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LIQUID-LIQUID EXTRACTION AND SPECTROPHOTOMETRIC CHARACTERIZATION OF SOME NEW ION-ASSOCIATED COMPLEXES OF Co(II) WITH INT: APPLICATION OF THE DEVELOPED METHOD FOR ANALYSIS OF SOIL COBALT CONTENT

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Abstract. The study presents a newly-developed method for extraction-spectrophotometric determination of Co(II) in samples by means of iodnitrotetrazolium chloride. The electronic spectrum of cobalt ion associated has a peak at 630 nm. At that wavelength the absorption is maximum. The ratio INT: $[Co(SCN)_4]$ in the triple ion-associate complex was 2:1, and due to the good solubility of the Co(II) ion associated and INT in 1,2 dichloroethane, maximum extraction in the organic phase was achieved after 30 s extraction. The molar absorptivity of the studied ion associate $INT_2[Co(SCN)_4]$ was $\varepsilon_{630} = 0.6\times10^3$ dm^3 mol^{-1} cm^{-1}. Sendel's sensitivity of the method was 9.8×10^{-2} mg cm^{-2}. The maximum quantity of Co extracted with INT was achieved at pH 2-7. The relationship between Co(II) concentration and absorption was linear in the range of 6 – 125 mg Co(II) in 10 cm^{-3} aqueous solutions.

Keywords: Co; determination; INT; soils; spectrophotometry

Introduction

It is widely known that Co content in agrochemical objects is insignificant (Sandell, 1959; Meyers, 2000; Cucinotta et al., 2008; Makarova & Kupalina, 2015; Toncheva et al., 2016; Çiftci et al., 2009). The scientific literature presents many methods for separation, preconcentration and determination of cobalt in samples (Makarova & Kupalina, 2015; Toncheva et al., 2016; Tewari, 2009; Sabil et al., 2009; Pouretedal et al., 2009; Çiftci , 2010; Berton & Wuilloud, 2011; Boggs et al., 2012; Divarova et al., 2013). The widely applied methods for determination of the element content are photo colorimetric, polarographic and spectral. Extraction-photometric methods are applied for determination of ultra-small Co quantities in agrochemical objects. Their major advantages are simplicity, rapidity and accessibility. In the analytical practice, the reaction between Co(II) and nitroso-R-salt is widely used. One of the base factors that reduces the precision of the photometric determination of Co micro quantities in soil samples is the presence of colored organic compounds, as well as Fe, Ni and Cu salts.

Till now literature presents only a few methods for Co determination in soil and plants. The following reagents are used: 1,10–phenantrolyne and eozine, thiodibenzoylmethane, picraminazo-4-cyclohexilrezorcine, diantipirilmethane, 2-(2-benzthiazolylazo)-5-dymethilaminobenzoic acid. Some of these methods require exact working pH and preliminary samples staying before Co determination. Other methods characterize with low sensibility and selectivity. Another method for quantitative determination of Co includes heating to 80° C. Besides, the complex formed is stable for only 20 min.[1-13]

The aim of the present study was the development of extraction-spectrophotometric method for Co(II) determination in soils, with selectivity and expressivity exceeding most of the up-to-date applied methods. The structure formula of INT is presented in Fig. 1.

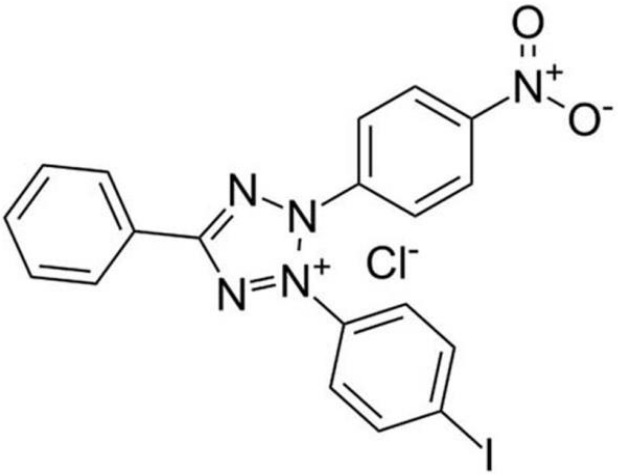

Fig. 1. Structure formula of INT (IUPAC name: *3-(4-Iodophenyl)-2-(4-nitrophenyl)-5-phenyl-2H-tetrazol-3-ium chloride;* Other names: *2-(4-Iodophenyl)-3-(4-nitrophenyl)-5-phenyltetrazolium chloride; Iodonitrotetrazolium chloride*, *INT*

For accomplishment of this goal the following objectives should be fullfilled: (I) to investigate the solubility of the ion-associated thiocyanate complex of Co(II) with iodnitrotetrazolium chloride (INT) in different organic solvents, to select the most appropriate of them; (II) to study the effect of pH; (III) to investigate the time necessary for Co extraction, and to estimate the time necessary for full metal extraction in organic phase in the form of ionic associate; (IV) to study the effect of the concentrations of the reagents participating in the extraction equilibrium of the system: the optimal established quantity of each of them would guarantee full extraction of Co(II) in the investigated monotetrazolium salt; (V) to assess the selectivity of the developed method towards side ions, their effect on the Co extraction and determination has to be analyzed.

Materials and methods

Apparatus

Absorbance measurements were made on a UV - VIS spectrophotometer, Germany, with a 1 cm quartz cuvette, 630 nm.

Reagents

The reagents applied were of analytical grade (p.a. Merck and Fluka).All solutions were prepared with distilled demineralized water.

Extraction procedure

In a separating funnel of 100 ml the following solutions: 1 cm^{-3} Co(II) 1×10^{-3} mol dm^{-3}, 1 cm^{-3} 4 mol dm^{-3} potassium thiocyanate, 7 cm^{-3} iodnitrotetrazolium chloride (INT) 1.5×10^{-3} mol dm^{-3} were added. Distilled water was added to the water phase to 10 cm^{-3}volume. The following step was extraction with 3 cm^{-3} 1,2-dichlorethane for 30 s. After delamination of the two phases, the organic phase was transferred through a paper filter into a cuvette b = 1 cm and subjected to photometric analyzes at 630 nm on UV - VIS spectrophotometer.

Results and discussion

Optimal condition

The extraction of the Co ion associate in different organic solvents: methyl ethyl ketone, 1,2-dichlorethane, chloroform, benzene, toluene, tetrachloromethane and diethyl ether, was studied.

The most appropriate organic solvent was chosen on the base of these investigations. 1,2-dichloroethane was the most suitable. The electronic spectrum of the cobalt ion associate had a maximum at 630 nm (Fig. 2). The maximum absorption was detected at this wavelength.

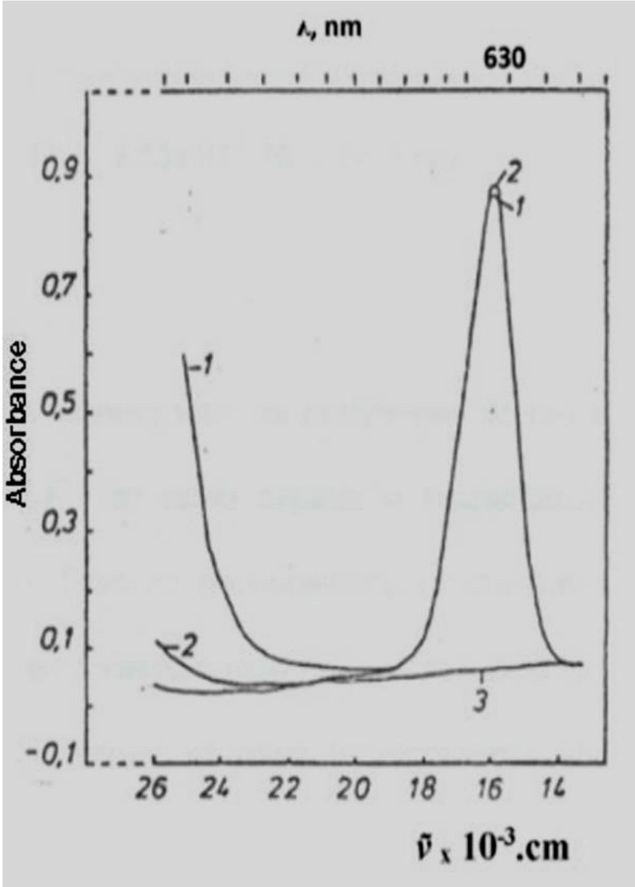

Fig. 2. 1 – Electron spectrum of $INT_2[Co(SCN)_4]$ in methyl ethyl ketone. Concentrations in the aqueous phase before extraction:$C_{Co(II)} = 8.25\times10^{-4}$ mol dm^{-3}, $C_{INT} = 1.65\times10^{-3}$ mol dm^{-3}, $C_{SCN} = 0.67$ mol dm^{-3}, b = 1 cm; 2 – Electron spectrum of $[Co(SCN)_4]^{2-}$ in methyl ethyl ketone. Concentrations in the aqueous phase before extraction: $C_{Co(II)} = 8.25\times10^{-4}$ mol dm^{-3}, $C_{SCN} = 0.67$ mol dm^{-3}, b = 1 cm; 3 – Electron spectrum of INT in dichloroethane. Electronic spectrum of INT in dichloroethane. Concentration in the aqueous phase before extraction of INT – 1.65×10^{-3} mol dm^{-3}, b = 1 cm

The bond in the molecule of the obtained ion associate, formed $[Co(SCN)_4]^{2-}$ and the tetrazolium salt was electrostatic. This was confirmed by the electronic spectra readings of the ion associate, and those of the constituent components (Fig.

2). Studies had shown that there was no shift in the absorption bands of the compounds. The spectra of the three-ion-associated complex and the thiocyanate complex ion had absorption bands at the same wavelength. This indicates that the bond is not coordinative.

Composition of the triple ion-associated complex

The composition of the triple ion-associated complex was proven by the Ostromislensky – Job method (Bulatov & Kalinkin, 1972). The present investigation displayed that the relationship INT: $[Co(SCN)_4]$ was 2:1 (Fig. 3).

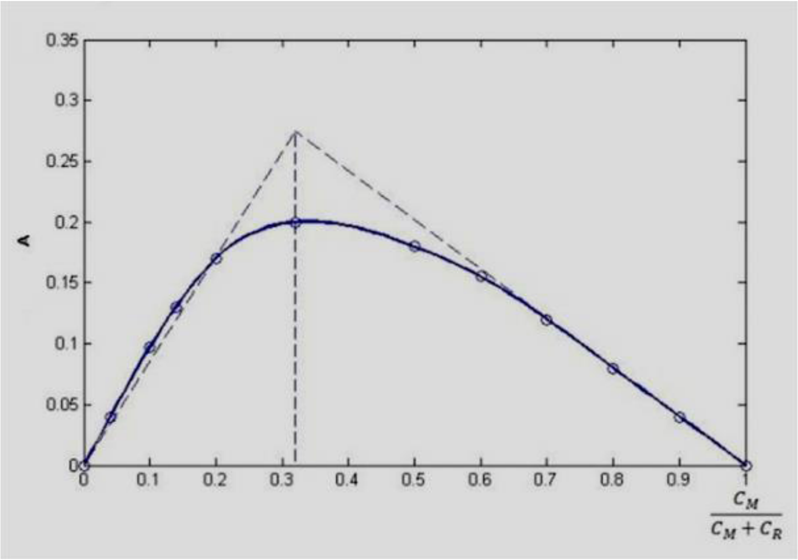

Fig. 3. Graphical determination of the molar ratio of the complex $INT_2[Co(SCN)_4]$ according to Ostromislensky – Job method: $C_{SCN} = 0.67$ mol dm^{-3}, b = 1 cm, $l_{max} = 630$ nm

Extraction time

The effect of time as a factor for achieving extraction equilibrium between the two phases was studied. Due to the good solubility of the ion-associated complex of cobalt (II) and INT in 1,2-dichloroethane, maximum extraction of the organic phase was obtained at 30 s extraction (Fig. 4).

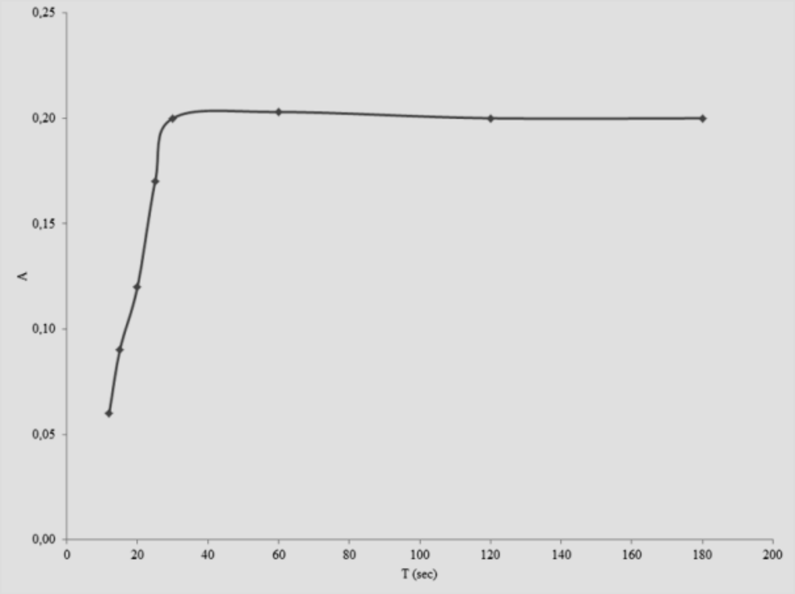

Fig. 4. Relationship between the change of light absorption and extraction time of the complex $INT_2[Co(SCN)_4]$: $C_{Co(II)} = 1\times10^{-4}$ mol dm^{-3}, $C_{INT} = 4\times10^{-4}$ mol dm^{-3}, $C_{SCN} = 0.8$ mol dm^{-3}, b = 1 cm

Determination of the molar absorbance of the ion triple associated thiocyanate complex of cobalt (II) and INT

Molar absorbance of the ion associate $INT_2[Co(SCN)_4]$ was determined by the method of Komar-Tolmachov (Bulatov & Kalinkin, 1972). The molar absorbance was determined by measuring of the light absorbance of solution with different concentration of the reagents at constant stoichiometry. The data from the experimental analyzes are presented in Table 1.

Table 1. Determination of the molar absorptivity of the ion-associated complex

Co(II) - 1.10^{-3} mol dm^{-3}	$C_{Co(II)}$	A	C.l / A = ε^{-1}	10^{-3}. ε^{-1}	$1/\sqrt[n+1]{A^n}$
0.1	0.00001	0.020	0.0005	0.50	7.09
0.2	0.00002	0.030	0.0007	0.76	5.78
0.8	0.00008	0.080	0.001	1.00	3.78
2	0.0002	0.160	0.00125	1.25	2.67

The molar absorbance of the studied ion associate $INT_2[Co(SCN)_4]$ was $e_{630} = 0.6\times10^3$ dm^3 mol^{-1} cm^{-1}. The sensitivity of the method according to Sendel [1] was 9.8×10^{-2} mg cm^{-2}.

Study of the medium acidity

The acidity of the medium is a factor that affects the amount of cobalt uptake by the organic phase. Fig. 5 illustrates the influence of pH of the aqueous phase on the change in light absorbance of the test solution. There is a very large pH range in which it has constant values. Experimental data showed that light absorption of neutral and acidic medium to pH 2 has a constant (maximum) value. At pH < 2, it begins to decrease and the determination becomes impossible. Maximum Co(II) uptake was achieved at pH 2-7 range. The too large pH range makes it possible to work without precisely controlling the pH, or to use buffer solution. This makes the method less pretentious.

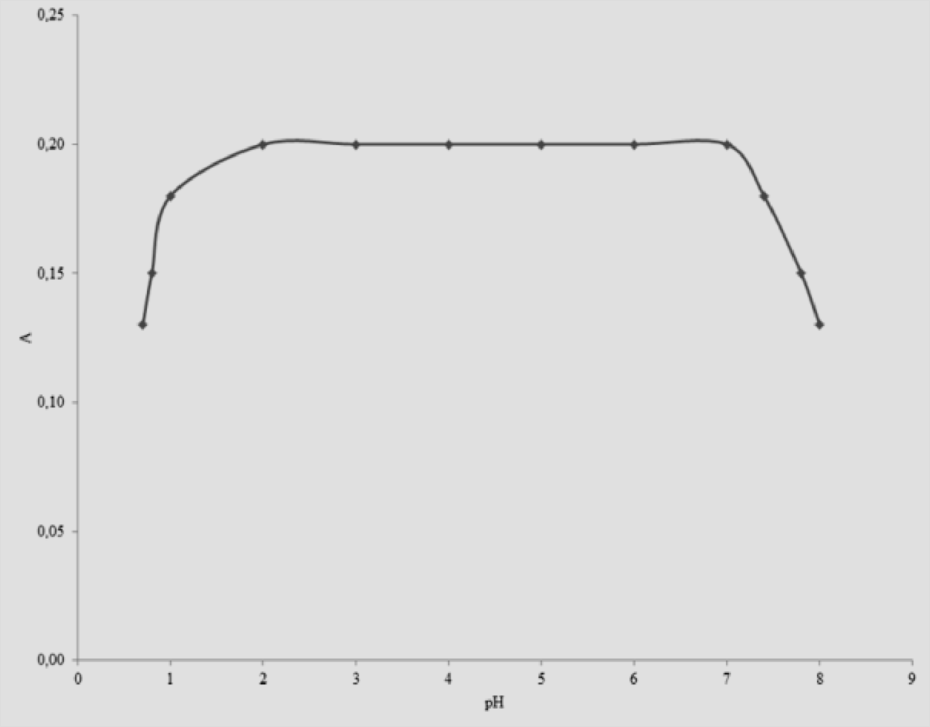

Fig. 5. Effect of pH on the light absorption during Co(II) extraction with INT. $C_{Co(II)} = 1\times10^{-4}$ mol dm^{-3}, $C_{INT} = 4\times10^{-4}$ mol dm^{-3}, $C_{SCN} = 0.8$ mol dm^{-3}, b = 1 cm

Reagents quantity

To develop optimal conditions and extraction of the thiocyanate complex of Co(II) with INT the influence of the tetrazole salt and thiocyanate ions was examined. The formation of the ion associate significantly depends on the concentration of the thiocyanate ions. In order to shift the equilibrium to the formation of the thiocyanate complex of Co(II) an excess of thiocyanate ions was required. This excess had no effect on the extraction equilibrium and facilitated the quantitative extraction of cobalt in the organic phase. By varying the amount of thiocyanate ions was found that at a concentration of ≥ 1 mol dm^{-3} in the water phase, the light absorbance of the extracts was the highest (Fig. 6).

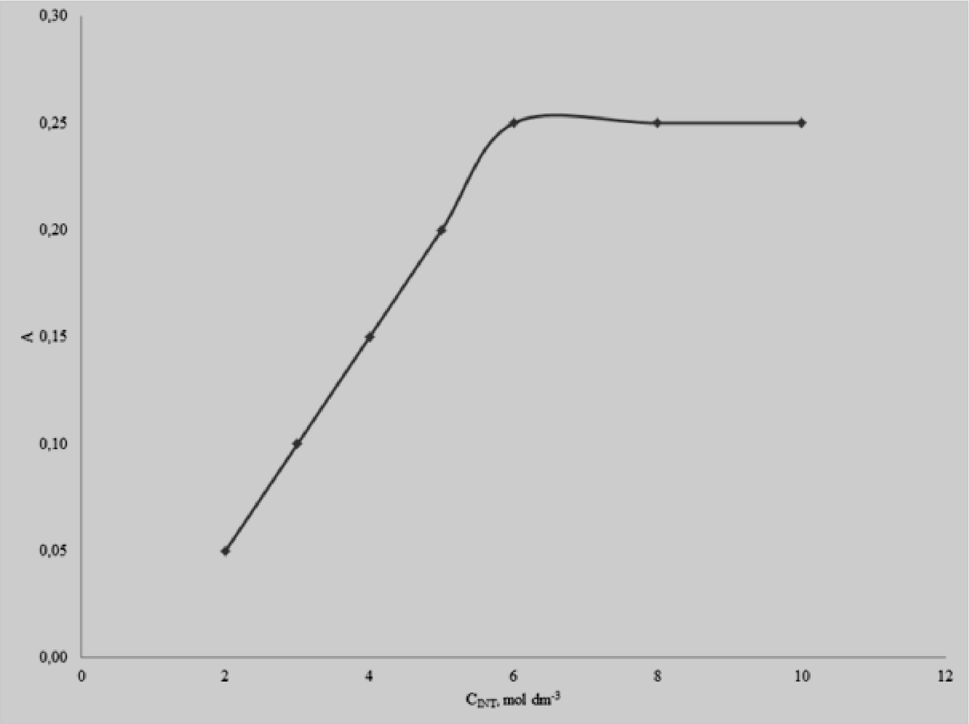

Fig. 6. Relationship between the change of light absorption and SCN$^-$ ions concentration:
$C_{Co(II)} = 1\times10^{-4}$ mol dm^{-3}, $C_{INT} = 3\times10^{-4}$ mol dm^{-3}, b = 1 cm

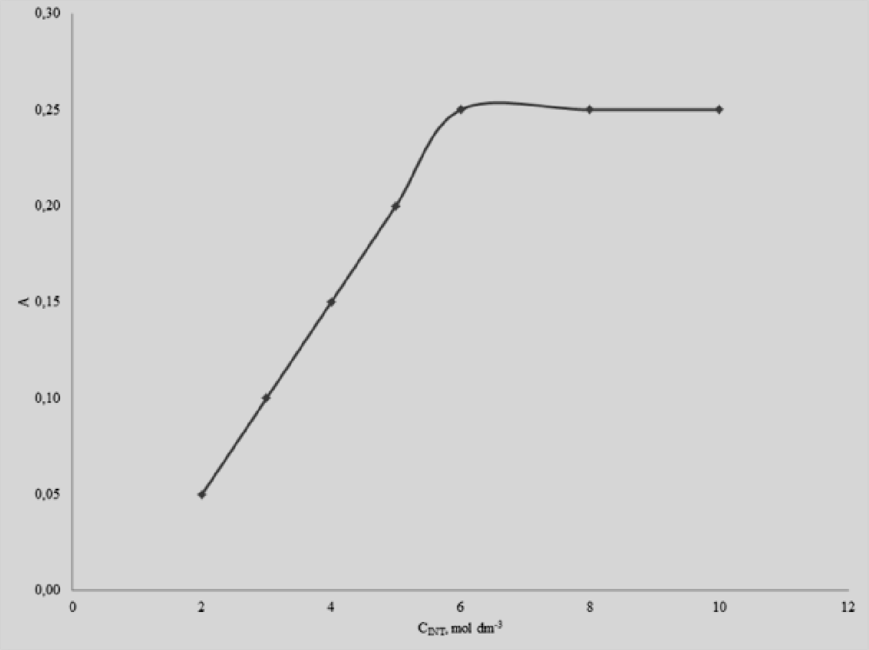

Fig. 7. Relationship between the change of associate light absorption and INT concentration:
$C_{Co(II)} = 1\times10^{-4}$ mol dm^{-3}, $C_{SCN} = 0.8$ mol dm^{-3}, b = 1 cm

An important factor in the photometric determination of cobalt is the tetrazolium salt. In order to maximize the recovery of the metal from the aqueous phase, the influence of different INT concentrations was investigated. The light absorption of the ion associate has a maximum value at a concentration of 6×10^{-4} mol dm^{-3} INT (Fig. 7). The figure shows that with increasing concentrations of the tetrazolium salt, light absorption of the associate remains constant.

Effect of Co(II) concentration on the light absorption

When INT was added to the thiocyanate solution of cobalt (II) pale green precipitate soluble in the organic solvent was obtained.

$$INT + [Co(SCN)_4]^{2-} \rightarrow [\,INT]_2\,[Co(SCN)_4]$$

The intensity of the precipitate colour increased with increasing cobalt (II) concentration. Fig.8 displays that the relationship between cobalt (II) concentration and light absorption is linear in the range of 6 mg to 125 mg Co(II) in 10 ml aqueous phase.

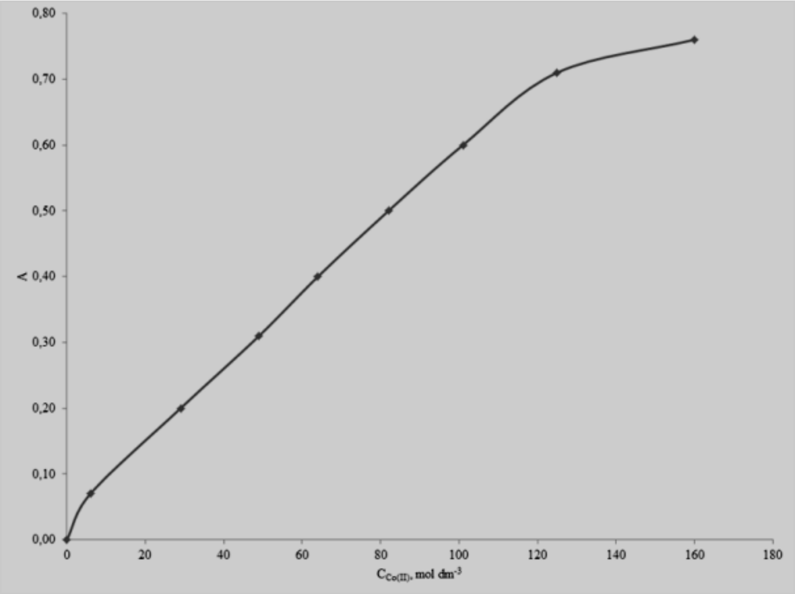

Fig. 8. Relationship between the change of light absorption and Co(II) concentration:
$C_{INT} = 10.5\times10^{-4}$ mol dm^{-3}, $C_{SCN} = 0.8$ mol dm^{-3}, b = 1 cm

Effect of side ions

To get a more complete picture of cobalt (II) extraction and to characterize the selectivity of the extraction, the influence of some ions, which would probably be contained in the analyzed samples, was studied. Experimental data are given in Table 2. The results qualify the tetrazolium salt used as a selective reagent for the determination of cobalt. Among all examined ions, only Fe (III) interferes the determination. The interference is removed by the addition of ascorbic acid as a masking agent. It has pronounced reduction properties.

Table 2. Effect of some ions on Co(II) extraction with INT: $C_{Co(II)} = 0.5\times10^{-4}$ mol dm^{-3}, $C_{INT} = 4.5\times10^{-4}$ mol dm^{-3}, $C_{SCN} = 0.8$ mol dm^{-3}

Side ion	Concentration limit of the side ion, mg	Limit ratio $C_x / C_{Co(II)}$, mg
K^+	300	10204:1
Na^+	100	3401:1
Sr^{2+};$S_2O_3^{2-}$	50	1700:1

$C_2O_4^{2-}$	20	680:1
Hg^{2+}	15	510:1
Al^{3+};Ca^{2+};Ni^{2+};BO_3^{3-}	10	340:1
Pb^{2+}	8	272:1
W^{6+}	7.4	251:1
Cd^{2+}	5	170:1
V^{5+}	0.5	17:1
Cr^{6+}	0.3	10:1
Br-	0.2	6.8:1
ЕДТА;NO_3-;J-;SO_4^{2-}	0.1	3.4:1
ClO_{4-}	0.05	1.7:1
Fe^{3+}	0.01	interfere

Application of the developed method for analysis of soil cobalt content

Accuracy and precision

Soil materials used for accuracy and precision tests include three certified soil samples corresponding to two main soil types in Bulgaria: (1) Light Alluvial–deluvial Meadow Soil PS-1, SOOMET No. 0001-1999 BG, SOD No. 310a-98; (2) Light Meadow Cinnamonic Soil PS-2, SOOMET No. 0002-1999 BG, SOD No.311a-98; (3) Light Alluvial–deluvial Meadow Soil PS-3, SOOMET No. 0003-1999 BG, SOD No. 312a-98.

For evaluation of the accuracy of the digestion and measuring procedures, we have used R criterion showing the extent of extraction of the element in percent from the certified value. When the measured value X is within the borders of $X_{CRM} \pm U_{CRM}$, where U_{CRM} is the indefiniteness of the certified value, we accept an extent of extraction to be 100%. In all the remaining cases, the extent of extraction is equal to $X / X_{CRM} \cdot 100$. As can be seen from the Table 1, the results obtained for all certified materials yield a recovery of 100% for Co.

Mineralization of the samples

The mineralization of the samples was carried out according to EPA Method 3052 procedure:[1)] 1g air - dry soil to the nearest 0.001 g in PTFE vessels was weighted. HNO_3, HF, HCl and H_2O_2, were added using a microwave system Multiwave 3000. The maximum power was 1400 W, and the maximum pressure in Teflon vessels - 40 bar.

Cobalt extraction

5 cm^3 soil samples, some drops of 1 mol dm^{-3} NaOH (for adjustment to pH 9.0-10.0) and 5 cm^3 0.02% dithizone in chloroform were consecutively placed in 100 cm^3 separating funnels. The systems were left to extract for 1min. Adequate quantity of HCl (1:1) (for adjustment of pH 1.0-2.0) and 2 cm^3 4 mol dm^{-3} thiocyanate solutions were added to the organic phase. Re-extraction for 1 min was accomplished. The organic phase was discharged, while 1 mol dm^{-3} NaOH (for pH 3.0-4.0), 0.6 cm^3 1.5×10^{-2} mol dm^{-3} INT and 2 cm^3 saturated solution of ascorbic acid (for masking of the interfering ions) were added to the aqueous phase. Distilled water was supplemented to a volume of 20 cm^3. Extraction with 3 cm^3 1,2-dichloroethane for 30 s was accomplished. After the stratification of both phases, the organic was filtered through a paper filter, placed in a cuvette, b = 1 cm, and photometered at $\lambda = 630$ nm.

A blank, not containing a soil sample, was also analyzed for reliability of the experimental results.

The experimental data are shown in Table 3. A good correlation of our results with data from included three certified soil samples was established.

Table 3. Determination of Co in soils

Element	Sample	Certified value	*INT* $X \pm \sigma$ mg kg^{-1}	*R*
Co	PS-1	11.42 ± 0.97	10.96 ± 0.023	96
	PS-2	10.56 ± 1.66	10.14± 0.019	96
	PS-3	12.5 ± 1.4	12.13± 0.036	97

Conclusions

The developed extraction spectrophotometric method for analysis of soil cobalt content with iodonitrotetrazolium chloride (INT) is simple, not expensive, express, characterized with selectivity and adequate acuracy.The good agreement of the results shows that INT can be used as a reagent for determination of microquantities of Co in soils and that pre-isolation of Co from most other ions is not necessary.

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NOTES

1. https://www.epa.gov/sites/production/files/2015-12/documents/3052.pdf

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