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

Mudigonda Naga Raju [1], Dr.Sanjeev Kumar [2], S.Swapna Rani [3], M.Sravan Kumar [4],
Dept.: Humanities & Science
Pallavi Engineering College,
Kuntloor(V),Hayathnagar(M),Hyderabad,R.R.Dist.-501505

ABSTRACT

The cobalt(II) - 4-(2- thiazolylazo)resorcinol (TAR) - 2,3,5-triphenyl-2H-tetrazolium chloride (TTC) - water - chloroform system was examined for complex formation and liquid-liquid extraction. Spectrophotometric measurements of the extraction yielded the best results. The interacting species' molar ratio was found to be 1:2:1. (Co:TAR:TTC). This study quantified three different equilibrium processes, including how $[Co3+(TAR)]$– and the tetrazoliumcation interact (Log =4.7), how the ternary complex is distributed across aqueous and organic phases (LogK =0.88), and how chloroform is extracted from water (LogK=LogD+LogK =5.6). The extraction was tested to see how extraneous ions and reagents affected it. A simple and sensitive extraction-spectrophotometric technique for the measurement of cobalt (525 ex=4.26104 l mol–1 cm–1) was devised.

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

INTRODUCTION

4-(2-pyridylazo)-resorcinol (PAR) and 4-(2-thiazolylazo)-resorcinol (TAR) are two examples of metal ions that create coloured binary species with azodyes [1-7]. With the addition of auxiliary chemicals [7, 8], these species may increase their colour and extraction characteristics. Reagents for liquid-phase ion-association were employed as follows: liquid extraction of $[Co(TAR)]^{z-}$ or $[Co(PAR)]^{z-}$ (z =1 or 2): zephiramine [9-12], xylometazoline hydrochlo- [13, 14], potassium-dicyclohex- yl-18-crown-6 [15], nitrogen [16], cetylpyridinium chloride [18], tetra-n-heptylammonium salts [18], tetrazolium [19] are some of the other compounds that have been used in the study. Complex generation and extraction in a Co(II), PAR, and 2,3,5-triphenyl-2H-tetrazolium chloride (TTC) system were previously reported [19]. The findings of a long-term study on a chromogenic extraction technique that uses TAR rather than PAR are reported here.

EXPERIMENTAL
Reagents and apparatus

Cobalt standard solution (1000 mg l−1; Co(NO3)2) was purchased from Merck Darmstadt (Germany).

Working solutions (CCo = 1.7x10–4 mol l−1) were prepared by diluting appropriate volumes of the stock solution. TAR (97 %, Sigma-Aldrich), dissolved in slightly alkalized distilled water, 2x10–3 mol l−1. TTC (LobaFeinchemie GMBH), 3.0x10–3mol 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

Separatory funnels were used to introduce aliquots of Co(II) solution, TAR solution, TTC solution, and buffer solution (5 ml; pH varying from 3.5 to 7.0). Dissolved oxygen in distilled water to make a final volume of 10 ml. To this solution, 10 ml of chloroform was added, followed by a period of shaking the funnels (up to 5.0 min). Excessively high absorbance readings were observed in a cell using an organic extract filter paper.

Procedure for extraction-spectrophotometric deter- mination of cobalt

In a separatory funnel, an aliquot of cobalt solution (0.19 - 1.5 g ml1) was put. Once all three solutions had been introduced, 5 cc of an acidic buffer solution with pH 5.5 was added. Chloroform and 10 ml of distilled water were combined with the resultant solution, and the funnel was agitated for one minute. The light absorbance of the organic extract was measured after it was filtered through a filter paper and placed in a cell. at λ_{max} 525 nm was recorded against a blank sample.

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 A_1 is the light absorbance measured after a single extraction at the optimum oper- ating conditions (Table 1, 25 ml final volume) and A_3 is the absorbance measured after a triple extraction underthe same conditions [20].

RESULTS AND DISCUSSION

Spectral characteristics and effect of Ph

Cobalt(II)-TAR species, which is readily generated in slightly acidic aqueous solution, may be effectively extracted in chloroform in the presence of TTC. [21] The maximum absorption wavelength shifts from 510 to 525 nm [21]. (Fig. 1). Fig. 2 shows that the highest and consistent extraction of the ternary compound is attained in the pH range of 5.2 to 5.8. As a result, pH 5.5 acetate buffer solution was utilised in all subsequent studies.

Effect of the shaking time

The extraction equilibrium is achieved lasting approx. 0.5 min. A prolonged shaking period (up to 5 min) did not impact the absorbance results. In order to minimize inadvertent mistakes, produced by the combination of short shaking durations and varied shaking rates, the subsequent studies were carried out with time of shaking 1 min.

Effect of reagents concentration

In Fig. 3, the absorbance of TAR and TTC concentrations is exhibited. Co extraction may be maximised with 10-fold TAR and 13-fold TTC excess, respectively. Table 1 shows the optimal reagent concentrations derived from the figure above.

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: $\varepsilon = (4.26\pm0.07)\times10^4 \ 1\,mol^{-1}\,cm^{-1}$
pH: 5.5 (acetate buffer)	True molar absorptivity: $\varepsilon' = (4.8\pm0.6)\times10^4 \ 1\,mol^{-1}\,cm^{-1}$
C_{TAR}: $1.6\times10^{-4}\,mol\,l^{-1}$	Adherence to Beer's law: up to $1.5\ \mu g\,ml^{-1}$
C_{TTC}: $2.7\times10^{-4}\,mol\,l^{-1}$	Limit of detection: $0.05\ \mu g\,ml^{-1}$
Shaking time: 1 min	Limit of quantification: $0.18\ \mu g\,ml^{-1}$
	Sandell's sensitivity: $1.38\ ng\,cm^{-2}$
	Relative standard deviation: 1.9 %
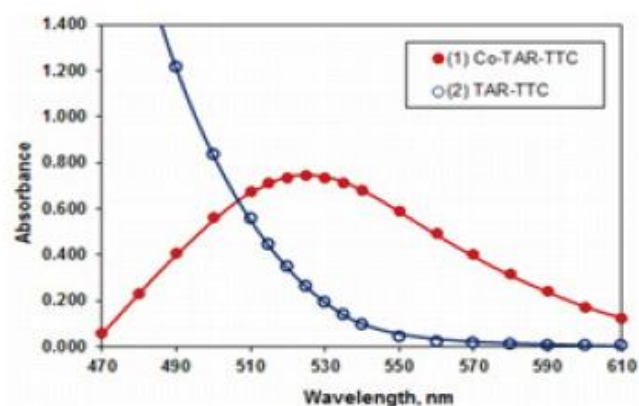
Fig. 1. Absorption spectra of the ternary Co-TAR-TTC complex and the blank (TAR-TTC); in chloroform. $C_{Co(II)} = 1.7\times10^{-5}\,mol\,l^{-1}$, $C_{TAR} = 1.6\times10^{-4}\,mol\,l^{-1}$, $C_{TTC} = 2.7\times10^{-4}\,mol\,l^{-1}$, pH 5.5.
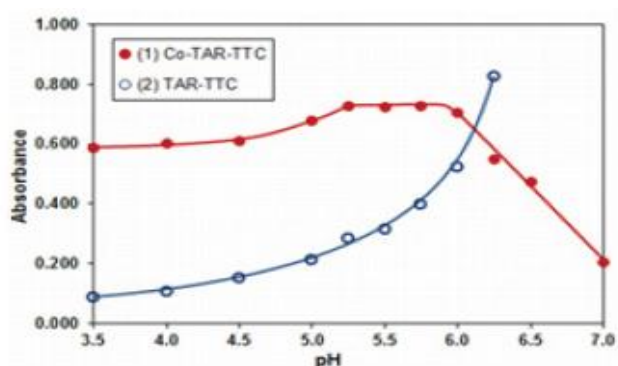

Fig. 2. Absorbance of Co-TAR-TTC extracts against blank (curve 1) and blank against chloroform (curve 2). $C_{Co(II)} = 1.7\times10^{-5}\,mol\,l^{-1}$, $C_{TAR} = 2.0\times10^{-4}\,mol\,l^{-1}$, $C_{TTC} = 3.0\times10^{-4}\,mol\,l^{-1}$, $\lambda=525$ nm.

Composition of the complex and suggested formula

The mobile equilibrium technique [22] (Fig. 4) and the Asmus straight-line method [23] were used to calculate the ternary compound's TAR:Co = 2:1 and TTC:Co = 1:1 molar ratios (Figs. 5 and 6). As a consequence of the findings [17, 24–26] and our prior experience with comparable systems [16, 19, 27], we may conclude that oxygen in the atmosphere oxidises cobalt(II) to cobalt(III) during the development of the complex. There are three atoms of Co^{3+} in the ternary combination, and the deprotonated form of $(TAR)2-$ appears in this formula.
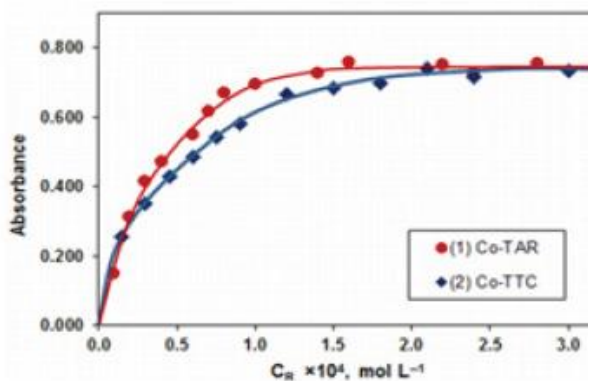

Fig. 3. Absorbance of the extracted ternary complex vs. concentration of the TTC (curve 1) and TAR (curve 2) plots. 1- $C_{Co(II)}$ = 1.7×10^{-5}mol l^{-1}, C_{TTC} = 3.0×10^{-4}mol l^{-1}, λ =525 nm; 2 - $C_{Co(II)}$ 1.7×10^{-5}mol l^{-1}, C_{TAR} = 1.6×10^{-4}mol l^{-1}, λ=525 nm.
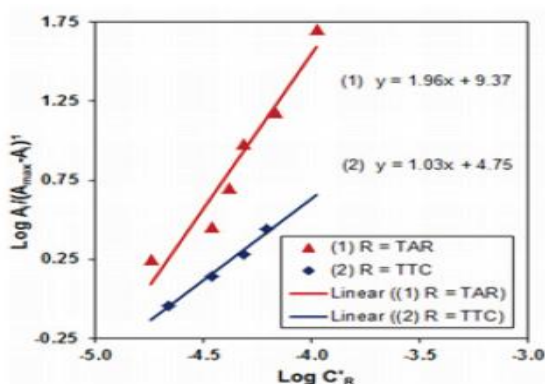

Fig. 4. Determination of the TAR-to-Co (straight line 1) and the TTC-to-Co (straight line 2) molar ratios by the mobile equilibrium method. 1- $C_{Co(II)}$= 1.7×10^{-5}mol l^{-1}, C_{TTC} = 3.0×10^{-4} mol l^{-1}, λ =525 nm; 2 - $C_{Co(II)}$= 1.7×10^{-5}mol l^{-1}, C_{TAR}= 1.6×10^{-4} mol l^{-1}, λ=525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

Fig. 6. Determination of the TAR-to-Co molar ratio by the method of Asmus. CCo(II) = 1.7×10–5mol l–1, CTTC = 3.0×10–4 mol l–1, l=525 nm and l = 1 cm.

Equilibria and equilibrium constants

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

• Formation in the aqueous phase:

$$TT^+_{aq} + [Co(TAR)_2]^-_{aq} \longleftrightarrow (TT^+)[Co(TAR)_2]_{aq} \qquad (1)$$

• Distribution:

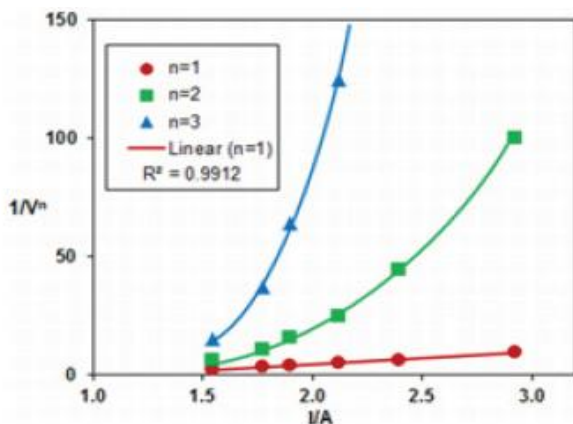$$(TT^+)[Co(TAR)_2]_{aq} \longleftrightarrow (TT^+)[Co(TAR)_2]_{org} \qquad (2)$$
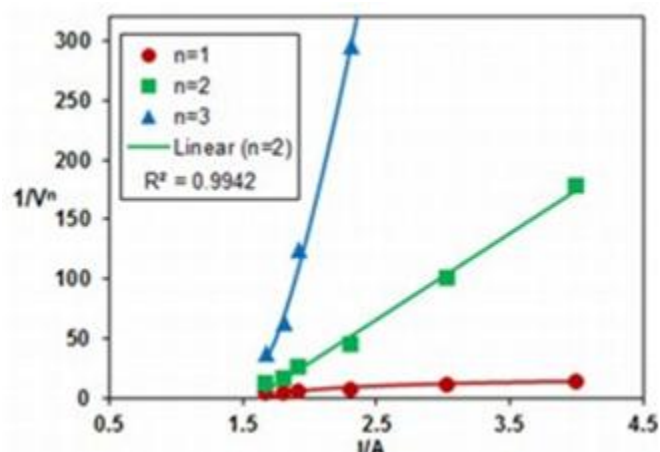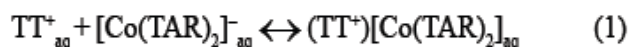

Fig. 5. Determination of the TTC-to-Co molar ratio by the method of Asmus. $C_{Co(II)}$ = 1.7×10^{-5} mol l^{-1}, C_{TAR} = 1.6×10^{-4}mol l^{-1}, λ=525 nm and l = 1 cm.
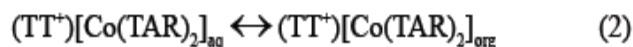
• Extraction from water into chloroform:

$$TT^+_{aq} + [Co(TAR)_2]^-_{aq} \leftrightarrow (TT^+)[Co(TAR)_2]_{org} \quad (3)$$
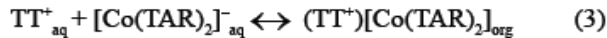
The equilibrium constants describing these processes are shown in Table 2. The association constant β was determined according to a strategy [28] by several independent methods, (Holme-Langmyhr method [29], Harvey-Manning method [30], Komar-Tolmachev method [31], and the mobile equilibrium method [22]), (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 Log β, Log K_D and Log K_{ex}.

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

[a]Calculated by the Holme-Langmyhr method;
[b]Calculated by the Harvey-Manning method;
[c]Calculated by the Komar-Tolmachev method;
[d]Calculated by the mobile equilibrium method;
[e]Calculated by the formula $K_{ex}=K_D\times\beta$ where β is determined by the Holme-Langmihr method;
[f]Calculated by the formula $K_{ex}=K_D\times\beta$ 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 $\sim 22°C$ and the calculations were carried out at a probability of 95 %.

Effect of foreign ions and reagents

Data on the extraction-spectrophotometric determination of cobalt(II) from 5 g cobalt are summarised in Table 3 (as shown). Large levels of alkaline ions, alkaline-earth ions, NH4+, W(VI), Mo(VI), Cl–, S O 2–, F–, NO –, SO 2–, PO 3–, tartrate, citrate, oxalate, and tiron might be presumed to be tolerated, as can moderate amounts of Cr(VI), Cr(III), Zn(II), and Cd(II), as well as modest amounts of Mn(I With regard to Co, there is a 1:1 ratio of interference from the following elements: Ni (II), Fe (II, III), Va (IV), Gd (III), In (III), and Tl (III) (II). It is possible to lessen the interference of some of these ions with the use of oxalate, citrate, or EDTA masking (see Table 3).

Beer's law and analytical characteristics

The adherence to Beer's law was studied underthe optimum extraction-spectrophotometric conditions (Table 1). The following straight line equation was ob-tained for the concentration interval 0.2 – 1.5 ⊡g ml^{-1} Co(II):

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

According to our calculations, the apparent molar absorptivity was a whopping 104 l mol-1 cm–1 = (4.260.07). Komar-technique Tolmachev's is statistically indistinguishable from this value [31]. A number of similar Co-containing chromogenic systems have shown promising results [32]. Table 1 provides further information on the Co-TAR-TTC-water-chloroform system's analytical applications. An artificial mixture comprising 0.5% Co(II), 10% Mg2+, 10% Ca2+, 10% K+, 10% Na+, 10% Sr2+, 10% Ba2+, 10% W(VI) and 10% Mo was used to compute the relative standard deviation (RSD = 1.9 percent) (VI).

CONCLUSIONS

The findings of an ex-traction-spectrophotmetric investigation on the ion-association for the synthesis and extraction of ternary complexes are presented in this paper. The equilibrium constants for ion-association, distribution, and extraction were determined. The researched system is well-suited for analytical use due to the colour reaction's high sensitivity and selectivity.

Acknowledgements

REFERENCES

1. H.R.Hovind, Thiazolylazo dyes and their applicationsin 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, Applica-tion of pyridylazo and thiazolylazo reagents in flow injection preconcentration systems for determinationof 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)resor- cinol complexes: characterization, thermal and optical properties, Spectrochim. Acta A, 73, 2009, 174-180.

7. F.I.Lobanov, G.K. Nurtaeva, E.E. Ergozhin, Ekstrak- tsiya kompleksov ionov metallov s piridinovymi oksiazosoedineniyami, Alma-Ata, Nauka, 1983, (inRussian).

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 determi- nation 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, Spectro-photometric 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 ex- traction-spectrophotometric determination of tracesof 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 xy-lometazoline hydrochloride, J. Indian Chem. Soc.,75, 1998, 176-177.

14. S.G. Mamuliya, I.V. Pyatnitskii, L.L. Kolomiets,

15. K.I. Grigalashvili, Solvent extraction of complexesof cobalt, nickel, copper, zinc and cadmium with 4-(2-pyridylazo)-resorcinol and diphenylguanidine, Zh. Anal. Khim., 35, 1980, 1306-1309, (in Russian).

16. 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.

17. 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-pyri- dylazo)resorcinol, and nitron, J. Mater., 2013, 7.

18. 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.

19. O.Navratil, R.W. Frei, The extraction-photomet- ric determination of cadmium and cobalt with 4-(2-thiazolylazo)-resorcinol and 1-(2-thiazolylazo)- naphthol, Anal. Chim. Acta, 52, 1970, 221-227.

20. V. V. Divarova, K. B. Gavazov, V. D. Lekova, A.

21. N. Dimitrov, Spectrophotometric investigations on liquid-liquid extraction systems containing cobalt, 4-(2-pyridylazo)-resorcinol and tetrazolium salts, Chemija, 24, 2013,81-87.

22. K.Gavazov, V. Lekova, A. Dimitrov, Extraction stud- ies on the system vanadium(V) – 4-(2-thiazolylazo)-

23. resorcinol – neotetrazolium chloride – water – chlo- roform, J.Univ. Chem. Technol. Met. (Sofia), 41, 2006, 217-220.

24. A.I.Busev, V.M. Ivanov, Z.I. Nemtseva, A spectro- photometric study of complex formation between cobalt and 4-(2-thiazolylazo)-resorcinol, Zh. Anal. Khim., 24, 1969, 414-421, (in Russian).

25. Z.Zhiming, M. Dongsten, Y. Cunxiao, Mobile equi- librium method for determining composition and stability constant of coordination compounds of theform MmRn, J. Rare Earths, 15, 1997, 216-219.

26. E.Asmus, Eine neue Methode zur Ermittlung der Zusammensetzung schwacher Komplexe, Fresenius' J. Anal. Chem., 178, 1960, 104-116.

27. 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.

28. V. Cucinotta, R. Caruso, A. Giuffrida, M. Messina,

29. G. Maccarrone, A. Torrisi, Separation and quanti- tation of metal ions by 4-(2-pyridylazo)resorcinol complexation in capillary electrophoresis–electro- spray ionisation mass spectrometry, J. Chromatogr.

A, 1179, 2008, 17-23.

30. J. Dolezal, L. Sommer, Reverse-phase high perfor- mance 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.

31. 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.

32. K.B.Gavazov, Extraction-Spectrophotometry of Ion-Association Complexes, Chemistry: Bulgarian Journal of Science Education, 22, 2013, 222-253.

33. A.Holme, F.J. Langmyhr, A modified and a new straight-line method for determining the composi- tion of weak complexes of the form AmBn, Anal. Chim. Acta, 36, 1966, 383-391.

34. 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.

35. M.I. Bulatov, I.P. Kalinkin, Prakticheskoe rukovod- stvo po fotokolorimetricheskim i spektrofotomet- richeskim metodam analiza, Leningrad, Khimiya, 1986, (in Russian).

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