

STUDY OF THE REACTION OF PLATINUM(IV) WITH DIMETHYLGLYOXIME BY UV SPECTROPHOTOMETRYMarija GEORGIEVA^{1,*} and Blagoja ANDONOVSKI²

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The complex formation of dimethylglyoxime and platinum(IV) in alkaline medium has been investigated by ultraviolet spectroscopy. This study has shown that more than one complex species exists in solution. The effects of pH variation of ammonia buffer solution from 6.0 to 13.0 were investigated with respect to the absorption spectra. The molar ratios method, the Job's method and the method of relative recovery of complex species were used. It was found that the stoichiometric ratio Pt(IV)/dimethylglyoxime was 1:1, 1:2 and 2:1. The molar absorptivity ($\log \epsilon = 4.1$ at 260 nm) and the formation constant of the complex ($\log K_{2,1} = 15.0$) were obtained. The stability constants of the $[\text{Pt}(\text{Hdmg})_2(\text{NH}_3)_2]$ complex determined by the molar ratios and Job's method were $\log \beta_2 = 9.2 \pm 0.2$ and $\log \beta_2 = 9.3 \pm 0.2$, respectively.

Keywords: Platinum complexes; Ultraviolet spectrophotometry; Dimethylglyoxime; Stability constants; Chelates.

All the platinum group metals (PGM) species in solutions are highly coordinated and complex. The complexity of chemical properties of the PGM and the kinetics of their reactions in solutions cause serious problems, especially in their separation and preconcentration by liquid chromatography and their spectrophotometric determination¹⁻⁴. Therefore, the most common spectrophotometric procedures for platinum usually require laborious enrichment steps and many organic reagents have been proposed for the determination⁵⁻¹².

Dimethylglyoxime (DMG) is a chelating agent, which can form strong complexes with some metal ions. Tshugaeff¹³ first used DMG as an analytical reagent for the gravimetric determination of Ni. DMG is also an excellent spectrophotometric reagent; it was used for adsorptive preconcentration of palladium on the stationary mercury electrode^{14,15}. There are no literature data on Pt(IV) complexes with DMG ligand. A variety of analytical

procedures, including mainly electroanalytical¹⁶⁻¹⁸, spectrophotometric^{19,20} and other methods have been developed for sensitive measurements of low platinum levels using various organic ligands.

The aim of this work is to establish the composition and optimum conditions for the complex formation of DMG and Pt(IV) and to evaluate the stoichiometric ratio and stability constants by ultraviolet spectrophotometry.

EXPERIMENTAL

All reagents were of analytical purity or suprapur quality. Water was deionized before use. Ammonia buffer of pH 9.2 was used as a blank solution. This was prepared by mixing appropriate amounts of 0.1 M NH_4OH and 0.1 M NH_4Cl . An ethanolic solution of 0.1 M dimethylglyoxime was prepared by dissolving DMG (butane-2,3-dione dioxime, Merck, Germany) in absolute ethanol. A platinum standard stock solution (2.41 mg ml^{-1}) was prepared by dissolving Pt wire in aqua regia (HCl-HNO_3 3:1) and standardized by a complexometric method²⁰. Working standards were prepared by serial dilution of the stock solution with 0.1 M HCl. A combined glass electrode and a pH meter were used for pH measurement.

The UV spectra were recorded in the 350–190 nm range on an HP 8452 A diode array computer controlled spectrometer (Hewlett Packard) equipped with a thermostatted cell compartment using 1-cm quartz thermostatted cells. The advantage of using this spectrometer is the possibility of measuring full spectra, rather than just the absorbance of a single wavelength. The metal ion concentration and the ligand for UV measurements were chosen in such a way that the absorbance ranged between 0.1 and 2.0 at the studied wavelength.

RESULTS AND DISCUSSION

Careful investigations were carried out to find the optimum conditions to achieve maximum absorbance in the studied reaction. Since both platinum and DMG can absorb in UV region, we investigated the behaviour of platinum, DMG and a combination of platinum and DMG.

Chemical interaction of PtCl_6^{2-} ions with DMG was investigated by UV spectroscopy following the spectral changes in the range from 350 to 190 nm. The UV spectrum of PtCl_6^{2-} ions in HCl solution (Fig. 1, curve 1) exhibits a single band with maximum absorption at 260 nm ($\log \varepsilon = 4.12$). According to the molecular-orbital theory²¹ (MO), this band corresponds to intramolecular charge-transfer (CT) reactions. In 0.1 M ethanolic solution of DMG, the UV spectrum of the ligand (Fig. 1, curve 2) shows a maximum absorption at 230 nm ($\log \varepsilon = 4.25$). This band probably results from $\pi \rightarrow \pi^*$ transitions. The most important feature of the UV spectrum of the Pt–DMG complex formed in ammonia buffer solution is the band centered at 210 nm of molar absorptivity $\log \varepsilon = 4.1$. In the UV spectrum, the band at 210 nm is certainly due to ligand charge-transfer to platinum ions, which can be as-

signed to $n(\text{DMG}) \rightarrow e_g(\text{Pt})$. Because of some transition peaks, $t_{2g} \rightarrow e_g$ have very small molar absorptivity (ϵ) and hence they are not observed in the UV spectrum. Therefore, the UV spectrum from 190 to 350 nm has no clear absorption peak. The absorption peaks whose wavelengths are smaller than 190 nm could not be measured under these conditions.

The optimum conditions of the complex formation were investigated and the effects of time, solution pH and the metal-to-ligand ratios on the reaction were also examined.

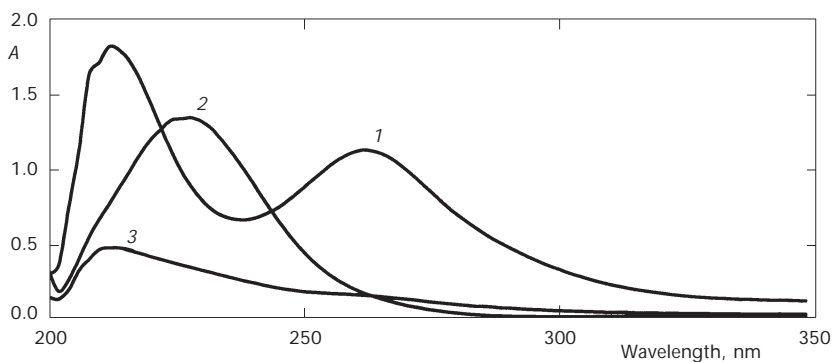


FIG. 1

UV spectra of PtCl_6^{2-} ions ($6.0 \times 10^{-5} \text{ mol l}^{-1}$ in 0.1 M HCl) (1), DMG ($5.0 \times 10^{-5} \text{ mol l}^{-1}$ in ethanol) (2) and of the Pt-DMG complex in ammonia buffer solution (3)

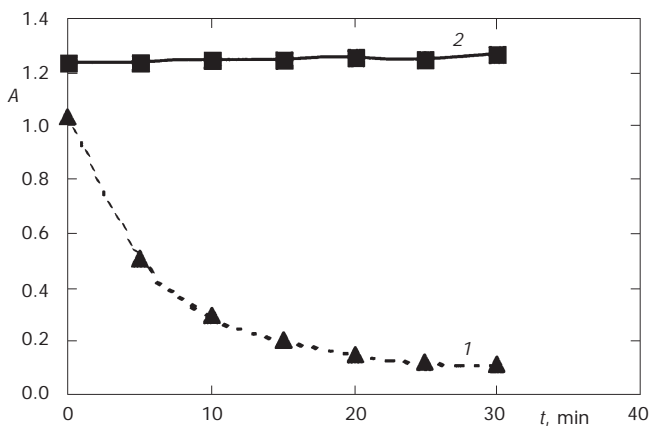


FIG. 2

Dependence of the absorbances on time: $\lambda = 260 \text{ nm}$ (PtCl_6^{2-} ions in 0.1 M HCl) (1) and $\lambda = 230 \text{ nm}$ (DMG) (2)

Effect of Time

The absorbance of the solution (25.0 ml) containing DMG ligand (dmg) ($4.5 \times 10^{-5} \text{ mol l}^{-1}$) and PtCl_6^{2-} ions ($4.5 \times 10^{-5} \text{ mol l}^{-1}$) in 0.1 M ammonia buffer solution of pH 9.2 was investigated for different periods of time (up to 30 min) at room temperature. It was found that the absorbances at 230 and 260 nm decrease approaching a stationary value at times higher than 20 min (Fig. 2). The appearance of the absorption band at 210 nm also indicated that complexation starts immediately after mixing and the absorbance decreases gradually, achieving a stationary value in 15 min. Over a period of time from 1 to 30 min, the reaction between the dmg ligand and PtCl_6^{2-} ions followed the rate law $-dA_{260}/dt = kc(\text{Pt})$, with a value of $k = 7.06 \times 10^{-4} \text{ s}^{-1}$, whereas the rate law $-dA_{230}/dt = kc(\text{DMG})$ had a value of $k = 4.33 \times 10^{-5} \text{ s}^{-1}$.

Effect of pH

The influence of pH on formation of the complex ions was followed by measuring the changes in UV spectrum of the reaction mixture containing dmg ligand and PtCl_6^{2-} ions in equimolar concentrations of $4.5 \times 10^{-5} \text{ mol l}^{-1}$. Ammonia buffer solutions covering pH values from 6.0 to 13.0 were used for the CT complex formation. The wavelength of the isosbestic point at 240 nm in the UV spectra indicated that complexation between the dmg ligand and PtCl_6^{2-} ions takes place at different pH values.

The results as shown in Fig. 3 confirmed that the complexation is weak in alkaline media of pH 7.0–8.5. The band of the complexed PtCl_6^{2-} ions de-

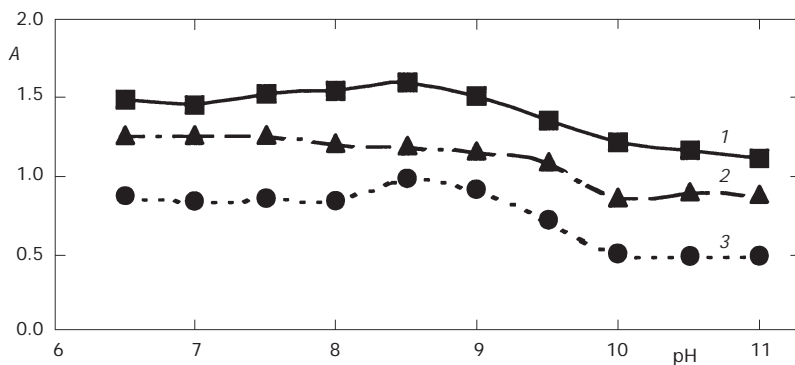


FIG. 3
Plot of absorbances at 230 (1), 210 (2) and 260 nm (3) versus pH

velops from pH 7.0 to 10.0, exhibiting minimum absorbance at pH 10. Then, the absorbance of the CT band decreases with increasing pH. Thus, pH between 9.0 and 10.0 is the optimum for further study, since it could be expected that the results would be highly reproducible at this pH value.

Stoichiometric Ratio of the Complex

The molar ratios method, the Job's method and the method of relative recovery of complex species²² were used for determining the stoichiometry of the reaction of dmg ligand and PtCl_6^{2-} ions. The molar ratios method was used at pH 9.2. Two series of solutions were prepared. At a constant metal concentration of $5.5 \times 10^{-5} \text{ mol l}^{-1}$, the concentration of DMG varied from 1.0×10^{-5} to $5.0 \times 10^{-5} \text{ mol l}^{-1}$. In the UV spectra the wavelengths of the isosbestic points at 204, 254 and 288 nm at different molar ratios of the components pointed out that the reaction of complex formation takes place. Absorbances were measured using an ammonia buffer solution of the corresponding concentration as a blank at 210, 230 and 260 nm. They are shown in Fig. 4. The intersection of straight lines, obtained at a molar ratio of $n = 0.5$, confirms the fact that the reaction occurs of the ratio $\text{Pt(IV)/DMG} = 1:2$. The presence of more than one complex species in the system is possible, but the exact determination of stoichiometric ratio of the reactants could not be made by the molar ratios method. The method was also used when the concentration of dmg ligand was constant ($4.0 \times 10^{-5} \text{ mol l}^{-1}$) but the concentration of metal ions varied from 8.0×10^{-6} to

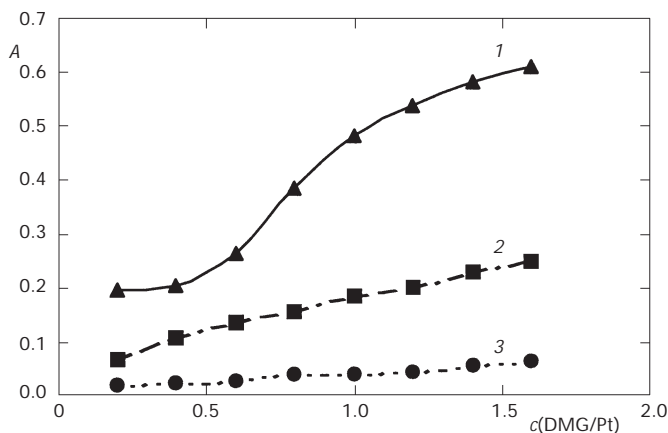


FIG. 4 Effect of absorbances at 210 (7), 230 (2) and 260 nm (3) of various DMG concentrations

$8.0 \times 10^{-5} \text{ mol l}^{-1}$. Absorbances were measured at 210, 230 and 260 nm. Within the range of these concentrations, the reaction at the ratio $\text{Pt(IV)}/\text{DMG} = 1:2$ or $2:4$ or $3:6$, *etc.* is possible.

The Job's method was used for determining the stoichiometric ratio of the reaction between dmg ligand and PtCl_6^{2-} ions. The influence of the ratio was followed by measuring the UV spectra of the mixed solutions. It is observed that the $\pi \rightarrow \pi^*$ band shifts hypsochromically with increasing Pt concentration while its intensity decreases. The gradual shift of $\lambda = 230 \text{ nm}$ results in convergence of the absorbances curves to an apparent isosbestic point at 216 nm. A similar convergence occurs at 256 nm for the formation of the complex species. The appearance of these isosbestic points is a clear evidence for the existence of complex species in the solution. As can be seen, the wavelength 210 nm is probably characteristic of the formation of the complex species.

The solutions for Job's method were prepared by mixing both components of equimolar concentration of $1.0 \times 10^{-5} \text{ mol l}^{-1}$, in the ratio from 0.1:0.9 to 0.9:0.1. Absorbances were measured at 210, 230 and 260 nm, using ammonia buffer solution as a blank. The Job's curves at different wavelengths are shown in Fig. 5. According to the appearance of Job's curves, it could be concluded that more than one complex species in the system are formed. The obtained curves 1 and 3 have slightly pronounced maxima at a molar fraction of $V(\text{DMG})/[V(\text{DMG}) + V(\text{Pt(IV)})] = 0.5$ and 0.7. This suggests that the complexes with the ratios $\text{Pt(IV)}/\text{DMG} = 1:1$ and $1:2$ prevail.

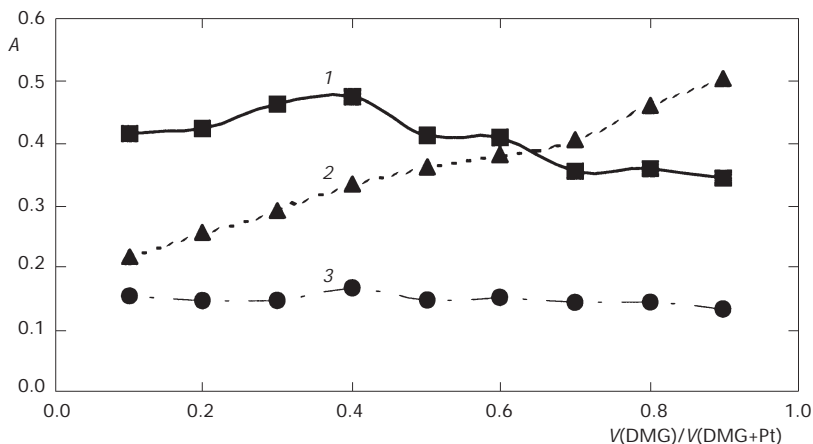


FIG. 5
Job's curves obtained at 230 (1), 210 (2) and 260 nm (3) at pH 9.2

Analysis of Job's curves shows the presence of mononuclear complex species whose appearance at pH 9.2 depends on the metal ions/ligand ratio. The presence of more than one complex species in the system simultaneously, is reflected in the shape of the curves shown in Fig. 5; this prevents the use of molar ratios method for the exact determination of the stoichiometric ratio of the reactants. The undefined maxima on Job's curves and the fact that the Job's method does not determine the amounts of the components but their relative ratio, determines the use of the method of relative recovery of the complex species.

In this method, the spectra from the molar ratios method at a fixed concentration of metal ions ($4 \times 10^{-5} \text{ mol l}^{-1}$) were used. From these spectral data the values $A/c(\text{DMG})$ and A/A_s were calculated, where A is the absorbance of the metal complex species, $c(\text{DMG})$ the initial concentration of DMG and A_s is the mean value of absorbances of the metal complex species on the curve's plateau (saturated) (Table I).

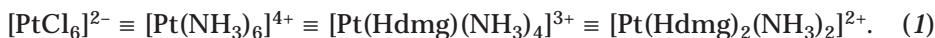
The absence of a maximum on the above dependence $A/c(\text{DMG}) = f(A/A_s)$ shows that the stoichiometric coefficient of the component with variable DMG concentration is equal to 1. This means that the formation of complex species $\text{Pt}_2\text{-DMG}$ or Pt-DMG is possible. In this case the formation of complex species $\text{Pt}_2\text{-DMG}$ could not be excluded because there is a deviation from linear dependence. Hence, the formed complexes are Pt-DMG and $\text{Pt}_2\text{-DMG}$ but not $\text{Pt}_2\text{-(DMG)}_2$ as Job's curves suggest.

TABLE I
Data of the method of relative recovery at a fixed concentration of metal ions ($4 \times 10^{-5} \text{ mol l}^{-1}$)

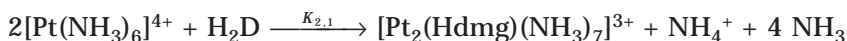
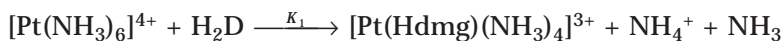
$c(\text{DMG}), \text{ mol l}^{-1}$	$A(210 \text{ nm})$	$A/c(\text{DMG})$ $\text{l mol}^{-1}\text{cm}^{-1}$	A/A_s
8.0×10^{-6}	0.9045	1.131×10^5	0.6685
1.6×10^{-5}	0.9691	6.057×10^4	0.7162
2.4×10^{-5}	0.9844	4.102×10^4	0.7275
3.2×10^{-5}	1.0580	3.306×10^4	0.7819
4.0×10^{-5}	1.1430	2.858×10^4	0.8447
4.8×10^{-5}	1.1840	2.467×10^4	0.8751
5.6×10^{-5}	1.2850	2.295×10^4	0.9491
6.4×10^{-5}	1.3030	2.036×10^4	0.9609

Determination of Stability Constants and Molar Absorptivity of the Complexes

Under the assumption of an octaedral coordination, the reactions in the bulk of solution in the presence of ammine and dimethylglyoximato (dmg) ligands involve the equilibria



In the absence of DMG²², the ammine species should be predominant at 0.1 M NH₃. In the presence of DMG, dynamic equilibria between the ammine species and DMG chelate exist.



H₂D represents the undissociated dmg ligand ($K_a = 10^{-10.5}$)²³ and Hdmg its dissociated form which enters into the chelate. Under the conditions used throughout the experiments – $c(\text{NH}_3) = 0.1 \text{ mol l}^{-1}$, $c(\text{H}_2\text{D}) = 4 \times 10^{-6} \text{ mol l}^{-1}$, pH 9.2 – if the stabilities of Pd–DMG complexes are high, the equilibria represented by Eq. (2) are shifted far to the right, *i.e.* platinum is chelated quantitatively by DMG. With ammonia concentration increasing to 1 mol l⁻¹ or more (at constant pH), the fraction of platinum–ammine complexes increases, which is reflected in the smaller concentration of $[\text{Pt}(\text{Hdmg})_2(\text{NH}_3)_2]^{2+}$.

Stability constants of the complexes and their molar absorptivities were calculated using the method for complexes of the type ML_{*n*} ($n = 1, 2, 3, \dots$), described by Bulatov and Kalinkin²⁴. The equilibrium constant expression for the above complex is described by the same authors.

$$\frac{c(\text{Pt})l}{A} = \frac{1}{\varepsilon_k} + Q \frac{1}{n+1\sqrt{A^n}} \quad (3)$$

Equation (3) indicates that a plot of $c(\text{Pt})l/A$ versus $1/n+1\sqrt{A^n}$ should be linear with the slope Q and the intercept $1/\varepsilon_k$. The values of $1/\varepsilon_k$, Q and $n = 2$ are

used for the calculation of K_r . The equations for the calculation of the reaction constant (K_r) is as follows

$$K_r = \frac{c^n (\text{H}^+) I^n}{n^n \epsilon_k Q} \quad (4)$$

according to our results, $K_r = 10^{4.84}$. The formation constant K_v of the complex species is

$$K_v = \frac{K_r}{K_a} = \frac{10^{4.84}}{10^{-10.5}} = 10^{15}. \quad (5)$$

The values of the complex formation constant and the molar absorptivity at pH 9.2 calculated by a graphical method are $\log K_{2,1} = 15.0$ for $n = 5$ (n is the number of absorbances, used for determination of the slope and intercept, $r = 0.956$) and $\log \epsilon = 4.1$, respectively. The values of the stability constant of the complex (pH 9.2) calculated by a numerical method using molar absorptivities are shown in Table II.

TABLE II
Values of the cumulative constants of the $[\text{Pt}(\text{Hdmg})_2]^{2+}$ complex

Molar ratios method ^a		Job's method ^a	
$\frac{c(\text{DMG})}{\alpha(\text{Pt(IV)})}$	$\log \beta_2$	$\frac{V(\text{DMG})}{V(\text{DMG}) + V(\text{Pt})}$	$\log \beta_2$
0.2	9.5	0.9	8.4
0.4	9.2	0.8	8.9
0.6	9.9	0.7	9.3
0.8	8.6	0.6	9.5
1.0	8.5	0.4	9.8
1.2	9.9	0.2	9.9
$\log \beta_2 = 9.2 \pm 0.2$		$\log \beta_2 = 9.3 \pm 0.2$	

^a Calculated by numerical method.

Conclusion

The interaction between Pt(IV) ions and DMG in aqueous ammonia results in the formation of the complexes $[\text{Pt}(\text{Hdmg})]^{3+}$, $[\text{Pt}(\text{Hdmg})_2]^{2+}$ and $[\text{Pt}_2(\text{Hdmg})]^{7+}$. These complex species at pH 9.2 show absorption bands in the range from 350 to 190 nm, with a maximum at 210 nm. By using ultraviolet spectrophotometry, it was found that the stoichiometric ratio Pt(IV)/DMG is 1:1, 1:2 and 2:1. The molar absorptivity $\log \epsilon = 4.1$ at 260 nm and the consecutive constant of dinuclear $[\text{Pt}_2(\text{Hdmg})]^{7+}$ complex at pH 9.2 calculated by a graphical method, $\log K_{2,1} = 15.0$ were obtained. Also, the cumulative constants of the $[\text{Pt}(\text{Hdmg})_2]^{2+}$ complex were calculated by the molar ratios method and Job's method (both are numerical methods): $\log \beta_2 = 9.2 \pm 0.2$ and $\log \beta_2 = 9.3 \pm 0.2$.

Further studies are in progress to exploit the formation of Pt-DMG complexes for determination of platinum(IV) by UV spectrophotometry.

SYMBOLS

A	absorbance
l	path length of radiation, cm
t	time, min
T	temperature, °C
λ	wavelength, nm
ϵ	molar extinction coefficient, $\text{l mol}^{-1} \text{cm}^{-1}$

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REFERENCES

1. Qu Bin Yi.: *Analyst* **1996**, *121*, 139.
2. Liu Q., Wang Y., Lin J., Cheng J.: *Anal. Sci.* **1993**, *9*, 523.
3. Basova M. E., Kazakova V. O., Bondareva G. L., Polenova V. T., Ivanov M. V.: *Zh. Anal. Khim.* **1993**, *48*, 1531.
4. Macka M., Borak J.: *J. Chromatogr.* **1993**, *641*, 101.
5. Kundu D., Roy K.: *Talanta* **1992**, *39*, 415.
6. Bhargava C., Tandon K. V.: *Asian J. Chem.* **1992**, *4*, 664.
7. Murthy R. V. G., Reddy S. T.: *Asian J. Chem.* **1993**, *5*, 1133.
8. Murthy R. V. G., Reddy S. T.: *Talanta* **1992**, *39*, 697.
9. Palaniappan R.: *Chim. Acta Turc.* **1990**, *18*, 483.
10. Kuroda R., Hayashibe Y., Yoshitsuka K.: *Fresenius' J. Anal. Chem.* **1990**, *336*, 494.
11. Tummavuori J., Hankala S., Siltaloppi L.: *Fresenius' J. Anal. Chem.* **1991**, *339*, 145.

12. Toral M. I., Richter P., Lara N., Escudero M. T., Soto C.: *Anal. Lett.* **2000**, 33, 93.
13. Tschugaeff L.: *Ber. Dtsch. Chem. Ges.* **1905**, 38, 2520.
14. Georgieva M., Pihlar B.: *Electroanalysis* **1996**, 8, 1155.
15. Georgieva M., Pihlar B.: *Fresenius' J. Anal. Chem.* **1997**, 357, 874.
16. Barefoot R. R., Van Loon J. C.: *Talanta* **1991**, 49, 1.
17. Messerschmidt J., Alt F., Tölg G., Angerer J., Schaller K. H.: *Fresenius' J. Anal. Chem.* **1992**, 343, 391.
18. Ezerskaya N. A.: *Khim. Farm. Zh.* **1996**, 6, 57.
19. Bochkova P. L., Borisova V. L., Korchemnaya K. E.: *Zh. Anal. Khim.* **1992**, 47, 809.
20. Schwarzenbach G., Flaschka H.: *Complexometric Titrations*, p. 251. Verlag, Stuttgart 1965.
21. Jafe H. H., Orchin M.: *Theory and Applications of Ultraviolet Spectroscopy*. J. Wiley, Inc., New York 1962.
22. Bjerrum J.: *Metal Formation in Aqueous Solution*. P. Haase, Copenhagen 1941.
23. Martell A. E., Smith R. M.: *Critical Stability Constants*, Vol. 3, p. 306. Plenum Press, New York 1977.
24. Bulatov M. I., Kalinkin I. P.: *Practical Manual of Photometric Analyses*, p. 241. Chemistry, Leningrad V Ed 1986.