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Extraction-Chromogenic System for Cobalt Based on 5-Methyl-4-(2-thiazolylazo) Resorcinol and Benzalkonium Chloride

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Abstract

The interaction between Co^{II} and 5-methyl-4-(2-thiazolylazo)-resorcinol (MTAR) was studied in a water-chloroform system, in the presence or absence of benzalkonium chloride (BZC) as a cationic ion-association reagent. The optimum pH, concentration of the reagents and extraction time for the extraction of Co were found. In the presence of BZC, the extracted ion-associate could be represented by the formula (BZ⁺)[Co^{III}(MTAR²⁻)₂], where MTAR is in its deprotonated form. The following extraction-spectrophotometric characteristics were determined: absorption maximum, molar absorptivity, Sandell's sensitivity, limit of detection, limit of quantification, constant of extraction, distribution ratio and fraction extracted. In the absence of BZC, the extraction is incomplete and occurs in a narrow pH range. The extracted chelate contains one deprotonated and one monoprotonated ligand: [Co^{III}(MTAR²⁻)(HMTAR⁻)].

Keywords: Cobalt; 4-(2-thiazolylazo)resorcinol; benzalkonium chloride; ternary complex; solvent extraction; spectro-photometry

1. Introduction

Cobalt is a group 9 transition metal that occupies position 27 in the periodic table. Because of its unique properties it is important for industry, agriculture, medicine and high technology development. As a highly wear- and corrosion-resistant metal which retains these properties even at high temperature, cobalt is an essential constituent of alloys for special uses.^{1,2} It is also applied in the manufacture of sintered cutting tools, catalysts, permanent magnets, pigments, siccative's and rechargeable (e.g., lithium-ion) batteries. Since the need of these batteries increases, some business experts predict a 47x increase in global demand for cobalt in 2030 compared to 2017.³

Cobalt is a relatively rare element. It is present in rocks, soils and sea water at very low concentrations and its average content in the continental crust is approximately 17.3 mg/kg.⁴ There are several commercially important

cobalt-containing minerals, such as heterogenite, linnaeite, cobaltite, smaltite, erythrite, carrolite, skutterudite and asbolite. However, in most deposits, this element is not in sufficient quantity to be economically minable alone and is obtained as a by-product of the metallurgy of copper, nickel, silver, gold, lead and zinc. 1,4,5

Cobalt is an essential trace element for all animals, including humans, and an active nutrient for bacteria, fungi and algae. It is utilized by animals only in the form of vitamin B-12, synthesized by certain bacteria and archaea in the presence of enough cobalt. Cobalt deficiency (or vitamin B-12 deficiency) in humans can lead to pernicious anemia and nerve damage.⁶ On the other hand, excess cobalt can provoke numerous negative effects on central metabolism.^{7,8} That is why its content in various samples should be monitored.^{8–11}

There are many analytical methods for cobalt. Azo dyes such as 4-(2-pyridylazo)resorcinol (PAR)¹²⁻²³ and

4-(2-thiazolylazo)resorcinol (TAR)²⁴⁻²⁷ have long been used for its preconcentration and subsequent determination. Due to the ability of these reagents to form anionic chelates with cobalt cations, analytical procedures are often associated with the addition of auxiliary reagents providing the necessary hydrophobicity and extraction characteristics.

The following cationic reagents have been used as components of Co-PAR and Co-TAR ternary complexes: diphenylguanidine, ¹⁵ dicyclohexyl-18-crown-6, ¹⁷ tetradecyl(trihexyl)phosphonium chloride, ²¹ xylometazoline hydrochloride, ¹⁹ tributylammonium bromide, ²² tetraphenylarsonium chloride, ^{28,29} tetraphenylphosphonium chloride, ^{28,29} nitron, ³⁰ tetrazolium salts, ^{27,31-33} and quaternary ammonium salts, ^{16,18,20,34-36}

5-Methyl-4-(2-thiazolylazo)resorcinol (MTAR)³⁷ is a TAR derivative that has been used in our laboratory for the liquid-liquid extraction of V^{IV,V} ^{38–42} and Ni^{II}. ⁴³ Its interaction with Co^{II} in water-ethanol medium has been studied by Kiryukhina. ⁴⁴ This reagent has also been used for the reversed-phase capillary high-performance liquid chromatographic determination of Co^{II}. ⁴⁵ There are no reports on the liquid-liquid extraction of Co complexes with MTAR, nor on the ternary Co-MTAR complexes with auxiliary reagents.

The objective of this work was to investigate the complex formation and liquid-liquid extraction of Co with MTAR in the presence and absence of benzalkonium chloride (BZC). BZC (Figure 1) is a mixture of quaternary ammonium chlorides used in pharmaceuticals, cosmetics and cleaning products due to its valuable bacteriostatic, bactericidal, fungicidal, algicide, spermicide and surfactant properties. 46,47 Its ability to form ion-pairs with bulky anions has been used in liquid-liquid extraction methods for its determination. 48

$$\begin{array}{c|c} & \oplus & C_nH_{2n+1} \\ \hline & & \\ H_3C & CH_3 & CI^{\bigcirc} \end{array}$$

Fig. 1. Structural formula of BZC. The index n can be 8, 10, 12, 14, 16 or 18 (constituents with n = 12, 14, and 16 predominate).

2. Experimental

2. 1. Reagents and Apparatus

Cobalt standard solution (1000 mg dm $^{-3}$, Co(NO₃)₂) was obtained from Merck, Germany. Working solutions

 $(c_{\text{Co}} = 4.0 \times 10^{-4} \text{ mol dm}^{-3})$ were prepared by appropriate dilution. MTAR (95%) and BZC (≥ 95%) were also Merck products. Neutral or slightly basic aqueous solutions of MTAR $(2.0 \times 10^{-3} \text{ mol dm}^{-3})$ were prepared by the addition of KOH. 40,41 BZC was dissolved in water ($c_{BZC} = 2 \times$ 10^{-2} mol dm⁻³ and 4×10^{-4} mol dm⁻³). Chloroform was redistilled and used repeatedly. The acidity of the aqueous phase was maintained constant by the addition of buffer solution, prepared by mixing 2 mol dm⁻³ aqueous solutions of acetic acid and ammonia. The resulting pH was checked by a WTW InoLab 720 pH-meter (Germany) with a precision of ±0.01 pH units. UV/vis spectrophotometers Ultrospec3300 pro and Camspec M508 UV-Vis (UK), equipped with 10-mm path-length cells, were employed for absorbance measurements. Distilled water was used in all experiments.

2. 2. General Procedure

Solutions of Co^{II}, buffer (pH 3.7–9.2), MTAR and BZC were sequentially transferred into a separatory funnel. Water was added to a total volume of 10 cm³. Then 10 cm³ of chloroform were buretted and the funnel was shaken for a fixed time interval. After a short wait for phase separation, a portion of the organic extract was transferred through a filter paper into the spectrophotometer cell. Absorbance was measured against chloroform or a simultaneously prepared blank.

2. 3. Determination of the Distribution Ratio and Fraction Extracted

The distribution ratio D was found from the equation $D = A_1/(A_3 - A_1)$, where A_1 is the absorbance measured after a single extraction under the optimum conditions in the presence of BZC (Table 1) and A_3 is the absorbance measured after a triple extraction under the same conditions. The total volume in both cases (single extraction and triple extraction) was 25 cm³.³⁹⁻⁴¹ The fraction extracted was calculated from the equation $E(\%) = 100 \times D/(D+1)$.

3. Results and Discussion

3. 1. Absorption Spectra and Effect of pH

Kiryukhina⁴⁴ reported that Co^{II} reacts with MTAR in a water-ethanol medium to form a 1:2-complex with an

Table 1. Optimum extraction-spectrophotometric conditions.

Extraction system	λ _{max} , nm	pН	c _{MTAR} , mol dm⁻³	c _{BZC} , mol dm⁻³	Shaking time, min
Co – MTAR – water –chloroform Co – MTAR – BZC– water –chloroform	509 550	5.5 7.5	4.0×10^{-4} 1.6×10^{-4}	- 1.4 × 10 ⁻⁴	3 ^a 3

^a quantitative extraction cannot be achieved

absorption maximum $\lambda_{\text{max}} = 520$ nm. She found that the optimum pH for complex formation was 6 – 8 but did not pay attention to the change in spectral characteristics as the pH changed.

Our extraction studies have shown that the extracted into organic phase complex in the Co-MTAR-water-chloroform system has an absorption maximum at 509 nm (Figure 2, spectrum 1). In the presence of BZC, the absorption maximum shifts to the higher wavelengths (about 549 –550 nm; spectrum 2) and the optimum pH range widens significantly and shifts to higher pH values (Figure 3).

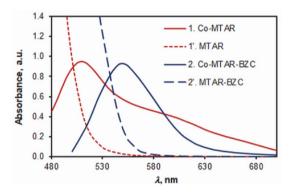


Figure 2. Absorption spectra in chloroform of the Co-MTAR binary complex (1) against blank (1') and Co-MTAR-BZC ternary complex (2) against corresponding blank (2'). $c_{\rm Co} = 4 \times 10^{-5}$ mol dm⁻³; $t_{\rm ex} = 3$ min; $c_{\rm MTAR} = 4.0 \times 10^{-4}$ mol dm⁻³ (1, 1') or 1.6×10^{-4} mol dm⁻³ (2, 2'); pH = 5.5 (1, 1') or 7.5 (2, 2'); $c_{\rm BZC} = 1.4 \times 10^{-4}$ mol dm⁻³ (2, 2').

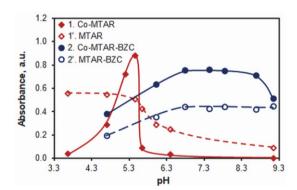


Figure 3. Absorbance of the Co-MTAR (1) and Co-MTAR-BZC (2) complexes and corresponding blanks (1' and 2') vs pH of the aqueous phase. $_{Co} = 4 \times 10^{-5}$ mol dm $^{-3}$ (1, 2); $c_{MTAR} = 4 \times 10^{-4}$ mol dm $^{-3}$ (1, 1', 2, 2'); $c_{BZC} = 1 \times 10^{-3}$ mol dm $^{-3}$ (2, 2'); $\lambda = 509$ nm (1,1') or 550 nm (2,2'); $t_{ex} = 3$ min.

3. 2. Effect of MTAR Concentration and the MTAR-to-Co Molar Ratio

The effect of MTAR concentration on the absorbance at 509 and 550 nm is shown in Figure 4, curves 1a-c. Processing of the data received in the presence or absence of BZC by the straight-line method of Asmus⁴⁹ (Figure 5) showed that in both cases the MTAR-to-Co molar ratio is 2:1. When the concentration of MTAR increases in the

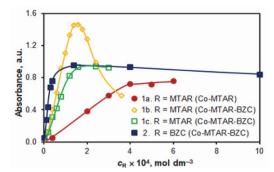
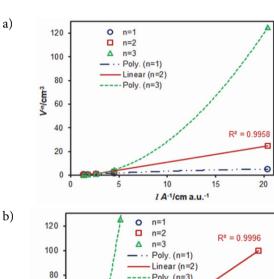
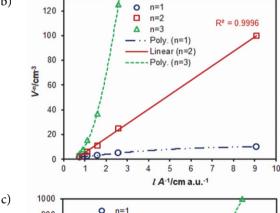


Figure 4. Effect of MTAR (1a,b,c) and BZC (2) concentration. (1a) $c_{\text{Co}} = 4 \times 10^{-5} \text{ mol dm}^{-3}$, pH 5.2, $t_{\text{ex}} = 3 \text{ min}$, $\lambda = 509 \text{ nm}$; (1b) $c_{\text{Co}} = 8.5 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{\text{BZC}} = 4 \times 10^{-4} \text{ mol dm}^{-3}$, pH 6.0, $t_{\text{ex}} = 3 \text{ min}$, $\lambda = 509 \text{ nm}$; (1c) $c_{\text{Co}} = 4.0 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{\text{BZC}} = 1.4 \times 10^{-4} \text{ mol dm}^{-3}$, pH 7.5, $t_{\text{ex}} = 3 \text{ min}$, $\lambda = 550 \text{ nm}$; (2) $c_{\text{Co}} = 4 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{\text{MTAR}} = 2 \times 10^{-4} \text{ mol dm}^{-3}$, pH 7.5, $t_{\text{ex}} = 3 \text{ min}$, $\lambda = 550 \text{ nm}$.





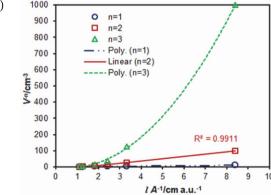


Figure 5. Determination of the MTAR-to-Co molar ratio by the straight-line method of Asmus. The experimental conditions are given in Figure 4, curves 1a-c, respectively.

presence of BZC, the absorption maximum shifts to lower wavelengths. This can be attributed to the simultaneous extraction of the binary Co–MTAR complex (λ_{max} = 509 nm).

3. 3. Effect of BZC Concentration and the BZC-to-Co Molar Ratio

The effect of BZC concentration is shown in Figure 4, curve 2. This curve allowed the BZC-to-Co molar ratio (1:1) to be determined by many methods: straight-line method of Asmus, ⁴⁹ Bent and French limited logarithm method^{50,51} (Figure 6), You and Jones method⁵² (Figure 7) and mobile equilibrium method⁵³ (Figure 8). Successful determination of the composition by all these methods is rarely possible since they have certain limitations related to the stability of the species and the presence of side processes. ^{51,54}

In addition to the aforementioned methods, the composition was determined by the Job's method of continuous variations (Figure 9).⁵⁵ The obtained curve shows that the complex is rather stable.

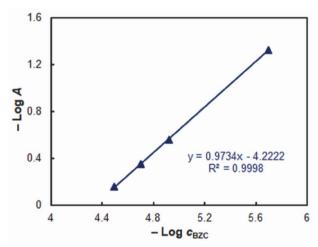


Figure 6. Determination of the BZC-to-Co molar ratio by the Bent-French limited logarithm method.

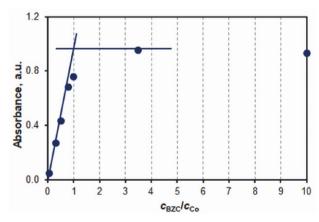


Figure 7. Determination of the BZC-to-Co molar ratio by the You and Jones method.

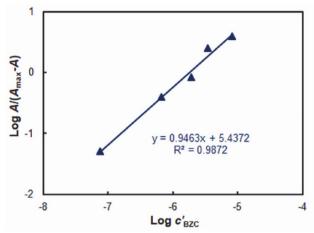


Figure 8. Determination of the BZC-to-Co molar ratio by the mobile equilibrium method.

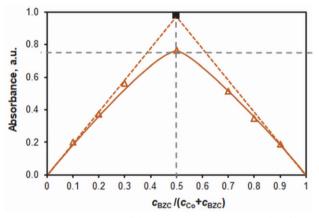


Figure 9. Determination of the BZC-to-Co molar ratio by the Job's method of continuous variations and $K_{\rm ex}$ by the Likussar-Boltz method. $k = c_{\rm Co} + c_{\rm BZC} = 8 \times 10^{-5} \, {\rm mol \ dm^{-3}}, \, c_{\rm MTAR} = 2 \times 10^{-4} \, {\rm mol \ dm^{-3}}, \, {\rm pH} \, 7.5, \, \lambda = 547 \, {\rm nm}.$

3. 4. Suggested Chemical Formulae and Equations

In order to propose correct formulae for the extracted species, the data for their composition must be synchronized with the information accumulated in the literature for the possible oxidation of Co^{II} to Co^{III} by the atmospheric oxygen. Numerous studies in this area allow us to summarize that in the presence of azo dyes^{17,27–31,56-61} such as PAR and TAR, (i) the oxidation proceeds rapidly (in seconds);^{58,61} (ii) the oxidation is quantitative;⁶⁰ (iii) Co^{II} is oxidized even in the presence of reducing agents such as ascorbic acid, sulfite or hydrazine;^{57,61} (iv) the protonation state of the azo dye in the complex can be estimated by the position and intensity of the spectral bands in the visible range.

The MTAR complex extracted in the absence of BZC has a composition of Co:MTAR = 1:2. Because of the requirement of electroneutrality, it is reasonable to assume that its formula is $[Co^{III}(HL^-)(L^{2-})]^0$ (L^{2-} and HL^- are the deprotonated and monoprotonated forms of the ligand $H_2L = MTAR$). A similar Co-PAR complex has been isolat-

ed and studied by Mochizuki et al.⁵⁸ The chloroform-extracted (at pH close to 4) Co-TAR binary complex²⁹ can probably be represented by the same formula.

It can be seen from Figure 3 (curve 1) that the Co-MTAR binary complex is formed in a narrow pH range (about pH 5.5), which corresponds well with the onset of the decrease in absorbance (curve 1 ') associated with the conversion of the neutral MTAR into a monoanion:

$$H_2L^0 \rightleftharpoons HL^- + H^+$$
 (1)

The course of curve 1' is in good agreement with the p K_a value determined by Menek et al.⁶² (Table 2; p K_{p-OH} = 5.7), characterizing Eq. 1.

As the pH increases the neutral complex is transformed into an anionic complex with a bathochromically shifted absorption maximum:

$$[Co^{III}(HL^{-})(L^{2-})]^{0} \rightleftharpoons [Co^{III}(L^{2-})_{2}]^{-} + H^{+}$$
 (2)

The anionic complex can also be formed by the direct interaction (Eq. 3) of the metal with the dominant form of the reagent under optimal conditions (i.e., HL⁻).

$$Co^{II}_{(aq)} + 2 HL^{-} \rightleftharpoons [Co^{III}(L^{2-})_{2}] + 2H^{+} + e^{-}$$
 (3)

The formation of the ternary ion-association complex can be described by Eq. 4, in which BZ⁺ is the cation of BZC.

$$[Co^{III}(L^{2-})_2]^- + BZ^+ \rightleftharpoons (BZ^+)[Co^{III}(L^{2-})_2]$$
 (4)

The overall process of complex formation and extraction at the optimum pH-range (see Figure 3, curve 2) is shown in Eq. 5.

$$\begin{array}{l} \text{Co}^{\text{II}}_{(aq)} + 2 \text{ HL}^{-}_{(aq)} + \text{BZ}^{+}_{(aq)} \rightleftarrows \\ \rightleftarrows (\text{BZ}^{+}) [\text{Co}^{\text{III}}(\text{L}^{2-})_{2}]_{(\text{org})} + 2\text{H}^{+}_{(aq)} + \text{e}^{-} \end{array} \tag{5}$$

It involves metal assisted deprotonation of the ligand HL⁻, oxidation of the initially formed labile Co^{II}-complex

to inert Co^{III}-complex in the presence of air, 16,58,63 and ion-association between BZ⁺ and the anionic complex. 54,64 The spectral characteristics and composition of the ternary complex (Co:MTAR:BZC = 1:2:1), and the optimal pHrange of its existence suggests that it contains two deprotonated ligands, as in the literature concerning similar ternary PAR- and TAR-complexes. $^{27-31}$ These azo dyes have pK_a values (Table 2) that are close to those reported for MTAR.

3. 5. Extraction Characteristics

The conditional equilibrium constant characterizing Eq. 5 was calculated by the mobile equilibrium method⁵³ (Figure 8), Likussar-Boltz method⁶⁷ (Figure 9) and Holme-Langhmyir method.⁶⁸ The obtained values are given in Table 3, along with the values for fraction extracted (E) and distribution ratio (D).

Table 3. Extraction characteristics.

Extraction characteristic	Value		
	$5.6 \pm 0.2^{a} (N=3)$		
Extraction constant (Log $K_{\rm ex}$)	$5.7 \pm 0.3^{\mathrm{a}} (N = 5)$		
0	$5.8 \pm 0.1^{\circ} (N = 5)$		
Distribution ratio (Log D)	$1.4 \pm 0.2 \ (N=4)$		
Fraction extracted (<i>E</i>), %	$96 \pm 2 \ (N = 4)$		

 $^{^{\}rm a}$ Likussar-Boltz method. $^{\rm b}$ Molar equilibrium method. $^{\rm c}$ Holme-Langmyhr method.

3. 6. Beer's Law and Analytical Characteristics

The relationship between the concentration of Co^{II} in the aqueous phase and the absorbance of the extracted ternary complex was studied under optimum conditions (Table 1). A good linearity was observed in the concentration range of $0.2 - 2.8 \, \mu g \, cm^{-3} \, (R^2 = 0.9994, \, N = 7)$. The linear regression equation was $A = 0.395 \, y + 0.004$, where A is the absorbance and y is the concentration ($\mu g \, cm^{-3}$). The standard deviations of the slope and intercept were

 Table 2. Dissociation constants of MTAR, TAR and PAR.

Azo dye	$\mathbf{p}K_{\mathbf{NH}}$	$egin{array}{lll} \mathbf{p}K_{\mathbf{a}} & & \mathbf{p}K_{\mathbf{NH}} & \mathbf{p}K_{\mathbf{p} ext{-}\mathrm{OH}} & \mathbf{p}K_{\mathbf{o} ext{-}\mathrm{OH}} & & \end{array}$		Conditions	Ref.
MTAR	_	5.7	11.8		62
TAR	1.25	6.0	9.3	0.1 mol dm ⁻³ NaC1O ₄	65, 66
	0.96	6.23	9.44	0.1 mol dm ⁻³ NaC1O ₄	
	-	6.16	9.59	I = 0.2	
	-	6.15	9.68		
PAR	2.7	5.83	12.5	$0.1 \text{ mol dm}^{-3} \text{ KNO}_3$	65, 66
	2.66	5.48	12.31	$0.1 \text{ mol dm}^{-3} \text{ NaC1O}_4$	
	3.1	5.6	11.9	I = 0.1	
	2.57	6.2	11.5		

0.004 and 0.008, respectively. The limits of detection (LOD) and quantitation (LOQ), calculated as 3- and 10 times standard deviation of the intercept divided by the slope, were LOD = 0.058 μg cm⁻³ and LOQ = 0.193 μg cm⁻³. The molar absorptivity (ϵ) and Sandell's sensitivity (SS) were ϵ = 2.33 × 10⁴ dm³ mol⁻¹ cm⁻¹ and SS = 2.53 × 10⁻³ μg cm⁻², respectively.

4. Conclusions

The present investigations shed light on the complex formation of $\mathrm{Co^{II}}$ with MTAR in the presence or absence of BZC. The conditions for formation of two electroneutral complex species, $[\mathrm{Co^{III}L(HL)}]$ and $(\mathrm{BZ^{+}})[\mathrm{Co^{III}(L)_{2}}]$, were found. The first one contains one monoprotonated MTAR and one deprotonated MTAR. It is extracted in a narrow pH-range (about 5.5) and shows an absorption maximum at 509 nm. In the presence of BZC, a ternary ion-association complex ($\lambda_{\mathrm{max}} = 550$ nm) is formed over a wider pH range (6.8–8.7). In both cases, the complex formation involves the oxidation of $\mathrm{Co^{II}}$ to $\mathrm{Co^{III}}$ by atmospheric oxygen.

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Povzetek

Proučevali smo interakcijo med Co^{II} in 5-metil-4-(2-tiazolilazo)-rezorcinolom (MTAR) v zmesi voda-kloroform, v prisotnosti ali odsotnosti benzalkonijevega klorida (BZC) kot kationskega iono-asociacijskega reagenta. Določili smo optimalni pH, koncentracijo reagentov in ekstrakcijski čas za ekstrakcijo Co. V prisotnosti BZC lahko ekstrahirani ionski kelat predstavimo s formulo (BZ+)[Co^{III}(MTAR²-)2], kjer je MTAR v deprotonirani obliki. Določili smo tudi naslednje ekstrakcijske in spektrofotometrične parametre: absorpcijski maksimum, molarno absorptivnost, Sandellovo občutljivost, mejo detekcije in kvantifikacije, konstanto ekstrakcije, porazdelitveno razmerje in delež ekstrakcije. V odsotnosti BZC je ekstrakcija nepopolna in poteka v ozkem območju pH. Ekstrahirani kelat vsebuje en deprotoniran in en monoprotoniran ligand, [Co^{III}(MTAR²-)(HMTAR^-)].



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