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SIMULTANEOUS DETERMINATION OF ALUMINUM (III) AND IRON (III) BY FIRST-DERIVATIVE SPECTROPHOTOMETRY IN ALLOYS

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A highly sensitive and selective first-derivative spectrophotometric method has been developed for the determination of aluminum and iron in mixtures. The method is based on the formation of the binary complexes of aluminum and iron with Alizarin yellow R (AYR) 5-[4-nitrophenylazo]salicylic acid at pH 2.0 with molar absorptivity of $1.1 \cdot 10^4$ *l·mol*$^{-1}$*·cm*$^{-1}$*. A zero-crossing technique is found suitable for the direct measurement of the first derivative value at the specified wavelength, so aluminum and iron were thus determined in the ranges 1.3–5.4 μg/ml and 1.1–8.3 μg/ml, respectively, in the presence of both components. The detection limits were found to be 1.4 ng/ml for aluminum and 2.8 ng/ml for iron. The relative standard deviations were in all cases less than 1.5%. The proposed method was successfully applied for the simultaneous determination of aluminum and iron in certified reference aluminum samples.*

Key words: *aluminum determination, iron determination, Alizarin yellow R, first-derivative spectrophotometry.*

Introduction. The chemistry of aluminum and iron is of great importance due to their presence in many alloys and steels, different drugs, plants, environmental waters, soils, and their biological activities in human body. Low amounts of aluminum can cause human acute toxicity. The role of iron is not invisible both in nearly all production sectors, with the metal industry in the first place, and in biological systems despite its presence at trace levels. High iron levels in drinking water in addition to its toxicity can result in poor taste and in staining of laundry, glassware, and dishes [1]. So, much attention is paid to the determination of both elements in different media by different ways at trace and sub-trace levels. Some of these ways are AAS methods and the volumetric determination [2], absorptive stripping voltametry (ASV), and graphite furnace atomic absorption spectrometry (GFAAS) [3]. The most acceptable ICP-MS analytical techniques and chromatography [4] have been reported for the determination of iron and aluminum. The spectrophotometric technique is always an acceptable analytical method due to its precision and accuracy and its lower cost compared with other techniques.

The simultaneous determination of multicomponents by the use of traditional UV-Vis spectrophotometric techniques is difficult without any separation process because of overlapping absorption spectra. Derivative techniques in the ultraviolet-visible region are very useful when overlap or interference exists; they offer a powerful tool for both qualitative and quantitative analysis of mixtures [5]. Derivative spectroscopy also permits one to resolve and determine binary mixtures of constituents [6–12]. Diverse computer programs have been applied to the analysis of multicomponent solutions using derivative spectra [13]. There were a lot of papers on the determination of different metals and components by derivative methods, which were collected by C. B. Ojeda [14]. Simultaneous determination of aluminum and iron in one shot in an easy way, with good static values and low interference from other metals, was not achieved in the previous work [4, 5, 15]. Hematoxylin was used for the simultaneous determination of aluminum and iron by first- and second-derivative spectrophotometry, but its calibration range is narrow, its detection limits are higher than in our method, and finally hematoxylin is an expensive reagent [16], so a rapid, sensitive, and inexpensive spectrophotometric determination of aluminum using AYR as a chromogenic reagent has been reported. A method for

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the simultaneous determination of aluminum and iron in mixtures by first-derivative spectrophotometry, using the zero-crossing technique, based on colored complexes that both aluminum and iron form with AYR, in 50% ethanol-water medium, has also been developed. The proposed method has been applied to the simultaneous determination of aluminum and iron in some certified reference aluminum samples.

Experimental. *Instruments.* Absorption measurements were made on a Shimadzu UV-21021 recording spectrophotometer using 10 mm matched quartz cells and a 2 nm wide slit. The pH-meter (HANNA HI 223) equipped with a radiometer combined glass electrode was used for pH measurements. The pH values in water-ethanol medium were corrected as described elsewhere [17]. Normal or derivative spectra of Al–AYR and Fe–AYR systems were measured against a reagent blank, similarly prepared but containing no metal ions.

Chemicals. All chemicals were of analytical reagent grade, and deionized water (or pure ethanol) was used to prepare solutions. A stock solution of $1 \cdot 10^{-3}$ mol/l AYR was prepared by dissolving an accurately weighed amount of the purified reagent in ethanol. A $1 \cdot 10^{-3}$ mol/l stock solution of aluminum(III) chloride was prepared by dissolving the required amount of analar product in deionized water. A $2 \cdot 10^{-3}$ mol/l stock solution of ferric(III) chloride was prepared by dissolving the required amount of analar product in deionized water. Al(III) and Fe(III) solutions were standardized compleximetrically with Oxine and EDTA (ethylenediaminetetraacetic acid) respectively [18]. The ionic strength of solutions was maintained at a constant value of I = 0.1 mol/l ($NaClO_4$). All measurements were made in 50% (v/v) ethanol-water medium at 25^{o}C.

Standard procedure. Into an aliquot containing 67.5 μg/25 ml of Al (III), 5 ml of $1 \cdot 10^{-3}$ mol/l solution of AYR, and 2.5 ml of 1 mol/l NaClO4 were added. After mixing with the appropriate amount of pure ethanol, the pH of the solution was adjusted to 2.0 with dilute $HClO_4$. The resulting solution was completed to 25 ml with deionized water while keeping a final 50% (v/v) ethanol content, and the absorbance was measured at 422 nm against a reagent blank similarly prepared but containing no Al(III).

Simultaneous determination of Al(III) and Fe(III). An aliquot of a sample solution containing up to 11.1 μg/ml of Fe(III) and up to 2.7 μg/ml of Al(III) was transferred into a 25 ml calibrated flask. Then 5 ml of AYR $1 \cdot 10^{-3}$ M was added. The pH was adjusted to 2.0 and diluted to volume while keeping a final 50% (v/v) ethanol content. The derivative spectrum was recorded in the range of 350–700 nm against a reagent blank. The absolute value of the first derivative was measured at 422 nm (zero crossing point of Al(III) complex) and 416 nm (zero crossing point of Fe(III) complex) to determine Al(III) and Fe(III) respectively.

Simultaneous determination of Al(III) and Fe(III) in different aluminum samples. A 0.1 g amount of the aluminum sample was accurately weighed and dissolved in 10 ml of aqua regia by heating, and the solution was evaporated to dryness. The residue was dissolved in 2 ml of 1:1 hydrochloric acid with heating, and the solution was diluted to 100 ml with deionized water. Suitable aliquots of the solution were taken for the simultaneous determination of aluminum and iron content by the recommended procedure.

Results and Discussion. *Acid-base properties of AYR.* In ethanol-water mixtures containing 50% (v/v) ethanol and at pH 1.4–12.5, AYR exists in four different forms (LH_3^+, LH_2, LH^-, and L^{2-}), exhibiting absorption maxima at 365, 380, 390, and 520 nm, respectively, as shown in Fig. 1. The mean pK_a values (equilibrium constants between ligand species) of the reagent are pK_{a1} (LH_2, LH^-) = 7.5 and pK_{a2} (LH^-, L^{2-}) = 10.5.

Complexation equilibria of aluminum with AYR. The complexation equilibria of Al^{3+} with AYR were studied in solutions containing 50% (v/v) ethanol in the pH range 1.3–8.2 (Fig. 2). The solution spectra were recorded in equimolar solutions and in solutions containing an excess of both the reagent and metal ions. The solution spectra reflect the formation of one complex species with λ_{max} = 422 nm and the existence of one chelate equilibrium in the pH range 1.3–2.5 (Fig. 3). The absorbance versus pH graphs at 422 nm for solutions of different component ratios show the range of the complex species formation and the existence of a single chelate equilibrium; above pH 2.5 the absorbance always shows an apparent decrease due to hydrolysis of the complex (Fig. 4).

The absorbance versus pH graphs for the Al–AYR system were interpreted using relations derived by Sommer et al. [19] and the generalized approaches described previously [20–22]. By considering the acid-base equilibria of AYR in 50% (v/v) ethanol–aqueous medium, we can assume that the monocationic form of the reagent is the prevalent ligand species in the pH range of complexation (Fig. 4). The direct and logarithmic analysis of the ascending parts of the absorbance–pH graphs gives the best fit for equilibrium (1) and the direct and logarithmic formation of [Al–AYR] complex species.

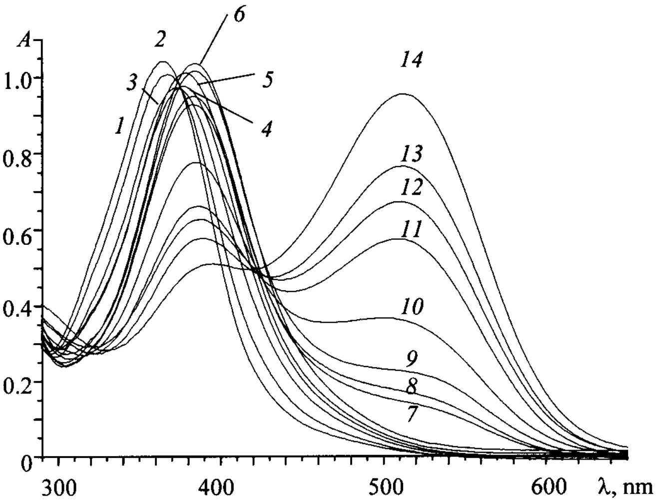

Fig. 1. Absorption spectra for 0.5·10^{-4} M of Alizarin yellow R at different pH values in the presence of 50à% ethanol, pH: 1.4 (1), 2.58 (2), 3.1 (3), 3.7 (4), 4.2 (5), 7.2 (6), 8.3 (7), 9.6 (8), 10.3 (9), 11.53 (10), 11.6 (11), 12.0 (12), 12.2 (13), 12.5 (14).

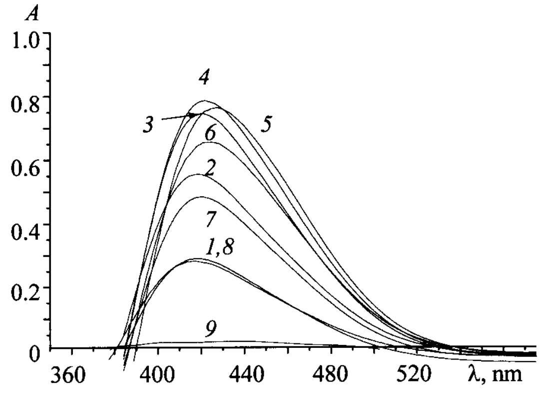

Fig. 2. Absorption spectrum of Al (III)–AYR, $C_{AYR} = C_{Al} = 1 \cdot 10^{-4}$ M, pH: 1.4 (1), 1.9 (2), 2.0 (3), 2.1 (4), 2.5 (5), 2.9 (6), 3.2 (7), 3.5 (8), 4.6 (9).

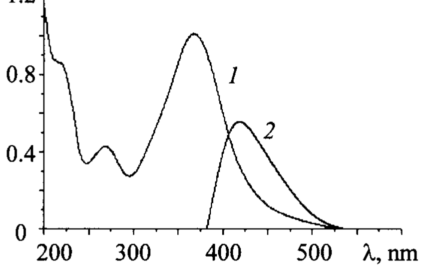

Fig. 3. Absorption spectra for 0.5·10^{-4} M of AYR (1) and for 1·10^{-3} M of AYR–Al(III) complex (2) at pH 2.

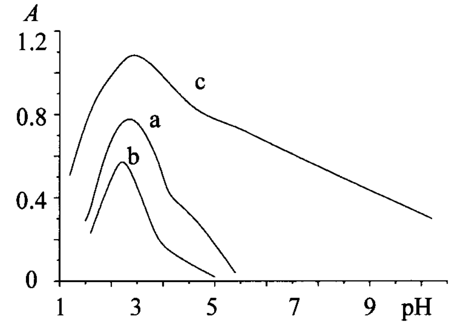

Fig. 4. Absorbance versus pH graphs for Al (III)–AYR system for various concentrations of components at λ = 420 nm: a) $C_{AYR} = C_{Al} = 1 \cdot 10^{-4}$ M; b) $C_{AYR} = 3 \cdot 10^{-4}$ M, $C_{Al} = 1 \cdot 10^{-4}$ M; c) $C_{AYR} = 3 \cdot 10^{-4}$ M, $C_{Al} = 1 \cdot 10^{-4}$ M.

TABLE 1. Mean Values of Equilibrium Constant (log K^*), Stability Constant (log β = log K^* + pK_2), and Molar Absorptivity (ε) of Al–AYR Complex Taken as Averages of Various Component Concentrations (I = 0.1 M $NaClO_4$, 25 ± 0.1°C)

Al^{3+} +LH_3^+ =[Al $LH_2]^{3+}$ +H^+		[Al $LH_2]^{3+}$ =$[Al]^{3+}$+[LH_2]
log K^*	ε, l·mole^{-1}·cm^{-1}	log β
(1.50 + 0.01)[a]		12.00 + 0.01
(1.34 + 0.02)[b]	$1.1 \cdot 10^4$	11.84 + 0.02
(1.45 + 0.01)[c]	λ_{max} = 422 nm	11.95 + 0.01

[a] Means for equimolar solutions.

[b] Means for excess ligand.

[c] Means for excess metal.

$$Al^{3+} + LH_3^+ = [Al\,LH_2]^{3+} + H^+ \tag{1}$$

The equations used for graphical and logarithmic transformations were given in a previous report [23]. The calculated values of the apparent equilibrium and stability constants of the Al–AYR system at pH 2.0 are $3.7 \cdot 10^{-2}$ and $8.5 \cdot 10^{11}$ respectively. The stoichiometry of the Al–AYR complex was further verified by the method of continuous variation [24] in solutions with $C_0 = C_M + C_L = 2 \cdot 10^{-4}$ mol/l at pH 2.0, and a component ratio of 1:1 (metal to ligand) was obtained. The stoichiometric ratio of the complex in solution was also determined by applying the molar ratio method [25].

Equilibrium and stability constants. The equilibrium constant K_{eq} was determined by considering the equilibrium (1). The stability constant (β) of aluminum–AYR complex is related to the equilibrium constant (K_{eq}) by the expression $\beta = K_{eq} K_{Al}^{-2}$. The calculated values of the apparent equilibrium constant (log K^*), stability constant (log β), and molar absorptivity of Al–AYR complex at pH 2.0 are given in Table 1.

Calibration graph and reproducibility. under the optimum conditions a linear calibration graph for the al–ayr complex was obtained up to the Al(III) concentration of 3.0 μg/ml with a molar absorptivity of $1.1 \cdot 10^4$ l·mol^{-1}·cm^{-1} at 422 nm. A Ringbom plot showed that the optimum concentration range for the determination of Al(III) was 1.0–2.0 μg/ml. Sandell's sensitivity [26] of the reaction was found to be $2.45 \cdot 10^{-3}$ μg/cm^2. The reproducibility of the method was checked by analyzing a series of five solutions with the Al(III) concentration of 2.3 μg/ml. The relative standard deviations are 0.789% and 1.37% for 1.5 and 2.5 μg/ml of Al(III) respectively.

Effect of diverse ions. In order to assess the usefulness of the proposed method, the effects of diverse ions that are often associated with Al(III) were studied. The tolerance of the method to foreign ions was investigated with solutions containing 55 μg of Al(III) per 25 ml and various amounts of foreign ions. Al(III) was determined as Al–AYR

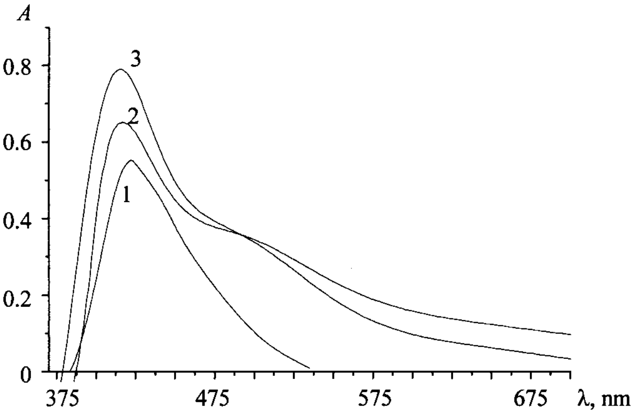

Fig. 5. Absorption spectra of Al(III)–AYR complex (1), Fe(III)–AYR (2), and mixture of Al(III)– and Fe(III)–AYR complexes (3); pH 2.0, 50% (v/v) ethanol.

under the optimum conditions as described in the experimental. The interference limit of an ion was attributed to the proportion in which a change of ±2% in absorbance from the expected value for aluminum occurred. The determination of aluminum as the Al–AYR was possible in the presence of Li^+, Na^+, K^+, NH_4^+, Mg^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, SO_4^{2-}, SO_3^{2-}, NO_3^-, Cl^-, Br^-, I^-, CN^-, and PO_4^{3-} (≈100-fold excess). The investigated Fe^{3+} ions interfered seriously even when present in very small amounts.

Reaction of Fe(III) with AYR. An aqueous Fe(III) solution reacts with an ethanolic solution of AYR at pH 2.0 to form a yellow-green complex species. The absorption spectrum shows an absorption maximum at 416 nm. The solution spectra reflected the formation of one complex species and the existence of one chelate equilibrium in the pH range of 1.0–2.8. However, the maximum absorption of the AYR reagent was at 365 nm within the pH range 1.0–2.8. The composition of the Fe (III) complex is determined by the continuous variation [13] and molar ratio [14] methods; only a 1:1 (M:L) complex was formed at pH 2.0 that obeyed Beer's law up to 0.55 μg/ml ($\varepsilon = 0.5 \cdot 10^4$ $l \cdot mol^{-1} \cdot cm^{-1}$).

Simultaneous Determination of Aluminum and Iron in Mixtures. *Spectral characteristics.* The absorption spectra of Al–AYR and Fe(III) complexes are shown in Fig. 5. The total absorption of aluminum and iron is presented by curve 3. Because of the large overlap of the spectra of the two complexes, the determination of aluminum and iron in their mixture by normal spectrophotometry is frequently difficult; this disadvantage has been overcome by using derivative spectrophotometry.

The first derivative spectra gave results of high accuracy and low detection limits. Figure 6 shows the first derivative spectra of Al–AYR, Fe(III)–AYR, and the mixture of the complexes. It is clear that the first derivative spectra of both complexes are not sufficiently resolved; therefore the zero-crossing approach was used to determine both analytes. The zero-crossing wavelengths of aluminum and iron in the first derivative spectra are obtained at 422 and 416 nm, respectively (Fig. 7). Figure 8 shows a series of first derivative spectra of a mixture of aluminum (III)– and iron (III)–AYR complexes. A series of first derivative spectra of a mixture of 1.1 μg/ml iron(III) and increasing amounts of aluminum(III) (0.538–5.400 μg/ml) is given in Fig. 8b. Figure 8a shows a series of 2.7 μg/ml of aluminum plus increasing concentrations of iron (1.11–11.1 μg/ml). The heights h_1 and h_2 in the first derivative spectrum of the mixtures corresponding to values taken at 416 nm (zero-crossing wavelength of iron complex) and 422 nm (zero-crossing wavelength of aluminum complex) are proportional to aluminum(III) and iron(III) concentrations, respectively.

Calibration graphs and statistical analysis of the results. The calibration graphs by the recommended procedure are linear over the ranges 1.3–5.4 μg/ml of aluminum in the presence of 11.1 μg/ml iron and 1.1–8.3 μg/ml of iron in the presence of 2.7 μg/ml aluminum. The calibration graphs were prepared by plotting the first-derivative values (h) versus aluminum or iron concentration. All of them give good linearity with negligible intercepts, confirming the mutual independence of the derivative signals of the two complexes (Fig. 9). In Table 2 the statistical parameters for calibration graphs are given. In order to test the accuracy and precision of the method, five successive measurements were carried out with the standard solution containing 2.7 μg/ml of aluminum(III) and 4.0 μg/ml of iron(III).

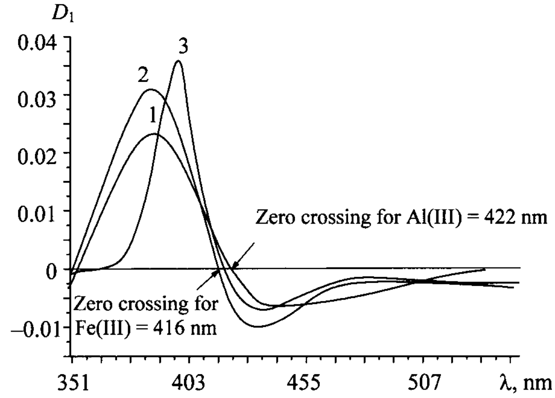

Fig. 6. First-derivative spectra of Al–AYR complex (1), Fe–AYR complex (2), and mixture of Al– and Fe–AYR complexes (3).

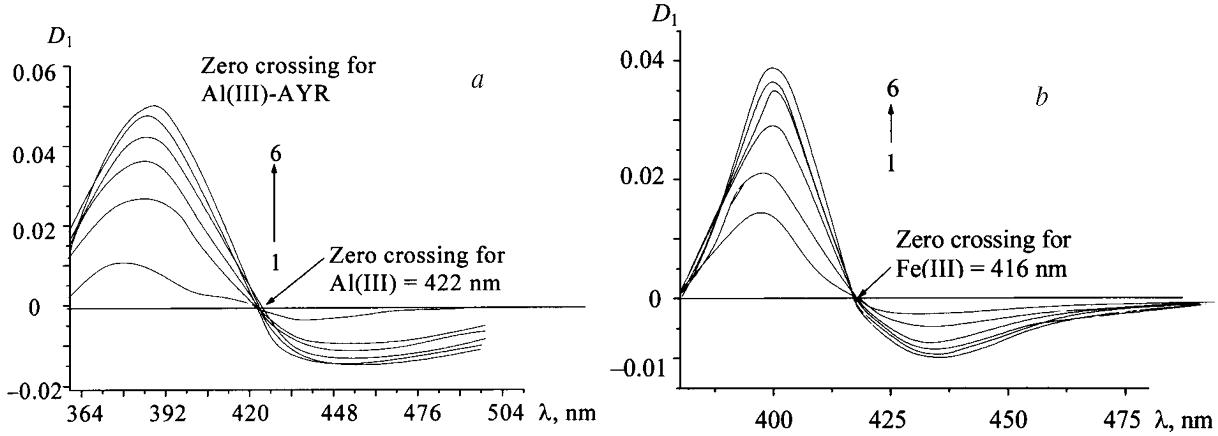

Fig. 7. First-order derivative for Al(III)–AYR (a) and Fe(III)–AYR (b) complexes; [Al(III)] = 0.539 (1), 1.300 (2), 2.160 (3), 2.700 (4), 4.000 (5), and 5.400 g/ml (6), [Fe(III)] = 1.116 (1), 2.790 (2), 4.460 (3), 5.580 (4), 8.370 (5), and 11.100 μg/ml (6); $C_{\mathrm{AYR}} = 2 \cdot 10^{-3}$ mol/l, 50% ethanol, pH = 2.0.

The relative standard deviations were 0.93 and 0.95 for aluminum and iron, respectively. The detection limits were 0.00144 μg/ml and 0.0028 μg/ml for aluminum and iron respectively. The minimum permissible levels of Fe and Al in drinking water are 0.3 μg/ml and 0.0036–0.0060 μg/ml, respectively, so our method can be used to detect the iron and aluminum amounts in water [27].

Effects of diverse ions. The effect of the presence of diverse ions on the simultaneous determination of aluminum and iron using AYR was studied under optimum conditions. Absorbance measurements in the first derivative mode proved useful in overcoming interferences in a number of cases where the use of masking agents could not help. The tolerance of the method to foreign ions was investigated with solutions containing 0.07 mg of Al and 0.1 mg of Fe in 25 ml and various amounts of foreign ions. The simultaneous determination of Al(III) and Fe(III) was possible in the presence of Li^+, Na^+, K^+, NH_4^+, Ba^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, SO_4^{2-}, SO_3^{2-}, NO_3^-, Cl^-, Br^-, I^-, and CN^- (≈100-fold excess), $B_4O_7^{2-}$ (≈50-fold excess), Ca^{2+}, Mg^{2+}, and Sr^{2+} (≈50-fold excess). EDTA and HPO_4^{2-} interfered seriously even when present in very small amounts.

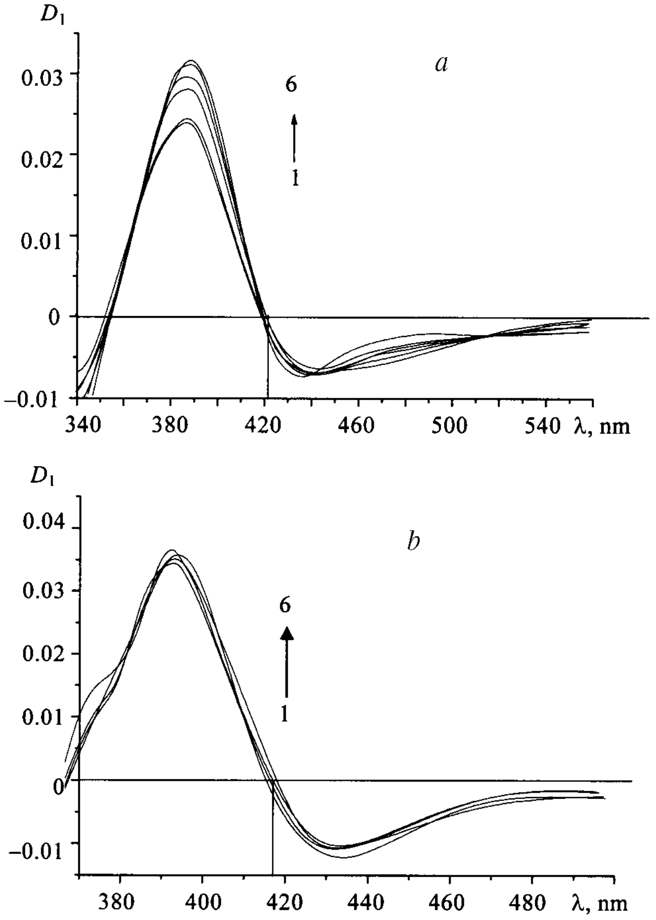

Fig. 8. First-order derivative spectra of mixture of Al(III)–AYR complex (a) and increasing concentrations of Fe(III)–AYR complex ([Al(III)] = 2.700 μg/ml, [Fe(III)] = 1.116 (1), 2.790 (2), 4.460 (3), 5.580 (4), 8.370 (5), and 11.100 μg/ml (6)), and spectra of mixture of Fe(III)–AYR complex (b) and increasing concentrations of Al(III)–AYR complex ([Fe(III) = 11.100 μg/ml, [Al(III)] = 0.539 (1), 1.300 (2), 2.160 (3), 2.700 (4), 4.000 (5), and 5.400 μg/ml (6)).

TABLE 2. Statistical Analysis of the Determination of Aluminum(III) and Iron(III) in Mixtures with AYR Using First-Derivative Spectrophotometry

Metal ion	λ_{max}, nm	Regression equation[b]	Correlation coefficient (τ)
Al(III)	416[a]	$D_1 = -0.00124 + 0.694 \cdot 10^{-4}\ C_{Al}$	0.998
Fe(III)	422[a]	$D_1 = 1.21 \cdot 10^{-4} + 0.153 \cdot 10^{-4}\ C_{Fe}$	0.993

[a] Recommended procedures.

[b] D_1 — derivative value; C — concentration, μg/ml.

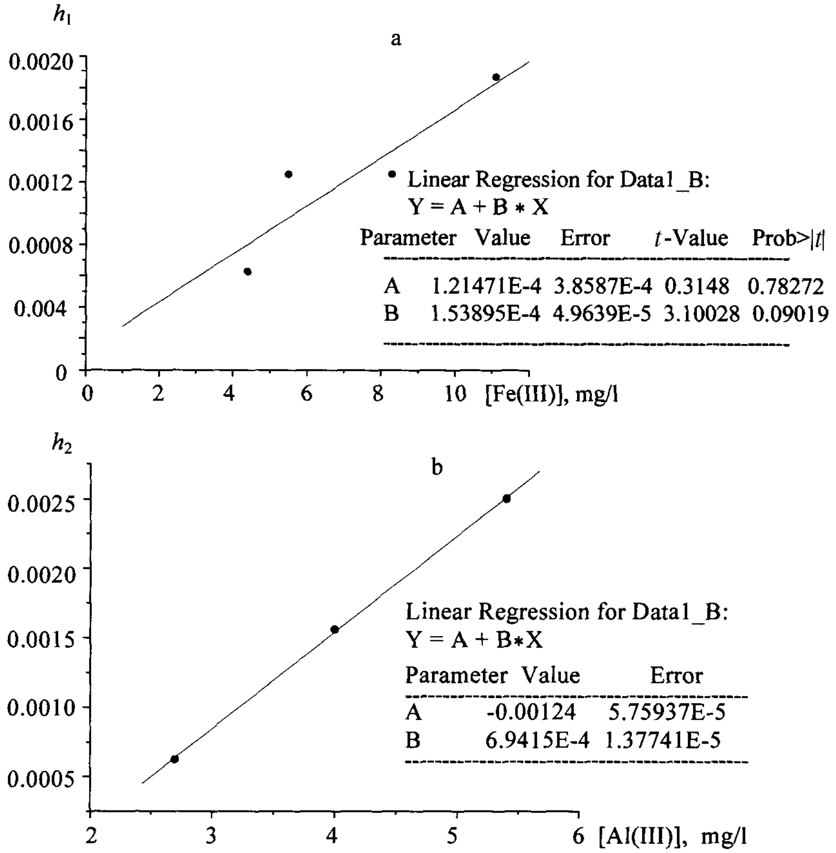

Fig. 9. Calibration curves for the determination of Al(III) and Fe(III) in solutions; values of h_1 (a) and h_2 (b) against concentrations of iron and aluminum, respectively.

TABLE 3. Simultaneous Determination of Aluminum and Iron in Diverse Aluminum Alloys Using First-Derivative Spectrophotometry

Sample no.	Certified value, %		Found, %		RSD%(n=5)		AAS for Fe (mg/l)	Recovery, %	
	Al(III)	Fe(III)	Al(III)	Fe(III)	Al(III)	Fe(III)		Al(III)	Fe(III)
1	99.83	0.09	99.85	0.09	0.80%	1.10%	0.09	100.02	100
2	99.9	0.08	99.85	0.075	0.92%	1.05%	0.07	99.95	98.21
Average (12)	99.79	0.075	99.8	0.074	0.95%	1.03%	0.074	99.99	99.39

Applications. To confirm the usefulness of the proposed method, aluminum and iron have been determined simultaneously in 12 aluminum samples and two aluminum alloys. The aluminum samples have nearly similar composition so we include only two of them in Table 3 with the average results for the 12 to show how our method succeeded in determining the very low concentration of iron in them. The results obtained (see Tables 3 and 4) are in good agreement with the certified values for aluminum samples and aluminum alloys, the RSD value being in the range of 1.0–1.2 % for iron(III) and 0.98–1.20 % for aluminum(III) in all different types of aluminum alloys.

TABLE 4. Simultaneous Determination of Aluminum and Iron in Diverse Alloys* Using First-Derivative Spectroscopy

Aluminum alloy and its composition	Certified value		Amount found by AAS, %	Amount found by proposed method		R.S.D, %		Recovery, %	
	Al(III)	Fe(III)	Fe(III)	Al(III)	Fe(III)	Al(III)	Fe(III)	Al(III)	Fe(III)
Cu 60.8; Sn 0.21; Zn 30.0; Al 3.34; Pb 0.023; Ni 0.16; Mn 1.36;Fe 1.56	3.34	1.56	1.55	3.34	1.55	0.95	1.1	100	99.3
Cu 40, Mn 1.7, Ni 2.12, Fe 0.031 and rest Al	56.1	0.031	0.031	56	0.03	0.98	1.2	99.8	96.7

*Aluminum samples and alloys were provided by Egypt Aluminum Company, Nag Hammady, Egypt.

Conclusion. As a result of the study, a new UV-vis spectrophotometric method was developed for the determination of iron(III) and aluminum(III) with acceptable static values in one shot with no interference from many ions like Li^+, Na^+, K^+, NH_4^+, Ba^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, SO_4^{2-}, SO_3^{2-}, NO_3^-, Cl^-, Br^-, I^-, CN^-, $B_4O_7^{2-}$, Ca^{2+}, Mg^{2+}, and Sr^{2+} in different aluminum samples and aluminum alloys; also our method can be tried to detect the two metals in drinking water. So we can conclude that spectrophotometric techniques continue to be widely popular in view of their rapidity, simplicity, precision, accuracy, and common availability of the instrumentation. The color reaction of aluminum and iron with AYR under the present experimental conditions provides a simpler, easier, and more rapid determination than other techniques. The present method has good reproducibility and excellent stability. It has high sensitivity and good selectivity when applied to the determination of nanograms of aluminum and iron in aluminum samples and aluminum alloys.

REFERENCES

1. M. A. Stoyanova, *Anal. Sci.*, **24**, 595–600 (2008).
2. P. C. Nascimento, C. L. Jost, M. V. Guterres, L. D. Del'Fabro, L. M. de Carvalho, and D. Bohrer, *Talanta*, **70**, 540–545 (2006).
3. H. B. Singh, N. K. Agnihotri, V. K. Singh, *Talanta*, **48**, 623–631 (1999).
4. C. A. I. Longfei and X. U. Chunxiu, *Anal. Sci.*, **24**, 775 (2008).
5. N. Aguerssif, *J. Trace Elem. Med. Biol.*, **22**, 175–182 (2008).
6. M. I Toral, B. Richter, *Anal. Lett.*, **28**, 1083 (1995).
7. F. Garcia, Hernandez, J. C. Marquez, *Anal. Chim. Acta*, **197**, 275 (1987).
8. B. Morelli, *Analyst*, **108**, 1506 (1983).
9. B. Morelli, *Anal. Chim. Acta*, **209**, 175 (1988).
10. M. I. Toral, P. Richter, *Talanta*, **40**, 1405 (1991).
11. P. Levillain, D. Fonpeydie, *Analysis*, **14**, 1 (1986).
12. A. I. Jimenez, F. Jimenez, and J. J. Arias, *Analyst*, **114**, 93 (1989).
13. F. Delaye, M. D. Gaye, and J. J. Aaron, *Anal. Chim. Acta*, **223**, 395 (1989).
14. C. B. Ojeda, *Talanta*, **42**, 1195–1214 (1995).
15. A. Safavi, H. Abdollahi, R. Mirzajani, *Spectrochim. Acta, A*, **63**, 196–199 (2006).
16. A. Youssef El-Sayed, *Fresenius J. Anal. Chem.*, **355**, 29–33 (1996).
17. G. Dougheret, *Bull. Soc. Chim. Fr.* (1967) p. 1412.
18. A. I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd ed., Longman, London (1973).
19. L. Sommer, P. Voznica, and J. Havel, *Folia Fac. Sc. Univ. Brno*, **11**, No. 1, 33 (1970).

20. K. A. Idriss, E. Y. Hashem, M. S. Abdel Aziz, and H. Ahmed, *Analyst*, **125**, 221–225 (2000).
21. E. Y. Hashem, H. Sedaira, K. A. Idriss, and S. A. Soliman, *Indian J. Chem.*, **39A**, 889–895 (2000).
22. E. Y. Hashem, M. S. A. Bakr, *Anal. Lett.*, **33**, No. 4 691–707 (2000) .
23. E.Y. Hashem, *J. AOAC Int.*, **84**, No. 2, 537–545 (2001).
24. P. Job, *Ann. Chem.*, **9**, 113 (1928).
25. J. H. Yoe, H. L. Jones, *Indian Eng. Chem., Anal. Ed.*, **16**, 111 (1944).
26. E. P. Sandell, *Colorimetric Determination of Trace Metals*, Vol. 3, Wiley, New York (1959) p. 97.
27. A. Maleki, B. Roshani, and F. Karakani, *J. Appl. Sci. Res.*, **1**, No. 1, 103–108 (2005).