

SPECTROPHOTOMETRIC DETERMINATION OF COBALT(II) IN A LIQUID-LIQUID EXTRACTION SYSTEM CONTAINING 4-(2-THIAZOLYLAZO) RESORCINOL AND 2,3,5-TRIPHENYL-2H-TETRAZOLIUM CHLORIDE

V. Divarova¹, P. Racheva², V. Lekova¹, K. Gavazov¹, A. Dimitrov¹

¹ Department of General and Inorganic Chemistry,
University of Plovdiv "Paissii Hilendarski",
24 Tzar Assen Str., 4000 Plovdiv, Bulgaria

² Department of Chemistry and Biochemistry,
Medical University Plovdiv,
15A Vassil Aprilov Blvd., 4002 Plovdiv, Bulgaria
E-mail: kgavazov@abv.bg

Received 11 July 2013
Accepted 25 October 2013

ABSTRACT

The complex formation and a liquid-liquid extraction in the cobalt(II) - 4-(2-thiazolylazo)resorcinol (TAR) - 2,3,5-triphenyl-2H-tetrazolium chloride (TTC) - water - chloroform system was studied. The optimum extraction-spectrophotometric conditions were found. The molar ratio of the reacting species was determined to be 1:2:1 (Co:TAR:TTC). The following equilibrium processes were quantitatively examined: the association between the anionic chelate, $[\text{Co}^{3+}(\text{TAR})_2]^-$, and the tetrazolium cation ($\text{Log}\beta = 4.7$); the distribution of the ternary complex between the aqueous and organic phases ($\text{Log}K_D = 0.88$); and the extraction from water to chloroform ($\text{Log}K_{\text{ex}} = \text{Log}\beta + \text{Log}K_D = 5.6$). The effect of foreign ions and reagents on the extraction was studied. A sensitive ($\epsilon_{525} = 4.26 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$) and simple extraction-spectrophotometric procedure for cobalt determination was developed.

Keywords: cobalt(III), azo compound, tetrazolium salt, ternary complex, solvent extraction.

INTRODUCTION

Many metal ions form coloured binary species with azodyes, such as 4-(2-pyridylazo)resorcinol (PAR) and 4-(2-thiazolylazo)resorcinol (TAR) [1-7]. Besides, the colour and extraction properties of these species can be improved by adding auxiliary compounds [7, 8]. The following ion-association reagents were used for liquid-liquid extraction of $[\text{Co}(\text{TAR})_2]^{z-}$ or $[\text{Co}(\text{PAR})_2]^{z-}$ ($z = 1$ or 2): zephiramine [9-12], xylometazoline hydrochloride [13], diphenylguanidine [14], potassium-dicyclohexyl-18-crown-6 [15], nitron [16], tetraphenylarsonium chloride [17], tetraphenylphosphonium chloride [17], cetylpyridinium chloride [18], tetra-n-heptylammonium salts [18], and tetrazolium salts [19]. In a previous paper the complex formation and extraction in a system containing Co(II), PAR and 2,3,5-triphenyl-2H-tetrazolium

chloride (TTC) has been described [19]. Here, results of systematic investigations on a similar extraction-chromogenic system, which involve TAR instead of PAR, are presented.

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.
- TAR (97 %, Sigma-Aldrich), dissolved in slightly alkalinized distilled water, $2 \times 10^{-3} \text{ mol l}^{-1}$.
- TTC (LobaFeinchemie GMBH), $3.0 \times 10^{-3} \text{ mol l}^{-1}$ aqueous solution.
- Acetate buffer solution, prepared from 2 mol l^{-1} aqueous

solutions of CH₃COOH and NH₄OH. The resulting pH was checked by HI 83140 pH meter (Romania).

- Chloroform (additionally distilled).
- A Camspec M508 spectrophotometer (United Kingdom), equipped with 10 mm path-length cells.

Procedure for determining the optimum extraction-spectrophotometric conditions

Aliquots of Co(II) solution, TAR solution (up to 1.6 ml), TTC solution (up to 1.2 ml) and buffer solution (5 ml; pH ranging from 3.5 to 7.0) 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 5.0 min). A portion of the organic extract was filtered through a filter paper into a cell and the absorbance was recorded against a blank sample.

Procedure for extraction-spectrophotometric determination of cobalt

An aliquot of cobalt solution (0.19 - 1.5 µg ml⁻¹) was placed in a separatory funnel. Then 0.7 ml TAR solution, 0.9 ml TTC solution, and 5 ml of acetate buffer with pH 5.5 were added. The resulting solution was diluted with distilled water to a total volume of 10 ml, 10 ml of chloroform were added and the funnel was shaken for 1 min. A portion of the organic extract was filtered through a filter paper into a cell and the light absorbance at λ_{max} 525 nm was recorded against a blank sample. The cobalt content was found from a calibration graph.

Procedure for determining the distribution constant

The distribution constant K_D was found from the

ratio $K_D = A_1 / (A_3 - A_1)$ where A₁ is the light absorbance measured after a single extraction at the optimum operating conditions (Table 1, 25 ml final volume) and A₃ is the absorbance measured after a triple extraction under the same conditions [20].

RESULTS AND DISCUSSION

Spectral characteristics and effect of pH

The coloured cobalt(II) - TAR species which is readily formed in slightly acidic aqueous medium [21] can be efficiently extracted in chloroform in the presence of the cationic ion-pair reagent TTC. The absorption maximum is shifted from 510 nm [21] to 525 nm (Fig. 1). It could be seen on Fig. 2 that the maximum and constant extraction of the ternary compound is achieved in the pH range from 5.2 to 5.8. Hence, acetate buffer solution with pH 5.5 in all further experiments was used.

Effect of the shaking time

The extraction equilibrium is reached for ca. 0.5 min. A longer shaking time (up to 5 min) did not affect the absorbance values. In order to avoid accidental errors, caused by the combination of short shaking times and different shaking rates, the further experiments were carried out with time of shaking 1 min.

Effect of reagents concentration

The effect of TAR and TTC concentrations on the absorbance is shown in Fig. 3. It could be accepted that 10-fold TAR excess and 13-fold TTC excess are sufficient for maximum Co extraction. The optimum reagents concentrations deduced from the mentioned figure are shown in Table 1.

Table 1. Optimum conditions and analytical characteristics of the Co(II)-TAR-TTC-water-chloroform system.

Optimum conditions	Analytical characteristics
Wavelength: 525 nm	Apparent molar absorptivity: $\epsilon = (4.26 \pm 0.07) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$
pH: 5.5 (acetate buffer)	True molar absorptivity: $\epsilon' = (4.8 \pm 0.6) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$
C _{TAR} : $1.6 \times 10^{-4} \text{ mol l}^{-1}$	Adherence to Beer's law: up to 1.5 µg ml^{-1}
C _{TTC} : $2.7 \times 10^{-4} \text{ mol l}^{-1}$	Limit of detection: 0.05 µg ml^{-1}
Shaking time: 1 min	Limit of quantification: 0.18 µg ml^{-1}
	Sandell's sensitivity: 1.38 ng cm^{-2}
	Relative standard deviation: 1.9 %

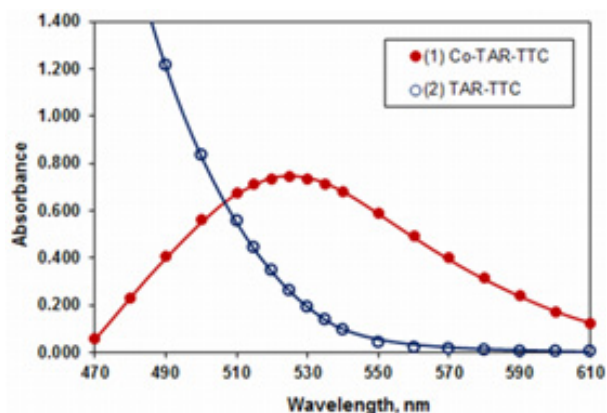


Fig. 1. Absorption spectra of the ternary Co-TAR-TTC complex and the blank (TAR-TTC); in chloroform. $C_{Co(II)} = 1.7 \times 10^{-5} \text{ mol l}^{-1}$, $C_{TAR} = 1.6 \times 10^{-4} \text{ mol l}^{-1}$, $C_{TTC} = 2.7 \times 10^{-4} \text{ mol l}^{-1}$, pH 5.5.

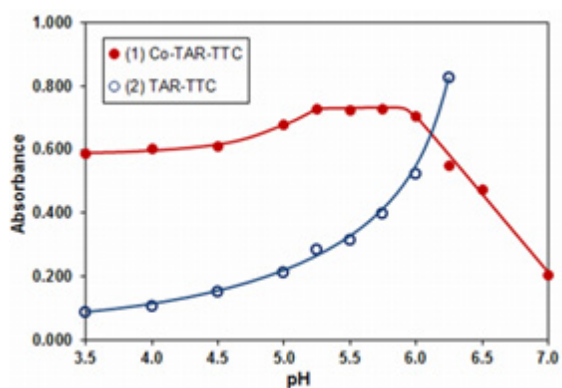


Fig. 2. Absorbance of Co-TAR-TTC extracts against blank (curve 1) and blank against chloroform (curve 2). $C_{Co(II)} = 1.7 \times 10^{-5} \text{ mol l}^{-1}$, $C_{TAR} = 2.0 \times 10^{-4} \text{ mol l}^{-1}$, $C_{TTC} = 3.0 \times 10^{-4} \text{ mol l}^{-1}$, $\lambda = 525 \text{ nm}$.

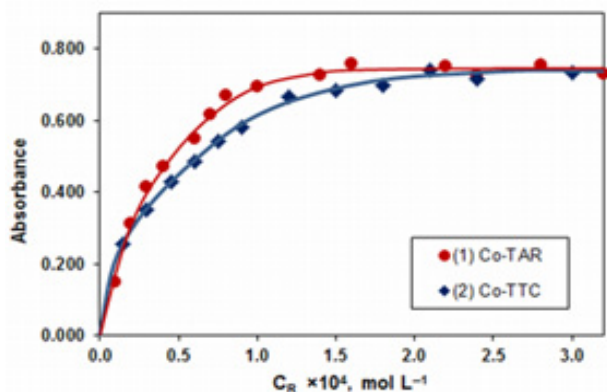


Fig. 3. Absorbance of the extracted ternary complex vs. concentration of the TTC (curve 1) and TAR (curve 2) plots. 1- $C_{Co(II)} = 1.7 \times 10^{-5} \text{ mol l}^{-1}$, $C_{TTC} = 3.0 \times 10^{-4} \text{ mol l}^{-1}$, $\lambda = 525 \text{ nm}$; 2- $C_{Co(II)} = 1.7 \times 10^{-5} \text{ mol l}^{-1}$, $C_{TAR} = 1.6 \times 10^{-4} \text{ mol l}^{-1}$, $\lambda = 525 \text{ nm}$.

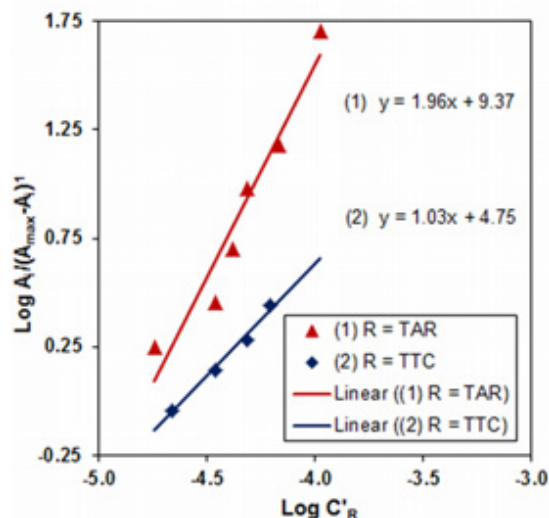


Fig. 4. Determination of the TAR-to-Co (straight line 1) and the TTC-to-Co (straight line 2) molar ratios by the mobile equilibrium method. 1- $C_{Co(II)} = 1.7 \times 10^{-5} \text{ mol l}^{-1}$, $C_{TTC} = 3.0 \times 10^{-4} \text{ mol l}^{-1}$, $\lambda = 525 \text{ nm}$; 2 - $C_{Co(II)} = 1.7 \times 10^{-5} \text{ mol l}^{-1}$, $C_{TAR} = 1.6 \times 10^{-4} \text{ mol l}^{-1}$, $\lambda = 525 \text{ nm}$.

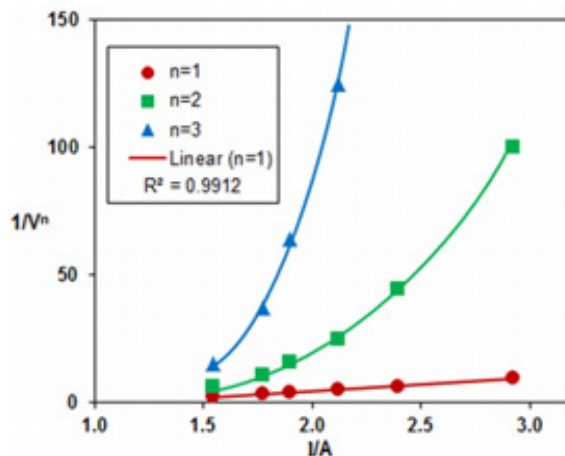


Fig. 5. Determination of the TTC-to-Co molar ratio by the method of Asmus. $C_{Co(II)} = 1.7 \times 10^{-5} \text{ mol l}^{-1}$, $C_{TAR} = 1.6 \times 10^{-4} \text{ mol l}^{-1}$, $\lambda = 525 \text{ nm}$ and $l = 1 \text{ cm}$.

Composition of the complex and suggested formula

The molar ratios in the ternary compound, TAR:Co = 2:1 and TTC:Co = 1:1, were determined by the mobile equilibrium method [22] (Fig. 4) and the straight-line method of Asmus [23] (Figs. 5 and 6). The obtained results, some conclusions [17, 24-26], and our previous experience with similar systems [16, 19, 27] suggest that cobalt(II) is oxidised to cobalt(III) by the atmospheric oxygen during the complex formation. Hence, we propose the following formula of the ternary compound: $(TT^+)[Co^{3+}(TAR)_2]$; in this formula TAR is in its depro-

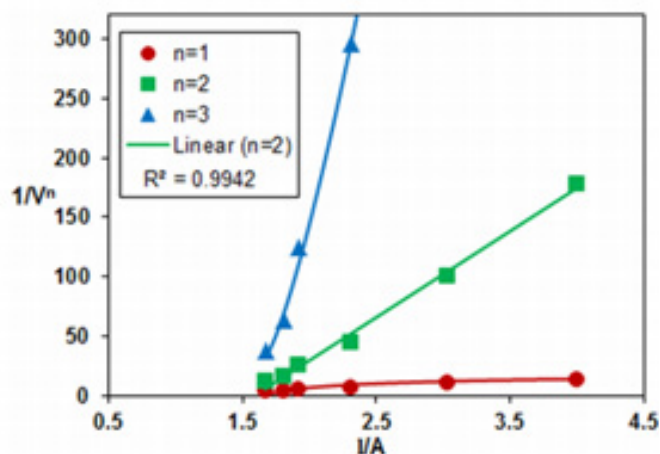


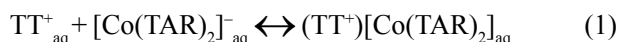
Fig. 6. Determination of the TAR-to-Co molar ratio by the method of Asmus. $C_{\text{Co(II)}} = 1.7 \times 10^{-5} \text{ mol l}^{-1}$, $C_{\text{TTC}} = 3.0 \times 10^{-4} \text{ mol l}^{-1}$, $\lambda = 525 \text{ nm}$ and $l = 1 \text{ cm}$.

tonated form $(\text{TAR})^{2-}$.

Equilibria and equilibrium constants

Several equilibrium processes are important when we describe quantitatively the formation and subsequent extraction of $(\text{TT}^+)[\text{Co}^{3+}(\text{TAR})_2]$.

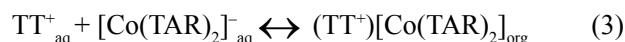
- Formation in the aqueous phase:



- Distribution:



- Extraction from water into chloroform:



The equilibrium constants describing these processes are shown in Table 2. The association constant β was determined according to a strategy [28] by several independent methods, (Holme-Langmyhr method [29], Harvey-Manning method [30], Komar-Tolmachev method [31], and the mobile equilibrium method [22]), (Fig. 4, straight line 2). The constant of distribution K_D was calculated from the absorption values obtained after single and triple extraction as described above. The constant of extraction K_{ex} was calculated by the formula

Table 2. Calculated values of $\text{Log } \beta$, $\text{Log } K_D$ and $\text{Log } K_{\text{ex}}$.

Equilibrium	Equilibrium constant	Value
1	$\beta = [(\text{TT}^+)[\text{Co}(\text{TAR})_2]_{\text{aq}}] / [\text{TT}^+]_{\text{aq}} \times [[\text{Co}(\text{TAR})_2]^-]_{\text{aq}}$	$\text{Log } \beta = 4.8 \pm 0.1^a$ $\text{Log } \beta = 4.7 \pm 0.1^b$ $\text{Log } \beta = 4.6 \pm 0.7^c$ $\text{Log } \beta = 4.7 \pm 0.3^d$
2	$K_D = [(\text{TT}^+)[\text{Co}(\text{TAR})_2]_{\text{org}}] / [(\text{TT}^+)[\text{Co}(\text{TAR})_2]_{\text{aq}}]$	$\text{Log } K_D = 0.88 \pm 0.01$
3	$K_{\text{ex}} = [(\text{TT}^+)[\text{Co}(\text{TAR})_2]_{\text{org}}] / [\text{TT}^+]_{\text{aq}} \times [[\text{Co}(\text{TAR})_2]^-]_{\text{aq}}$	$\text{Log } K_{\text{ex}} = 5.7 \pm 0.1^e$ $\text{Log } K_{\text{ex}} = 5.6 \pm 0.1^f$

^aCalculated by the Holme-Langmyhr method;

^bCalculated by the Harvey-Manning method;

^cCalculated by the Komar-Tolmachev method;

^dCalculated by the mobile equilibrium method;

^eCalculated by the formula $K_{\text{ex}} = K_D \times \beta$ where β is determined by the Holme-Langmyhr method;

^fCalculated by the formula $K_{\text{ex}} = K_D \times \beta$ where β is determined by the Harvey-Manning method.

Table 3. Effect of foreign ions on the extraction of 5 µg cobalt (II).

Foreign ions and reagents (FI)	mg	FI-to-Co ratio	Co found	R, %
Mg ²⁺	30	6000	5.18	103.5
Na ⁺	30	6000	5.11	102.2
K ⁺	15	3000	5.01	100.2
W(VI)	10	2000	4.88	97.7
NH ₄ ⁺	10	2000	5.02	100.5
Sr ²⁺	10	2000	5.11	102.3
Mo(VI)	10	2000	4.85	97.0
Ca ²⁺	9	1800	5.09	101.8
Ba ²⁺	2.5	500	5.15	103.1
Cr(VI)	0.5	100	4.91	98.2
Cr ³⁺	0.3	60	4.80	96.0
Cd ²⁺	0.1	20	4.86	97.2
Zn ²⁺	0.05	10	5.14	102.9
	0.1 ^a	20	5.04	100.8
Mn ²⁺	0.03	6	5.15	103.0
Sn ²⁺	0.03	6	4.96	99.0
Cu ²⁺	0.03	6	5.17	103.4
Ni ²⁺	0.005	1	4.56	91.3
Al ³⁺	0.005	1	5.08	101.6
	0.1 ^b	20	4.82	96.4
	0.1 ^c	20	4.89	97.8
Fe(II)	0.005	1	4.25	85.0
Fe(III)	0.005	1	5.90	118.0
	0.1 ^b	20	5.05	101.0
V(IV)	0.005	1	7.10	142.0
V(V)	0.005	1	6.60	132.0
Ga ³⁺	0.005	1	5.55	111.0
In ³⁺	0.005	1	4.69	93.8
Tl ³⁺	0.005	1	4.61	92.1
Tartrate ²⁻	10	2000	5.02	100.5
SCN ⁻	0.025	50	5.13	102.6
Cl ⁻	10	2000	5.20	104.0
S ₂ O ₃ ²⁻	10	2000	4.92	98.5
F ⁻	5	1000	5.20	104.0
NO ₃ ⁻	5	1000	5.02	100.3
SO ₄ ²⁻	5	1000	5.03	100.5
Citrate ³⁻	5	1000	4.94	98.0
PO ₄ ³⁻	3.5	700	5.10	102.0
EDTA	0.75	150	4.85	97.0
Oxalate ²⁻	2.5	500	5.15	103.1
Tiron	2.5	500	5.11	102.5
Ascorbic acid	0.5	100	5.12	102.6
ClO ₄ ⁻	0.005	1	4.73	94.6
CDTA	0.005	1	3.95	79.0

^a in the presence of 0.75 mg EDTA; 15 min extraction time;^b in the presence of 2.5 mg oxalate;^c in the presence of 3.0 mg citrate.

$K_{ex} = K_D \times \beta$. All experiments were performed at room temperature of $\sim 22^\circ\text{C}$ and the calculations were carried out at a probability of 95 %.

Effect of foreign ions and reagents

The effect of various ions and reagents on the extraction-spectrophotometric determination of 5 μg cobalt(II) is summarised in Table 3. It can be assumed that large amounts of alkaline ions, alkaline-earth ions, NH_4^+ , W(VI), Mo(VI), Cl^- , $\text{S}_2\text{O}_3^{2-}$, F^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , tartrate, citrate, oxalate and tiron; moderate amounts of Cr(VI), Cr(III), Zn(II) and Cd(II); and small amounts of Mn(II), Sn(II), Cu(II), Al(III), ascorbic acid and SCN⁻ are tolerable. Ni(II), Fe(II,III), V(IV,V), Ga(III), In(III), and Tl(III) interfere seriously at a ratio of 1:1 with respect to Co(II). However, the interfering effect of some of these ions can be reduced by masking with oxalate, citrate or EDTA (see Table 3).

Beer's law and analytical characteristics

The adherence to Beer's law was studied under the optimum extraction-spectrophotometric conditions (Table 1). The following straight line equation was obtained for the concentration interval 0.2 – 1.5 $\mu\text{g ml}^{-1}$ Co(II):

$$Y=0.7059X+0.0087 \quad (R^2=0.9988).$$

Calculated apparent molar absorptivity was $\varepsilon = (4.26 \pm 0.07) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$. This value is statistically indistinguishable from that obtained by Komar-Tolmachev method [31]. It could compete successfully with the values reported for many similar Co-containing chromogenic systems [32]. Some additional characteristics concerning the analytical application of the Co-TAR-TTC-water-chloroform system are given in Table 1. The relative standard deviation (RSD = 1.9 %) was calculated from the results of four replicate analyses of an artificial mixture containing 0.5 $\mu\text{g ml}^{-1}$ Co(II) and 10 $\mu\text{g ml}^{-1}$ of each of the following foreign ions: Mg^{2+} , Ca^{2+} , K^+ , Na^+ , Sr^{2+} , Ba^{2+} , W(VI) and Mo(VI).

CONCLUSIONS

This work represents the results of a detailed extraction-spectrophotometric study on the ion-association

system of cobalt-TAR and TTC. The optimum conditions for ternary complex formation and extraction were found. The constants characterizing the equilibria of ion-association, distribution and extraction were determined. The relatively high sensitivity and selectivity of the colour reaction make the studied system appropriate for analytical applications.

Acknowledgements

The authors would like to thank the Research Fund of the University of Plovdiv "Paisii Hilendarski" for its financial support (contract NI-13-HF006).

REFERENCES

1. H.R.Hovind, Thiazolylazo dyes and their applications in analytical chemistry. A review, *Analyst*, 100, 1975, 769-796.
2. V.A. Lemos, E.S. Santos, M.S. Santos, R.T. Yamaki, Thiazolylazo dyes and their application in analytical methods, *Microchim. Acta*, 158, 2007, 189-204.
3. R.G. Anderson, G. Nickless, Heterocyclic azo dye-stuffs in analytical chemistry. A review, *Analyst*, 92, 1967, 207-238.
4. P.X. Baliza, S.L.C. Ferreira, L.S.G. Teixeira, Application of pyridylazo and thiazolylazo reagents in flow injection preconcentration systems for determination of metals, *Talanta*, 79, 2009, 2-9.
5. A.V. Ivanov, Progress in and prospects for the use of heterocyclic azo-compounds in analytical chemistry, *Russ. Chem. Rev.*, 45, 1976, 213-226.
6. F. Karipcin, E. Kabalcilar, S. Ilican, Y. Caglar, M. Caglar, Synthesized some 4-(2-thiazolylazo)resorcinol complexes: characterization, thermal and optical properties, *Spectrochim. Acta A*, 73, 2009, 174-180.
7. F.I.Lobanov, G.K. Nurtaeva, E.E. Ergozhin, Ekstraktsiya kompleksov ionov metallov s piridinovymi oksiazosodineniyami, *Alma-Ata, Nauka*, 1983, (in Russian).
8. K.B. Gavazov, A.N. Dimitrov, V.D. Lekova, The use of tetrazolium salts in inorganic analysis, *Uspekhi Khim.*, 76, 2007, 187-198, (in Russian).
9. K.Ueda, Spectrophotometric Study on the extraction of 4-(2-thiazolylazo)resorcinol chelates of cobalt(II), nickel(II), copper(II), and zinc(II) with zephiramin, *Anal. Lett.*, 11, 1978, 1009-1021.

10. K.Ueda, The extraction spectrophotometric determination of cobalt(II) with 4-(2-thiazolylazo)resorcinol and zephiramin, *Bull. Chem. Soc. Jpn.*, 52, 1979, 1215-1216.
11. T.Yotsuyanagi, R. Yamashita, K. Aomura, Spectrophotometric determination of traces of metals by solvent extraction with 4-(2-pyridylazo)-resorcin-quaternary ammonium salt-polyaminocarboxylic acid system, *Jpn. Anal.*, 19, 1970, 981-982.
12. R.Yamashita, T. Yotsuyanagi, K. Aomura, The extraction-spectrophotometric determination of traces of iron and cobalt with 4-(2-pyridylazo)-resorcinol, *Jpn. Anal.*, 20, 1971, 1282-1288.
13. S.N. Bhadani, M. Tewari, A. Agrawal, C. Sekhar, Extractive-photometric determination of cobalt(II) in steels using 4-(2-pyridylazo)resorcinol and xylometazoline hydrochloride, *J. Indian Chem. Soc.*, 75, 1998, 176-177.
14. S.G. Mamuliya, I.V. Pyatnitskii, L.L. Kolomiets, K.I. Grigalashvili, Solvent extraction of complexes of cobalt, nickel, copper, zinc and cadmium with 4-(2-pyridylazo)-resorcinol and diphenylguanidine, *Zh. Anal. Khim.*, 35, 1980, 1306-1309, (in Russian).
15. A.G. Gaikwad, H. Noguchi, M. Yoshio, Solvent extraction studies of metal-4-(2-pyridyl-azo)-resorcinol complexes with potassium-dicyclohexyl-18-crown-6 complex, *Anal. Lett.*, 24, 1991, 1625-1641.
16. P.V. Racheva, K.B. Gavazov, V.D. Lekova, A.N. Dimitrov, Complex formation in a liquid-liquid extraction system containing cobalt(II), 4-(2-pyridylazo)resorcinol, and nitron, *J. Mater.*, 2013, 7.
17. L. Marić, M. Široki, Z. Štefanac, M. J. Herak, Extraction of cobalt-[4-(2-thiazolylazo)resorcinol] complexes, *J. Inorg. Nucl. Chem.*, 43, 1981, 3357-3361.
18. O.Navratil, R.W. Frei, The extraction-photometric determination of cadmium and cobalt with 4-(2-thiazolylazo)-resorcinol and 1-(2-thiazolylazo)-naphthol, *Anal. Chim. Acta*, 52, 1970, 221-227.
19. V. V. Divarova, K. B. Gavazov, V. D. Lekova, A. N. Dimitrov, Spectrophotometric investigations on liquid-liquid extraction systems containing cobalt, 4-(2-pyridylazo)-resorcinol and tetrazolium salts, *Chemija*, 24, 2013, 81-87.
20. K.Gavazov, V. Lekova, A. Dimitrov, Extraction studies on the system vanadium(V) – 4-(2-thiazolylazo)-resorcinol – neotetrazolium chloride – water – chloroform, *J.Univ. Chem. Technol. Met. (Sofia)*, 41, 2006, 217-220.
21. A.I.Busev, V.M. Ivanov, Z.I. Nemtseva, A spectrophotometric study of complex formation between cobalt and 4-(2-thiazolylazo)-resorcinol, *Zh. Anal. Khim.*, 24, 1969, 414-421, (in Russian).
22. Z.Zhiming, M. Dongsten, Y. Cunxiao, Mobile equilibrium method for determining composition and stability constant of coordination compounds of the form $MmRn$, *J. Rare Earths*, 15, 1997, 216-219.
23. E.Asmus, Eine neue Methode zur Ermittlung der Zusammensetzung schwacher Komplexe, *Fresenius' J. Anal. Chem.*, 178, 1960, 104-116.
24. M. Široki, L. Marić, Z. Štefanac, M. J. Herak, Characterization of complexes involved in the spectrophotometric determination of cobalt with 4-(2-pyridylazo)resorcinol, *Anal. Chim. Acta*, 75, 1975, 101-109.
25. V. Cucinotta, R. Caruso, A. Giuffrida, M. Messina, G. Maccarrone, A. Torrisi, Separation and quantitation of metal ions by 4-(2-pyridylazo)resorcinol complexation in capillary electrophoresis-electrospray ionisation mass spectrometry, *J. Chromatogr. A*, 1179, 2008, 17-23.
26. J. Dolezal, L. Sommer, Reverse-phase high performance liquid chromatography of metal chelates of 4-(2-pyridylazo)resorcinol and 4-(2-thiazolylazo)resorcinol. Simultaneous determination of low concentrations of Co, Ni and Fe, *Collect. Czech. Chem. Commun.*, 59, 1994, 2209-2226.
27. F.Genç, K.B. Gavazov, M. Türkyilmaz, Ternary complexes of vanadium(IV) with 4-(2-pyridylazo)-resorcinol (PAR) and ditetrazolium chlorides (DTC), *Cent. Eur. J. Chem.*, 8, 2010, 461-467.
28. K.B.Gavazov, Extraction-Spectrophotometry of Ion-Association Complexes, *Chemistry: Bulgarian Journal of Science Education*, 22, 2013, 222-253.
29. A.Holme, F.J. Langmyhr, A modified and a new straight-line method for determining the composition of weak complexes of the form $AmBn$, *Anal. Chim. Acta*, 36, 1966, 383-391.
30. A.E. Harvey, D.L. Manning, Spectrophotometric Methods of Establishing Empirical Formulas of Colored Complexes in Solution, *J. Am. Chem. Soc.*, 72, 1950, 4488-4493.
31. M.I. Bulatov, I.P. Kalinkin, *Prakticheskoe rukovod-*

stvo po fotokolorimetričeskim i spektrofotometričeskim metodam analiza, Leningrad, Khimiya, 1986, (in Russian).

32. G.Ram, R.S. Chauhan, A.K. Goswami, Review of spectrophotometric methods for determination of cobalt(II), *Rev. Anal. Chem.*, 22, 2003, 255-317.