Determination of Cobalt in Soils and Natural Waters Using Silica Gel Modified with Polyhexamethylene Guanidine and Nitroso-N-Salt

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Abstract
Highly sensitive and simple method was developed for preconcentration and determination of trace amounts of cobalt in natural waters and soils using diffuse reflectance spectroscopy was developed. Method is based on the application of the new sorbent – silica gel sequentially modified with polyhexamethylene guanidine and 2-nitroso-1-naphthol-4-sulfonic acid sodium salt (nitroso-N-salt). Optimal conditions of solid-phase extraction of cobalt (II) such as stirring time, pH and volume of the solution, surface concentration of the reagent were determined. During sorption, intensively colored complex of cobalt (III) with nitroso-N-salt, that have a stripe in diffuse reflectance spectrum with maximum at 530 nm, was formed. Sorption-photometric method of cobalt determination directly in the sorbent phase by the color of its complex with nitroso-N-salt using diffuse reflectance spectroscopy was developed. The linearty of calibration curve depended on the surface concentration of nitroso-N-salt. For the surface concentration of nitroso-N-salt of 2.8 $\mu mol\ g^{-1}$ the linearty was maintained in the concentration range of 0.05 – 5.0 μg Co per 0.100 g of the sorbent, or 0.005 – 0.50 $\mu g\ mL^{-1}$ if the sorption was carried out from 10 mL of the solution. As the surface concentration of the reagent decreased, the range of linearty of the calibration curve narrowed. The detection limit was calculated as 0.01 μg per 0.100 g of the sorbent (or 1 ng mL^{-1} if the sorption was carried out from 10 mL of the solution) and didn't depend on the surface concentration of the reagent. Method was applied to the determination of cobalt in natural waters and soils. The accuracy of the results was confirmed by inductively coupled plasma optical emission spectroscopy and recovery test of spiked samples.

Keywords: Cobalt Modified Silica Gel, Polyhexamethylene Guanidine, 2-Nitroso-1-Naphthol-4-Sulfonic Acid, Solid-Phase Extraction, Diffuse Reflectance Spectroscopy, Visual Test Method.

Introduction
An increased attention to cobalt determination in natural materials (soils, waters) is associated with the fact, that the content of cobalt in these samples is very low, but it plays an important role for plants, animals and human being. There is certain content of cobalt that is necessary for living organisms [1,2]. Physiological and pathophysiological effects of cobalt are various [3,4]. In plants cobalt has a positive effect on photosynthesis, activates enzymes of protein metabolism. In the animal body cobalt is a part of vitamin B12. However, an excess of it leads to toxic effects on the body [5,6]. Soil and natural waters are contaminated with cobalt as a result of chemical, metallurgical and metal processing companies activity, as well as due to the leaching of cobalt ores.

Cobalt compounds are found in natural waters in dissolved and suspended states. Rivers and lakes contain dissolved cobalt in the oxidation state +2 in the form of complexes with organic compounds.

Graphite furnace atomic absorption spectrometry, flame atomic absorption spectrometry (including combination with the preconcentration), X-ray fluorimetric spectroscopy, optical emission spectroscopy, adsorptive stripping voltammetry, flow injection chemiluminesce and chemiluminescent determination coupled with liquid cation-exchange chromatography [7-17].

Photometric method is the most widely used method for cobalt determination [18-25]. This method is highly sensitive and selective, with low matrix interference and uses quite simple equipment. Organic reagents, which form intensively colored complex compounds with cobalt are used for the photometric determination of cobalt: 4-(6-nitro-2-benzothiazolylazo) resorcinol, dithizone, 5-(6-methoxy-2-benzothiazoleazo)-8-aminoquinoline, ninhydrin, *p*-methylisonitrosoacetophenonehydrazone, 3-(2'-thiazolylazo)-

2,6-diaminopyrodine, iodine nitrotetrazole chloride, 2-hydroxy-1-naphthaldehyde-p-hudroxybenzoichydrazone, 5-[3-(1,2,4-thiazolylazo]-2,4-dihydroxy-benzaldehyde,5,7-dichlorquinolin-8-ol-rhodamine 6G, 2-hydroxy-4n-butoxy-5-bromo propiophenon oxime, di-2-pyridyl ketone benzoylhydrazone, 4,4'-diazobenzenediazoaminoazobenzene, 2,6-pyridinedicarboxaldehyde, thiosemicarbazone, 2,2'-dipyridyl ketoxime [19-33].

For the determination of trace concentrations of cobalt photometric method was combined with preliminary solid-phase extraction [34]. Gelatin films, chitosan, cellulose, Amberlite XAD resins, C_{18} membrane disk and silica gel were used as the sorbents for cobalt preconcentration [35-40].

Silica gels have several advantages compared with other sorbents: they don't have own color, its particles are mechanically strong, have a relatively high chemical resistance and the possibility of chemical or noncovalent attachment to their surface of various functional groups.

One of the most group of common reagents for the photometric determination of cobalt is nitrosonaphthols [18, 35, 40]. Its sulphonated derivatives – 1-nitroso-2-naphthol-3,6-disulfonic acid (nitroso-R-salt, **NRS**) and 2-nitroso-1-naphthol-4-sulfonic acid (nitroso-N-salt, **NNS**) – as well as their complexes with cobalt(III) are readily soluble in water. This avoids the use of organic solvents for cobalt determination.

Techniques for the photometric determination of cobalt using 2-nitroso-1-naphthol derivatives are more sensitive compared to 1-nitroso-2-naphthol derivatives [41]. During complexation of cobalt with nitrosonaphthols it is oxidized to cobalt (III).

In this paper, a new sorbent for preconcentration and determination of cobalt was proposed. The conditions for synthesis of the sorbent, based on sequential modification with polyhexamethylene guanidine (**PHMG**) and NNS, were investigated, and cobalt (II) sorption properties of the sorbent were studied. Methods coupling solid-phase extraction of cobalt and its photometric and visual determination directly in the sorbent phase were developed. Methods were applied to the determination of cobalt in soil extracts and natural waters.

Presence of silanol groups on the surface of silicon oxide prevents effective fixation of NNS on its surface due to mutual repulsion between negatively charged deprotonated silanol groups and sulfonic groups of the organic reagent. Therefore, formation of intermediate layer of polymeric polyamine that is able to interact with both surface silanol groups and sulfonic groups of the reagent was suggested. This approach has been used previously for synthesis of silica based sorbent sequentially modified with PHMG and NRS [42].

Experimental
Apparatus
Inductively coupled plasma optical emission spectrometer Optima 5300DV (Perkin-Elmer, USA) was used to determine cobalt concentration in aqueous phase after contact with the sorbent. The wavelength used for cobalt was 228.616 nm.

The UV-Vis spectra were registered using Cary 100 spectrophotometer (Varian, Australia). Diffuse reflectance spectra over the range of 380-720 nm were registered using Pulsar spectrophotocolorimeter (Himavtomatika, Russia). Spectra were plotted against coordinates calculated using the Kubelka-Munk function, that is, $F(R) = (1–R)^2/2R$ – wavelength (nm).

The pH measurements were carried out with a SevenEasy pH Meter S20 (Mettler-Toledo, Switzerland) calibrated against four standard buffer solutions of pH 1.65, 4.01, 7.00 and 9.18. A mechanical shaker WU-4 (Poland) was used for preparation of the sorbent. Peristaltic pump Masterflex L/S (Thermo Fisher Scientific, USA) was used for pumping solutions through a mini column.

Glass mini-column (inner diameter of 3 mm, length of 5 cm) containing 0.100 g of the sorbent, sequentially modified with PHMG and NNS, was used for the preconcentration of cobalt (II) in dynamic mode.

Reagents and solutions
All reagents were of analytical grade. Deionized water was used for the preparation of the solutions.

A stock standard solution of Co(II) 100 mg L^{-1} was prepared by dissolving 403.7 mg of $CoCl_2\cdot6H_2O$ in 0.1 mol L^{-1} HCl into a 1000 mL volumetric flask. The standard working solutions were diluted daily prior to use.

Nitroso-N-salt solution was prepared by dissolving of accurately weighted portion of Aldrich chemical in deionized water.

Silica gel Silokhrom S-120 (0.1 – 0.2 mm fraction, specific surface area of ~120 m^{2}g^{-1}, average pore diameter of ~45 nm) was used as a matrix for the sorbent synthesis.

Polyhexamethylene guanidine chloride solution was prepared by dissolving of commercially available chemical (purity more then 95%).

The required pH was adjusted by adding HNO$_3$, NaOH, or acetic buffer solution (pH 4.0-7.0), prepared from 1.0 mol L^{-1} CH$_3$COOH and 1.0 mol L^{-1} CH$_3$COONa, or ammonium chloride buffer solution (pH 7.5-8.5), prepared from 1.0 mol L^{-1} NH$_4$OH and 1.0 mol L^{-1} NH$_4$Cl.

## Modification of silica surface by sequential adsorption of PHMG and nitroso-N-salt from aqueous solutions
In order to activate the surface a portion of silica gel of 15 g was soaked with the NaOH solution at pH 9.0 for 1 hour, and then washed with deionized water until pH 7.0. Then 100 mL of 7.5% PHMG solution was added to the silica gel at the rate 1 mL min^{-1} under continuous stirring. Prepared sorbent (**SiO$_2$- PHMG**) was washed with deionized water until no positive reaction to PHMG in the rinsing water and dried at 70°C. Presence of PHMG in the rinsing water was determined visually by the test with bromophenol blue.

Portions of the SiO$_2$-PHMG sorbent of 0.100 g were placed into a test tubes with a ground glass stoppers, 10.0 mL of 6.8•10^{-6} – 1.8•10^{-3} mol L^{-1} solution of NNS was added, and stirred for 5 min. The resulting sorbent (**SiO$_2$-PHMG-NNS**) was separated from the solution by decantation.

In order to investigate desorption of the organic reagent SiO$_2$-PHMG-NNS was treated with 0.001 – 6.0 mol L^{-1} solutions of HCl, HNO$_3$, or NaCl.

The solid-phase extraction of nitroso-N-salt was monitored by its own light absorbance at 383 nm (for the solutions of pH<6.0) and 424 nm (for the solutions of pH>6.0).

Fixation of PHMG on the inorganic oxides surface occurs due to formation of multicentered hydrogen bonds between amino groups of polyamine and hydroxyl groups of silica gel. Fixation of NNS occurs due to interaction between negatively charged sulfonic groups of a reagent and protonated amino groups of PHMG that immobilized onto silica surface. The scheme of the modified silica gel is represented in (Figure 1).
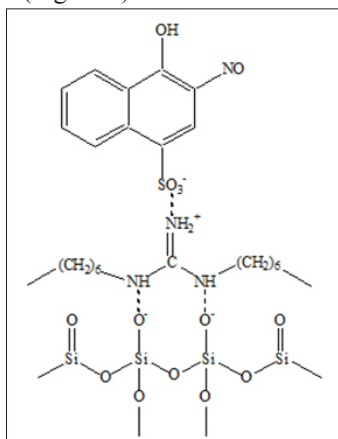
Figure 1: Scheme of the modified silica gel

Adsorption of cobalt (II) onto SiO2-PHMG-NNS surface
Solid-phase extraction of cobalt (II) was studied at room temperature both in batch and dynamic modes. In the batch experiment, 1.0 mL of Co(II) solution with the concentration of $0.05 – 10.0$ µg mL^{-1} in 0.1 mol L^{-1} HCl was placed into a graduated test tube with ground plug; NaOH and HNO$_3$ solutions (to adjust pH $1.0 – 3.0$) or acetic buffer solution (to adjust pH $4.0 – 7.0$) or ammonium chloride buffer solution (to adjust pH $7.5 – 8.5$) and water to the total volume of $10.0 – 50.0$ mL were added. SiO$_2$-PHMG-NNS sorbent (0.100 g) was put into the test tube with the solution, the test tube was plugged, the solution with the sorbent was stirred for $1 – 30$ min. The sorbent was isolated from the solution by decantation, moved into a fluoroplastic cell, the excess of water was removed by filter paper, and the diffuse reflectance coefficients were measured in the range of $380 – 720$ nm.

Under dynamic conditions, $10.0 – 100.0$ mL of Co(II) containing solution with pH 6.2 was passed through the mini column using peristaltic pump at the rate of $0.5 – 5.0$ mL min^{-1}. Metal ions concentration in the solutions before and after adsorption was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of the aqueous phase.

Construction of calibration curve for cobalt determination using sorption-photometric technique
Solutions (5.0 mL) containing from 0.05 to 10.0 µg of cobalt (II) were put into a series of graduated test tubes with ground plugs; NaOH, acetic buffer solution (until pH 6.2) and deionized water (to a total volume of 10.0 mL) were added. The solutions were intensively stirred with 0.100 g of SiO$_2$-PHMG-NNS sorbent for 10 min. Then the sorbent was isolated from solution by decantation, moved into fluoroplastic cell, the excess of water was removed by filter paper, and a diffuse reflectance coefficient (R) at 530 nm was measured.

Preparation of soil and water samples for the analysis
Soil samples were dried at 80oC for 72 h. Weighted portions of 2.00 g of the powder of dry samples were placed into a beakers, 10.0 mL of 0.5 mol L^{-1} HNO$_3$ was added, mixed with the samples and heated at 900C for 3 h under continuous stirring. Then samples were cooled, filtered through a membrane filters into volumetric flasks and diluted to the total volume 50.0 mL with deionised water.

The preparation of natural river water was as followed: concentrated nitric acid was added to the 100.0 mL of the sample up to pH 1.0, then, the sample was boiled for 30 min to decompose the organic compounds. The samples were cooled, filtered through a membrane filter and diluted to 100.0 mL with deionised water in a volumetric flask.

Analysis of soil extracts and natural water samples
For cobalt determination in batch mode 0.5 mL (if cobalt concentration > 0.5 µg mL^{-1}) or 10.0 mL (if cobalt concentration < 0.5 µg mL^{-1}) of soil extract or 20.0 mL of natural water was placed in graduated test tube with ground plug, NaOH and acetic buffer solution (until pH 6.2) and deionized water (to a total volume 25.0 mL) were added. The solutions were intensively stirred with 0.100 g of SiO$_2$-PHMG-NNS sorbent for 10 min. Then the solutions were decanted; 10.0 mL of hot (70oC) 1 mol L^{-1} HNO$_3$ was added to the sorbent and stirred for 20 min for the total destruction of the complexes of iron(II), copper(II), and nickel(II) with NNS. Then test tubes were cooled, the sorbent was isolated from solution by decantation, moved into fluoroplastic cell and a diffuse reflectance coefficient (R) at 530 nm was measured.

Determination of cobalt in real samples using mini-column
For visual test detection of cobalt the sorption was carried out in dynamic mode. Prepared soil extract (10.0 mL) or river water (100.0 mL) with pH 6.2 was passed through the mini-column filled with 0.100 g of the sorbent with the flow rate 2.0 mL min^{-1}. Then, 10.0 mL of hot (70ºC) 1 mol L^{-1} HNO$_3$ was passed through the column. The content of cobalt was determined by the length of red-colored zone of the sorbent in mini-column.

Results and discussion
Immobilisation of nitroso-N-salt on the surface of SiO2-PHMG
Sorbent SiO$_2$-PHMG quantitatively extracted (recovery > 98%) nitroso-N-salt in the range of pH $4.0 – 8.0$ (Figure 2, curve 1). During sorption of NNS the surface of the sorbent became yellow colored. Diffuse reflectance spectra (DRS) were wide structureless band with maximum of absorbance at 430 nm. The intensity of color was maximum in the range of pH $4.0 – 8.0$ (Figure 2, curve 2).
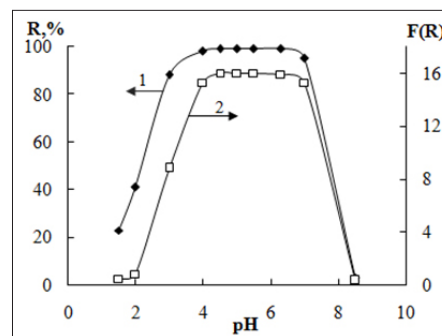
Figure 2: Effect of pH on the recovery *(1)* and F(R) *(2)* of NNS by SiO$_2$-PHMG (C_{NNS}=2.8·10^{-5} mol L^{-1}, *(1)*, λ = 430 nm *(2)*, 0.100 g of the sorbent, V=10.0 mL)

The sorption capacity of SiO$_2$-PHMG for NNS determined by the horizontal section of the isotherm of sorption was 88 μmol g^{-1}. The sorption isotherm of nitroso-N-salt by SiO$_2$-PHMG can be attributed to L-type. The quantitative extraction of the reagent is achived in Henry section; this allows to obtain sorbents with any surface concentration of the reagent within the sorption capacity of SiO$_2$-PHMG for nitroso-N-salt.

Stability of fixation of NNS on the surface of SiO$_2$-PHMG was studied by treating of the sorbent with surface concentration of NNS 14 μmol g^{-1} with solutions of NaCl, HCl and HNO$_3$. The results are represented in (Table 1). With rising the acid concentration the desorption of the reagent was increased. This process occurs due to protonation of sulfonate groups of NNS. The nature of the acid did not significantly affect the desorption of the reagent. At equal concentrations of HNO$_3$ and HCl the desorption of the reagent was comparable. Presence only one sulfonate group in the NNS molecule causes weaker fixation of NNS on the surface of SiO$_2$-PHMG than NRS, having two sulfonate groups [42].

Table 1: Desorption of nitroso-N-salt from the surface of SiO$_2$-PHMG-NNS with nitric acid, hydrochloric acid and sodium chloride solutions.

	Desorption of NNS, %		
C, mol L^{-1}	HNO$_3$	HCl	NaCl
0.001	10	6	0.5
0.01	50	45	5
0.1	71	77	23
1	81	86	61
6	97	97	-

Interaction of cobalt (II) with NNS immobilized onto SiO$_2$-PHMG
Effect of stirring time
Stirring time enough for attainment of sorption equilibration was studied. In this experiment recovery of 1.0 μg Co (II) by SiO$_2$-PHMG-NNS sorbents with various surface concentration of the reagent (2.8 μmol g^{-1}, 1.4 μmol g^{-1}, 0.7 μmol g^{-1}) was investigated. As it can be seen from (Figure 3), if the surface concentration of NNS was more than 2.8 μmol g^{-1}, the equilibration time of cobalt (II) extraction was less than 5 min. Decrease of the surface concentration of the reagent up to 1.4 μmol g^{-1} and further to 0.7 μmol g^{-1} leads to an increase in the equilibration time up to 15 and 30 min, respectively.
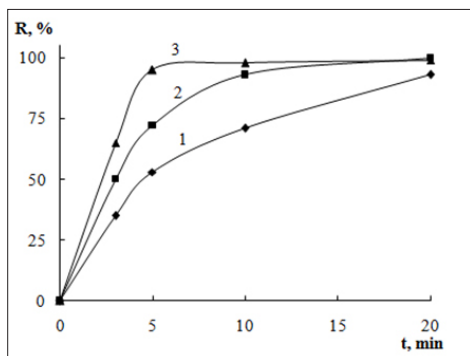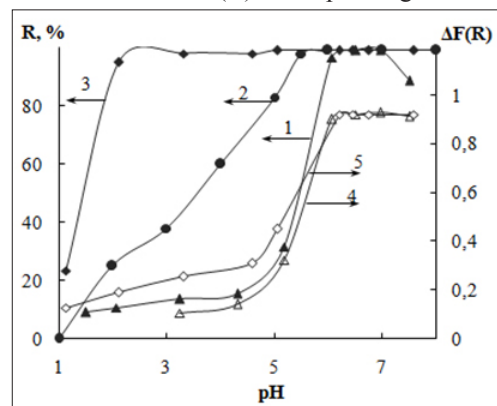

Figure 3: Effect of stirring time on the recovery of Co(II) by SiO$_2$-PHMG-NNS at various surface concentration of nitroso-N-salt (C$_{NNS}$, μmol g^{-1}: 2.8 (1), 1.4 *(2)*, 0.7 *(3)*)

Effect of volume
Varying the volume of the solution during Co (II) extraction in the batch mode can affect the equilibration time. The volume of the solution was varied from 10.0 to 50.0 mL with the same total content of Co (II) equal to 1.0 μg. Varying the volume of the solution from 10.0 to 30.0 mL did not affect the equilibration time if 0.100 g of the sorbent with surface concentration of NNS more than 2.8 μmol g^{-1} was used. Increasing the volume of the solution up to 50.0 mL leads to rising the equilibration time from 5 to 10 min.

Effect of pH
Effect of pH on the sorption of Co (II) was studied in solutions of pH range 1.0 - 8.0. The pH range of quantitative extraction of cobalt (II) depends on the surface concentration of NNS. If the surface concentration of the reagent was 0.7 μmol g^{-1} the quantitative extraction of cobalt (II) from solutions was attained in pH range of 6.0 – 7.0 (Figure 4, curve 1). The range of quantitative extraction of cobalt (II) by SiO$_2$-PHMG-NNS sorbent shifted into more acid area if the surface concentration of the reagent increased: if surface concentration of the NNS was 2.8 μmol g^{-1} the pH range of quantitative extraction of cobalt was 5.5 – 8.0 (Figure 4, curve 2); if surface concentration of the NNS was equal or more than 28 μmol g^{-1} the pH range of quantitative extraction of cobalt was 2.0 – 8.0 (Figure 4, curve 3). The partition coefficient under optimal conditions of solid phase extraction was $5\times10^3 – 1\times10^4$ cm^3 g^{-1}. SiO2-PHMG sorbent did not extract cobalt (II) in the pH range of 1.0 – 8.0.

Figure 4: Effect of pH on the recovery (1 - 3) and ΔF(R) (4, 5) of cobalt (II) by SiO$_2$-PHMG-NNS at various surface concentration of nitroso-N-salt (CNNS, μmol g-1: 0.7 (1, 4), 2.8 (2), 28 (3, 5), 0.100 g of the sorbent)

Sorption capacity
Sorption capacity of SiO$_2$-PHMG-NNS sorbent for cobalt (II) depends on the surface concentration of the reagent. Isotherms of cobalt (II) sorption are represented on (Figure 5). Comparison of sorption capacity for cobalt (II) with surface concentration of NNS indicates the formation of complexes on the surface of the sorbent with the stoichiometry of Co: NNS = 1:3 independent on surface concentration of the reagent. An increase of cobalt (II) concentration in solution leads to the formation of complexes on the surface of the sorbent with stoichiometry of Co: NNS = 1:2.
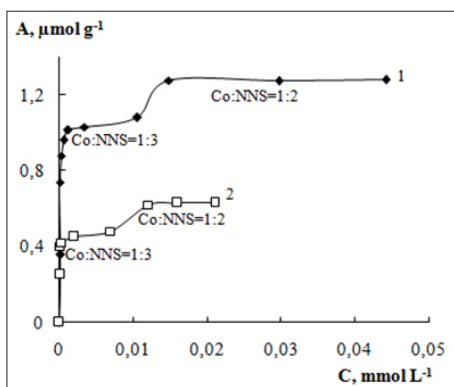
Figure 5: Isoterms of cobalt (II) sorption by SiO$_2$-PHMG-NNS (C$_{NNS}$, μmol g^{-1}: 2.8 *(1)*, 1.4 *(2)*, stirring time of 10 min, pH 6.2)

Diffuse reflectance spectra

During the sorption of Co (II) the sorbent SiO$_2$-PHMG-NNS became red colored, that is evident of formation of cobalt (III) complex compounds with NNS.

The diffuse reflectance spectrum of Co (III) complexes with NNS on the surface of SiO$_2$-PHMG is the band with maximum at 430 nm, attributed to the adsorbed NNS, and shoulder at 530 nm, attributed to the surface complex of cobalt(III) with NNS. As cobalt amount on the surface increases, the intensity of the band at 430 nm decreases, and intensity at 530 nm increases proportional to the content of cobalt(III) (Figure 6). Maximum color intensity of the surface complex of cobalt (III) with NNS was observed in the pH range of 6.0 – 8.0 and did not depend on the surface concentration of NNS (Figure 4, curves 4 - 5).
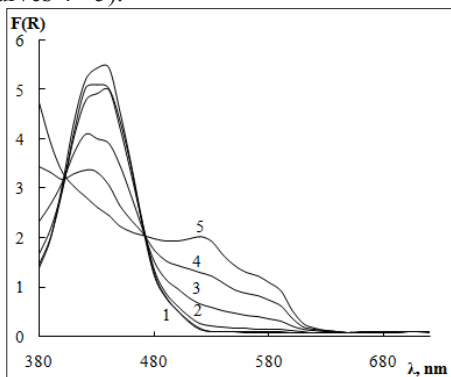
Figure 6: Diffuse reflectance spectra of cobalt (III) complex on the surface of SiO$_2$-PHMG-NNS (C$_{Co}$, μg: 0 *(1)*; 0.1 *(2)*; 0.5 *(3)*; 1 *(4)*; 2.5 *(5)*; 0.100 g of the sorbent, C$_{NNS}$ =1.4 μmol g^{-1})

Analytical features

As the cobalt amount on the sorbent surface increases color intensity of the sorbent increases proportionally. The calibration curve for the determination of cobalt was prepared according to the proposed procedure in the optimum conditions. Nitroso-N-salt has its own intensive yellow color and colors sorbent in yellow in sorption process. As the surface concentration increase, the intensity of the sorbent color rises. For construction the calibration curves for cobalt determination SiO$_2$-PHMG-NNS sorbents with the reagent surface concentrations of 0.7, 1.4, и 2.8 μmol g^{-1} were used. The linearty of calibration curve depends on the surface concentration of the reagent and rises with its growth (Figure 7).
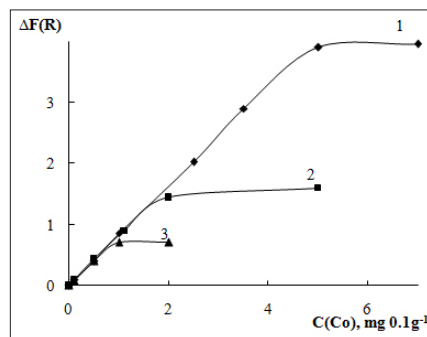
Figure 7: Calibration curves for cobalt (II) determination using SiO$_2$-PHMG-NNS with various surface concentration of the reagent (C$_{NNS}$, μmol g^{-1}: 2.8 *(1)*, 1.4 *(2)*, 0.7 *(3)*, 0.100 g of the sorbent)

A comparison of cobalt amounts corresponding to the upper boundary of linear range with a surface concentration of the reagent indicates that the linearity of calibration curves is maintained up to a ratio Co:NNS=1:3. In the case of NNS surface concentration of 2.8 μmol g^{-1} the linearty of calibration curve was maintained in the concentration range of 0.05 – 5.0 μg Co (II) per 0.100 g of the sorbent. It corresponds to 0.005 – 0.5 μg mL^{-1} in the case of sorption from 10.0 mL of solution.

The equation of the line is $\Delta F(R)_{530} = (0.788 \pm 0.005)C_{Co}$ (R^2=0.999), where $\Delta F(R)_{530}$ is the difference between the Kubelka-Munk function of sorbent before and after treatment by cobalt solution, C$_{Co}$ is concentration of cobalt (μg per 0,100 g of the sorbent); and the equation is independent on the functional group concentration.

Limit of detection was calculated as 0.01 μg Co(II) per 0.100 g of the sorbent (it corresponds to 1 ng mL^{-1} if volume of solution was 10.0 mL and 0.2 ng mL^{-1} if volume of solution was 50.0 mL), based on three times the standard deviation of the blank signal. The relative standard deviation (RSD) of sorption-photometric technique was less than 0.05.

Effect of interference ions

In order to assess the selectivity of proposed method, the effect of some foreign ions (major components of natural waters and soils) on cobalt (II) determination was examined. For this purpose, binary solutions containing 1.0 μg of Co (II) and many times larger amounts of foreign ions. The effect of each ion was considered interfering if the analytical signal changed more than ± 5%. The results are summarized in (Table 2).

Table 2: Effect of foreign ions on the determination of 1.0 μg Co(II) per 0.100 g sorbent using SiO2-PHMG-NNS (relative error ± 5.0 %)

Foreign ions	Tolerance limit, μg
Na+, K+, Sr2+, Ca2+, Mg2+, Ba2+	10,000
Mn2+, Pb2+, Cd2+	1,000
Sn2+, Cr3+, Cr6+	300
Zn2+, Al3+	200
Fe3+	25
Na2CO3	20,000
NaCl, Na2SO4, Na2SO3	10,000

Cu(II), Ni(II) and Fe(II) interfered with the determination of Co(II)

at the same concentration, since iron(II) forms green complexes with NNS, and Cu(II) and Ni(II) form orange complexes. Natural waters and soil extracts contain Cu (II), Ni(II) and Fe(II) at the concentrations of mach higher then cobalt content that requires the elimination of the interfering effect.

To eliminate the interference with these ions masking agents were used in the earlier work EDTA, citrate and acetate ions. However, as we have shown previously, these masking agents are ineffective to eliminate the interfering effect of the Cu (II), Ni (II) and Fe (II) in the sorption-photometric determination of cobalt using silica, sequentially modified with PHMG and NRS [40,42,43].

During cobalt determination using nitrosonaphthols and its sulfonic derivatives in the presence of Fe(II), Fe(III), Cu(II) and Ni(II), forming colored complexes, their decomposition by heating in acidic media (1 mol L^{-1} HCl, 1 mol L^{-1} HNO_3) was used while cobalt(III) complex with nitrosonaphthols remained unchanged [40,44].

Complexes of Fe (II), Cu(II), and Ni(II) with NNS on the surface of SiO_2-PHMG-NNS can be decomposed by treating with hot (70°C) 1 mol L^{-1} HNO_3 for 10 min; 100-fold amounts of these ions do not interfere cobalt determination. The cobalt (III) complex with NNS - $[Co (NNS)_3]^{6-}$ was stable to boiling the solution HNO_3 and remained unchanged on the sorbent surface.

Higher selectivity of cobalt determination in the presence of Fe (II) can be attained by its preliminary oxidation up to iron (III) using ammonium persulfate and hydrogen peroxide. Cobalt (II) sorption in the presence of 0.001 – 0.02 mol L^{-1} $(NH_4)^2S_2O_8$ or 1-3% H_2O_2 and subsequent treatment with hot 1 mol L^{-1} HNO_3 solution allows to determine cobalt on the surface of SiO_2-PHMG-NNS sorbent in the presence of 200-fold amounts of Fe(II).

The desorption of the reagent occur during treatment with 1 mol L^{-1} HNO_3 resulting in an increase the contrast of cobalt determination and an improvement of the detection limit up to 0.005 µg Co(II) per 0.100 g of the sorbent irrespective of initial surface concentration of NNS.

Since Fe (II), Fe (III), Cu (II) and Ni (II) form complexes with NNS, cobalt determination in the presence of these ions should be carried out using sorbents with maximum surface concentration of the reagent.

Preconcentration of cobalt (II) in mini-column
In the process of cobalt (II) sorption in dynamic mode the upper layer of the sorbent in mini-column became colored in reddish-brown that was clearly visible on the background of yellow color of the reagent. During 1 – 3 h the color of the sorbent changed from reddish-brown to red due to the oxidation of cobalt (II) to cobalt(III). Oxidizing agents are dissolved oxygen and the reagent by itself [45]. At pH > 4.0 the oxidation of cobalt (II) proceeds more due to dissolved oxygen; oxidation due to reagent is much slower reaction. In the weakly acidic media the role of the reagent as an the oxidant increases.

Since, during passing the solution through a mini-column the oxygen supply to the sorbent is limited, the oxidation of cobalt (II) in the sorption process proceeds more due to reagent – NNS.

If 1 mol L^{-1} solution of acid was passed through a mini-column filled with SiO_2-PHMG-NNS sorbent after passing the solution of cobalt (II) the color of the sorbent changed almost instantly from reddish-brown to red.

In order to increase the rate of oxidation of cobalt (II) various oxidants were added in a solution containing 1.0 g of cobalt(II): $(NH_4)^2S_2O_8$, H_2O_2; the resulting solutions were passed through the mini-columns filled with the sorbent. In the presence of 2.5•10^{-3} mol L^{-1} $(NH_4)^2S_2O_8$ or 3% H_2O_2 the top layer of the sorbent in mini-column turns red immediately. The length of red colored zone of the sorbent in mini-column depends on cobalt (II) content in initial solutions and is extended in proportion to increase of its concentration.

The following factors affect the length of the colored zone corresponding to the Co(III) complex with NNS: surface concentration of NNS, flow rate of the solution, and volume of the solution.

Effect of surface concentration of NNS was studied using sorbents with surface concentration of the reagent of 7, 14, 28, 56 µmol g^{-1}. If the concentration of NNS was more than 14 µmol g^{-1}, the length of colored zone after solid-phase extraction of the same amount of cobalt (II) was equal for all three adsorbents and was 2.5 ± 0,5 mm for 1.0 µg of cobalt. If the concentration of NNS was 7 µmol g^{-1} the length of red colored zone was extended approximately 2 times and was 5.0 ± 0.5 mm for 1.0 µg of cobalt.

Effect of flow rate of the solution passed through the column on the length of red colored zone was studied. For this purpose, 10.0 mL of the solution with Co(II) concentration of 0.1 µg mL^{-1} was passed through the mini-column filled with the sorbent with surface concentration of reagent of 14 µmol g^{-1} with the flow rate of 0.5, 1.0, 2.0, 3.0 or 5.0 mL min^{-1}. For the solution flow rates between 0.5 and 2.0 mL min^{-1} the length of colored zone was the same and was 2.5 ± 0.5 mm for 1.0 µg of cobalt. For the solution flow rates more than 3.0 mL min^{-1} the bottom edge of colored zone was eroded, leading to error rising in cobalt determination by the length of colored zone.

The length of the colored zone was not changed on passing through the mini-column different volumes of solutions (1.0 to 100.0 mL) with the same content of cobalt in solution volume equal to 1.0 µg at flow rate of 1 mL min^{-1}. Iron (II), copper(II), and nickel(II) ions are present at real samples and are also extracted by SiO_2-PHMG-NNS sorbent in dynamic mode, and they interfere with the visual determination of cobalt.

For decomposition of complexes of iron(II), copper(II), and nickel(II) with NNS 1.0, 2.0, and 6.0 mol L^{-1} hot (70°C) solutions of HNO_3 were used. After passing of 10.0 mL of 1 mol L^{-1} HNO_3 through the sorbent in a column complexes of iron(II), copper(II), and nickel(II) with NNS were decomposed, the reagent was desorbed, and the length of red colored zone remained unchanged. After passing through the column 2.0 mol L^{-1} HNO_3 the red colored zone two times lengthened. After passing through the column 6.0 mol L^{-1} HNO_3 the colored zone was eroded long the entire height of the sorbent in mini column and a partial desorption of cobalt(III) complex with NNS occurred, and eluate became red. 1 mol L^{-1} HNO_3 was chosen as an optimal one. This approach allows cobalt determination by the length (l) of colored zone of the sorbent in mini-column. The calibration function is as follows: l(mm) = (2.5±0.5)C, where C is cobalt content, µg.

Determination of cobalt in soils

The developed method of sorption-photometric determination of cobalt was applied for determination of mobile cobalt species in soils around the Tuvakobalt decommissioned plant for processing cobalt ore (Khovu-Aksy, the Tuva Republic, Russia). Soil samples were taken directly in the waste storage of the plant (Sample 1, Sample 2), at a distance of 300 m (Sample 3), 500 m (Sample 4), and 5 km (Sample 5) from it. In determination of cobalt content in soils sorbent with the surface concentration of the reagent 56 μmol g^{-1} was used. The accuracy of obtained results was confirmed by ICP-OES analysis (Table 3).

Table 3: Determination of cobalt in the soil using SiO$_2$-PHMG-NNS (n=5, P=0.95)

Sample	Found , x ± t$_p$S/√n, μg mL^{-1}	
	Proposed method	ICP- OES
Sample 1[a]	10.4 ± 0.5	10.67 ± 0.03
Sample 2[a]	12.5 ± 0.5	12.64 ± 0.03
Sample 3[b]	0.28 ±0.01	0.265 ±0.004
Sample 4[b]	0.10 ± 0.01	0.096 ±0.003
Sample 5[b]	0.065 ±0.003	0.064 ±0.002

Notes: [a]Sample volume: 0.5 mL
[b]Sample volume: 10 mL

Determination of cobalt in waters

The applicability of SiO2-PHMG-NNS was tested with various water samples. Water from rivers Elegest and Ongacha (the Tuva Republic, Russia) flowing near waste storage of the plant, water from river Us (Krasnoyarsk Krai, Russia), mineral water "Arjaan Suu" (the Tuva Republic, Russia) were chosen as real samples of water. The results are represented in (Table 4). The accuracy of the results was confirmed by recovery test of spiked samples of river water. There was a good agreement between the added and the found amounts of the analyte. The results indicate that the developed procedure can be applied for determination of cobalt in the various water samples.

Table 4: Determination of cobalt in the water samples using SiO$_2$-PHMG-NNS

Sample	Cobalt (ng mL^{-1})		Recovery (%)
River water[a]	Added	Found	
	0.0	ND	-
	10.0	9.9 ± 0.2	99
River water[b]	20.0	20.5 ± 0.4	102.5
	0.0	ND	-
	10.0	10.4 ± 0.4	104
	20.0	19.8 ± 0.5	99
River water[c]	0.0	4.8 ± 0.2	-
	5.0	9.9 ± 0.3	102
	10.0	15.0 ± 0.3	102
Mineral water	0.0	ND	-
	20.0	20.0 ± 0.3	100
	40.0	40.5 ± 0.5	101.2

Notes: sample volume: 20 mL.

Conditions: pH 6.2; 0.100 g sorbent; 530 nm
[a] River Elegest
[b] River Ongatcha
[c] River Us

Visual color-scale cobalt determination using SiO2-PHMG-NNS

For color scale preparation, from 0.01 to 10.0 μg of Co(II) as a solutions in 0.1 mol L^{-1} HCl were added into a series of test tubes; NaOH and acetic buffer solution up to pH 6.2 were added, and volume of solution was adjusted to 10.0 mL with deionized water. Then, 0.100 g of the sorbent with the surface concentration of 14 μmol g^{-1} was placed into a test tubes, and the solutions were strongly stirred for 10 min. Then, the solutions were decanted, 10.0 mL of hot (70°C) 1 mol L^{-1} HNO$_3$ was added to the sorbents in the test tubes and stirred for 20 min. The sorbent was then isolated from the solution by decantation, moved into fluoroplastic cell plate in the order of increasing concentrations of cobalt. Sorbent with unknown cobalt concentration after cobalt solid-phase extraction from natural waters or soil extracts was placed in the cell of separate fluoroplastic plate, which was moved along the color scale. The color of the sorbent was visually compared with the scale colors. Minimum quantity of copper that might be detected visually is 0.05 μg (using 0.100 g of the sorbent).

The photography of color scale for cobalt determination in three real samples is represented on the (Figure 8).
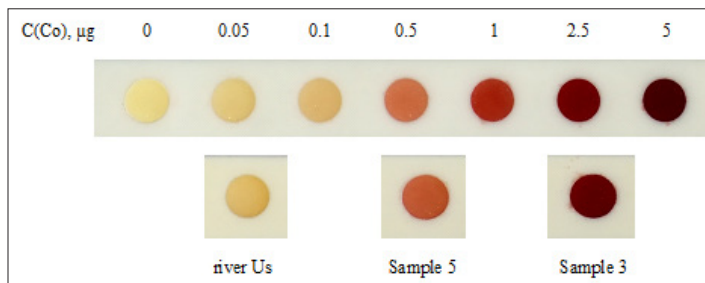
Determination of cobalt (II) in river water and soil extracts by the length of colored zone in mini-column

Mini-column filled with SiO$_2$-PHMG-NNS sorbent was used in cobalt determination in water of river Us and soil extracts Sample 3, Sample 4, Sample 5). River water (100.0 mL) or prepared soil extract (10.0 mL) at pH 6.2 was passed through the mini-column at flow rate of 2.0 mL min^{-1}. Then, 10.0 mL of hot 1 mol L^{-1} HNO$_3$ was passed in order to eliminate the interference of iron(II) and other metal ions. The content of cobalt was determined by the length of colored zone of the sorbent in mini-column. The results are represented in (Table 5).

Table 5: Determination of cobalt in the water and the soil samples using mini-column

Sample	Length of colored zone, mm	Cobalt content, μg per 0.100 g of the sorbent	Cobalt content in the sample, μg mL^{-1}
River Us[a]	1.0 ± 0.5	0.5±0.25	0.0050 ± 0.0025
Soil, Sample 3[b]	8.0 ± 0.5	3.0 ± 0.2	0.30 ± 0.02
Soil, Sample 4[b]	2.5 ± 0.5	1.0 ± 0.2	0.10 ± 0.02
Soil, Sample 5[b]	1.0 ± 0.5	0.5 ± 0.25	0.050 ± 0.025

Notes: [a] Sample volume 100.0 mL; b Sample volume 10.0 mL

Results obtained using mini-column are in good agreement (considering the error) with the results of developed sorption-photometric and ICP-OES determination.

Comparison with other methods
A comparison of the proposed procedure with other preconcentration systems which use various adsorbents for the determination of cobalt can be seen in (Table 6). Analytical features such as detection range, detection limits and precision are comparable to the methods presented in the literature [37,38,40,42,44,46-49].

Table 6: Comparison of the results of the proposed method with the other published works for the determination of cobalt

Solid support	Spectrophotometric agent	Samples	Detection range (μg mL^{-1})	LOD (ng mL^{-1})	Volume solution (mL)	RSD %	Ref.
Cobalt(II) sorption as a complex with organic reagent							
Waters Porapak Sep-Park C18 disk	N,N'-disalicylidene-ethylenediamine	Drinking water	0.01-0.4	10	250	2.54	[46]
C18 disk	5-(2-benzothiazolylazo)-8-hydroxyquinolene	Biological, water, soil and pharmaceutical preparation samples	0.01–0.38	3.1	100	1.37	[47]
C18 disk	2-(2-quinolinylazo)-5-diethylaminoaniline	Biological samples, water	0.01-0.6	0.02	200	1.18	[48]
Silochrom C-80 – TPPS	1-nitroso-2-naphthol-3.6-disulfonic acid	Tap waters, alloy samples	0.0025-0.05	2.5	200	-	[40]
Cobalt (II) sorption by immobilized surface of the sorbent							
Chitosan film	1-nitroso-2-naphthol-3.6-disulfonic acid	Waste water, SUT water reservoir	1-60 0.035-0.40	820 12	3 300	1.7 0.41	[49]
Cellulose acetate membrane	pyrogallol red immobilization	pyrogallol red immobilization	0.1 – 8.97	21	-	0.8 – 2.1	[37]
Amberlite XAD-7	2-(4-pyridylazo)resorcinol (PAR)	2-(4-pyridylazo) resorcinol (PAR)	0.01 – 1000	20	-	1.78	[38]
Amberlite CG-400	1-nitroso-2-naphthol-3.6-disulfonic acid	Natural water	0.06 – 0.24 0.0075 – 0.05	27 1.8	50 400	7.6 6.6	[44]
Silochrom C-120 - PHMG	1-nitroso-2-naphthol-3.6-disulfonic acid (NRS)	Soil samples	0.01 – 0.5	5.0	10	7.0	[42]
Silochrom C-120 - PHMG	2-nitroso-1-naphthol-4-sulfonate (NNS)	River water, soil samples	0.005 – 0.5	1.0	10	5.4	This work

Conclusion
In the present work the possibility of preparation a new sorbent based on silica non-covalently modified with polyhexamethylene guanidine and nitroso-N-salt was considered. The procedure of preparation of suggested sorbent is simple, fast, cost-effective and uses available reagents. The limit of detection of developed sorption-photometric method is comparable with the limit of detection of ICP-OES determination; the obtained results have good accuracy and reproducibility. Application of the sorbent with functional groups of NNS allows two times reduce the detection limit of cobalt determination compared with limit of detection of cobalt determination using silica modified with PHMG and NRS [42]. Application of mini-column filled with SiO2-PHMG-NNS sorbent allows rapid and reliable visual estimation of cobalt content in natural waters and soil extracts in the field.

Acknowledgment

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