Spectrophotometric Investigation of 2-(2-Pyridylmethyleneamino)phenol Complexes with Cobalt(II) and Nickel(II) in Methanol—Water Solutions

Z. GRABARIĆ*, B. S. GRABARIĆ, N. KOPRIVANAC, and I. EŠKINJA

Faculty of Chemical Engineering and Technology, University of Zagreb,
41000 Zagreb, Croatia

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The stability constants of Co(II) and Ni(II) complexes with 2-(2-pyridylmethyleneamino)phenol (PMAP) have been determined by three methods at constant temperature θ = (25 ± 1) °C, ionic strength I = 0.5 mol dm^{-3} ($NaNO_3$), in methanol—water medium of volume fraction φ(methanol) = 10 %, and at different pH in order to optimize the experimental conditions for using PMAP as a spectrophotometric reagent for Co and Ni determination in beryllium bronzes. PMAP has the main advantages over other reagents due to the fact that it does not form complexes with Be and that the interferences of Zr can be avoided by pH adjustment. The influence of the interferences present in Be and Zr bronzes has also been investigated.

Schiff bases form complexes with many metal ions and can be used either as spectrophotometric reagents [1] or as a dyestuff in textile and other industries [2]. In this work the complexation of 2-(2-pyridylmethyleneamino)phenol (PMAP) as a Schiff base (azomethine) dyestuff with Co(II) and Ni(II) ions has been investigated. The complexation of this dyestuff with some metal ions has been investigated by *Geary et al.* [3, 4] and *Pollard et al.* [5] in dioxane—water medium, and by *Capitan et al.* [6—8] in water and ethanol—water media. Application of PMAP as a reagent for extractive spectrophotometric analysis has also been reported [9].

Some discrepancies, however, have been reported in those papers concerning the water solubility of PMAP, and also concerning the stability constants of PMAP metal ion complexes. The former can be attributed to the purity of PMAP synthesized, while the latter can be caused by the differences in used medium, besides the impurity of PMAP. Moreover, the stability constants obtained by potentiometric and spectrophotometric methods, published so far have not been determined statistically using computerized data evaluation, and for many investigated systems the estimated errors reported are unacceptable for the present standards. Some of the reported stability constants had a standard error of ± 0.3 log units which implies ± 100 % of error on absolute scale and this in turn means that the stability constants reported statistically do not differ from zero by Student's *t*-test [10].

EXPERIMENTAL

The PMAP ligand has been synthesized by the procedure described in the literature [3, 11], purified and characterized using elemental analysis, mass and IR spectroscopy.

UV—VIS spectra of the ligand and the complexes formed have been recorded on a spectrophotometer, model DMS-80 (Varian, USA) at c(PMAP) = 1.82 mmol dm^{-3}, φ(methanol) = 10 vol. %, θ = (25 ± 1) °C and I = 0.5 mol dm^{-3} ($NaNO_3$); pH of the solutions have been measured with microprocessor-controlled pH-meter, model MA 5740 (Iskra, Slovenia) using combined glass/reference electrode. Experimental data evaluations have been performed on an IBM compatible PC AT/286 computer.

RESULTS AND DISCUSSION

Absorption spectra of PMAP ligand are shown in Fig. 1 at different pH in methanol—water solution. The mixed methanol—water medium has been used due to lower solubility of the PMAP ligand in water.

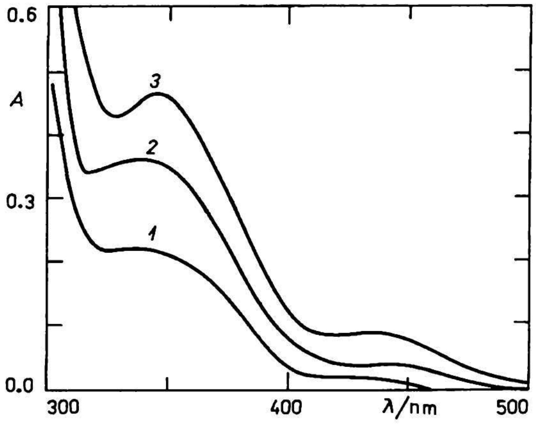

Fig. 1. Absorption spectra of PMAP at different pH. *1.* pH = 4; *2.* pH = 6; *3.* pH = 8.

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*The author to whom the correspondence should be addressed.

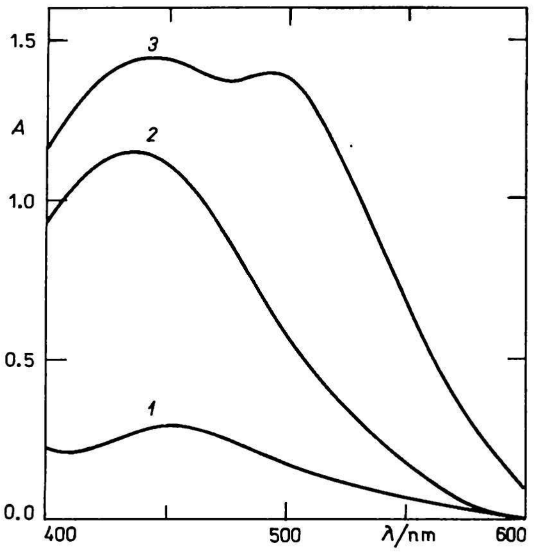

Fig. 2. Absorption spectra of Co(II)—PMAP complexes at different pH. *1.* pH = 4; *2.* pH = 6; *3.* pH = 8.

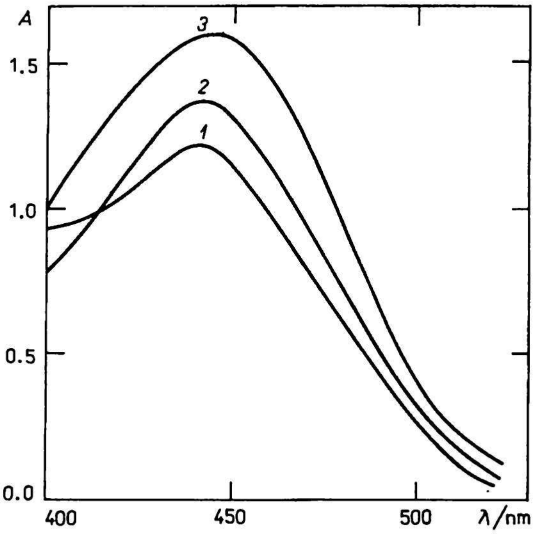

Fig. 3. Absorption spectra of Ni(II)—PMAP complexes at different pH. *1.* pH = 4; *2.* pH = 6; *3.* pH = 8.

Absorption spectra of Co(II) and Ni(II) complexes with PMAP using the same experimental conditions are given in Figs. 2 and 3, respectively. All absorption spectra increase with increasing the pH of the solutions. The Co(II)—PMAP complexes at pH = 8 show two maxima, probably due to formation of mixed Co(II)-hydroxo—PMAP complexes. All subsequent measurements have been performed at λ = 440 nm for the investigated systems.

Time stability investigation of the complexes formed at different pH shows that Co(II)—PMAP complexes are slightly more time-unstable because the absorbance reached the constant value at all investigated pH within 20 min. Ni(II)—PMAP complexes show better time stability and practically after 10 min the absorbance was constant at all investigated pH values.

The composition and stability constants using the model of the single predominant complex species have been determined by two methods. The first one used was the mole fraction variation method (Job's method) using computerized algorithm proposed by *Likussar et al.* [12—14] based on iterative successive approximation of the theoretical equation describing the absorbance *vs.* mole fraction curves. The experimental curves obtained by this method are shown in Fig. 4.

The second method used assuming again the existence of a single predominant complex species was the method of mole ratio variation. The algorithm for computerized statistical evaluation of experimental data proposed by *Chriswell* and *Schilt* [15] was used. An example of curves obtained by this method is given in Fig. 5.

Log values of stability constants measured at θ = (25 ± 1) °C and I = 0.5 mol dm^{-3} (NaNO$_3$) together with their relative standard errors obtained by these

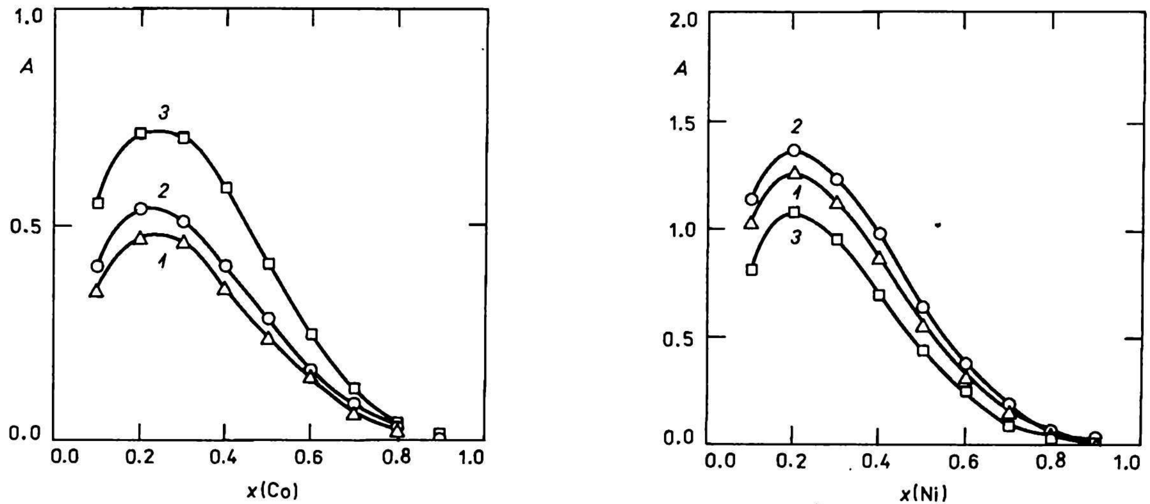

Fig. 4. Absorption *vs.* metal ion mole fraction curves for Co(II)—PMAP and Ni(II)—PMAP complexes. *1.* pH = 4; c(M) + c(PMAP) = 2 mmol dm^{-3} for Co and Ni; *2.* pH = 6; c(M) + c(PMAP) = 1 mmol dm^{-3} for Co and Ni; *3.* pH = 8; c(M) + c(PMAP) = 1 mmol dm^{-3} for Co and 0.5 mmol dm^{-3} for Ni.

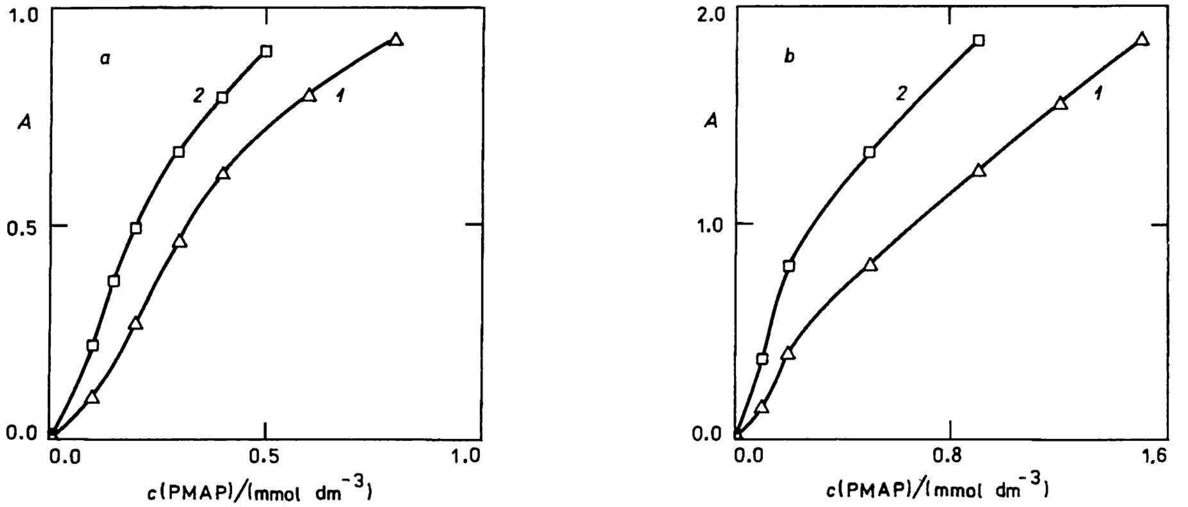

Fig. 5. Absorption *vs.* metal ion-to-ligand mole ratio curves for Co(II)—PMAP (*a*) and Ni(II)—PMAP (*b*) complexes. *1.* c'(Co) = 0.2 mmol dm^{-3}; d' = 1 cm; c'(Ni) = 1 mmol dm^{-3}; *2.* c''(Co) = 0.1 mmol dm^{-3}; d'' = 2 cm; c''(Ni) = 0.5 mmol dm^{-3}.

two methods are summarized in Tables 1 and 2 for Co(II)—PMAP and Ni(II)—PMAP complexes, respectively. Some discrepancies, however, have been obtained concerning the composition of the single predominant complex species present in solution judged by the value of the relative standard errors obtained. The first method is giving lower standard deviations for complex species with higher ligand-to-metal ratios, while the second one is favouring complex species with lower ligand-to-metal ratios, which is not surprising considering different experimental conditions used in these two methods. In the first one all ratios of mole fractions of metal ion have been scanned, favouring higher complex species, while in the second method only up to 20-fold excess of ligand concentration over the metal ion concentration was experimentally possible to investigate. Therefore, the second method will favour lower complex species as the obtained results suggest. The reason for these discrepancies is the possibility that Co(II) and Ni(II) form with PMAP consecutive complexes simultaneously present in the solution.

One of the simplest methods of this kind is the method of corresponding solutions proposed by Bjerrum, and its computerized version by *Grabarić et al.* [16]. It is interesting to notice that this method beside its simplicity is not much used in the literature. The method needs to scan at least two mole ratio plots using two constant total metal ion concentrations and fulfilling the condition that $c'(\mathrm{M}) \cdot d' = c''(\mathrm{M}) \cdot d''$. This means that the curves for two-fold metal ion concentration should be recorded in spectrophotometric cell with one half of the optical path length. The curves obtained in this way are shown in Fig. 5. Corresponding solutions are those two (or more) having the same absorbance and different total metal ion and ligand concentrations and their basic property is that such solutions have

Table 1. Log β_i for Co(II)—PMAP Complexes Obtained at Different pH

pH	i*	Mole fraction variation	Method of mole ratio variation	Corresponding solutions
		log β_i ± standard error		
4	1	2.84 ± 0.26	2.45 ± 0.03	3.33 ± 0.04
	2	6.06 ± 0.14	6.30 ± 0.03	6.44 ± 0.02
	3	9.95 ± 0.08	10.82 ± 0.08	
	4	13.34 ± 0.09	15.52 ± 0.27	
6	1	3.33 ± 0.23	2.20 ± 0.02	3.82 ± 0.08
	2	6.97 ± 0.10	6.10 ± 0.02	7.24 ± 0.03
	3	11.77 ± 0.07	10.61 ± 0.02	
	4	15.23 ± 0.09	15.29 ± 0.19	
8	1	3.44 ± 0.21	< 0	4.47 ± 0.07
	2	7.10 ± 0.05	6.76 ± 0.06	7.57 ± 0.03
	3	12.05 ± 0.06	11.31 ± 0.19	
	4	15.79 ± 0.09	16.07 ± 0.60	

*i-th complex species ML$_i$.

Table 2. Log β_i for Ni(II)—PMAP Complexes Obtained at Different pH

pH	i*	Mole fraction variation	Method of mole ratio variation	Corresponding solutions
		log β_i ± standard error		
4	1	2.92 ± 0.25	2.95 ± 0.09	3.59 ± 0.05
	2	6.19 ± 0.12	6.27 ± 0.02	6.93 ± 0.01
	3	10.34 ± 0.07	10.11 ± 0.01	
	4	13.72 ± 0.08	14.19 ± 0.02	
6	1	3.05 ± 0.27	3.27 ± 0.14	3.97 ± 0.01
	2	6.51 ± 0.15	6.79 ± 0.07	7.36 ± 0.02
	3	10.27 ± 0.07	10.86 ± 0.05	
	4	14.87 ± 0.08	15.20 ± 0.09	
8	1	3.34 ± 0.26	3.96 ± 0.08	4.58 ± 0.01
	2	6.95 ± 0.09	6.97 ± 0.09	7.69 ± 0.05
	3	11.17 ± 0.02	11.67 ± 0.32	
	4	16.73 ± 0.05	16.56 ± 1.45	

*i-th complex species ML$_i$.

Table 3. Experimental Data for the Co(II)—PMAP System at pH = 8

Mole fraction method		Mole ratio and corresponding solution methods			
$c(\text{Co}) = 0.5\ \text{mmol dm}^{-3}$ $c(\text{PMAP}) = 0.5\ \text{mmol dm}^{-3}$		$d' = 1$ cm, $c'(\text{Co}) = 0.2\ \text{mmol dm}^{-3}$		$d' = 2$ cm, $c''(\text{Co}) = 0.1\ \text{mmol dm}^{-3}$	
$x(\text{Co})$	$A_{440\ \text{nm}}$	$c'(\text{PMAP})/(\text{mmol dm}^{-3})$	$A'_{440\ \text{nm}}$	$c''(\text{PMAP})/(\text{mmol dm}^{-3})$	$A''_{440\ \text{nm}}$
0.1	0.907	0.0	0.000	0.0	0.000
0.2	1.833	0.1	0.104	0.1	0.221
0.3	2.153	0.2	0.274	0.15	0.370
0.4	2.050	0.3	0.463	0.2	0.492
0.5	1.679	0.4	0.620	0.3	0.670
0.6	1.280	0.6	0.800	0.4	0.792
0.7	0.917	0.8	0.927	0.5	0.899
0.8	0.556				
0.9	0.218				

Table 4. Experimental Data for the Ni(II)—PMAP System at pH = 8

Mole fraction method		Mole ratio and corresponding solution methods			
$c(\text{Ni}) = 0.25\ \text{mmol dm}^{-3}$ $c(\text{PMAP}) = 0.25\ \text{mmol dm}^{-3}$		$d' = 1$ cm, $c'(\text{Ni}) = 1\ \text{mmol dm}^{-3}$		$d' = 2$ cm, $c''(\text{Ni}) = 0.5\ \text{mmol dm}^{-3}$	
$x(\text{Ni})$	$A_{440\ \text{nm}}$	$c'(\text{PMAP})/(\text{mmol dm}^{-3})$	$A'_{440\ \text{nm}}$	$c''(\text{PMAP})/(\text{mmol dm}^{-3})$	$A''_{440\ \text{nm}}$
0.1	0.806	0.0	0.000	0.0	0.000
0.2	1.079	0.1	0.150	0.1	0.372
0.3	1.129	0.2	0.405	0.2	0.805
0.4	1.102	0.3	0.819	0.5	1.330
0.5	0.932	0.4	1.252	0.9	1.850
0.6	0.734	0.6	1.560		
0.7	0.451	0.8	1.852		
0.8	0.219				
0.9	0.076				

the same fraction of successive complex species, *i.e.* they have the same average number of ligands bound per one central metal ion $\bar{n}$ and free ligand concentration [L]. These parameters can be obtained very simply by the relations

$$\bar{n} = \frac{c'(\text{L}) - c''(\text{L})}{c'(\text{M}) - c''(\text{M})} \qquad c'(\text{M}) > c''(\text{M})$$

$$[\text{L}] = \frac{c'(\text{M}) \cdot c''(\text{L}) - c''(\text{M}) \cdot c'(\text{L})}{c'(\text{M}) - c''(\text{M})}$$

Plotting the function $\bar{n}/[\text{L}]$ *vs.* [L] function and using numerical integration, the function $F_0([\text{L}])$ which is a polynomial with cumulative stability constants as coefficients can be obtained

$$F_0([\text{L}]) = \exp\left(\int_0^{[\text{L}]} (\bar{n}/[\text{L}])\,\delta[\text{L}]\right) = 1 + \sum_1^N \beta_i [\text{L}]^i$$

where i is the number of ligand(s) bound to a metal ion, *i.e.* i-th complex species ML_i in the solutions.

Using weighted nonlinear least squares fitting and the criteria in reference [16] the cumulative stability constant can be statistically obtained.

The results of this method are also given in Tables 1 and 2 showing that this model is more suitable than the model of a single complex species in the solution giving statistically the most reliable results with very acceptable standard errors. These results at the same time suggest that the stability constants and compositions of complex species in the solutions obtained by the assumption of a single predominant complex species, which is very frequently used in the literature, should be taken only as an approximation, and only in the case when two methods based on this assumption are giving unambiguous results. This was not true for the investigated complex systems. From the results given in Tables 1 and 2 it can be also seen that the most reliable stability constants obtained by the method of corresponding solutions increase with the increase of the pH of solution. This can be explained by the different extent of protonation of the ligand bound to the central metal ions. In solutions with lower pH values the ligand is more protonated, giving the complex species with lower stability and *vice versa*. Examples of numerical results obtained at pH = 8 for calculation of the stability constants of the investigated systems are given in Tables 3 and 4.

The practical use of PMAP ligand as a spectrophotometrical reagent for Co and Ni determination in Be and Zr bronzes was tested in this work. Calibration diagrams for Co and Ni determination are linear in the concentration range up to 100 μmol dm^{-3} for Co and Ni, with the lowest concentration detection limit of approximately 5 μmol dm^{-3} using standard 1 cm cell. Regression lines are given with the following equations (A = absorbance, c = concentration in μmol dm^{-3}) together with the corresponding correlation coefficients

Cobalt

pH = 4; $A = (2 \pm 12) \times 10^{-3} + (2.6 \pm 0.1) \times 10^{-3}\{c\}$; $r = 0.998$
pH = 6; $A = (5 \pm 22) \times 10^{-3} + (8.0 \pm 0.2) \times 10^{-3}\{c\}$; $r = 0.998$
pH = 8; $A = (-6 \pm 8) \times 10^{-3} + (9.0 \pm 0.2) \times 10^{-3}\{c\}$; $r = 0.999$

Nickel
pH = 4; $A = (2 \pm 8) \times 10^{-3} + (6.5 \pm 0.1) \times 10^{-3}\{c\}$; $r = 0.999$
pH = 6; $A = (1 \pm 2) \times 10^{-3} + (14.3 \pm 0.2) \times 10^{-3}\{c\}$; $r = 0.999$
pH = 8; $A = (-1 \pm 5) \times 10^{-3} + (19.0 \pm 0.4) \times 10^{-3}\{c\}$; $r = 0.999$

All regression lines show that the intercepts on the *y* axes have the standard errors greater than the value of the intercept, which means that the intercepts do not statistically differ from zero judged by the *t*-test.

The influence of the interferences present in beryllium and zirconium bronzes has also been investigated. Beryllium does not form complexes with PMAP. At pH = 4 and 6 (citrate buffer) the presence of Zr, Al, Fe, and Mn does not interfere, while at pH = 8 (borate buffer) Zr and Al do not interfere but Mn, Zn, and Fe slightly interfere in determination of Co and Ni. Of course, Co interferes for Ni determination and *vice versa*.

The proposed method of Co and Ni determination with PMAP was tested in real standard samples of beryllium and zirconium bronzes with the known composition (Table 5) according to DIN and it gave the declared results within ± 1.5 % in aliquots of 10 μmol dm^{-3} concentration level, which in determination of Co and Ni gave an error in total metal mass fraction in bronzes between 1—2 %. The results obtained show that this reagent gives reliable results and that it can be used with advantages over the other reagents for Co and Ni determination in Be and Zr bronzes samples.

Table 5. Mass Fraction of Co and Ni in Standard Samples of Beryllium and Zirconium Bronzes Obtained Spectrophotometrically Using PMAP at $\theta = (25 \pm 1)$ °C, $I = 0.5$ mol dm^{-3} ($NaNO_3$) and pH = 8 after Electrogravimetric Separation and Determination of Copper

Alloy	$w(\text{Co})_{\text{calc.}}$ / %	$w(\text{Co})_{\text{found}}$ / %	$w(\text{Ni})_{\text{calc.}}$ / %	$w(\text{Ni})_{\text{found}}$ / %
CuNi2Be.00	–	–	1.76	1.80
CuCoBe.00	2.83	2.80	–	–
CuCrZr.00	–	–	0.35	0.34

CONCLUSION

In this investigation it has been demonstrated that the model of the single complex species, usually presumed in the literature, is not reliable due to the simultaneous presence of two or more complex species in solution. Therefore, the values of stability constants obtained using the methods based on the single-complex model (mole fraction and mole ratio variation methods) are in such systems erroneous. These methods can be used only for very rough estimation of the stability constants of metal ion complexes (Tables 1 and 2).

Using the method of corresponding solution the number of single ligand complex species with different metal ion-to-ligand stoichiometry is simultaneously present in the solution and their stability constants can be determined.

The investigated Co(II)—PMAP and Ni(II)—PMAP complexes gave two species simultaneously present in the solution, in the investigated concentration range, and the stability constants obtained by this method (Tables 1 and 2) are the most reliable ones. Even this model can fail when determining the stability constants in systems where mixed ligand and/or polynuclear complexes are also present in the solution. In such a case one has to use more sophisticated methods [17].

Knowing the stoichiometry and the stability constants of the complex species formed, the analytical application for quantitative determination of the metal ion concentration using the investigated complexing reagent can be optimized. In the present work it has been shown that Shiff base, PMAP, can be successfully used as the reagent for spectrophotometric determination of Co and Ni in bronzes and using controlled experimental conditions, linear calibration graphs can be obtained in the concentration range of metal ions between 5 and 100 μmol dm^{-3}.

PMAP has special advantage over other spectrophotometric reagents for determination of Co and Ni in beryllium and zirconium bronzes, because many metals present in these bronzes do not interfere. The estimated error of quantitative determination of Co and Ni in real samples of beryllium and zirconium bronzes, using PMAP as spectrophotometric reagent, is between 1 and 2 %.

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