



DIRECT DETERMINATION OF ZIRCONIUM AND CHROMIUM BY FIRST-DERIVATIVE SPECTROPHOTOMETRY

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(Received 15 April 1994. Revised 16 June 1994. Accepted 29 June 1994)

Summary—The solution properties of zirconium complex with the Schiff's base 2-(2-pyridylmethyl-eneamino)phenol have been studied by zero-order absorption spectrophotometry. The influence of pH, stability of the complexes with time and stability constants were investigated. The use of first-derivative spectrometry eliminates the interference of chromium and enables the simultaneous determination of zirconium and chromium without previous separation. The relative overall standard errors, of five independent simultaneous determinations of zirconium and chromium at the 1.0 $\mu\text{g/ml}$ concentration level, were 2 and 4%, respectively. The proposed method has been successfully applied to the analysis of some real samples of zirconium/chromium bronzes.

Schiff's bases have wide applications as spectrophotometric reagents in analytical chemistry due to their relatively stable complexes in solutions.^{1–3} In our previous work, the complexation of Cr(III),⁴ Mn(II),⁵ Co(II)⁶ and Ni(II)⁶ with the azomethine dye 2-(2-pyridylmethyl-eneamino)phenol (PMAP) in solutions has been investigated. The metal/dye-complexes were isolated and characterized by elemental analysis. IR and mass spectrometry. The Cr(III)–PMAP dye was applied to wool and studies were made for the estimation of the stability of the bonding between the dye and wool at pH 4.5 and 5.5. The crystalline Mn(II)–PMAP complex offers some potential as a dye for wool and PA 66 fibres. It was found that spectrophotometric determination of Mn(II) with PMAP is four times more sensitive than with formaldoxime, which is very often used. PMAP has special advantage over other chromogens for determination of Co(II) and Ni(II) in beryllium and zirconium bronzes, because many metals present in such bronzes do not interfere. To overcome the interferences in different matrices first-derivative spectrophotometry can be used. Simultaneous first-derivative spectrophotometric determination of Ni(II) and Mn(II),⁷ and Zn(II) and Ni(II)⁸ complexes with PMAP has been proposed.

The aim of this work was to investigate the solution properties of Zr(IV)/PMAP-complexes [the properties of Cr(III)/PMAP-complexes has been previously reported⁴] and the possibility of simultaneous determination of zirconium and chromium, which are important components in some types of bronzes. Bronzes with zirconium mass fraction, $w(\text{Zr}) = 0.02\text{--}0.15\%$, have high thermal and electrical conductivity and good mechanical properties.⁹ Addition of chromium gives bronzes additional high stretching qualities.¹⁰ Mechanical properties of Cr–Zr bronzes can also be enhanced by heating at 950–1000°. The fraction of chromium and zirconium in bronzes can vary yielding bronzes of different properties and uses, so the concentration of each metal should be strictly controlled.

To find out the best conditions for determination of Zr and Cr, the solution properties of both metal complexes with PMAP have to be known. The solution properties of Cr–PMAP complexes in methanol/water (methanol volume ratio, $\varphi = 0.1$) at constant temperature ($25 \pm 1^\circ$) and different pH (4, 6, 8 and 10) were determined spectrophotometrically.⁴ It was found that the stoichiometry of the complex in the solution was the same as in the solid state, *i.e.* ML_2 . The solution properties of Zr–PMAP complex are investigated in this paper and the conditions for the simultaneous determination

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of zirconium and chromium in their bronzes without prior separation are established.

EXPERIMENTAL

Apparatus

DMS-80 UV/vis-spectrophotometer, Varian, with 1.00 cm cells was attached to a PL3 X-Y recorder, Lloyd. The scanning was at 500–360 nm (100 nm/min) with chart speed of 50 nm/min (slit width = 2 nm).

Model MA-5740, Iskra, pH-meter with combined glass/reference electrode was used.

Potentiograph E-436, Metrohm, with Pt as working and Ag/AgCl as reference electrode (both Metrohm) were used for potentiometric redox titration.

Data evaluations for stability constants have been performed on a PC 386 computer using programs written in QBASIC according to Likussar and Boltz,¹⁵⁻¹⁷ and Chriswell and Schilt.²¹

Reagents and solutions

Standard solution of Cr(III), 0.175 mg/ml, was prepared by dissolving aliquot masses of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, Kemika, in bidistilled water. The solution was standardized with Fe(II) ion solution by potentiometric redox titration.¹¹

Standard solution of Zr(IV), 0.500 mg/ml, was prepared by $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, Kemika, in conc H_2SO_4 in order to avoid hydrolysis and to depolymerize zirconium in the solution¹². The hydrolysis of the zirconium is irreversible, usually causing decrease of the sensitivity of the methods reported in the literature.¹³ The final concentration of the H_2SO_4 should be 1.25M at 0.1M level of zirconium.

Standard buffer solutions Titrival, Kemika, were used for pH adjustment.

All other chemicals and solvents were of reagent grade, Merck or Aldrich, and used without further treatment.

Solutions for zero-order and first-derivative spectrophotometric characterization of Zr-PMAP complex and determination of Zr-PMAP and Cr-PMAP complexes were prepared by adding to aliquots of metal solutions 1 ml of the ligand ($c \neq 10$ mM in methanol/water solvent of volume ratio 0.5; due to the low solubility of the ligand in water) and 2 ml of the corresponding buffer in 5-ml volumetric flask. The absorption spectra were recorded 30 min after mixing the reagents in the range from 500 to 360 nm against a blank

solution prepared in the same way without the metals. Three calibration diagrams were recorded. One without the interfering ion and two with 1.0 and 5.0 $\mu\text{g/ml}$ of interfering ion.

Concentrations of Zr and Cr were determined from the magnitude of first-derivative signals at the zero-crossing point for Cr (436 nm) and Zr (424 nm), respectively, and comparing the value with the appropriate calibration diagram.

Samples of bronzes, obtained by courtesy of casting company 'Strojar', Bistra, were treated according to the previously described procedure¹⁴ and zirconium and chromium were simultaneously determined in the same manner as was described for the calibration graphs.

RESULTS AND DISCUSSION

The solution properties of Zr-PMAP complexes were investigated by recording the absorption spectra in citrate and acetate (pH 3, 4, 5) and borate (pH 8) buffers. Special care was taken to avoid irreversible hydrolysis and polymerization when handling Zr(IV) solutions. The solution of ligand was slowly added to an acidic Zr(IV) solution and then the pH was adjusted by addition of appropriate buffer. In citrate and borate buffers the absorption maxima in the visible region of absorption spectrum was not observed, while in the acetate buffer the absorption maximum at 430 nm was obtained. It can be concluded that zirconium forms more stable complexes with citrate and borate than with PMAP. Increase of pH in the solution causes increases of the light absorption with molar absorption coefficients (ϵ) of 2375, 2750 and 4050 $\text{l. mol}^{-1} \cdot \text{cm}^{-1}$ at pH 4, 5 and 6, respectively.

At lower pH (4, 5) about 30 min are needed for full development of complexes and then the absorption remains constant. At pH 6 the absorbance changes for 0.4 absorbance units up to 30 min, and after that a slight, but permanent increase of absorbance occurs.

All further investigations were made 30 min after the preparation of the solutions.

The composition and stability constants using the model of the single predominant complex species have been determined by two methods at constant temperature, $t = 25 \pm 1^\circ$, ionic strength, $I = 0.5\text{M}$ (KNO_3) in methanol/water of methanol volume ratio, $\varphi = 0.1$ and different pH. The first method used was the mole fraction variation method (Job's method) using computerized algorithm proposed by Likussar *et al.*¹⁵⁻¹⁷

Table 1. Composition and stability constants of the Zr-PMAP complex species ML, obtained with mole fraction (MF) and mole ratio (MR) method at different pH values for various assumed stoichiometry

		log $\beta_i \pm SE$		
	<i>i</i>	pH 4	pH 5	pH 6
MF	1	2.93 ± 0.28	3.27 ± 0.14	3.54 ± 0.16
	2	5.91 ± 0.05	7.14 ± 0.03	7.15 ± 0.06
	3	7.34 ± 0.09	10.42 ± 0.19	10.81 ± 0.11
	4	9.23 ± 0.17	14.00 ± 0.21	14.20 ± 0.19
MR	1	3.04 ± 0.08	4.14 ± 0.09	2.89 ± 0.21
	2	6.03 ± 0.02	7.63 ± 0.02	7.55 ± 0.09
	3	8.25 ± 0.11	11.20 ± 0.17	11.32 ± 0.31
	4	10.17 ± 0.25	14.87 ± 0.28	14.83 ± 0.36

		log $\beta^*(Zr-PMAP_2)$		
	<i>i</i>	pH 4	pH 5	pH 6
	2	5.97 ± 0.06	7.39 ± 0.25	7.35 ± 0.20

β_i : Cumulative stability constants.

SE: standard errors.

*Average values from both methods.

based on iterative successive approximation of the theoretical equation describing the absorbance vs. mole fraction curves. As there is no literature data for Zr-PMAP complexes the results were compared with those for its azo-homologue PAR. The composition of the Zr-PAR complex varies from 1:1 to 1:4 according to the author and pH of the solution. At pH 2.5 and 3.5 the stoichiometry of Zr:PAR complexes was found to be 1:1 with $\epsilon = 6750$ and $13,400 \text{ l. mol}^{-1} \cdot \text{cm}^{-1}$, respectively.^{18,19} The stability constant was determined only at pH 2.5, and $\log K = 5.66 \pm 0.2$ was reported. At pH 8 the composition reported¹³ was Zr:PAR = 1:2 with $\epsilon = 66,000 \text{ l. mol}^{-1} \cdot \text{cm}^{-1}$, while Tselinski and Lapitskaya²⁰ found the composition of

Zr:PAR = 1:4 with $\epsilon = 6200 \text{ l. mol}^{-1} \cdot \text{cm}^{-1}$ at 500 nm. Due to these discrepancies in the results and resemblance of azomethine PMAP to azo-compound PAR, the second method for determination of composition and stability constants, the mole ratio variation method, was used. The algorithm for computerized statistical evaluation of experimental data proposed by Chriswell and Schilt²¹ was employed. Log values of stability constants together with their relative standard errors obtained by these two methods are summarized in Table 1. The composition of the complex species present in the solution, judged by the smallest value of the relative standard errors, is Zr-PMAP₂, with $\log \beta^*(Zr-PMAP_2) = 5.97, 7.39$ and 7.35 for pH 4, 5 and 6, respectively.

The effects of different metal ions on absorbance of Zr-PM complexes are presented in Table 2. It can be seen that the presence of Cr(VI), Zn(II), Co(II), Al(III) and Fe(III) influence the determination of zirconium, giving a positive error of approximately 20% for Co(II) and Al(III) and above 100% for other elements. Be(II) and Mn(II) do not interfere in determination of zirconium. As in the zirconium bronzes another element, in addition to copper which is most often separated electrogravimetrically, is chromium, a method for simultaneous determination of zirconium and chromium was developed.

From the studies of time stability, influence of pH on composition and stability of complexes the optimal conditions for the formation of Zr-PMAP complexes and the procedure for the determination of zirconium was proposed. All measurements were made at pH 5 after 30 min.

Table 2. Influence of some interfering metal ions on the absorption of Zr-PMAP complexes

Metal ion	γ ($\mu\text{g/ml}$)	$A_{430 \text{ nm}}$
Cr(III)	2.0	1.562
Mn(II)	16.5	0.475
Mn(II)	33.0	0.480
Zn(II)	2.5	0.980
Ni(II)	2.0	1.030
Co(II)	1.3	0.613
Al(III)	5.4	0.542
Fe(III)	0.2	1.381
Be(II)	2.0	0.481
Be(II)	10.0	0.475

γ : Mass concentration of metal ion in $\mu\text{g/ml}$;
 $c(\text{PMAP}) = 2 \text{ mM}$; $\text{pH} \neq 5$; $t = 30 \text{ min}$;
 $\varphi(\text{methanol/water}) = 10\%$. The absorbance of Zr-PMAP was 0.477 for $c(\text{Zr}) = 0.2 \text{ mM}$ in the absence of other metal ions.

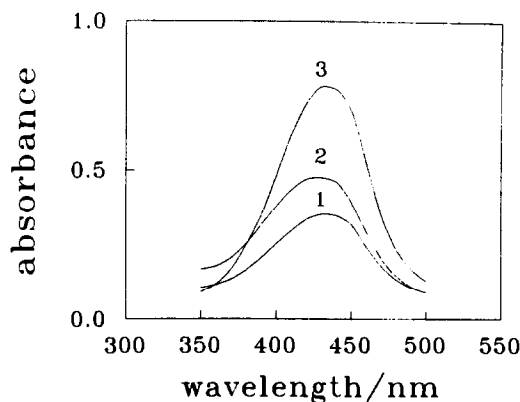


Fig. 1. Absorption spectra of (1) Cr-PMAP, (2) Zr-PMAP and (3) Cr-Zr-PMAP complexes. $c(\text{PMAP}) = 2 \text{ mM}$;
 $\gamma(\text{Zr}) = 20 \mu\text{g/ml}$; $\gamma(\text{Cr}) = 1.0 \mu\text{g/ml}$; $t = 30 \text{ min}$; $\text{pH} \neq 5$;
 $\varphi(\text{methanol/water}) = 10\%$.

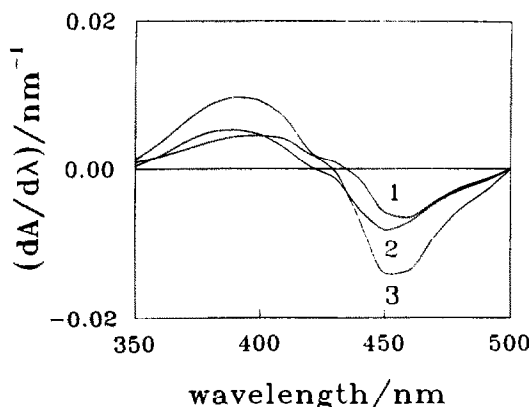


Fig. 2. First-derivative spectra of (1) Cr-PMAP, (2) Zr-PMAP and (3) Cr-Zr-PMAP complexes. $c(\text{PMAP}) = 2 \text{ mM}$; $\gamma(\text{Zr}) = 20 \text{ } \mu\text{g/ml}$; $\gamma(\text{Cr}) = 1 \text{ } \mu\text{g/ml}$; $t = 30 \text{ min}$; $\text{pH} \neq 5$; $\varphi(\text{methanol/water}) = 10\%$.

Figure 1 shows the absorption (zero-order) spectra of Zr-PMAP, Cr-PMAP and Zr-Cr-PMAP complexes at pH 5 with broad absorption maxima at about 430 nm for Zr and 438 nm for Cr and the mixture of Zr and Cr complexes. Because of the large overlap of the spectral bands of the two components, the absence from the total zero-order spectrum of any spectral feature, *e.g.* a shoulder, is evident. To resolve the problem of closely overlapping spectra the first-derivative spectrophotometry was used. Figure 2 shows the first-derivative spectra of the zero-order spectra given in Fig. 1. The most common techniques used to prepare analytical calibration graphs are peak-to-peak and base-line measurements, commonly called graphical measurements, and zero-crossing measurements.^{22,23} Graphical methods are more often used in spite of some advantages of zero-crossing measurements. The validity of the measurement depends on its total error, which is the sum of the systematic error plus twice the random error.²² The systematic error is defined as the relative percentage difference between the magnitude of a measurement with and without the overlapping band of a second component, and the random error is the standard deviation of replicate determinations of the analyte, which results from the presence of random noise in the spectrum. The zero-crossing method is superior in terms of systematic error, but is more sensitive to small drifts of the band of the other component. As the overlapping spectra are not well resolved in the first-derivative mode, the zero-crossing method was used. In this technique a suitable wavelength is chosen, at which the $dA/d\lambda$, measured as h_1 , is proportional to

the concentration of one metal and where the other metal does not interfere (zero-crossing in first-derivative spectrum) and *vice versa* for the other interfering metal, measured as h_2 . The zero-crossing point in the first-derivative spectrum of the Zr-PMAP complex is found at 424 nm, while that for the Cr-PMAP complex is found at 436 nm. The zero-crossing wavelengths of the first derivatives do not correspond exactly to the maxima of the zero-order spectra. The differences probably arise from the large number of instrumental variables to be controlled.²⁴ Reading $dA/d\lambda$ for the mixture of both metal ions at 424 and 436 nm the interference due to zirconium or chromium is avoided and chromium or zirconium concentration, respectively, can be determined. Table Genitizer Model GT 1212B, Genius, was subsequently used to input h_1 and h_2 determination. Linear regression of calibration diagram can be displayed. Linear regression equations coefficients and corresponding standard errors together with correlation coefficients are given in Table 3. The adherence of calibration graphs to the Beer's law is validated by the high value for the correlation coefficients. From the results it can be concluded that the mass concentration up to 5 $\mu\text{g/ml}$ of zirconium does not interfere with the determination of chromium and *vice versa*. Using the proposed method zirconium can be determined in the presence of 10-fold excess of chromium mass concentration and chromium can be determined in the presence of 10-fold excess of zirconium mass concentration.

Table 3. Regression lines $dA/d\lambda = A + B\gamma$ for determination of zirconium and chromium in mixtures by first-derivative spectrophotometry

Determination of Zr with Cr as interference			
$\gamma(\text{Cr})$ $\mu\text{g/ml}$	A \pm SE	B \pm SE	r^2
—	$(2.4 \pm 1.2) \times 10^{-4}$	$(1.84 \pm 0.06) \times 10^{-4}$	0.996
1.0	$(2.0 \pm 1.0) \times 10^{-4}$	$(1.87 \pm 0.05) \times 10^{-4}$	0.997
5.0	$(2.1 \pm 0.9) \times 10^{-4}$	$(1.84 \pm 0.05) \times 10^{-4}$	0.997
Determination of Cr with Zr as interference			
$\gamma(\text{Zr})$ $\mu\text{g/ml}$	A \pm SE	B \pm SE	r^2
—	$(-1.5 \pm 2.6) \times 10^{-4}$	$(1.71 \pm 0.05) \times 10^{-3}$	0.999
1.0	$(-0.5 \pm 1.3) \times 10^{-4}$	$(1.62 \pm 0.03) \times 10^{-3}$	0.999
5.0	$(-3.3 \pm 1.1) \times 10^{-4}$	$(1.74 \pm 0.02) \times 10^{-3}$	0.999

$\gamma(\text{Zr}) = 0.5\text{--}20 \text{ } \mu\text{g/ml}$; $\gamma(\text{Cr}) = 1.1\text{--}5.3 \text{ } \mu\text{g/ml}$.

γ : Mass concentration in $\mu\text{g/ml}$; A: Y-axis intercept in $(dA/d\lambda) (\text{nm}^{-1})$ units; B: slope; SE: standard error; r^2 : squared correlation coefficient.

Each calibration graph is an average of three independent measurements.

Table 4. Mass fractions of Zr and Cr in copper alloy sample determined in real samples of CuCrZr.00 bronze by first-derivative spectrophotometry (FDS) and atomic absorption spectrometry (AAS)

Sample	FDS		AAS	
	w(Zr)(%)	w(Cr)(%)	w(Zr)(%)	w(Cr)(%)
1	0.11 ± 0.01	0.63 ± 0.02	0.10 ± 0.01	0.63 ± 0.01
2	0.15 ± 0.01	0.80 ± 0.02	0.14 ± 0.01	0.81 ± 0.02

w: Mass fraction of metal ions in %.

Average values ± standard deviations of five independent simultaneous determinations.

The validity of the proposed method was checked on two different samples of copper alloy CuCrZr.00 (DIN nomenclature⁹). The results obtained for chromium and zirconium mass fraction in the bronze are compared with those obtained by atomic absorption spectrometry (Table 4). It can be concluded that the proposed method gives satisfactory results, as far as the sensitivity and precision are concerned, although atomic absorption spectrometry might be preferred method due to more direct determination of chromium and zirconium and good selectivity.²⁵ However, the proposed spectrophotometric method may be a good alternative for those laboratories where chromium and zirconium have to be simultaneously determined using UV/vis spectrophotometry.

Acknowledgement— The authors acknowledge the financial support of Croatian Ministry of Science for the Project No. 2-13-047.

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