surface became emerald-green, which is the color of the Fe(II) complex with NRS [19]. In the adsorption of Co(II) in the presence of 30-fold and higher amounts of Fe(III), the color of the adsorbent became similar to the color of adsorbents in the adsorption of Co(II); however, this color with time slowly changed to green; the intensity and time of color development depended on the concentration of Fe(III) on the adsorbent surface. A similar change of adsorbent color was observed in the adsorption of Fe(III) from its individual solutions. In neutral or alkaline aqueous solutions, Fe(III) with NRS formed complexes of brown color, slowly changing to green [20]. The color change in this case was associated with the reduction of Fe(III) to Fe(II) and the formation of a complex with NRS by the latter ion. The change of adsorbent color after the adsorption of Co(II) in the presence of Fe(III) was, probably, also connected with the reduction of Fe(III) to Fe(II) and the formation of Fe(II)–NRS complexes on the surface of the SiO_2–PHMG–NRS adsorbent.

To eliminate the interference with iron(III) and iron(II), the authors of the works [10, 11, 20, 21] proposed the use of EDTA, citrate and acetate ions, etc. In the presence of 0.005–0.05 M EDTA, Fe(II), Fe(III), and Co(III) did not form complexes with NRS on the surface of SiO_2–PHMG–NRS. A comparison of the stability constants of the Co(II), Co(III), Fe(II), and Fe(III) complexes with EDTA and NRS ($\log\beta_{CoY^{2-}} = 16.3$, $\log\beta_{CoY^{-}} = 40.6$, $\log\beta_{FeY^{2-}} = 14.2$, $\log\beta_{FeY^{-}} = 24.2$ [22], $\log\beta_{Co^{2+}(HPC)_3} = 13.3$ [23], $\log\beta_{Co^{3+}(HPC)_3} = 35.15$ [24]) showed that the Co(II) and Co(III) complexes with EDTA are more stable than the corresponding complexes of Fe(II) and Fe(III) and more stable than their complexes with NRS. This explains the absence of complex formation by Co(III) on the surface of SiO_2–PHMG–NRS in the presence of EDTA. No complex formation between Co(III) and NRS in solutions in the presence of EDTA was noted in [6]. The low values of stability constants for Fe(II) and Fe(III) citrate ($\log_{Fe(II)} = 4.4$ and $\log_{Fe(III)} = 11.4$ [22]) and acetate ($\log_{Fe(II)} = 8.3$ and $\log_{Fe(III)} = 8.7$ [22]) complexes prevent the use of citrate and acetate ions for masking.

In determining cobalt with nitrosonaphthols and their sulfo derivatives in the presence of Fe(II), Fe(III), Cu(II), and Ni(II), forming colored complexes with NRS, analysts utilize their ability to decompose on heating in acid media (1 M HCl, 1 M HNO_3), in which the cobalt(III)–NRS complex remains unchanged [1]. We studied the influence of Fe(II) and Fe(III) on the adsorption preconcentration of Co(II) and its subsequent determination after the decomposition of iron complexes with NRS in the medium of 1 M HNO_3 on heating in the batch mode. One- to 150-fold amounts of Fe(III), Fe(II), Ni(II), and Cu(II) were added to a solution containing 0.5 μg of Co(II), after which 5 mL of an acetate buffer solution to pH 6 and water to a volume of 10 mL were added. A 0.1-g portion of a SiO_2–PHMG–NRS adsorbent with the surface concentration of the reagent 27 μM/g was introduced, because in the determination of cobalt in solutions in the presence of interfering elements an excess of the reagent was recommended [1]; the mixture was stirred for 10 min. The solution was decanted, 10 mL of 1 M HNO_3 was added to the adsorbent, and the mixture was heated to 70–80°C on stirring.

The Fe(II)–NRS complex formed on the adsorbent surface was rather stable and did not decompose in 1 M HNO_3 at 70–80°C within 20 min. For its complete decomposition, the adsorbent could be boiled in 1 M HNO_3 for 1 h. After the disappearance of the emerald-green color, indicative of the decomposition of the Fe(II)–NRS complex, the adsorbent became colorless, which was indicative of the absence of the formation of a surface complex of Co(III) with NRS.

After the adsorption of Co(II) in the presence of Fe(III) and treatment with 1 M HNO_3 at 70–80°C for 10 min, the adsorbent became red, which corresponded to the color of the Co(III)–NRS complex. However, the effect of Fe(III) was determined by its amount on the adsorbent surface and the time after adsorption before treatment with an acid solution, because Fe(III) on the adsorbent surface was with time reduced to Fe(II), and the latter ion formed a complex with NRS. Treatment of the adsorbent with 1 M HNO_3 at 70–80°C for 1 h after adsorption ensured the determination of cobalt in the presence of 100-fold amounts of Fe(III).

Therefore, Fe(II) much more strongly interferes with the adsorption preconcentration and determination of cobalt in comparison to Fe(III). This can be due to the fact that Fe(II) as a reductant ($E^0_{Fe^{3+}/Fe^{2+}} = 0.77$ V) prevents the oxidation of Co(II) to Co(III) ($E^0_{Co^{3+}/Co^{2+}} = 1.85$ V) and, forming a more stable complex with NRS ($\log\beta_1 = 7.60$, $\log\beta_2 = 15.04$, $\log\beta_3 = 22.13$ [25]), hinders the formation of the less stable complex of Co(II) with NRS [23]. It is likely that iron(III) in the course of adsorption, like in aqueous solutions [20], favors the oxidation of Co(II) to Co(III), i.e., is reduced to Fe(II), which forms a complex with NRS.

To eliminate the interference with Fe(II), we used the oxidation of Fe(II) to Fe(III) with ammonium

Table 3. Sorption–photometric determination of mobile cobalt species (mg/L) in soils using SiO_2–PHMG–NRS ($n = 5$, $P = 0.95$

Sample code	Sorption—photometry	ICP AES
K1-P1	10.80 ± 0.05	10.67 ± 0.03
K1-P2	12.90 ± 0.04	12.64 ± 0.03
L3-2	0.32 ± 0.02	0.29 ± 0.02
Background	0.15 ± 0.03	0.13 ± 0.02

persulfate and hydrogen peroxide. Ammonium persulfate and hydrogen peroxide not only oxidize Fe(II) in solution to Fe(III), but also prevent the reduction of Fe(III) to Fe(II) on the adsorbent surface with the formation of a Fe(II)–NRS complex. In the presence of 0.001–0.01 M $(NH_4)_2S_2O_8$ or 1–3% H_2O_2, at least 100-fold amounts of Fe(II) did not interfere with the adsorption preconcentration and subsequent determination of cobalt.

The Cu(II) and Ni(II) complexes of NRS formed on the adsorbent surface decomposed with hot 1 M HNO_3 within 10 min and in up to 100-fold amounts did not interfere with the determination of cobalt.

The results obtained allowed us to use the SiO_2–PHMG–NRS adsorbent for the sorption–photometric determinaltion of mobile cobalt species in soils around the Tuvakobalt dead plant (Khovu-Aksy, Republic of Tyva, Russia). We analyzed soil samples taken directly in the sludge storage (samples K1–P1 and K1-P2) and at distances of 300 m (sample L3-2) and 5 km from it (background).

Procedure for the determination of mobile cobalt species in soils. The soil samples were treated with 1 M HNO_3 according to recommendations [26]. Aliquot portions of 1 mL (for Co concentrations <5 μg/mL) or 0.5 mL (for Co concentration > 5μg/mL) of a solution were placed in graduated test tubes; 1 mL of a 0.1 M solution of ammonium persulfate, NaOH, and an acetate buffer solution to pH 6 were added; 0.1 g of a SiO_2–PHMG–NRS adsorbent with the surface concentration 27 μM/g was added; and stirring for 10 min was performed. The solutions were decanted, 10 mL of hot (70–80°C) 1 M HNO_3 was added to the adsorbent, and stirring for 20 min was performed. Then the solution was decanted, the adsorbent was transferred into a fluoroplastic cell, and the coefficient of diffuse reflection was measured at 510 nm. The concentration of cobalt was determined from a calibration graph constructed under similar conditions.

Using the desorption of the free reagent from the adsorbent surface, the contrast of the determination of cobalt was increased and the limit of detection for cobalt was reduced to 0.01 μg/0.1 g, irrespectively of the initial surface concentration of NRS. The accuracy of the results obtained was compared with the data of inductively coupled plasma atomic emission spectrometry (Table 3).

Test procedures for the determination of cobalt with SiO_2–PHMG–NRS. The formation of an intensely colored Co(III) complex with NRS on the adsorbent surface was used for its test determination in the versions of color scales and indicator tubes [27].

Method of color scales. For the preparation of a reference scale, from 0.01 to 10 μg of Co(II) as its solution in 0.1 M HCl was placed in a series of test tubes and NaOH, an acetate buffer solution to pH 6, and water to a total volume of 10 mL were added. Then 0.1 g of an adsorbent with the surface concentration 13.5 μM/g was introduced and the mixture was stirred for 10 min. The solutions were decanted, 10 mL of hot (70–80°C) 1 M HNO_3 was added to the adsorbent, and stirring for 20 min was performed. Then the solution was decanted and the adsorbents were transferred into cells of a fluoroplastic plate, consecutively increasing the concentration of cobalt. An adsorbent with an unknown concentration of cobalt was placed in a cell in a separate plate. By moving the control plate along the scale, the observer visually found a correspondence between the color of an adsorbent with an unknown concentration of cobalt and that of an adsorbent in the control plate. The error of the visual determination of 1–5 μg cobalt was ±0.3 μg.

Method of indicator tubes. An increase in the length of the colored adsorbent zone in a microcolumn with an increase in the concentration of cobalt in the test solution was used for the test determination of cobalt in the version of indicator tubes.

To study the possibility of determining cobalt in the presence of Fe(III) or Fe(II) in the dynamic mode of preconcentration, NaOH and an acetate buffer solution were added to a solution containing 1 μg of Co(II) and 50-fold amounts of Fe(III) or Fe(II) to adjust pH 6 and then water was added to 20 mL. The solutions were pumped through a microcolumn, and then 10 mL of hot (70–80°C) 1 M HNO_3 was passed through it. In the adsorption of Co(II) in the presence of Fe(II), an emerald-green coloration was observed within the whole adsorbent layer in the microcolumn. After passing 10 mL of hot (70–80°C) 1 M HNO_3 and the disappearance of the green color, the adsorbent became red within the whole height of its layer. In the adsorption of Co(II) in the presence of Fe(III) and treatment with hot 1 M HNO_3, the length of the red zone corresponded to the length of zone in the adsorption of Co(II) from its individual solution.

After the oxidation of Fe(II) to Fe(III) with ammonium persulfate or H_2O_2 and adsorption, the color of the adsorbent became red, which corresponded to the color of the Co(III)–NRS complex. In the use of 1–3% H_2O_2, the length of the colored zone corresponded to the length of zone in the adsorption of Co(II) from its individual solutions. In the presence of 0.01 M ammonium persulfate, we observed an increase in the length of the colored zone, which was due to the higher salt content of the solution than in the use of H_2O_2. An increase in salt content let to a partial desorption of the reagent, the reduction of its surface concentration and, as a result, an increase in the length of the colored zone. The effect of the salt background was taken into account in the test determination of mobile cobalt species in real samples using the added–found method. The error of the determination of 5 μg cobalt was ±0.3 μg. The lower boundary of the analytical range for cobalt in the test method in the versions of color scales and indicator tubes was 0.02 μg.

The developed procedures of the sorption–photometric determination of cobalt in the limits of detection were comparable with those of atomic spectroscopic methods, characterized by simplicity and rapidity, and did not require complex and expensive equipment; in the version of test methods, these can be used in work places and in the field.

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