

# Fluorescence of Metal–Ligand Complexes of Mono- and Di-Substituted Naphthalene Derivatives

M. I. Rodríguez-Cáceres,<sup>1</sup> R. A. Agbaria,<sup>2</sup> and I. M. Warner<sup>2,3</sup>

Received May 25, 2004; accepted October 8, 2004

In this work, metal ion complexes for several naphthalene derivatives have been investigated. Different working pH values were chosen: 2.5 for complexes with Zr(IV), 4.0 for complexes with Fe(III), 5.0 for complexes with Al(III), and 7.5 for complexes with Cu(II). A stoichiometry of 1:1 for all complexes except two has been established by use of the Benesi–Hildebrand method and the stability constants have been calculated. All complexes between naphthalene derivatives and Cu(II) and Fe(III) show fluorescence quenching. In the case of Al(III), all complexes provided enhanced fluorescence. For Zr(IV), only the complex with 3-hydroxy-2-naphthoic acid provided enhanced fluorescence. The value of the stability constants as a function of the substituents of naphthalene derivatives has been analyzed. One can conclude that Cu(II) showed the largest binding affinity for the mono-substituted derivatives. However, Al(III) and Zr(IV) produced greater selectivity for the di-substituted derivatives. Iron(III) showed no specific binding with any of the naphthalene derivatives.

**KEY WORDS:** Naphthalene derivatives; steady-state fluorescence; stability constants; metal ions.

## INTRODUCTION

Complexes between naphthalene derivatives and different metal ions have been studied since the early 1960s. In these studies, different methods, such as voltammetry [1,2], spectrophotometry [2–7], and flame atomic-absorption spectrometry [8,9] have been used to examine these complexes. As examples, several references on potentiometric studies of complexes of Cu(II) with 1-hydroxy-2-naphthoic acid (1H2NA) [10–12] and 3-hydroxy-2-naphthoic acid (3H2NA) [12,13] have been found. In all cases, an organic:aqueous solution (ethanol:water [10,11] or dioxane:water [12,13]) was used. It is also noted that a ternary complex between 1H2NA or 2-hydroxy-1-naphthoic acid (2H1NA)

with Cu(II) and 2,2-bipyridine has been reported by Datta *et al.* [14].

The compound 3H2NA is one example of a naphthalene derivative that has been frequently used for the determination of metal ions. For example, 3H2NA has been used for the determination of Al(III) by spectrofluorimetry [15,16]. In addition, 3H2NA has been used for the fluorimetric determination of Be(II) [15–18] and Sc(III) [19]. Likewise, an extraction-photometric method has been proposed for the determination of V(V) [20]. Casassas *et al.* determined trace amounts of copper(II) by use of a catalytic spectrophotometric method [21], and Abdel-Ghani *et al.* proposed the spectrophotometric determination of some lanthanoids using 3-hydroxy-2-naphthoic acid azo-dyes [22]. Kasiura proposed a method for the determination of Ca(II) and Mg(II) by formation of binary complexes with 3H2NA [23]. A comparison between 1- and 2-naphthoic acid as an extracting agent for Co(II), Ni(II) and Cu(II) has also been studied by Yamada *et al.* [24].

In this paper, the complexes of 11 naphthalene derivatives (mono- and di-substituted with hydroxy and carboxylic groups) and several metal ions (Cu(II), Al(III),

<sup>1</sup> Department of Analytical Chemistry, University of Extremadura, 06071 Badajoz, Spain.

<sup>2</sup> Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803.

<sup>3</sup> To whom correspondence should be addressed. E-mail: iwarner@lsu.edu

Fe(III) and Zr(IV)), are systematically studied by use of spectrofluorimetry. The Benesi–Hildebrand method was applied to determining the stoichiometry of these complexes. The logarithm of the stability constants were then tabulated and a comparison is made for variations in the functional group attachments.

## EXPERIMENTAL

### Apparatus

Fluorescence spectra were acquired by use of a Fluorolog-2 (Yvon-Horiba, New Jersey, USA) spectrofluorimeter equipped with a 450-W Xenon arc lamp and controlled by a software DataMax, version 2.2. Samples were measured in a 1 quartz cell with excitation and emission slit bandwidths of 4 nm. Excitation and emission wavelengths were different for each of the naphthalene derivatives and are therefore summarized in Table I. All measurements were taken at room temperature. All pH measurements were made with an Orion 410A (Cambridge, MA, USA) digital pH-meter using a combined glass-calomel electrode.

### Materials

The compounds 1-naphthoic acid (1NA), 2-naphthoic acid (2NA), 1-hydroxy-2-naphthoic acid (1H2NA), 3-hydroxy-2-naphthoic acid (3H2NA), 6-hydroxy-2-naphthoic acid (6H2NA), 2-hydroxy-1-naphthoic acid (2H1NA), 1-naphthol (1NOH), 2-naphthol (2NOH), 1,4-naphthalenedicarboxylic acid (14NDA),

2,3-naphthalenedicarboxylic acid (23NDA) and 2,6-naphthalenedicarboxylic acid (26NDA) were purchased from Aldrich (Milwaukee, WI, USA) and used as received. Triple distilled, de-ionized water (Purelab UV/UF, US filter) was used in all experiments. Glycine, Tris, ZrCl<sub>4</sub>, Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·7H<sub>2</sub>O were all obtained from Sigma and CuSO<sub>4</sub>·5H<sub>2</sub>O was obtained from Fisher Scientific (Pittsburg, PA, USA)

### General Procedure for Fluorescence Measurements

A 3.5 × 10<sup>-3</sup> M stock solution of all reagents was prepared by weighing the appropriate amount of each compound and dissolving in methanol. Only in the case of 2,6-naphthalenedicarboxylic acid was the solvent DMF:MeOH (10:90 v/v) used. To prepare dilute solutions, an aliquot of stock solution was placed in a 5 mL volumetric flask and filled to the mark with distilled water. Spectra were recorded immediately after sample preparation in the optimum wavelength range for each compound (see Table I).

The interactions of naphthalene derivatives with metal ions were studied at several pH values by use of fluorescence measurements. For determination of the stability constants of the complexes, the concentrations of reagents were held constant at 2.0 × 10<sup>-5</sup> M, while the concentrations of metal ions were varied in the range of 0.0–2.0 mM. In the case of Cu(II), the complex is so weak that the concentration of metal ion was increased to 18 mM to monitor variations in fluorescence. The buffers (0.5 M) used were glycine/HCl pH 2.5 for the complexes with Zr(IV), NaAc/HAc pH 4.0 for the complexes with Fe(III), NaAc/HAc pH 5.0 for the complexes with Al(III) and Tris/HCl pH 7.5 for the complexes with Cu(II). The order of addition was constant using the following scheme: naphthalene derivative + buffer + metal ion.

**Table I.** Name, Abbreviation and Excitation and Emission Wavelength for the Different Analytes

Name	Abbreviation	$\lambda_{ex}/\lambda_{em}$ (nm)
1-Naphthoic acid (I)	1NA	312/400
2-Naphthoic acid (II)	2NA	334/386
1-Hydroxy-2-naphthoic acid (III)	1H2NA	344/417
3-Hydroxy-2-naphthoic acid (IV)	3H2NA	354/504
6-Hydroxy-2-naphthoic acid (V)	6H2NA	313/453
2-Hydroxy-1-naphthoic acid (VI)	2H1NA	342/414
1-Naphthol (VII)	1NOH	320/460
2-Naphthol (VIII)	2NOH	327/417
1,4-Naphthalene-dicarboxylic acid (IX)	14NDA	324/432
2,3-Naphthalene-dicarboxylic acid (X)	23NDA	342/390
2,6-Naphthalene-dicarboxylic acid (XI)	26NDA	340/370

### Determination of Stoichiometries and Association Constants of the Complexes

The stoichiometries and stability constants of the complexes with the metal ions were established by use of the Benesi–Hildebrand method [25]. Assuming that the metal ions form 1:1 inclusion complexes with the naphthalene derivatives, Eq. (1) is applicable:

$$\frac{1}{F - F_0} = \frac{1}{(F_\infty - F_0)K[Me]_0} + \frac{1}{(F_\infty - F_0)} \quad (1)$$

In this approach, a graph of 1/(F - F<sub>0</sub>) versus 1/[Me]<sub>0</sub>, was made where F is the observed fluorescence

at each concentration tested,  $F_0$  is the fluorescence intensity of analyte in the absence of metal ion, and  $[Me]$  is the concentration of metal ion. A linear plot is required for this double reciprocal plot in order to conclude 1:1 stoichiometry.

In the case where a 2:1 stoichiometry is predominant, the applicable equation is:

$$\frac{1}{F - F_0} = \frac{1}{(F_\infty - F_0)K[Me]_0^2} + \frac{1}{(F_\infty - F_0)} \quad (2)$$

For a 2:1 complex, a straight line would be obtained when  $1/(F - F_0)$  is plotted against  $1/[Me]_0^2$ .

If the stoichiometry is 1:1, a linear relationship has to be obtained when  $1/(F - F_0)$  versus  $1/[Me]_0$  is plotted. In contrast, a downward concave curvature is obtained when these same data are fitted to a 2:1 complex, with the use of Eq. (2). This observation suggests that the stoichiometry of the complex is not 2:1.

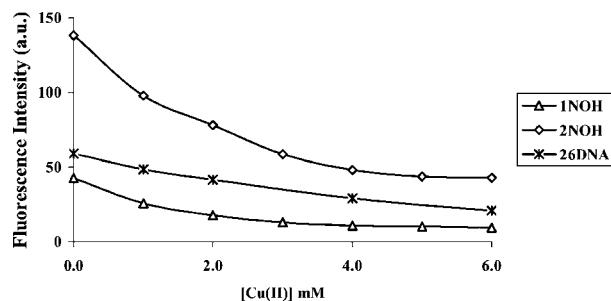
The association constant is determined by dividing the intercept by the slope of the straight line obtained in the double-reciprocal plot.

## RESULTS AND DISCUSSION

### Complexes with Cu(II)

A study of the complexes with Cu(II) was performed at pH 7.5. This pH was chosen to avoid precipitation of copper hydroxide. Three out of the four, mono-substituted naphthalene derivatives yielded complexes with Cu(II). The logarithms of the equilibrium constants values ( $\log K$ ) (Table II) vary between 2.54 and 2.82. A comparison between OH and COOH groups revealed that the complexes with the COOH group were stronger than those with the OH group.

For di-substituted naphthalene with different substituents, the  $\log K$  values varied between 1.78 and 2.78. Interestingly, 6H2NA has a similar  $\log K$  value to 2NA. However, the  $\log K$  values for 1H2NA and 3H2NA are



**Fig. 1.** Influence of concentration of Cu(II) on the fluorescence intensity of some mono- and di-naphthalene derivatives. Concentration of naphthalene derivatives: 4  $\mu\text{g/mL}$ . pH 7.5 (Tris/HCl, 0.1 M).

lower. In general, the  $\log K$  values for the di-substituted derivatives were smaller than either one of the mono-substituted parent compounds, i.e. naphthoic acid or naphthol. This lead to the conclusion that the second substituent in the *ortho* position is interfering with the complexation of Cu(II). The 2H1NA is the only reagent which has a stoichiometry of 1:2 under the same conditions as the others ( $\log K = 5.48$ ). In this case, the representation of  $1/(F - F_0)$  versus  $1/[Me]_0^2$  gave a straight line with a  $R^2 = 0.998$ .

Figure 1 shows the influence of concentration of Cu(II) on the fluorescence intensity of several reagents. It is worth nothing that di-substituted 26DNA and 6H2NA behave similar to mono-substituted NA due to the *para* position of the substituents. All of the di-substituted reagents have very similar  $\log K$  values.

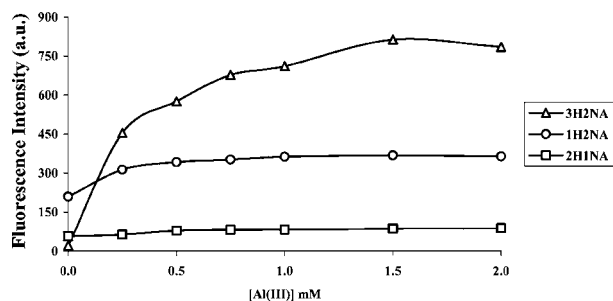
### Complexes with Al(III)

The change in fluorescence intensity of the complex 1H2NA-Al(III) as a function of pH was examined. An increment of the fluorescence signal was observed when the pH increased between pH 2.3 and 3.5. After this pH, the fluorescence intensity remained constant until pH 5.0. For pH higher than 5.5, a white precipitate is observed. For this reason, pH 5.0 was chosen for the

**Table II.** The  $\log K$  Values for the Naphthalene Derivatives-Metal Ions Complexes

Analyte/Metal	1NA	2NA	1H2NA	3H2NA	6H2NA	2H1NA	1NOH	2NOH	14DNA	23DNA	26DNA
Cu(II)	—	2.82	1.78	2.00	2.78	5.48	2.60	2.54	—	—	2.05
Al(III)	1.18	1.40	3.82	3.60	—	3.52	—	—	—	2.00	1.45
Fe(III)	3.40	3.78	3.70	3.82	3.40	4.00	3.70	3.78	3.15	3.78	3.45
Zr(IV)	4.48	—	3.35	3.30	—	—	—	—	1.85	3.52	—

*Note.* All the complexes that present enhancement of fluorescence are represented with grey bottom. For the other analytes there are quenching of fluorescence. All the complexes present stoichiometry 1:1 except, the ones in black bottom, that present stoichiometry 1:2. The buffer used were: 0.1 M glycine/HCl, pH 2.5 for Zr(IV), 0.1 M AcNA/HAc, pH 4.0 for Fe(III) and 5.0 for Al(III), and 0.1 M Tris/HCl, pH 7.5 for Cu(II).



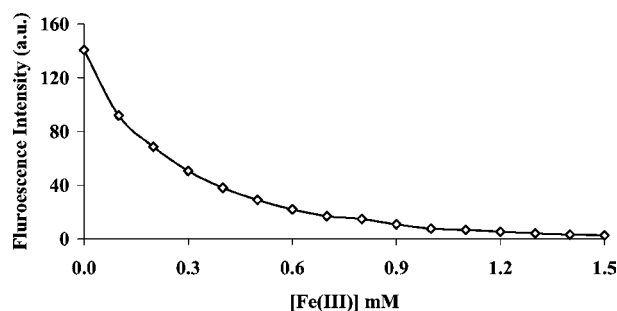
**Fig. 2.** Influence of concentration of Al(III) on the fluorescence intensity of 1H2NA, 3H2NA and 2H1NA. Concentration of naphthalene derivatives: 4  $\mu\text{g/mL}$ . pH 5.0 (NaAc/HAc, 0.1 M).

study of the complexes with Al(III). Only complexes with the mono-substituted reagents and Al(III) were formed for the COOH substituent. In the case of 1NA and 2NA, enhancement of fluorescence was observed. However, the complexes were not very strong. The measured  $\log K$  values are 1.18 and 1.40 for 1NA and 2NA, respectively. If we compare the di-substituted reagents, we observe that the strongest complexes are formed between Al(III) and the reagents, which have two different substituents. Figure 2 illustrates the variation of the fluorescence intensity of the three *ortho* di-substituted naphthalene derivatives. The maximum fluorescence intensity was reached when the substituents were in positions 2 and 3.

### Complexes with Fe(III)

For the study of the complexes with Fe(III), a pH 4.0 buffer using 0.10 M of NaAc/HAc was chosen. In this case, all reagents investigated formed a red 1:1 complexes and produced quenching fluorescence. The influence of Fe(III) concentration on the fluorescence of 2NA is presented in Fig. 3. As seen, the fluorescence intensity decreases and almost disappears at Fe(III) concentrations higher than 1 mM. The Benesi–Hildebrand's plots for the calculation of stoichiometry and stability constants of the 2NA:Fe(III) complex are presented in Fig. 4. In Fig. 4A, the plot of  $1/(F - F_0)$  versus  $1/[\text{Fe(III)}]$  gives a straight line, which is indicative of 1:1 stoichiometry. In Fig. 4B, the plot of  $1/(F - F_0)$  versus  $1/[\text{Fe(III)}]^2$  does not give a straight line, which is consistent with a 1:1 stoichiometry for the 2NA:Fe(III) complex.

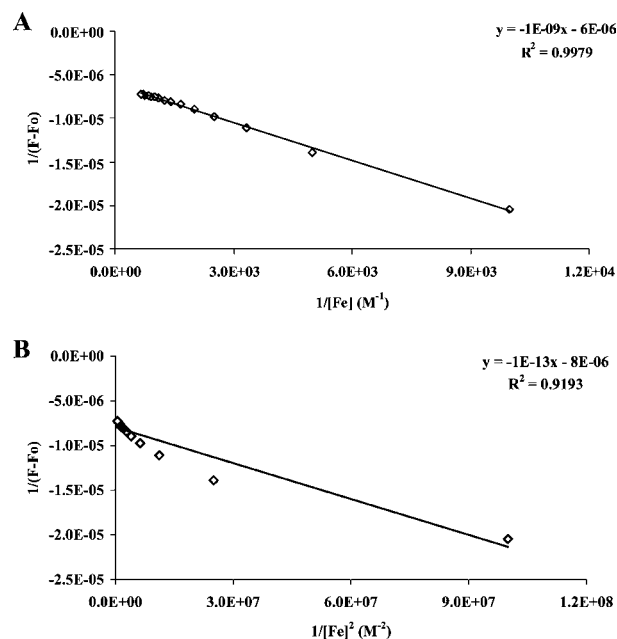
All complexes with iron showed stoichiometry 1:1. This is likely because all the reagents have hydroxy and carboxylic groups. It is well known that the interaction between these two groups and iron can form complexes with different stoichiometry at different pH values. For example, Martínez Vidal [26] studied the reaction between



**Fig. 3.** Influence of concentration of Fe(III) on the fluorescence intensity of 2NOH. [2NOH] = 4  $\mu\text{g/mL}$ ;  $\lambda_{\text{ex}}$  = 312 nm;  $\lambda_{\text{em}}$  = 400 nm; pH 4.0 (0.1 M NaAc/AcH).

5,5'-metylendisalicic acid with iron and obtained three different complexes as a function of pH. The complex was violet at pH 1.6 (stoichiometry 1:2), red at pH 6.5 (stoichiometry 1:1) and yellow at pH 10 (stoichiometry 3:2). In our case, all complexes have been studied at pH 4; all the complexes had red color; for this reason, it is reasonable to find a 1:1 stoichiometry for all of them. All of the analytes present acidic ligands, and react with the iron in the following manner: OH and COOH lose a  $\text{H}^+$  and then there is a coordination with the metal forming a metallic chelate [27].

This suggests a difference between the naphthalene derivatives and other iron complexes such as



**Fig. 4.** Benesi–Hildebrand's plots for the 2NA:Fe(III) complex. (A) Assuming 1:1 stoichiometry; (B) Assuming 1:2 stoichiometry.

[Fe(bipy)<sub>3</sub>]<sup>3+</sup> or [Fe(phen)<sub>3</sub>]<sup>3+</sup> where one molecule of iron is binding three molecules of ligand. In this case, the N of the heteroatom provides electrons to bond to the iron. This kind of basic ligands, acts as  $\sigma$ -donors because of the presence of the sp<sup>2</sup> donor orbital on the N atoms. However, it can also function as acceptors due to the presence of delocalized  $\pi$  orbitals associated with their aromatic ring systems.

### Complexes with Zr(IV)

For the study of complexes with Zr(IV), a pH of 2.5 was chosen because at higher pH values, the Zr(IV) precipitates as Zr(OH)<sub>4</sub>. Of the four metal ions, Zr(IV) yielded the most interesting results. With the mono-substituted naphthalene derivatives, only the formation of a complex with stoichiometry 1:2 (log *K* = 4.48) is observed between 1NA and Zr(IV). With di-substituted naphthalene derivatives, we observe complexes only when the substituents are in the *ortho* position. The most interesting result is the different behavior of 1H2NA and 3H2NA. The only difference in these two compounds is the position of the OH group. However, this change has a great influence on the fluorescence, since enhancement and quenching of fluorescence is observed (Fig. 5).

### CONCLUSIONS

The results reported here support the formation of a variety of complexes between naphthalene derivatives and various metal ions. Fe(III) showed no specific binding with any of the derivatives.

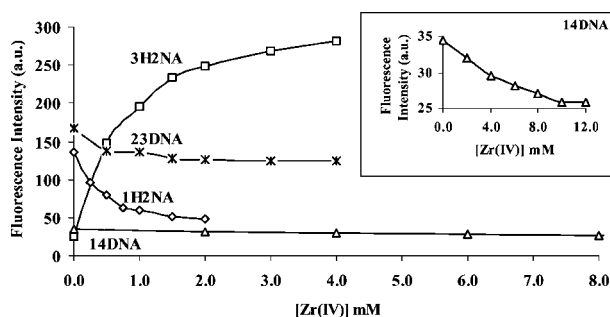
Cu(II) did not enhance or quench the fluorescence of any of the 1-naphthoic derivatives. However, all but one

of the 2-naphthoic derivatives produced significant fluorescence quenching with Cu(II). Furthermore, the mono-substituted derivatives showed the highest binding affinity for Cu(II), indicating that the binding is not co-operative between the two adjacent groups, as observed for Zr(IV) and Al(III).

The fluorescence intensities of all mono- and di-substituted naphthalene derivatives were enhanced by Al(III). Furthermore, the binding affinity reached its maximum for the di-substituted naphthalene derivatives with *ortho* COOH and OH groups. In comparison, the binding affinity was lower when both groups were COOH. However, the weakest binding affinity was found for mono-substituted naphthoic acid or when the two COOH groups of the di-substituted naphthoic acid were not *ortho*. In contrast, the fluorescence of the naphthols was quenched by Al(III).

Complexes with Zr(IV) showed very interesting results. The fluorescence of 2-naphthoic acid was quenched by Zr(IV) when the 1-position was substituted with an OH group. In contrast, substitution of an OH in the 3-position of 2-naphthoic acid resulted in enhanced fluorescence. For Al(III) the highest binding affinity was observed when the *ortho* groups were COOH and OH. In contrast, the highest binding affinity for Zr(IV) was achieved when the *ortho* groups were both COOH.

The studies reported here are interesting for two main reasons. First, the variation in fluorescence intensity as a result of position and substitution is worthy of further study, since the reasons for these variations are not entirely apparent. Therefore, further studies are warranted for scientific reasons alone. Second, these or similar molecules may serve as sensors for metal ions due to the variation in response to different metal ions. Finally, understanding the interactions reported here may lead to the development of novel kinds of sensor molecules.



**Fig. 5.** Influence of concentration of Zr(IV) on the fluorescence intensity of 1H2NA, 3H2NA, 23DNA and 14DNA. Concentration of reagents: 4  $\mu$ g/mL. pH 2.5 (glycine/HCl, 0.1 M). The small graph is a detail of the interaction of 14DNA with Zr(IV).

### ACKNOWLEDGMENTS

Funding for this study was provided by the National Institutes of Health and the National Science Foundation. M.I. Rodríguez Cáceres is also grateful to the Ministry of Education, Culture and Sports of Spain for the grant that made possible her research in Professor Warner's laboratory.

### REFERENCES

1. M. Esteban, C. Arino, I. Ruisanchez, M. S. Larrechi, and F. X. Rius (1994). *Anal. Chim. Acta* **285**(3), 377.

2. E. Gorodkiewicz and Z. Figaszewski (2000). *Chem. Anal.* **45**(6), 867.
3. J. Kobylecka and E. Skiba (1993). *Chem. Anal.* **38**(5), 599.
4. I. Singh and Sushma (2000). *Indian J. Chem. Sect. A Inorganic Bio-ionorganic Phys. Theor. Anal. Chem.* **39**(5), 545.
5. J. Nozaki and H. Zhou (1987). *Anal. Lett.* **20**(3), 361.
6. E. Malinowska and K. Kasiura (1986). *Chem. Anal.* **31**(5–6), 797.
7. E. Casassas, A. Izquierdo-Ridorsa, L. Garcia-Puignou, and J. Dunach (1985). *Anal. Lett.* **18**(A18), 2239.
8. J. R. Chen and K. C. Teo (2001). *Anal. Chim. Acta* **450**(1–2), 215.
9. I. Narin, M. Soylak, L. Elci, and M. Dogan (2001). *Anal. Lett.* **34**(11), 1935.
10. S. S. Shandhu, J. N. Kumaria, and R. S. Shandhu (1976). *Indian J. Chem.* **14A**, 816.
11. M. S. Rizk, N. T. Abdel-Ghani, Y. M. Issa, and Sahar M. Atwa (1993). *Egypt J. Chem.* **36**(6), 449.
12. R. M. Sathe and S. Y. Shetty (1970). *J. Inorg. Nucl. Chem.* **32**, 1383.
13. E. Casassas, G. Forondona, and R. Tauler (1987). *Polyhedron* **6**, 1517.
14. P. K. Datta, M. Chandra, and A. K. Dey (1980). *J. Indian Chem. Soc.* **LVII**, 931.
15. K. Kasiura (1975). *Chemia Analityczna* **20**, 389.
16. G. F. Kirkbright, T. S. West, and C. Woodward (1965). *Anal. Chem.* **37**(1), 137.
17. V. Kuban, J. Havel, B. Patockova (1989). *Collect Czech. Chem. Commun.* **54**(7), 1777.
18. P. N. Kariuki (1980). *Kenya J. Sci. Technol. Ser. A* **1**(1), 27.
19. D. B. Gladilovich, N. N. Grigor'ev, and K. P. Stolyarov (1980). *Zh. Anal. Khim.* **35**(7), 1283.
20. N. K. Rustamov and A. N. Gurbanov (2001). *Zavod. Lab. Diagn. Mater.* **67**(4), 12.
21. E. Casassas, A. Izquierdo-Rtidorsa, and L. Puignou (1988). *Talanta* **35**(3), 199.
22. N. T. Abdel-Ghani, Y. M. Issa, and A. A. Salem (1989). *Microchem. J.* **39**(3), 283.
23. K. Kasiura (1975). *Chem. Anal.* **20**, 389.
24. H. Yamada, Y. Matsui, Y. Kuroki, and H. Wada (1997). *Anal. Sci.* **13**(2), 237.
25. H. Benesi and J. H. Hildebrand (1949). *J. Am. Chem. Soc.* **71**, 2703.
26. F. Capitán, F. Salinas, and J. L. Martínez Vidal (1975). *Afinidad* **XXXII**(327), 455.
27. *Chelating Agents and Metal Chelates* (1964). Dwyer and Mellor, Academic Press.