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Spectrophotometric Determination of Microamounts of Yttrium with 1-Amino-4-Hydroxyanthraquinone

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Summary. 1-amino-4-hydroxyanthraquinone (*AMHA*) is proposed as a spectrophotometric reagent for the determination of yttrium. The solution equilibria of *AMHA* complexes with Y(III) have been studied spectrophotometrically in 50% (v/v) ethanol at 25 °C and an ionic strength of $I = 0.1$ mol·dm^{-3} ($NaClO_4$). The complexation reactions were investigated and characterized using graphical logarithmic analysis of the absorbance graphs. The composition, molar absorptivities, and stability constants of the chelates of *AMHA* with Y(III) have been determined spectrophotometrically. A simple, rapid, selective, and sensitive method for the spectrophotometric determination of microamounts of Y(III) is developed based on the formation of the violet YLH^+ complex with $\lambda_{max} = 580$ nm at *pH* 6.2($\varepsilon = 0.98 \times 10^4$ l·mol^{-1}·cm^{-1}). Interferences and their elimination have been studied. Many foreign ions are tolerated in considerable amounts; 45–60 fold amounts of rare earths do not interfere with the determination of yttrium. In the determination of yttrium in synthetic polymetallic samples the relative error and relative standard deviation of the method were found to be better than 1 and 0.5%, respectively.

Keywords. Spectrophotometric determination of yttrium; complexation equilibria; Stability constants.

Spektrophotometrische Bestimmung von Mikromengen Yttrium mit 1-Amino-4-hydroxyanthrachinon

Zusammenfassung. 1-Amino-4-hydroxyanthrachinon (*AMHA*) wird als spektrophotometrisches Reagens zur Bestimmung von Yttrium vorgeschlagen. Die Gleichgewichte von Komplexen aus *AMHA* und Y(III) in Lösung wurden in 50% (v/v) Ethanol bei 25 °C und einer Ionenstärke von $I = 0.1\ M$ ($NaClO_4$) untersucht. Die Komplexierungsreaktionen wurden durch graphische logarithmische Analyse der Extinktionskurven charakterisiert. Die Zusammensetzungen, die molaren Extinktionen und die Stabilitätskonstanten der Chelate von *AMHA* mit Y(III) wurden spektrophotometrisch bestimmt. Eine einfache, schnelle, selektive und empfindliche Methode zur spektrophotometrischen Bestimmung von Mikromengen Y(III) wurde entwickelt. Sie basiert auf der Bildung des violetten YLH^+-Komplexes mit $\lambda_{max} = 580$ nm bei *pH* 6.2 ($\varepsilon = 0.98 \times 10^4$ l·mol^{-1}·cm^{-1}). Störungen und ihre Beseitigung werden ebenfalls diskutiert. Viele Fremdionen werden in beträchtlichen Mengen toleriert; 45–60 facher Überschuß an Seltenen Erden stört die Bestimmung von Yttrium nicht. Der relative Fehler und die relative Standardabweichung der Methode bei der Bestimmung von Yttrium in synthetischen polymetallischen Proben waren besser als 1 bzw 0.5%.

Introduction

Although several procedures have been proposed during the last decade for the direct or extractive spectrophotometric determination of yttrium [1–6], there is a need for a simple, rapid and sensitive method with faster colour development which does not require rigid control of *pH*. In a previous paper [7], we proposed a method for facilitating the spectrophotometric analysis of yttrium with 5,8-dihydroxy-1,4-naphthoquinone (*NAZA*). The results showed that the method was applicable to yttrium. In this method, however, some metal ions caused serious interferences. Moreover, the stability constant of Y-*NAZA* (B_1) was rather small. Therefore we reexamined the spectrophotometric determination of yttrium with the analogous compound 1-amino-4-hydroxyanthraquinone (*AMHA*) in order to test the hypothesis that the stability constants of the complexes depend linearly on the pK_a of the ring hydroxyl groups. Previous studies from this laboratory have shown that *AMHA* possesses a unique combination of properties that enable this reagent to be utilized in some novel applications. The analytical aspects of *AHMA* for Zr(IV) [8] and Pd(II) [9] have recently been explored. The spectrophotometric determination of yttrium by means of this colour reaction is described in this communication. The molar absorptivity is $0.98 \times 10^4 \text{ l} \cdot \text{mole}^{-1} \cdot \text{cm}^{-1}$ at $\lambda_{max} = 580$ nm. The stability constant B_1 of Y-*AMHA* is about 80 times that of the *NAZA* complex. Moreover, this method tolerates a larger number of diverse ions.

Results and Discussion

AMHA shows four differently coloured acid-base forms: LH_3^+, LH_2, LH^-, and L^{2-}. Detailed studies have been carried out on the acid-base properties of *AMHA* and the results obtained promted us to symbolize the molecular form of the reagent as LH_2. According to our results, the acid-base equilibria existing in *AMHA* solution within the *pH* range ~0.3–12.0 can be represented as

$$\underset{pH < 1.0}{LH_3^+} \rightleftharpoons \underset{pH = 1.5\text{–}9.5}{LH_2} \rightleftharpoons \underset{pH = 10\text{–}11.5}{LH^-} \rightleftharpoons \underset{pH > 11.5}{L^{2-}}$$

The acid dissociation constants (pK_a) corresponding to these ionization steps have been calculated by treating the nonlinear dependences $A = f(pH)$ as described

Table 1. Values of pK_a and λ_{max} for various forms of *AMHA* and *NAZA* in 50% (v/v) ethanol; species in parentheses

Equilibrium	pK_a			
	AMHA	$\lambda_{max,(nm)}$	*NAZA*[7]	$\lambda_{max,(nm)}$
		525 (LH_2)		505 (LH_2)
$LH_2 \rightleftharpoons LH^- + H^+$	10.50 ± 0.03		8.25 ± 0.02	
		555 (LH^-)		555 (LH^-)
$LH^- \rightleftharpoons L^{2-} + H^+$	11.62 ± 0.02		11.22 ± 0.02	
		595 (L^{2-})		600 (L^{2-})

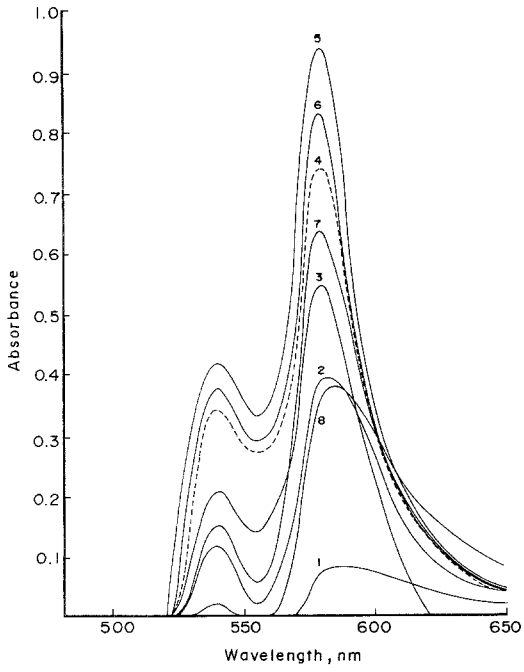

Fig. 1. Absorption spectra of Y(III)-*AMHA* complexes; $C_L = C_M = 1 \times 10^{-4} M$, 50% (v/v) ethanol; *pH*: 1, 5.75; 2, 6.0; 3, 6.2; 4, 6.3; 5, 6.5; 6, 6.6; 7, 6.8; 8, 7.0

elsewhere [10]. The mean pK_a value are given in Table 1. The experimental data can be obtained from the authors.

Complexation Equilibria of Y(III) with AMHA

The complexation equilibria of Y(III) with *AMHA* were studied in 50% (v/v) ethanol-water in the *pH* range 3.5–8.0. The visible absorption spectra of solutions were recorded in presence of an excess of the metal ion, in equimolar solutions, and in presence of excess reagent. The absorption spectra of equimolar solutions and of solutions with an excess of metal ion at various *pH* values are analogous and exhibit an absorption band with λ_{max} at 580 nm. In presence of excess reagent, the solution spectra reflect the formation of a complex with $\lambda_{max} = 590$ nm at *pH* 6.7–7.2. The absorbance *vs. pH* graphs for solutions containing an excess of metal ions or equimolar solutions at 580 nm are analogous and indicate the existence of a single chelate equilibrium in the *pH* range 5.6–6.4, probably through interaction of Y(III) with the LH_2 form of the ligand *AMHA* according to the general equilibrium

$$mY^{3+} + nLH_x \overset{K_1^*}{\rightleftharpoons} Y_mL_nH_z + qH^+ \qquad 1$$

Above *pH* ~ 6.5, the absorbance decreases rapidly owing to the hydrolysis of the ligand. In presence of excess metal ions, the hydrolysis starts at *pH* 6.4.

The absorbance *vs. pH* graphs for solutions containing excess ligand (see Fig. 2) indicate the existence of two basic equilibria within the *pH* range 5.6–7.2 that are sufficiently separated. In addition to equilibrium 1, the second ascending portion of these graphs is obtained in the *pH* region 6.7–7.2, probably as a step-wise complex transition with further coordinated ligand species.

$$Y_mL_nH_z + pLH_x \overset{K_2^*}{\rightleftharpoons} Y_mL_{n+p}H_c + qH^+ \qquad 2$$

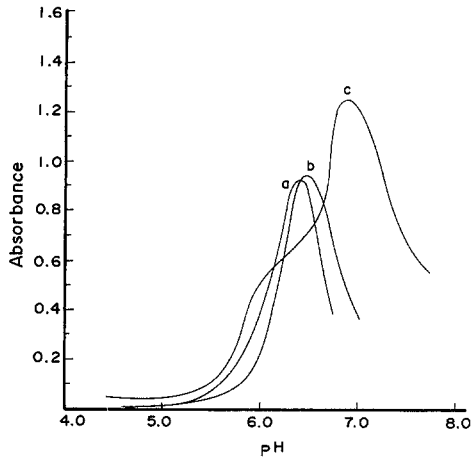

Fig. 2. Absorption *vs. pH* graphs for Y(III)-*AMHA* systems of various concentrations of components; a, $C_M = 5 \times 10^{-4} M$, $C_L = 1 \times 10^{-4} M$; b, $C_M = C_L = 1 \times 10^{-4} M$; c, $C_M = 1 \times 10^{-4} M$, $C_L = 5 \times 10^{-4} M$; $\lambda = 580$ nm, $I = 0.1 M$ $NaClO_4$, 50% (v/v) ethanol

The graphs have a descending branch above *pH* 7.3 due to the hydrolysis of the complex.

The absorbance *vs. pH* graphs for all solutions investigated were interpreted using the previously derived slope intercept transformations [7, 11] of the equilibrium constants or conditional stability constants of the assumed chelates for conditions under which a single complex equilibrium predominates, and for selected wavelengths.

Considering the values of the dissociation constants of *AMHA* under our experimental conditions, it can be concluded that the neutral form (LH_2) is the predominating ligand species in the *pH* range of complexation. From the graphical logarithmic analysis of the absorbance *vs. pH* graphs, the following equilibrium was proved to be present in solutions containing excess metal ions or in equimolar solutions.

$$Y^{3+} + LH_2 \overset{K^*_{11}}{\rightleftharpoons} YLH^{2+} + H^+ \qquad 3$$

For solutions with excess reagent, the analysis of the graphs confirm the presence of equilibrium 4 at *pH* 6.7–7.2 in addition to 3 at *pH* 5.6–6.6.

$$YLH^{2+} + LH_2 \overset{K^*_{21}}{\rightleftharpoons} Y(LH)_2^+ + H^+ \qquad 4$$

The equilibrium constants K^*_{11} and K^*_{21} are related to the stability constants B_{nm} by equations 5 and 6.

$$\log B_{11} = \log K^*_{11} + pK_{a1} \qquad 5$$

$$\log B_{21} = \log K^*_{21} + \log B_{11} + pK_{a1} \qquad 6$$

The set of absorbance *versus pH* curves for varying metal ion excess was analyzed under the conditions of the so-called corresponding solutions [7, 12] according to Eq. 7.

$$(pH)_i = m/q(-\log C_M) + \text{constant} \qquad 7$$

$(pH)_i$ represents the *pH* values for corresponding solutions, m is the number of metal ions bound in the chelate, and q is the number of protons liberated during

Table 2. Mean values of equilibrium constants ($\log K^*_{nm}$), stability constants ($\log B$), and molar absorptivities of Yttrium(III) complexes with *AMHA*. Values are taken as averages for various component concentrations, 50% (v/v) ethanol, $I = 0.1\ M$ ($NaClO_4$), and 25 °C; charges are omitted

Equilibrium	constant	log(constant)	molar absorptivity ($l \cdot mol^{-1} \cdot cm^{-1}$)
$[MLH][H]/[M][LH_2]$	K^*_{11}	-2.06 ± 0.01[a]	0.98×10^4
		-1.50 ± 0.01[b]	
		-1.66 ± 0.02[c]	
$[M(LH)_2][H]/[MLH][LH_2]$	K^*_{21}	-2.36 ± 0.03[c]	1.25×10^4
$[MLH]/[M][LH]$	B_1	8.76[d]	
$[M(LH)_2]/[M][LH]^2$	B_2	16.90[e]	

[a] From the absorbance *vs. pH* graphs for solutions with excess of metal ion; [b] from the absorbance *vs. pH* graphs for solutions of equimolar concentrations; [c] from the absorbance *vs. pH* graphs for solutions with excess ligand; [d] $B_1 = 6.904$ for *NAZA* [7]; [e] $B_2 = 16.3$ for NAZA

complexation. The results obtained reveal no evidence for the presence of any dinuclear complex in solution under the experimental conditions.

The stoichiometry of the Y-*AMHA* complexes was further verified by the method of continuous variation. In solutions with $C_0 = C_M + C_L = 3 \times 10^{-3}\ mol \cdot l^{-1}$ at $pH = 6.2$, the maximum of the *Job* plot corresponds to a component ratio of 1:1 (metal to ligand). At *pH* 6.9, a component ratio of 1:2 was confirmed. The calculated values of the molar absorptivities, equilibrium constants, and stability constants of the Y-*AMHA* complexes are given in Table 2.

The analysis of representative species distribution curves of Y(III) complexes (Fig. 3) reveals that the concentration of YLH^{2+} increases rapidly and reaches a limiting value ($\simeq 70\%$) at *pH* 6.2. Overlap with $Y(LH)_2^+$ is quite apparent at $pH \geq 6.0$. At any *pH* value, the concentration of each species tends to approach a limiting value, and the total concentration of metal present in various species was found to be nearly 100%.

There is a good correlation between the stability constants and the pK_{a1} values of *AMHA* in comparison with *NAZA* (Tables 1 and 2), particularly in the Yttrium(III) complexes. The stability constants increases as the pK_a values for the dissociation of the hydroxy group of the ligands increase. One should also note

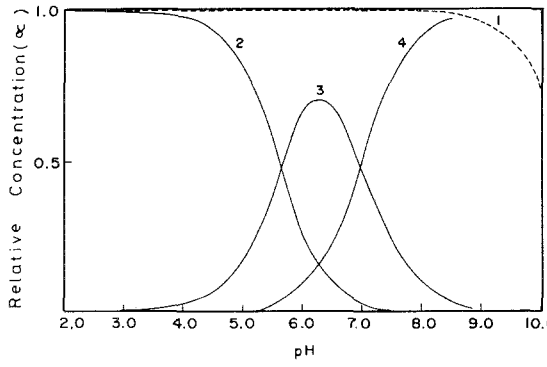

Fig. 3. Distribution curves for the components in the Y^{3+}-*AMHA* system (50% (v/v) ethanol, $I = 0.1\ M$ $NaClO_4$); 1, $\alpha = [LH_2]/C_L$; 2, $[Y^{3+}]/C_M$; 3, $\alpha = [YLH]/C_M$; 4, $\alpha = [Y(LH)_2]/C_M$; $C_L = C_M = 1 \times 10^{-4}\ M$

that the expected increase in stability constants of *AMHA* with respect to *NAZA* may be attributed to the larger size of the conjugated system over which the charge can be delocalized.

Calibration Graph and Reproducibility

According to the results of this work, the formation of the YLH^{2+} complex which possesses a greater stability and a higher molar absorptivity can serve as a suitable base for the spectrophotometric determination of Yttrium(III) under optimum conditions. The YLH^{2+} complex does not require a rigid control of *pH* and possesses a reasonable stability. The optimum *pH* range for quantitative formation of the complex according to Eq. 3 is 6.0–6.4. The LH_2/LH^- acid-base equilibrium of the ligand does not play a significant role in the complexation reaction at this *pH* range. At *pH* 6.0–6.4, the system obeys *Beer*'s law up to a concentration of 8.9 $\mu g \cdot ml^{-1}$ Y(III). The molar absorptivity of the complex at 580 nm is 0.98×10^4 $l \cdot mol \cdot cm^{-1}$. A *Ringbom* plot shows an optical working range for the determination of Y(III) from 3.0 to 8.5 $\mu g \cdot ml^{-1}$. *Sandell*'s sensitivity [13] of the reaction of Y(III) was found to be 1.18×10^{-3} $\mu g \cdot cm^{-2}$. The reproducibility of the method was checked by analyzing two series of solutions (ten determinations each) with Y(III) concentrations of 5.2 and 7.0 $\mu g \cdot ml^{-1}$. The relative standard deviations were found to be 0.6 and 0.5%, respectively.

Comparison with other Methods

The formation of yttrium complexes is known to be very dependent on *pH*. In earlier investigations, little information on the complexation equilibria has been obtained. The results obtained about complexation equilibria in this study will aid in choosing optimal experimental conditions to increase selectivitiy. The reagent offers clear advantages over many of the other chromogenic reagents used for the same purpose. The proposed method is simple and selective and gives a violet coloured complex which is stable for a long time. With this method, yttrium(III) can be determined directly in aqueous solution with no need for extration into organic solvents. The method described above is one of the most sensitive ones available and competes favourably with others for the spectrophotometric determination of yttrium(III). The sensitivities of a series of methods are listed in Table 3.

Effect of Diverse Ions

The tolerance of the method to foreign ions was investigated with solutions containing less than 220 μg of yttrium(III) per 25 ml and various amounts of foreign ions. Yttrium(III) was then determined as YLH^{2+} under optimum conditions as described above. The tolerance limit of foreign ions was taken as that value which caused an absorbance error of not more than ±2%. The results of this work indicate that the ions chloride, bromide, nitrate, sulfate, borate, alkali, and alkaline earth elements did not interfere in the determination of Yttrium as Y-*AMHA*. The tolerance limits in mg of other ions shown in parentheses. The determination of yttrium(III) was possible in the presence of La(III), Zn(II), Cd(II), VO_3^-, CrO_4^{2-},

Table 3. Comparison of spectrophotometric reagents used for the determination of Yttrium(III)

Reagent	range of concentration (μg/ml)	molar absorptivity ($l \cdot mol^{-1} \cdot cm^{-1}$)	*pH*	λ_{max}(nm)	Ref.
2-(2-thiazolylazo)-4-methyl phenol, zephiramine (as ternary complex)	0.10–1.20	3.7×10^4	7.5	610	14
1,4-*bis*-(4′-methylanilino)-anthraquinone	7.12–28.5	4.6×10^3	7.7	565	4
pyrocatechol violet, zepheramine (as ternary complex)	0.10–1.20	3.3×10^4	9.0	660	3
chrome azurol S, cetyltrimethyl ammonium (as ternary complex)	0.50–1.60	8×10^3	5.1	610	3
purpurin (as mixed metal complexes)[a,b]	0.05–0.40	4.5×10^4	7.5	570	15
m-carboxychlorophospho-*NAZO*[b]	0.10–0.80	1.03×10^5	2.0	669	16
5,8-dihydroxy-1,4-naphthoquinone (*NAZA*)	1.95–8.86	1.15×10^4	5.5	595	7
1-amino-4-hydroxyanthraquinone (*AMHA*)	0.44–8.89	0.98×10^4	6.2	580	this paper

[a] By solvent extraction; [b] total rare earth elements

Table 4. Determination of Y(III) in synthetic samples

Sample	Sample composition (%)													Y found (%)	std. dev. (%)
	Sc	La	Pr	Ho	Sm	Zn	Al	Ca	Th	Fe^{3+}	Zr	Cu	Y		
1	9.9	15.2	13.8	13.2	16.1	–	–	22.4	7.2	–	–	–	2.2	2.22	0.01
2	8.5	18.4	16.3	10.8	15.3	20.7	–	–	–	–	–	6.2	3.8	3.77	0.03
3	12.3	21.3	–	8.9	16.4	25.3	–	–	2.5	10.2	–	–	3.1	3.13	0.02
4	6.3	12.1	10.2	6.5	9.1	19.1	4.1	25.4	3.3	–	2.1	–	1.8	1.82	0.02

MoO_4^{2-}, WO_4^{2-}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+} (14 mg); Ho^{3+}, Er^{3+}, Yb^{3+}, Sc^{3+}, Mn^{2+}, Co^{2+} (10 mg); Cu^{2+}, Ni^{2+}, Hg^{2+}, Th(IV), Zr(IV) (4 mg); Fe^{3+}, Ru^{3+}, Al^{3+}, Ti(IV) (3 mg). Fluoride, oxalate, and citrate decrease the reactivity of yttrium with *AMHA* and therefore must be absent. Suitable amounts of certain metal ions that react with *AMHA* may be masked by addition of a masking agent, *e.g.* Ni^{2+}, Hg^{2+}, Fe^{3+}, and Ru^{3+} (up to 8 mg) by adding pottasium cyanide (*ca.* 40 fold excess), 7.0 mg of Cu^{2+} by thiourea (35 fold excess), or 6.0 mg Zr(IV) and Th(IV) by tartaric acid. Interference caused by Al^{3+} and Ti(IV) (up to 5 mg) could be prevented by presence of sulfosalicyclic acid.

To evaluate the application of our procedure for the determination of Y(III), we have analyzed four synthetic samples prepared from analytical grade reagents and including cations that could be present in different mineral matrices with yttrium(III). Table 4 shows the composition of samples and the results obtained.

Experimental

Reagents

Analytical grade reagents, deionized water, and pure ethanol were used for the preparation of solutions. A stock solution of 2×10^{-3} *M AMHA* was prepared by dissolving the accurately weighted amount of the purified reagent in ethanol. Dilute solutions were obtained by appropriate dilution. A 5×10^{-3} *M* solution of yttrium nitrate was prepared by dissolving the required amount of the salt in bidistilled water. The metal content of the solution was determined as recommended [17]. Standard solutions of NaOH (0.1 *M*) and $HClO_4$ (0.1 *M*) were also prepared. Solutions of lower concentrations were obtained by accurate dilution. Solutions of diverse ions used for interference studies were prepared using the nitrates, acetates, or percholorates of metal ions and potassium or sodium salts of the anions to be tested. The acidity of the solutions investigated was adjusted by the addition of either dilute perchloric acid or sodium hydroxide. *Thiel* buffers (boric acid, succinic acid, and sodium sulfate) of *pH* 3–9 were for *pH* adjustment in the interference experiments.

Apparatus

The absorption spectra of the solutions were recorded on a Perkin-Elmer Lambda 3B spectrophotometer in the range of 400–700 nm using 1 cm matched stoppered silica cells. *pH* values were measured using a Radiometer *pH*-meter (Model M 63) equipped with a Radiometer combined-glass electrode (GK 2301 C). The *pH* meter was calibrated before use with standard buffer solutions. The *pH* values in 50% (v/v) ethanol were corrected as described by *Douheret* [18].

Standard Procedure

An aliquot of standard solution of Y(III) containing less than 220 µg of yttrium was introduced into a 25 ml calibrated flask. Then, 2 ml of 2×10^{-3} *M AMHA* solution in ethanol were added. The *pH* was adjusted to 6.2, 2.5 ml of 1 *M* $NaClO_4$ were added, and the solutions was diluted to volume with doubly distilled water while keeping concentration of ethanol at 50% (v/v). After thorough mixing, the absorbance was measured at 580 nm against a reagent blank similarly prepared but containing no yttrium.

References

[1] Broekaert J. A. C. (1981) Anal. Chim. Acta **124**: 421
[2] Tikhonov V. N., Fedotova S. N. (1982) Zh. Anal. Khim **37**: 1888
[3] Jarosz M., Marczenko Z. (1984) Anal. Chim. Acta **159**: 309
[4] Idriss K. A., Hassan M., Abu-Bakr M., Sedaira H. (1984) Analyst **109**: 1389
[5] Desal D. D., Shinde V. M. (1985) Anal. Chim. Acta **167**: 413
[6] Sen Gupta J. G. (1987) Talanta **34**(12): 1043
[7] Idriss K. A., Saleh M. S. (1993) Analyst **118**: 223
[8] Idriss K. A., Seleim M. M., Saleh M. S., Abu-Bakr M. S., Sedaira H. (1988) Analyst **113**: 1643
[9] Idriss, K. A., Saleh M. S., Seleim M. M., Hassan F. S., Idriss S. K. (1990) Monatsh. Chem. **121**: 625
[10] Kuban V., Havel J. (1973) Acta Chem. Scand. **27**: 528
[11] Sommer L., Kuban V., Havel J. (1970) Folia Fac. Sci. Nat Univ. Brno; 11, Chemie, Part 1
[12] Chiacchierini E., Gocchieri G., Sommer L. (1973) Collec. Czech Chem. Comm. **38**: 1478
[13] Sandell E. B. (1959) Colorimetric determination of traces of metals, 3rd edn. Interscience, New York, p. 97
[14] Tsurumi C., Furuga K., Kamada H. (1980) Anal. Lett. **13**(A4): 319–330
[15] Ramirez A. A., Linares C. J. (1986) Talanta **33**(12): 1021
[16] Hsu C. G., Lian X. M., Pan J. M. (1991) Talanta **38**(9): 1051
[17] Scott W., Furmay H. (1962) Standard methods of chemical analysis, 6th edn. Van Nostrand, New York
[18] Douheret G. (1967) Bull. Soc. Chim. Fr. **1412**

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