

SELECTIVE EXTRACTION-SPECTROPHOTOMETRIC METHOD FOR DETERMINING COBALT WITH 1-(2- PYRIDILAZO)-2-NAPHTHOLE (PAN)

¹Rakhmatullaeva Nargiza Tulkunovna, ²Giyasov Anvar Sharipovich, ³Shokhakimova
Aziza Alimdzhanovna, ⁴Otakuzieva Vazira Usmonjonovna

^{1,2,3}Tashkent State Technical University, Tashkent

⁴Tashkent State Technical University, Kokand branch, Tashkent

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Abstract. *The conditions for selective extraction of cobalt (II) with inert organic solvents from a strongly acidic medium in the presence of dimethylformamide (DMF) and its complexation with the PAN reagent directly in the organic phase were studied. As a result, a selective extraction-spectrophotometric method for the determination of cobalt with PAN was developed. The developed method is recommended for the determination of cobalt from ores, concentrates, steels and other materials with complex chemical compositions without prior separation of associated elements.*

Keywords: *selective, ecoanalytical, extraction-photometric, extraction-spectrophotometric, spectra of extracts, equilibrium shift method, solvation number, hydrate-solvation mechanism.*

Introduction. The development of science, industry and the introduction of new technological processes leads to increasing environmental pollution. Increasing requirements for environmental protection in the Republic put forward the task of analytical chemists to develop simple, rapid, sensitive and selective methods for determining microconcentrations of substances, in particular heavy and toxic elements that are ecotoxicants.

Considering the ever-increasing scale of production and use of heavy toxic metals, their high toxicity and carcinogenicity, the ability to accumulate in the human body and have harmful effects even in low concentrations, these chemical pollutants are considered a priority. Such ecotoxicants also include copper, cadmium, cobalt, nickel and other elements. Therefore, the search for selective ecoanalytical methods for determining cobalt in materials with complex chemical composition is an urgent task.

Methods and materials. Modern environmental analytical methods of analysis, such as chromatography-spectrometry, chromatography-mass spectrometry, atomic absorption, plasma, X-ray fluorescence, etc., do not always allow solving this problem due to the complexity and inaccessibility of the equipment.

Existing photometric and extraction-photometric methods for the determination of cobalt using organic dyes [1, 2, 3] are highly sensitive, but poorly selective. Since the complexation of cobalt with organic reagents in the above methods is carried out in an aqueous solution. In this case, many accompanying ions form complex compounds and interfere with the determination of cobalt.

To increase the selectivity of methods for determining elements, extraction of colorless complexes of elements with inert organic solvents is used, followed by the addition of organic

dyes to the extract and the formation of colored complex compounds as a result of the interaction of metal ions with organic dyes directly in the organic phase [4, 5].

This work discusses a new, selective and simple method based on the extraction of cobalt thiocyanate complex with inert organic solvents and its complexation with PAN directly in the organic phase.

Experimental part. A stock solution of cobalt 2 mg/ml was prepared from $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ grade "xk" by weight. The solution titer was determined potentiometrically by titration with potassium bromate [6]. A chloroform solution of PAN (Reanal, BHP) was used. The spectra of cobalt complexes and the reagent were recorded on an SF-26 spectrophotometer ($l=1$ cm). The optical densities of the complexes were measured on an SF-26 spectrophotometer, and the pH of the solutions was controlled on a pH-340 pH meter.

Cobalt(II) from a solution containing H_2SO_4 , thiocyanate ions and dimethylformamide (DMF), easily extracted with chloroform. Study of cobalt (II) extraction with chloroform depending on concentration H_2SO_4 , thiocyanate ions and DMF showed that the optimal conditions for cobalt extraction are: 1,25–3,5 M H_2SO_4 , 0,5–3,0 M potassium thiocyanate, 0,13–0,3 M DMF selectively extracted with chloroform by shaking the phases for 3-5 s. With equal volumes of the aqueous and organic phases, the recovery of cobalt during a single extraction is 99.9% and does not change until the phase volume ratio is 40:1.

The composition of the extracted cobalt(II) thiocyanate complex was determined by the equilibrium shift method [7]. For this purpose, the dependence of the distribution coefficient of cobalt (II) on the concentration of sulfuric acid (0.05–1.50 M) was studied at constant concentrations of potassium thiocyanate (1 M), DMF (0.2 M) and ionic strength ($\mu = 1,3$); potassium thiocyanate (0,05–0,7 M), at constant concentrations of sulfuric acid (2 M), DMF (0,2 M) and ionic strength ($\mu = 1,3$); DMF (0,02–0,15 M), at constant concentrations of sulfuric acid (2 M), potassium thiocyanate (1 M) and ionic strength ($\mu = 1,3$).

The cobalt concentration in the extract was determined by the photometric method with the PAN reagent.

Results and its discussion. The obtained data show that in logarithmic coordinates $\lg D_{\text{Co}^{+2}} - \lg C_{\text{H}^+}$, $\lg D_{\text{Co}^{+2}} - \lg C_{\text{CNS}^-}$, $\lg D_{\text{Co}^{+2}} - \lg C_{\text{DMF}}$ (where D – distribution coefficient, C – equilibrium concentration) there is a linear relationship with the slopes of the straight lines equal to 2, 4 and 4, respectively (Tables 1, 2, 3 and Fig. 1, 2, 3).

Table 1

Determination of the number of hydrogen ions involved in the extraction of cobalt with chloroform. $A_{\text{np}} = 0,53$; $(C_{\text{Co}} = 1,695 \cdot 10^{-4} \text{ M})$

| $C_{\text{H}_2\text{SO}_4}, \text{ mol}$ | A | D | $\lg D$ | $-\lg C_{\text{H}_2\text{SO}_4}$ |
|--|-------|-------|---------|----------------------------------|
| 0,05 | 0,330 | 1,524 | 0,183 | 1,301 |
| 0,06 | 0,347 | 1,896 | 0,278 | 1,255 |
| 0,07 | 0,360 | 2,120 | 0,326 | 1,155 |
| 0,08 | 0,385 | 2,655 | 0,424 | 1,097 |
| 0,10 | 0,410 | 3,417 | 0,534 | 1,000 |
| 1,12 | 0,426 | 4,096 | 0,612 | 0,921 |

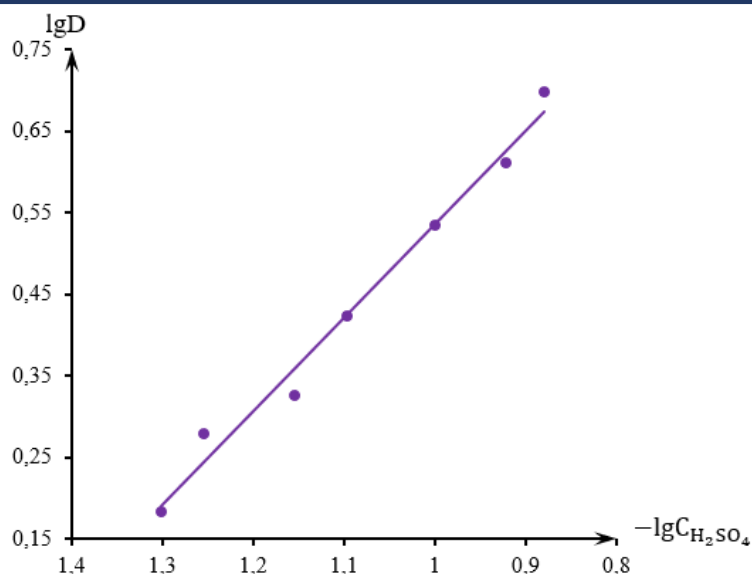


Figure. 1. Determination of the number of hydrogen ions involved in the extraction of cobalt with chloroform using the equilibrium shift method. $V_o = 10 \text{ ml}$; $l = 1 \text{ cm}$

Table 2

Determination of the number of thiocyanate ions involved in the extraction of cobalt with chloroform

| $C_{\text{KCNS}}, \text{ mol}$ | A | D | $\lg D$ | $-\lg C_{\text{KCNS}}$ |
|--------------------------------|-------|---------|---------|------------------------|
| 0,05 | 0,225 | 0,6923 | -0,160 | 0,222 |
| 0,10 | 0,328 | 1,4774 | 0,169 | 0,097 |
| 0,15 | 0,410 | 2,9285 | 0,467 | 0,0 |
| 0,20 | 0,460 | 5,1111 | 0,708 | -0,079 |
| 0,25 | 0,510 | 12,7500 | 1,105 | -0,146 |
| 0,30 | 0,525 | 22,0000 | 1,342 | -0,204 |
| 0,40 | 0,535 | 33,2540 | 1,512 | -0,313 |
| 0,50 | 0,500 | 40,2800 | 1,740 | -0,400 |

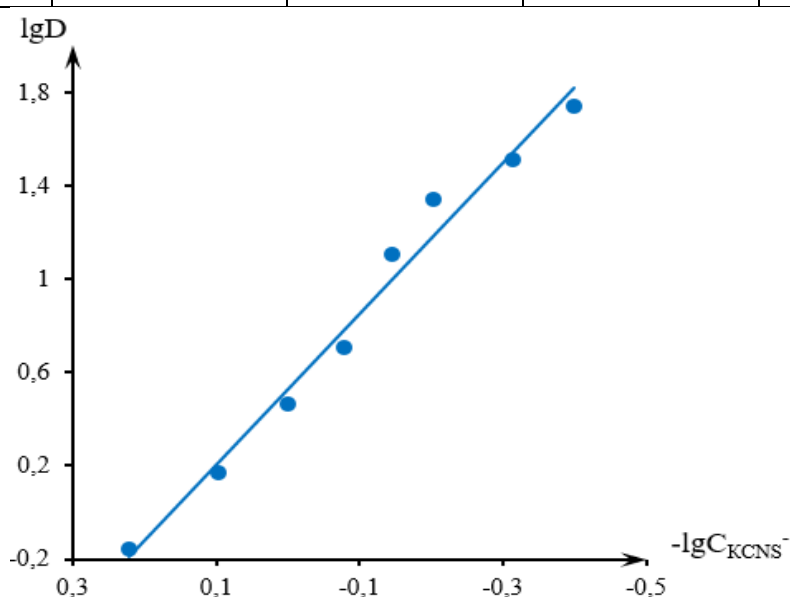


Figure. 2. Determination of the number of thiocyanate ions involved in the extraction of cobalt with chloroform.

Table 3

Determination of the number of DMF molecules involved in the extraction of cobalt with chloroform

| C_{DMF} | A | D | $\lg D$ | $-\lg C_{DMF}$ |
|-----------|-------|--------|---------|----------------|
| 0,1324 | 0,167 | 0,450 | -0,3372 | 0,880 |
| 0,2698 | 0,332 | 1,677 | 0,2246 | 0,580 |
| 0,3972 | 0,350 | 1,944 | 0,4487 | 0,450 |
| 0,5296 | 0,440 | 4,889 | 0,6832 | 0,276 |
| 0,6620 | 0,468 | 7,548 | 0,8779 | 0,179 |
| 0,7944 | 0,480 | 9,600 | 0,9823 | 0,100 |
| 0,9268 | 0,500 | 16,667 | 1,2221 | 0,003 |

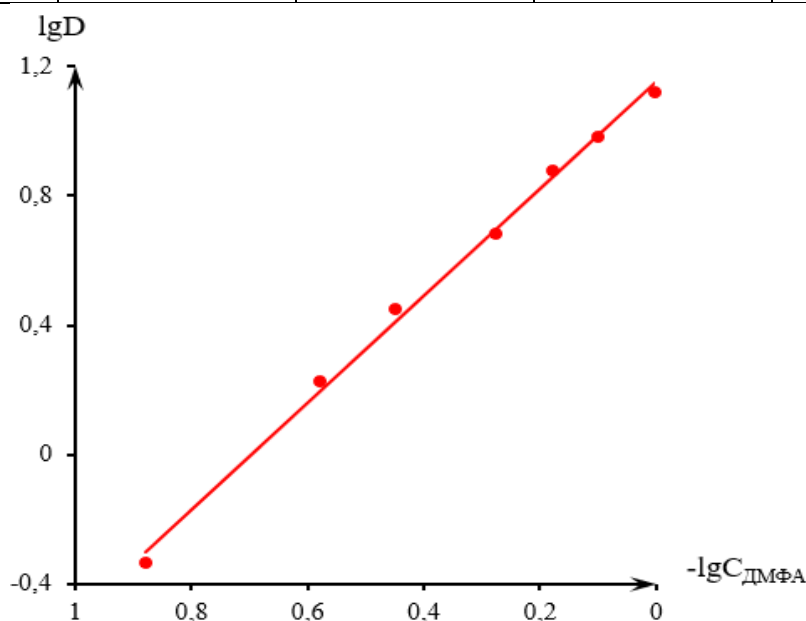
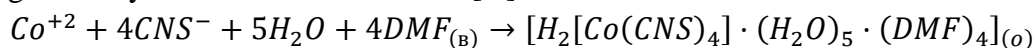


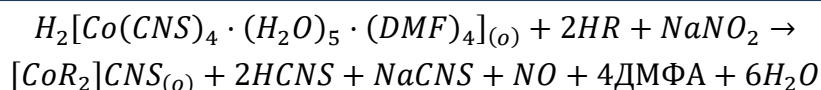
Figure. 3. Determination of the number of DMF molecules involved in the extraction of cobalt with chloroform.

Consequently, cobalt is extracted by chloroform in the form $H_2[Co(CNS)_4]$; solvate number $H_2[Co(CNS)_4]$ in the extract is 4. The number of water molecules bound in chloroform, determined by spectrophotometry [8], is 5. Based on experimental data, apparently, the cobalt thiocyanate complex from acidic solutions in the presence of DMF is extracted with chloroform according to the hydrate-solvate mechanism [6].



After extraction of cobalt with chloroform, we studied the conditions for the complexation of cobalt with the reagent with PAN directly in the organic phase. The study showed that when adding the PAN reagent, a buffer solution containing 0.2% sodium nitrite, to the extract of the cobalt thiocyanate complex to oxidize cobalt (II) ions to cobalt (III) and shaking the phases for 10-15 s, the ions cobalt (III), simultaneously interacts with PAN and a colored complex compound is formed directly in the organic phase. Then the colored extract is treated with an ammonia acetate solution containing 10% sodium sulfite (to prevent the formation of turbidity in the extract).

Consequently, the reaction of cobalt complexation with PAN in the organic phase can be briefly represented by the following scheme:



The cobalt complex with PAN is stable for more than 24 hours. The absorption spectrum of cobalt with PAN in the extract has two maxima at 590 and 640 nm. (Fig. 4). The apparent molar absorption coefficient is $2,4 \cdot 10^4$ and $2,0 \cdot 10^4$ respectively. The cobalt complex with PAN obeys Beer's law in the range of 2–200 µg of cobalt in 10 ml of extract. Reproducibility of determination is in the range of 2-5%.

It has been established that complete complexation of cobalt with PAN occurs in the pH range = 3-5.5. Using the equilibrium shift method [7], it was found that cobalt (III) interacts with PAN in the organic phase in a molar ratio of 1:2 (Table 4, Fig. 4).

Table 4

Determination of the composition of the cobalt complex with PAN
equilibrium shift method. $C_{Co} = 1,77 \cdot 10^{-5}$ M. $l = 1$ sm.

| $C_{PAN}, M \cdot 10^5$ | A | D | lg D | $[PAN]_{equal} \cdot 10^5, M$ | $-\lg [PAN]_{equal}$ |
|-------------------------|------|---------|---------|-------------------------------|----------------------|
| 1,184 | 0,10 | 0,1886 | -0,7244 | ≈ 0,9050 | 5,0443 |
| 2,368 | 0,20 | 0,4651 | -0,3324 | 1,8060 | 4,7433 |
| 3,552 | 0,28 | 0,8000 | -0,0969 | 2,7654 | 4,5583 |
| 4,736 | 0,43 | 2,1500 | 0,3324 | 3,5280 | 4,4525 |
| 5,920 | 0,48 | 3,2000 | 0,5051 | 4,5715 | 4,3400 |
| 11,184 | 0,59 | 14,7500 | 1,1687 | 10,1824 | 3,9922 |
| 17,768 | 0,61 | 30,5000 | 1,4843 | 16,0420 | 3,7500 |
| 23,680 | 0,61 | | | | |

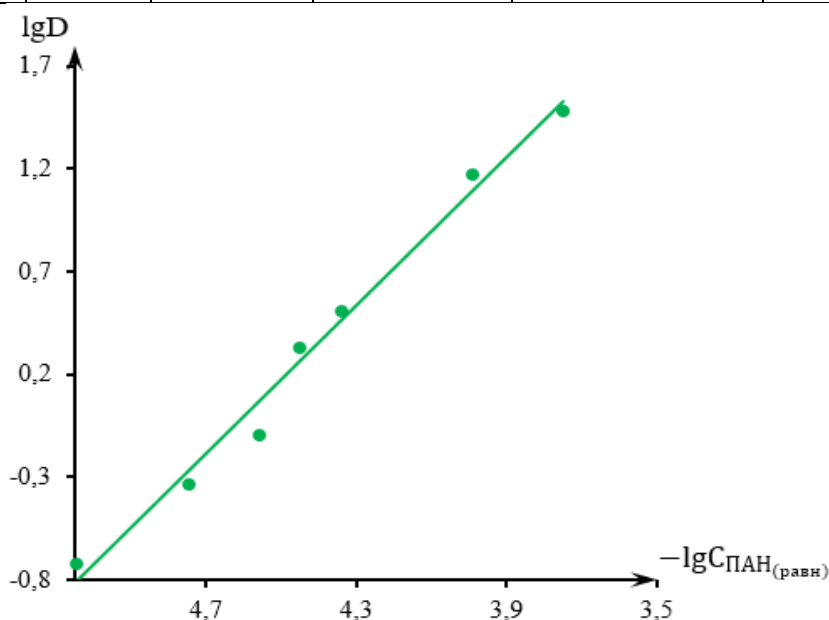


Figure. 4. Determination of the composition of the cobalt complex with PAN by the equilibrium shift method.

$$C_{Co} = 1,77 \cdot 10^{-5} \text{ M}; l = 1 \text{ cm.}$$

Method for determining cobalt in pure solutions. The test solution containing 2–200 µg of cobalt is added to a measuring cylinder (25 ml) with a ground-in stopper add 3 ml of 2 M sulfuric

acid, 1 ml of 10 M potassium thiocyanate and the volume of the solution is adjusted to 8.5 ml with water, add 1.5 ml of DMF, 5 ml of chloroform and shake for 3-5 seconds. The mixture is transferred to another separatory funnel. Add 5 ml of 0.06% chloroform solution of PAN and 2 ml of acetate buffer solution with pH 4 containing 0.2% sodium nitrite to the extract and shake for 10-15 seconds. The resulting colored extract is poured into another separatory funnel, and again 2 ml of an acetate buffer solution with pH 4 containing 10% sodium sulfite is added to the extract and shaken for 10-15 seconds. The colored extract is filtered through filter paper and photometered relative to the blank solution.

Then we studied the influence of foreign ions under optimal conditions for the extraction of cobalt (II) and its complexation with PAN directly in the organic phase.

Experiments have shown that under optimal cobalt extraction conditions, lead (II), copper (II), palladium (I), iron (III), bismuth (III), gold (III), rhodium (III), chromium (III) ions are partially extracted), arsenic (III), titanium (IV), selenium (IV), vanadium (V), uranium (VI), molybdenum (VI), tungsten (VI). However, under the conditions of complexation of cobalt with PAN in the organic phase, the above ions do not form complex compounds and do not interfere with the determination.

The determination of cobalt with PAN is interfered with by copper, iron, bismuth and tungsten ions in large multiples. The interfering influences of iron and bismuth are eliminated by adding sodium fluoride and thiourea to the buffer solution; copper and tungsten are eliminated by adding thiourea and tartaric acid to the extraction mixture. The influences of many foreign ions on the determination of cobalt with PAN have also been studied and are shown in Table 5.

Table 5

***Determination of cobalt with PAN in the presence of foreign ions
(25 mcg cobalt taken)***

| M | M/Co | M | M/Co | M | Co |
|---------|--------------------|----------|--------------------|------------------------------|--------------------|
| Ag (I) | 4 000 | Au (III) | 400 | Cr (VI) | 2 000 |
| Zn (II) | 200 | Rh (III) | 400 | W (VI) | 200 |
| Pb (II) | 20 000 | Ru (III) | 400 | W (VI) | 1 000 ³ |
| Cu (II) | 4 000 ¹ | In (III) | 4 000 | Te (VI) | 4 000 |
| Mn (II) | 20 000 | Ga (III) | 20 000 | Mn (VII) | 4 000 |
| Cd (II) | 40 000 | Cr (III) | 1 000 | Os (VIII) | 400 |
| Hg (II) | 8 000 | La (III) | 4 000 | F ⁻ | doesn't interfere |
| Ca (II) | 20 000 | Ti (IV) | 2 000 | Cl ⁻ | doesn't interfere |
| Ba (II) | 20 000 | Ti (IV) | 8 000 ² | Br ⁻ | doesn't interfere |
| Mg (II) | 40 000 | Zr (IV) | 20 000 | I ⁻ | doesn't interfere |
| Pd (II) | 400 | Se (IV) | 2 000 | NO ₃ ⁻ | doesn't interfere |

| | | | | | |
|----------|--------------------|---------|-------|---|-------------------|
| Be (II) | 2 000 | Th (IV) | 2 000 | PO ₄ ⁻³ | doesn't interfere |
| Ni (II) | 20 000 | Pt (IV) | 2 000 | C ₂ O ₄ ⁻² | doesn't interfere |
| Al (III) | 40 000 | As (V) | 1 000 | CH ₃ COO ⁻ | 5 000 |
| Fe (III) | 4 | Sb (V) | 1 000 | S ₂ O ₃ ⁻² | doesn't interfere |
| Fe (III) | 400 ² | V (V) | 200 | ЭДТА | doesn't interfere |
| Tl (III) | 2 000 | Nb (V) | 1 000 | Thiourea | doesn't interfere |
| Bi (III) | 40 | U (VI) | 400 | Wine acid | doesn't interfere |
| Bi (III) | 8 000 ¹ | Mo (VI) | 2 000 | Limon acid | doesn't interfere |
| | | | | Ascorbic acid | doesn't interfere |

M – ion or compound; M/Co – permissible mass ratio to cobalt;

1 – in the presence of 100 mg thiourea; 2 – in the presence of 150 mg NaF in buffer;

3 – in the presence of 200 mg of tartaric acid.

The developed method for the extraction-spectrophotometric determination of cobalt (II) with PAN was tested in the analysis of model solutions compiled according to the type of rocks and ores of the Almalyk Mining and Metallurgical Plant, also in steels and ores.

To determine cobalt with PAN in model solutions, aliquots (0.5–4 ml) of the model solution are taken into a measuring cylinder (25 ml) with a ground stopper and then proceed according to the procedure for determining cobalt with PAN in pure solutions (Table 6).

Table 6

Results of determination of cobalt (II) in model solutions composed according to the type of ores and rocks of the Almalyk production (n = 4; P = 0.95)

| Name and No. sample | Certified Chem. composition of Art. samples, % | ($x \pm \Delta x$), % | S_r |
|-----------------------------|---|-------------------------|-------|
| Cobalt-nickel ore № 1347-78 | SiO ₂ – 31; TiO – 0,192; Al ₂ O ₃ – 7,1; Fe ₂ O ₃ – 6,03; MnO – 0,25; CaO – 18,7; MgO – 4,24; Zn – 0,039; Ni – 1,57; Cu – 0,39; As – 5,77; S – 0,4; Co – 1,13 | -1,120 ± 0,024 | 0,013 |
| Scarn copper ore № 48-85 | SiO ₂ – 33,77; Ti – 0,882; Al ₂ O ₃ – 5,47; Fe – 15,9; CaO – 29,75; MgO – 0,66; MnO – 0,36; P ₂ O ₅ – 0,11; K ₂ O – 0,13; Na ₂ O – 0,01; CO ₂ – 2,73; Cu – 1,98; Mo – 0,02; Co – 0,43 | 0,450 ± 0,016 | 0,022 |

| | | | |
|-------------|--|----------------|-------|
| Breed № 519 | SiO ₂ – 49,1; Ti – 1,11; Al ₂ O ₃ – 7,1; FeO – 10,26; Mn – 0,21; CaO – 10,2; MgO – 5,74; Na ₂ O – 2,49; K ₂ O – 0,7; P ₂ O ₅ – 0,21; H ₂ O – 0,97; W – 0,0007; Nd – 0,0015; Zn – 0,015; F – 0,023; Co – 0,046 | 0,05 ± 0,003 | 0,037 |
| Breed № 521 | SiO ₂ – 46,4; Ti – 1,026; Al ₂ O ₃ – 14,88; Fe ₂ O ₃ – 11,66; MnO – 7,0; Na ₂ O – 2,82; K ₂ O – 2,96; P ₂ O ₅ – 1,01; H ₂ O – 0,83; Nd – 0,007; W – 0,0001; Zn – 0,012; As – 0,001; Co – 0,018 | 0,026 ± 0,0016 | 0,041 |

Method for determining cobalt in steels. Place a sample (0.1–0.3 g) in a conical flask (250 ml), add 10 ml of hydrochloric acid and 3 ml of nitric acid (pl = 1.4) and evaporate to wet salts, add 30–40 ml of 4 M sulfuric acid and stir, then transfer to a volumetric flask (100 ml). The solution is diluted with 4 M sulfuric acid to the mark. An aliquot of the solution is taken into a measuring cylinder (25 ml) with a ground stopper and determined according to the method for determining cobalt with PAN in pure solutions (Table 7).

Table 7

Results of determination of cobalt with PAN in steels (n = 4; P = 0,95)

| Steel standard number | Certified cobalt content of steel, % | (x ± Δx), % | Δx/x · 100, % |
|-----------------------|--------------------------------------|---------------|---------------|
| 156 | 10,50 | 10,52 ± 0,14 | 1,33 |
| 157 | 5,47 | 5,48 ± 0,11 | 2,01 |
| 158 | 10,35 | 10,34 ± 0,155 | 1,49 |
| 164 ^a | 4,36 | 4,38 ± 0,05 | 1,14 |

Methodology for determining cobalt in ores. A sample (0.5–1.0 g) is placed in a platinum cup, 1–2 ml of 70% perchloric acid, 3–5 ml of water and 5–10 ml of hydrofluoric acid (35%) are added. Heat on hotplate and evaporate twice to moist salts. Add 10–15 ml of 2 M hydrochloric acid to the residue and heat, if necessary, to dissolve all substances. The solution is filtered through a paper filter into a volumetric flask (50–100 ml). The filtrate is diluted with water to the mark and the cobalt content is determined from an aliquot of the solution using the method for determining cobalt with PAN in pure solutions, adding masking agents to the solution (Table 8).

Table 8

Results of determination of cobalt with PAN in ores (n = 4; P = 0,95)

| Steel standard number | Certified cobalt content of steel, % | (x ± Δx) · 10 ² , % | S _r |
|-----------------------|--------------------------------------|--------------------------------|----------------|
| 1347-78 | 1,130 | 115,00 ± 2,76 | 0,015 |
| 3032-84 | 0,200 | 22,00 ± 0,62 | 0,018 |
| 616-75 | 0,094 | 9,10 ± 0,30 | 0,021 |
| 3597-86 | 0,170 | 15,60 ± 0,59 | 0,024 |
| 90131-78 | 0,025 | 3,00 ± 1,86 | 0,389 |

Thus, the developed method is recommended for the analysis of ores, concentrates, steels and other materials with complex chemical compositions without preliminary separation of associated elements.

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