

Spectrophotometric investigations on liquid-liquid extraction systems containing cobalt, 4-(2-pyridylazo)-resorcinol and tetrazolium salts

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Complex formation and liquid-liquid extraction were studied in systems containing Co(II), 4-(2-pyridylazo)resorcinol (PAR), tetrazolium salt (TZS) {2,3,5-triphenyl-2H-tetrazolium chloride (TTC) or 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT)}, water and chloroform. The optimum conditions for the extraction of Co were found: pH, extraction time, concentration of the reagents PAR and TZS. The results show that the extracted species could be represented with the general formula $(TZ^+)[Co(PAR)_2]$, where Co is in its +3 oxidation state and PAR is in a doubly deprotonated form. The following key constants and characteristics were established for both systems: constants of extraction (K_{ex}), constants of association (β), constants of distribution (K_D), recovery factors (R%), wavelengths of maximum absorption (λ_{max}), molar absorptivities, Sandell's sensitivities, intervals of adherence to Beer's Law, limits of detection and limits of quantification. The ion-associate with INT is more stable and extractable ($\text{Log } \beta = 5.0$, $\text{Log } K_{ex} = 6.1$, $\text{Log } K_D = 1.12$, $R = 92.8\%$). Beer's law for the system with this reagent is observed in a wider concentration interval (0.26–2.6 $\mu\text{g mL}^{-1}$ Co) with a higher molar absorptivity coefficient ($\epsilon' = 5.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ at $\lambda_{max} = 515 \text{ nm}$).

Key words: cobalt-PAR chelate, iodonitrotetrazolium chloride, triphenyltetrazolium chloride, ternary complex, solvent extraction

INTRODUCTION

Cobalt is a transition element of high industrial importance because of its valuable alloying, dyeing, magnetic, catalytic and plating properties. It is also of biological significance thanks to its ability to be an active center of coenzymes, e. g. vitamin B₁₂. As such, it is an essential trace element for all animals and an active nutrient for bacteria, fungi and algae. It is known that long-term cobalt deficiency can result in demyelination of large nerve trunks and the spinal cord, reduced white blood cells, pernicious anemia and reduced resistance to parasite and microbial infections. On the other hand, co-

balt can be toxic in high doses, causing polycythemia, bone marrow hyperplasia, pancreatic failure, congestive heart failure and cardiomyopathy [1, 2]. That is why its content in various systems should be monitored [3–5].

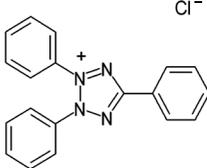
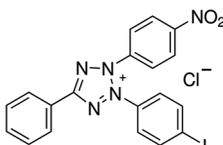
There are many methods for separation, preconcentration and determination of cobalt [3, 6–8]. 4-(2-pyridylazo)resorcinol (PAR) is among the most important reagents for all these purposes [5–50] because of the high stability and molar absorptivity of Co-PAR species, and the ability of these species to react readily with additional compounds and form ternary complexes with better extraction and color properties. The following reagents have been used as components of Co-PAR ternary complexes: tetradecyl(trihexyl)phosphonium chloride [18], xylometazoline hydrochloride [40],

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dicyclohexyl-18-crown-6 [42], diphenylguanidine [43], tetraphenylarsonium chloride [44], tetraphenylphosphonium chloride [44], 1,10-phenanthroline [51], 2,2'-bipyridyl [51] and quaternary ammonium salts [25–35].

Tetrazolium cations ($\text{TZ}^{\text{n}+}$) have been reported to form analytically important ion-association complexes with $\text{Co}(\text{SCN})_4^{2-}$ [52, 53] and M-PAR anionic chelates, where M is V(V), V(IV), In(III) and Ga(III) [53–58]. There is no information in the literature with respect to ternary Co-PAR-TZ complexes and their liquid-liquid extraction properties. Hence, the aim of the present study was to fill this gap. Two widely used TZS were selected for the experiments: 2,3,5-triphenyl-2H-tetrazolium chloride (TTC) [58–62] and 2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (INT) [52, 54, 55, 63]. Their structural formulae are given in Table 1.

Table 1. Tetrazolium salts in the present study

Structural formula	Name and abbreviation
	2,3,5-triphenyl-2H-tetrazolium chloride (TTC)
	2-(4-iodophenyl)-3-(4-nitrophenyl)-5-phenyl-2H-tetrazolium chloride (Iodonitrotetrazolium chloride, INT)

EXPERIMENTAL

Reagents and apparatus

Cobalt standard solution (1000 mg L^{-1} ; $\text{Co}(\text{NO}_3)_2$) was purchased from Merck Darmstadt (Germany). Working solutions ($C_{\text{Co}} = 1.7 \times 10^{-4} \text{ mol L}^{-1}$) were prepared by diluting appropriate volumes of the stock solution. Aqueous solutions of the reagents were used: PAR from Sigma-Aldrich Chemie GMBH, Steinheim, Germany ($2 \times 10^{-3} \text{ mol L}^{-1}$), TTC from Loba Feinchemie GMBH, Fischamend, Austria ($3 \times 10^{-3} \text{ mol L}^{-1}$), and INT from Sigma-Aldrich Chemie GMBH; ($2 \times 10^{-3} \text{ mol L}^{-1}$). The chloroform was redistilled and used repeatedly. The acidity of the aqueous medium was set by the addition of buffer solution, prepared by mixing 2 mol L^{-1} aqueous solutions of CH_3COOH and NH_4OH . The resulting pH was checked by HI 83140 pH meter (Italy). A Camspec M508 spectrophotometer (United Kingdom), equipped with 10 mm path-length cells, was employed for reading the absorbance.

Table 2. Optimum extraction-spectrophotometric conditions

Extraction systems	Extraction time, min	pH	$C_{\text{PAR}}, \text{mol L}^{-1}$	$C_{\text{TZS}}, \text{mol L}^{-1}$	$\lambda_{\text{max}}, \text{nm}$
Co-PAR-TTC	2	5.5	1.4×10^{-4}	4.5×10^{-4}	515
Co-PAR-INT	1	4.7	1.4×10^{-4}	1.8×10^{-4}	515

Procedure for establishing the optimum operating conditions

Aliquots of Co(II) solution, PAR solution (up to 1.6 mL), TZS solution (TTC or INT; up to 1.8 mL) and buffer solution (5 mL; pH ranging from 3.0 to 9.0) were introduced into 250-mL separatory funnels. The resulting solutions were diluted with distilled water to a total volume of 10 mL. Then 10 mL of chloroform were added and the funnels were shaken for a fixed time (up to 3.0 min). A portion of the organic extract was filtered through a filter paper into a cell and the absorbance was read against a blank.

Procedure for determination of the distribution constants

The distribution constants K_D were found from the ratio $K_D = A_1/(A_3 - A_1)$, where A_1 and A_3 are the absorbances (measured against blanks) obtained after a single and triple extraction of cobalt, respectively. The single extraction and the first stage of the triple extraction were performed with 10 mL of chloroform, under the optimum extraction-spectrophotometric conditions (Table 2). The organic layers were transferred into 25-mL calibrated flasks and the flask for the single extraction was brought to volume with chloroform. The second stage of the triple extraction was performed by adding a 7-mL portion of chloroform to the aqueous phase, which remained after the first stage. The third stage was performed in the same manner. The two successive organic layers were transferred to the flask containing the organic layer obtained after the first stage. The volume was brought to the mark with chloroform and shaken for homogenization before the spectrophotometric measurement [55, 57, 62].

RESULTS AND DISCUSSION

Absorption spectra

Absorption spectra of the extracted into chloroform ternary complexes Co-PAR-TZS are shown in Fig. 1. The maxima in both cases are recorded at 515–516 nm. They are shifted to 5–6 nm as compared to the maximum of the binary Co-PAR complex in aqueous medium (510 nm; pH = 3.5–10 [6, 35, 43–49]).

Effect of pH

The effect of pH on the extraction is represented in Fig. 2. The ternary complex with TT^+ is extracted in a great extent at pH 5–6, while that with INT^+ is extracted at pH 4.5–5.0. The difference in the pH intervals for maximum extraction could be explained by different ability of TT^+ and INT^+ to facilitate the deprotonation of 1-hydroxyl group in the complexed PAR in aqueous medium [64] during the formation of ternary species.

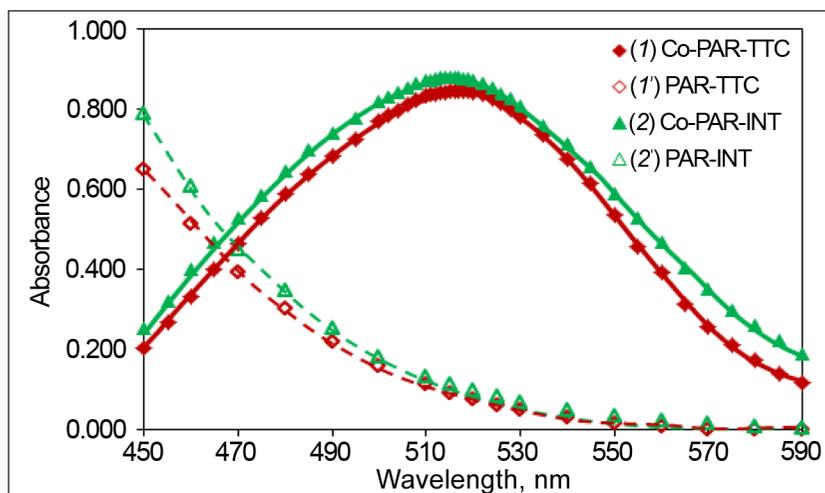


Fig. 1. Absorption spectra of the ternary complexes (curves 1, 2) and blank samples (curves 1', 2') in chloroform. $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{PAR} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$, $C_{TTC} = 4.5 \times 10^{-4} \text{ mol L}^{-1}$, $C_{INT} = 3.0 \times 10^{-4} \text{ mol L}^{-1}$, pH 5.0

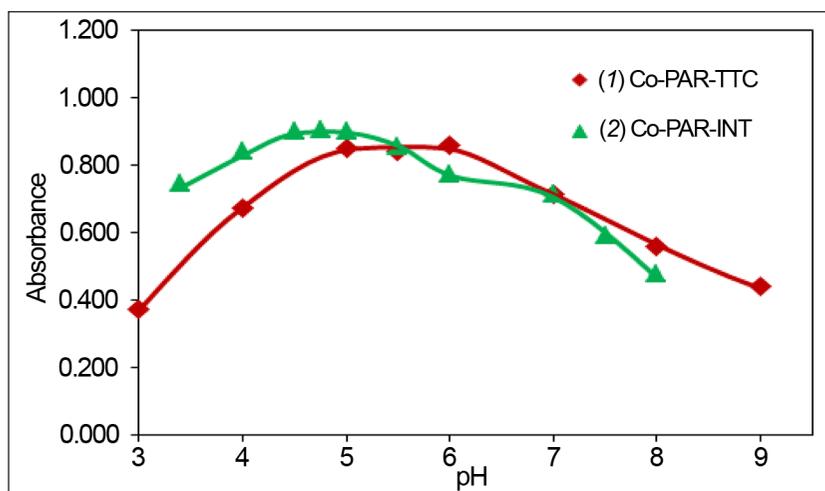


Fig. 2. Absorbance of Co-PAR-TZS extracts against PAR-TZS extracts vs. pH of the aqueous phase plots. 1 - $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{PAR} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$, $C_{TTC} = 4.5 \times 10^{-4} \text{ mol L}^{-1}$, $\lambda = 515 \text{ nm}$; 2 - $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{PAR} = C_{INT} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$, $\lambda = 515 \text{ nm}$

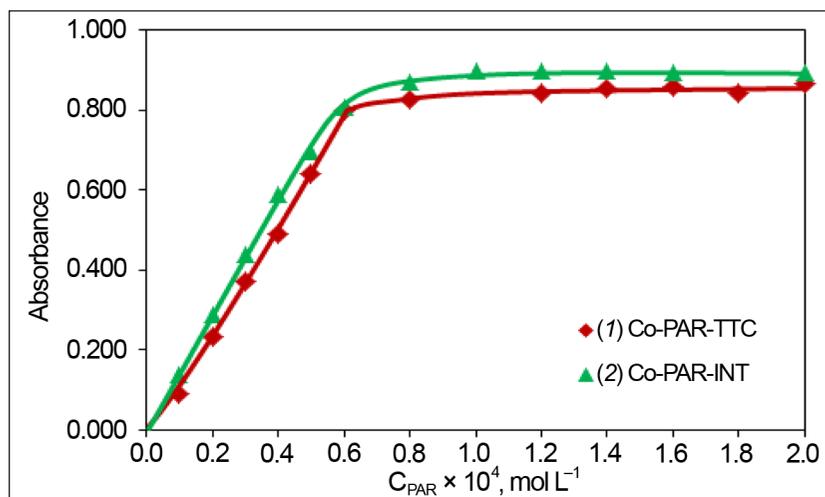


Fig. 3. Absorbance of the extracted ternary Co-PAR-TZS complexes vs. concentration of the PAR plots. 1 - $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{TTC} = 4.5 \times 10^{-4} \text{ mol L}^{-1}$, pH 5.5, $\lambda = 515 \text{ nm}$; 2 - $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{INT} = 1.8 \times 10^{-4} \text{ mol L}^{-1}$, pH 4.7, $\lambda = 515 \text{ nm}$

Effect of shaking time

The extraction equilibrium for Co-PAR-TTC system is reached for about 90 seconds and that for Co-PAR-INT system is reached for about 15 seconds. In both cases, longer shaking time does not affect the absorbance. In order to avoid accidental errors, caused by the combination of short shaking times and different shaking rates, we extracted in our further experiments for 2 min and 1 min, respectively (Table 2).

Effect of reagents concentration

The effect of PAR and TZS concentrations on the absorbance of the extracted species is shown in Fig. 3 and Fig. 4, respectively. The saturation curves with PAR are similar (Fig. 3). It could be seen from Fig. 4 that the saturation with INT is reached more easily. This is an indication that INT^+ forms a more stable ion-associate than TT^+ .

Composition of the complexes and suggested general formula

The molar PAR-to-Co and TZS-to-Co ratios were determined by the mobile equilibrium method [65] (Fig. 5) and the Asmus method [66] (Table 3). The results show that ternary complexes with a ratio of 1 : 2 : 1 (Co : PAR : TZS) are extracted into an organic phase. Having in mind the obtained molar ratios and several reports, which demonstrate that the labile Co(II)-PAR complex is oxidized to an inert Co(III)-PAR complex, $[\text{Co}^{3+}(\text{PAR})_2]^-$, by the atmospheric oxygen [11, 27, 29, 38, 42, 44, 51, 64], we suggest the following general formula of the extracted ternary species: $(\text{TZ}^+)[\text{Co}^{3+}(\text{PAR})_2]$. In this formula PAR is in its deprotonated form (PAR^{2-}).

Equilibrium constants, recovery factors and molar absorptivities

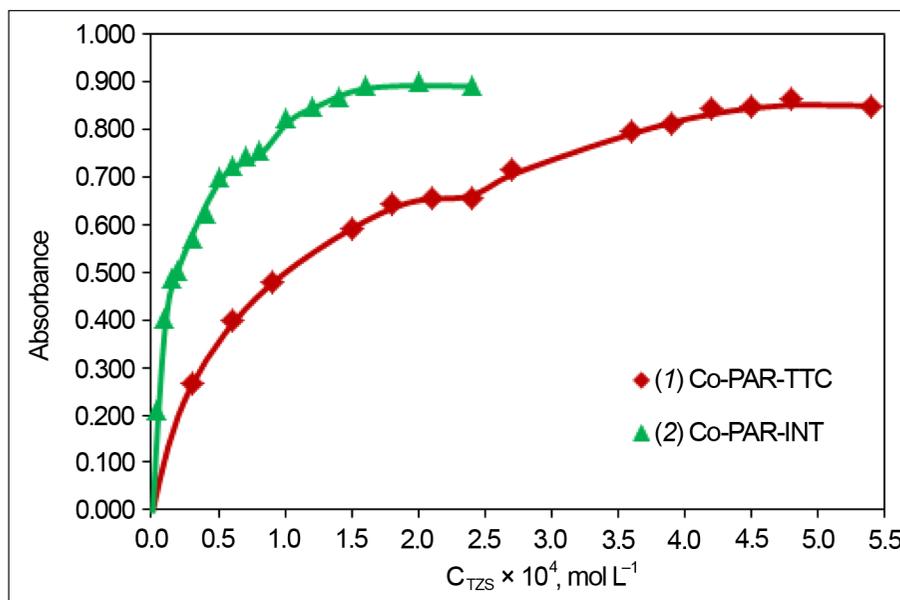
Several processes should be taken into account for the system of Co, PAR, TZ^+ (TT^+ or INT^+), water and chloroform:

(i) Formation of ion-associate complexes in the aqueous phase, $\text{TZ}^+ + [\text{Co}(\text{PAR})_2]^- \leftrightarrow (\text{TZ})[\text{Co}(\text{PAR})_2]$, with equilibrium constants $\beta = \frac{[(\text{TZ})[\text{Co}(\text{PAR})_2]]}{[\text{TZ}^+] \times [[\text{Co}(\text{PAR})_2]^-]}$;

Table 3. Determination of the PAR-to-Co and TZS-to-Co molar ratios (n and m, respectively) by the Asmus method [66] from the experimental data given in Fig. 4 and Fig. 5, respectively

Extraction system	Correlation coefficient squared values (CC ²) corresponding to molar ratios 1, 2 and 3	
	PAR : Co	TZS : Co
Co-PAR-TTC-water-chloroform	CC ² = 0.964 (n = 1)	CC ² = 0.992 (m = 1)
	CC ² = 0.989 (n = 2)	CC ² = 0.903 (m = 2)
	CC ² = 0.949 (n = 3)	CC ² = 0.821 (m = 3)
Co-PAR-INT-water-chloroform	CC ² = 0.977 (n = 1)	CC ² = 0.993 (n = 1)
	CC ² = 0.998 (n = 2)	CC ² = 0.920 (n = 2)
	CC ² = 0.985 (n = 3)	CC ² = 0.864 (n = 3)

Fig. 4. Absorbance of the extracted ternary Co-PAR-TZS complexes vs. concentration of the TZS plots. 1 – $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{PAR} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$, pH 5.5, $\lambda = 515 \text{ nm}$; 2 – $C_{Co} = 1.7 \times 10^{-5} \text{ mol L}^{-1}$, $C_{PAR} = 2.0 \times 10^{-4} \text{ mol L}^{-1}$, pH 4.7, $\lambda = 515 \text{ nm}$



(ii) Distribution of the complexes between the aqueous and the organic phase, $(TZ)[Co(PAR)_2]_{aq} \leftrightarrow (TZ)[Co(PAR)_2]_{org}$, with distribution constants $K_D = [(TZ)[Co(PAR)_2]_{org}] / [(TZ)[Co(PAR)_2]_{aq}]$;

(iii) Extraction from water into chloroform, $[Co(PAR)_2]_{aq}^- + TZ_{aq}^+ \leftrightarrow (TZ)[Co(PAR)_2]_{org}$, with extraction constants $K_{ex} = [(TZ)[Co(PAR)_2]_{org}] / [TZ^+]_{aq} \times [[Co(PAR)_2]^-]_{aq}$.

The association constants β were calculated by several independent methods: Holme-Langmihr method [67], Harvey-Manning method [68], Mobile equilibrium method [65] (Fig. 5, straight lines 1 and 2) and Komar-Tolomachev method [69] (Fig. 6). It should be mentioned that $(INT^+)[Co(PAR)_2]^-$ has a high constant of association (Table 4). The obtained value ($\text{Log } \beta = 5.0$) is higher than all reported val-

Table 4. Calculated values ($P = 95\%$) of the extraction constants (K_{ex}), distribution constants (K_D), association constants (β), recovery factors ($R\%$) and true molar absorptivities (ϵ)

Extraction system	Log β	Log K_D	Log K_{ex}	R%	$\epsilon, \text{ L mol}^{-1} \text{ cm}^{-1}$
Co-PAR-TTC-H ₂ O-chloroform	4.3 ± 0.1^a	0.96 ± 0.01	$5.3 \pm 0.1^{e,f}$	89.3 ± 0.1	$(4.9 \pm 0.4) \times 10^4^d$
	4.3 ± 0.1^b				
	4.2 ± 0.1^c				
	4.5 ± 0.6^d				
Co-PAR-INT-H ₂ O-chloroform	4.9 ± 0.2^a	1.12 ± 0.01	6.0 ± 0.2^e	92.8 ± 0.1	$(5.0 \pm 0.3) \times 10^4^d$
	5.1 ± 0.2^b				
	4.9 ± 0.3^c				
	5.0 ± 0.6^d				

a – calculated by the Holme-Langmihr method [67];

b – calculated by the Harvey-Manning method [68];

c – calculated by the Mobile Equilibrium method [65];

d – calculated by the Komar-Tolomachev method [69];

e – calculated by the equation $\text{Log } K_{ex} = \text{Log } \beta + \text{Log } K_D$, where β is the value obtained by the Holme-Langmihr method;

f – calculated by the equation $\text{Log } K_{ex} = \text{Log } \beta + \text{Log } K_D$, where β is the value obtained by the Harvey-Manning method.

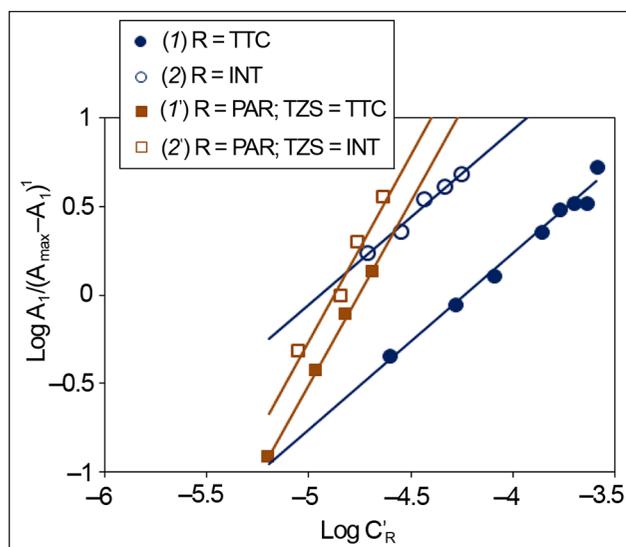


Fig. 5. Straight lines obtained by the Mobile Equilibrium method [65] during the determination of TZS-to-Co (lines 1 and 2) and PAR-to-Co (lines 1' and 2') molar ratios from the experimental data given in Fig. 5 and Fig. 4, respectively. Straight line equations: (1) $y = 1.00x + 4.22$; (2) $y = 0.99x + 4.91$; (1') $y = 2.08x + 9.88$; (2') $y = 2.06x + 10.13$

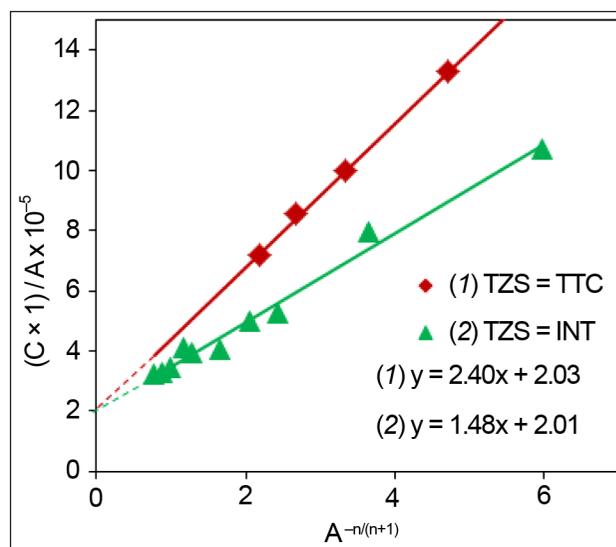


Fig. 6. Straight lines obtained by the Komar-Tolmachev method [69] during the determination of the constants of association (β) and true molar absorptivities (ϵ). $C_{TZS} = C_{Co}$, $C_{PAR} = 2.0 \text{ mol L}^{-1}$, $\lambda = 515 \text{ nm}$, pH 5.5 (straight line 1) or 4.7 (straight line 2)

Table 5. Characteristics concerning the application of the ternary complexes for extractive-spectrophotometric determination of cobalt

Analytical characteristics	Co-PAR-TTC-H ₂ O-CHCl ₃	Co-PAR-INT-H ₂ O-CHCl ₃
Apparent molar absorptivity (ϵ')	$5.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$	$5.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$
Sandell's sensitivity (SS)	1.18 ng cm^{-2}	1.11 ng cm^{-2}
Adherence to Beer's Law	up to $1.8 \mu\text{g mL}^{-1}$	up to $2.6 \mu\text{g mL}^{-1}$
Limit of detection (LOD)	$0.047 \mu\text{g mL}^{-1}$	$0.077 \mu\text{g mL}^{-1}$
Limit of quantification (LOQ)	$0.16 \mu\text{g mL}^{-1}$	$0.26 \mu\text{g mL}^{-1}$

ues [53, 55] for similar ion-association complexes of the type $(\text{INT}^+)[\text{ML}_n]^-$, where M is Cr, Hg, La, Mn, Mo, Nb, Re, V, W [53], Ga and In [55]. This advantage could be of importance in the development of a selective method for cobalt extraction and determination.

The Komar-Tolmachev method also allows calculating the true molar absorptivities of the complexes. The obtained values (Table 4) agree well with these found from Beer's Law (Table 5); this is an indication for absence of serious side-reactions [69].

The distribution constants K_D were calculated from the absorption values obtained after the single and triple extraction as described above. The extraction constants K_{ex} and recovery factors R% were calculated by the formulae $K_{ex} = K_D \times \beta$ and $R\% = 100K_D/(K_D + 1)$. The results are presented in Table 4. All experiments were performed at room temperature of $\sim 22^\circ\text{C}$ and the calculations carried out at a probability of 95%.

Beer's Law and analytical characteristics

Linear dependences between the absorbance of the complexes $(\text{TZ}^+)[\text{Co}(\text{PAR})_2]$ and cobalt concentrations are observed up to $1.8 \mu\text{g mL}^{-1}$ Co (when $\text{TZ}^+ = \text{TT}^+$) and $2.6 \mu\text{g mL}^{-1}$ Co (when $\text{TZ}^+ = \text{INT}^+$). The following straight-line equa-

tions were obtained: $y = 0.8521x - 0.002$ ($\text{TZ}^+ = \text{TT}^+$) and $y = 0.8785x + 0.0085$ ($\text{TZ}^+ = \text{INT}^+$). The corresponding squared correlation coefficients CC^2 were 0.9994 and 0.9991. Some important analytical characteristics of the investigated systems are shown in Table 5. It should be mentioned that the obtained molar absorptivities of both complexes are higher than these reported for many similar systems, e. g. Co(II)-thiocyanate-tetrazolium salt-H₂O-organic solvent [$\epsilon = (1.08 \times 10^3 - 1.2 \times 10^4) \text{ L mol}^{-1} \text{ cm}^{-1}$] [70-74], Co-4-(2-thiazolylazo)resorcinol (TAR)-tetra-n-heptylammonium chloride-H₂O-benzene ($\epsilon = 2.5 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [75], Co-TAR-zephiramin-H₂O-chloroform ($\epsilon = 3.42 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [76], Co-4-(2-thiazolylazo)naphthol-tetra-n-heptylammonium chloride-H₂O-benzene ($\epsilon = 3.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [75], and Co-PAR-xylometazoline hydrochloride-H₂O-chloroform ($\epsilon = 4.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) [40].

CONCLUSIONS

1. Cobalt(II) forms well chloroform-extractable ternary ion-association complexes with PAR and tetrazolium cations (TZ^+ : TT^+ and INT^+). The anionic part of the complexes, $[\text{Co}(\text{PAR})_2]^-$, ensures intensive red coloration, while the

cationic part, TZ^+ , guarantees their poor solubility in water. The obtained molar ratios, $Co : PAR = 1 : 2$ and $Co : TZ = 1 : 1$, and literature data about similar extraction-chromogenic systems suggest that during the complex formation $Co(II)$ is oxidised to $Co(III)$ by the atmospheric oxygen.

2. The following conditional constants are calculated: constant of association (β), constant of distribution (K_D) and constant of extraction (K_{ex}). The complex with participation of INT has a very high constant of association: $\log \beta = 5.0$. This value is higher than all reported values for similar ion-association complexes of the type $(INT^+)[ML_n]^-$, where M is Cr, Hg, La, Mn, Mo, Nb, Re, V, W, Ga and In.

3. The apparent molar absorptivities of the complexes are rather high ($\epsilon'_{(INT)[Co(PAR)_2]} = 5.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$; $\epsilon'_{(TT)[Co(PAR)_2]} = 5.0 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$). In this criterion, they could compete successfully with many complexes used for spectrophotometric determination of cobalt.

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References

- D. G. Barceloux, D. Barceloux, *Clin. Toxicol.*, **37**, 201 (1999).
- B. B. Tewari, *Rev. Bol. Quim.*, **26**, 30 (2009).
- R. A. Meyers (ed.), *Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation*, Wiley, Chichester (2000).
- M. Jakubowski, M. Trzcinka-Ochocka, *J. Occup. Health*, **47**, 22 (2005).
- A. Tsuyoshi, H. Hoshino, T. Yotsuyanagi, *Chem. Lett.*, **30**, 302 (2001).
- I. V. Pyatnitskii (ed.), *Analytical Chemistry of Cobalt* (in Russian), Nauka, Moscow (1965).
- Z. Marczenko, M. Balcerzak, *Separation, Preconcentration and Spectrophotometry in Inorganic Analysis*, Vol. 10, Elsevier, Amsterdam (2000).
- G. Ram, R. S. Chauhan, A. K. Goswami, *Rev. Anal. Chem.*, **22**, 255 (2003).
- Z. Marczenko, M. Balcerzak, *UV-Vis Spectrophotometric Methods in Inorganic Analysis* (in Russian), BINOM. Laboratoriya znaniy, Moscow (2007).
- S. Tokalioglu, S. Kartal, *Bull. Korean Chem. Soc.*, **27**, 1293 (2006).
- V. Cucinotta, R. Caruso, A. Giuffrida, M. Messina, G. Maccarrone, A. Torrisi, *J. Chromatogr., A*, **1179**, 17 (2008).
- Z.-T. Jiang, J. C. Yu, H.-Y. Liu, *Anal. Sci.*, **21**, 851 (2005).
- M. L. Fernandez-de Cordova, A. Molina-Diaz, M. I. Pascual-Reguera, L. F. Capitan-Vallvey, *Anal. Lett.*, **25**, 1961 (1992).
- C. C. Nascentes, M. A. Z. Arruda, *Talanta*, **61**, 759 (2003).
- J. E. DiNunzio, R. W. Yost, E. K. Hutchison, *Talanta*, **32**, 803 (1985).
- I. Vyshcherevichand, I. Kalinichenko, *J. Water Chem. Technol.*, **32**, 33 (2010).
- R. E. Taljaard, J. F. V. Staden, *Anal. Chim. Acta*, **366**, 177 (1998).
- P. Berton, R. G. Wuilloud, *Anal. Methods*, **3**, 664 (2011).
- H. Ciftci, *Curr. Anal. Chem.*, **6**, 154 (2010).
- M. Ince, G. Kaya, M. Yaman, *Environ. Chem. Lett.*, **8**, 283 (2010).
- L. L. Kolomiets, L. A. Pilipenko, I. M. Zhmud', I. P. Panfilova, *Zh. Anal. Khim.*, **54**, 34 (1999).
- E. Gómez, J. M. Estela, V. Cerdà, M. Blanco, *Fresen. J. Anal. Chem.*, **342**, 318 (1992).
- M. A. Z. Arruda, E. A. G. Zagatto, N. Maniasso, *Anal. Chim. Acta*, **283**, 476 (1993).
- H. Ciftci, A. Ölçücü, A. Ozkaya, T. Ciftci, *Asian J. Chem.*, **21**, 2643 (2009).
- C. E. Säbel, J. L. Shepherd, S. Siemann, *Anal. Biochem.*, **391**, 74 (2009).
- B. F. Liu, L. B. Liu, J. K. Cheng, *J. Chromatogr., A*, **848**, 473 (1999).
- T. Okutani, A. Sakuragawa, M. Murakami, *Anal. Sci.*, **7(Suppl.)**, 109 (1991).
- K. Sato, T. Goto, *Bunseki Kagaku*, **47**, 735 (1998).
- J. B. Noffsinger, N. D. Danielson, *J. Liq. Chromatogr. Relat. Technol.*, **9**, 2165 (1986).
- H. R. Pouretedal, P. Sononi, M. H. Keshavarz, A. Semnani, *Chemistry*, **18**, 22 (2009).
- H. Okochi, *Bunseki Kagaku*, **21**, 51 (1972).
- R. Yamashita, T. Yotsuyanagi, K. Aomura, *Jpn. Analyst*, **20**, 1282 (1971).
- T. Yotsuyanagi, R. Yamashita, K. Aomura, *Jpn. Analyst*, **19**, 981 (1970).
- J. Dolezal, L. Sommer, *Collect. Czech. Chem. Commun.*, **59**, 2209 (1994).
- N. T. Sizonenko, L. V. Gudzenko, *Zavod. Lab.*, **51**, 9 (1985).
- S. A. Akhmedov, O. A. Tataev, R. R. Abdullaev, *Zavod. Lab.*, **37**, 756 (1971).
- M. I. Zaboeva, G. N. Zus', M. P. Dorofeeva, *Zavod. Lab.*, **36**, 1158 (1969).
- C. Baiocchi, F. Cantone, A. Marchetto, M. Gennaro, E. Mentasti, C. Sarzanini, *Chromatographia*, **23**, 736 (1987).
- A. V. Ivanov, V. N. Figurovskaya, V. M. Ivanov, *Vest. MGU. Ser. 2. Khimiya*, **33**, 570 (1992).
- S. N. Bhadani, M. Tewari, A. Agrawal, C. Sekhar, *J. Indian Chem. Soc.*, **75**, 176 (1998).
- D. Nonova, B. Evtimova, *Anal. Chim. Acta*, **62**, 456 (1972).
- A. G. Gaikwad, H. Noguchi, M. Yoshio, *Anal. Lett.*, **24**, 1625 (1991).
- S. G. Mamuliya, I. V. Pyatnitskii, L. L. Kolomiets, K. I. Grialashvili, *Zh. Anal. Khim.*, **35**, 1306 (1980).
- M. Siroki, L. Maric, Z. Stefanac, M. J. Herak, *Anal. Chim. Acta*, **75**, 101 (1975).

45. A. I. Busev, V. M. Ivanov, Z. I. Nemtseva, *Zh. Neorg. Khim.*, **13**, 511 (1968).
46. A. I. Busev, V. M. Ivanov, *Zh. Anal. Khim.*, **18**, 208 (1963).
47. V. M. Ivanov, N. I. Ershova, V. N. Figurovskaya, A. V. Ivanov, *J. Anal. Chem.*, **56**, 143 (2001).
48. F. H. Pollard, P. Hanson, W. J. Geary, *Anal. Chim. Acta*, **20**, 26 (1959).
49. T. Yotsuyanagi, R. Yamashita, K. Aomura, *Anal. Chem.*, **44**, 1091 (1972).
50. A. Hol, U. Divrikli, L. Elci, *Environ. Monit. Assess.*, **184**, 3469 (2012).
51. M. S. Sastary, R. Ghose, A. K. Ghose, *B. Chem. Soc. Ethiopia*, **4**, 61 (1990).
52. L. Dospatliev, N. V. Georgieva, A. I. Pavlov, Z. Yaneva, *Trakia J. Sci.*, **8**, 16 (2010).
53. K. B. Gavazov, A. N. Dimitrov, V. D. Lekova, *Usp. Khim.*, **76**, 187 (2007).
54. K. Gavazov, Z. Simeonova, A. Alexandrov, *Talanta*, **52**, 539 (2000).
55. K. B. Gavazov, K. T. Stojnova, T. S. Stefanova, G. K. Toncheva, V. D. Lekova, A. N. Dimitrov, *Chemija*, **23**, 278 (2012).
56. T. S. Stefanova, K. B. Gavazov, *Cent. Eur. J. Chem.*, **11**, 280 (2013).
57. T. S. Stefanova, G. K. Toncheva, K. B. Gavazov, *Chem. J.*, **2**, 146 (2012).
58. K. T. Stojnova, K. B. Gavazov, G. K. Toncheva, V. D. Lekova, A. N. Dimitrov, *Cent. Eur. J. Chem.*, **10**, 1262 (2012).
59. D. Kostova, *J. Anal. Chem.*, **66**, 384 (2011).
60. A. G. F. Elsaid, N. M. H. Rizk, A. B. H. Matter, *Asian J. Chem.*, **22**, 1736 (2010).
61. G. Toncheva, K. Gavazov, V. Lekova, K. Stojnova, A. Dimitrov, *Cent. Eur. J. Chem.*, **9**, 1143 (2011).
62. V. Lekova, P. Racheva, K. Stojnova, A. Dimitrov, K. Gavazov, *Chemija*, **21**, 106 (2010).
63. M. Boggs, L. Gribat, C. Boele, N. Wall, *J. Radioanal. Nucl. Chem.*, **293**, 843 (2012).
64. A. Corsini, Q. Fernando, H. Freiser, *Inorg. Chem.*, **2**, 224 (1963).
65. Z. Zhiming, M. Dongsten, Y. Cunxiao, *J. Rare Earth.*, **15**, 216 (1997).
66. E. Asmus, *Fresen. J. Anal. Chem.*, **178**, 104 (1960).
67. A. Holme, F. J. Langmyhr, *Anal. Chim. Acta*, **36**, 383 (1966).
68. A. E. Harvey, D. L. Manning, *J. Amer. Chem. Soc.*, **72**, 4488 (1950).
69. M. I. Bulatov, I. P. Kalinkin, *Practical Handbook on Photocolorimetric and Spectrophotometric Methods of Analysis* (in Russian), Khimiya, Leningrad (1986).
70. M. C. Mehra, D. LeBlanc, *Microchem. J.*, **24**, 435 (1979).
71. A. K. Singh, D. Kumar, M. Katyal, *Anal. Chim. Acta*, **172**, 303 (1985).
72. M. Kamburova, A. Alexandrov, K. Trifonov, *Chem. Anal. (Warsaw)*, **39**, 639 (1994).
73. M. Kamburova, A. Alexandrov, *Chem. Anal. (Warsaw)*, **43**, 1021 (1998).
74. M. Kamburova, A. Aleksandrov, *Zh. Anal. Khim.*, **54**, 277 (1999).
75. O. Navratil, R. W. Frei, *Anal. Chim. Acta*, **52**, 221 (1970).
76. K. Ueda, *Bull. Chem. Soc. Jpn.*, **52**, 1215 (1979).

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SKYSTINĖS EKSTRAKCIJOS SISTEMOS, TURINČIOS KOBALTO, 4-(2-PIRIDILAZO)-REZORCINOLIO IR TETRAZOLIO DRUSKŲ, SPEKTROFOTOMETRINIS TYRIMAS

S a n t r a u k a

Buvo tiriamas kompleksų susidarymas ir skystinė ekstrakcija sistemoje, turinčiose Co(II), 4-(2-piridilazo)rezorcinolio, kelių skirtingų tetrazolio druskų, vandens ir chloroformo. Nustatytos optimalios kobalto ekstrakcijos sąlygos: tirpalo pH, proceso trukmė ir reagentų koncentracijos.