

Fluorometric Determination of Aluminum with Morin and Sodium Dodecyl Sulphonate (SDS)

Y. Z. Hussein, S. H. Etaiw* and A. A. Abuel Ela

Chemistry Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo, Egypt.

* Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt.

Summary: Fluorometric determination of aluminum was carried out based on the formation of fluorescent complexes between aluminum and morin in absence and presence of anionic surfactant SDS at pH 3.5. The formed complexes exhibit fluorescence with maximum emission at 495 nm when excited at 421 nm and 425 nm in both aqueous and micellar medium, respectively. The linear range of both two complexes were followed up to 1.9 and 2.2 ng/ml, respectively and the detection limit was 0.01 ppb of aluminum. The stoichiometry of aluminum complexes in the systems Al: morin and Al: morin : SDS were 1:2 and 1:2:1, respectively. The proposed method was applied to the determination of trace aluminum in water and alloys.

Introduction

The need of methods for the determination of metal ions at the ng ml^{-1} level was increased in both industrial and environmental analysis. Few reagents was encountered for the fluorometric determination of aluminum compared to spectrophotometric reagents, but it has clear advantage in terms of sensitivity and selectivity in most cases. Salicylaldehyde derivatives were considered the most common reagents which give fluorescence with aluminum through fluorometric determination⁽¹⁻⁷⁾. The sensitization of CTAB of the fluorometric reaction of

aluminum with 8-hydroxyquinoline-5-sulfonic acid⁽⁸⁾ and ferron⁽⁹⁾ were enhanced the fluorescence intensity many times. On the other hand, a fluorescence measurement of aluminum -lumogallion in the absence and presence of nonionic surfactant Triton X-100 was determined⁽¹⁰⁻¹¹⁾.

In the work reported here, several surfactants and protective colloids were examined for their effect on the fluorescence of the aluminum with morin complex. The solvation effect on the sensitivity of the developed method was also studied .

Experimental

Apparatus

A Perkin-Elmer luminescence spectrometer model LS 50B with transparent cell of 1-cm path length was used for luminescence measurements.

The pH was measured using ion analyzer model Crison Digit-501 pH meter equipped with a combination glass-calomel electrode.

Ion exchange column, a portion of 10 ml graduated glass tubing was used. A glass stopcock was placed at the end of the glass tube. A small plug of glass wool was placed in the bottom of the test tube to prevent the exchange resin from moving through the tubing.

Reagents

All chemicals used were of analytical reagent grade. Aqueous solutions were prepared with bi-distilled water. Standard aluminum stock solution of $5 \times 10^{-3} \text{M}$, was prepared by dissolving 2.371 g of aluminum potassium sulphate ($\text{AlK}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$) in water containing 10 ml of concentrated hydrochloric acid and the solution was diluted to 1.0 liter. Morin (2',3,4,5,7-pentahydroxy flavone) solution of $1 \times 10^{-2} \text{M}$, was prepared by dissolving 0.7556 g of morin in ethanol and diluted to 250 ml. Sodium dodecyl sulphonate (SDS) solution of 0.1 M, was prepared by dissolving 2.884 g of SDS in hot water and diluting to 250 ml. Acetate buffer solution of pH 3.5, was prepared by adjusting the pH of 0.2 M acetic acid solution with 0.2 M sodium acetate solution to the desired pH value. The surfactants and protective colloids were prepared as $1 \times 10^{-2} \text{M}$ for cationic surfactant, 1% for nonionic surfactant and 0.1% for protective colloid. Ion exchange resin, Dowex chloride-form anion exchange resin of 50-100 mesh with 10% divinyl benzene (DVB).

Procedures

1) Determination of Aluminum with Morin and SDS in Water

A water sample containing not more than 19 ng of aluminum (III) was transferred into a 25 ml volumetric flask. Add 0.5 ml of morin reagent of $1 \times 10^{-2} \text{M}$ maintaining ethanol content of 5% v/v followed by 1.0 ml of SDS of 0.1 M and

completed to the mark with acetate buffer solution of pH 3.5. Measure the fluorescence intensity immediately at 495 nm.

2) Determination of Aluminum with Morin and SDS in Alloys

Decompose about 0.2 g of dry alloy sample by heating gently with hydrochloric or perchloric acid. Evaporate to dryness and dilute with 9 M hydrochloric acid. If chromium is present in an amount greater than aluminum, add concentrated hydrochloric acid and evaporate the fumes again to volatilize chromyl chloride until no more red fumes⁽¹²⁾. Pipette an aliquot of the sample to Dowex 1 resin. Allow to drain completely, allow 15 ml of 9 M hydrochloric acid to pass through the column. Evaporate the effluent to dryness, then cool it to room temperature and dilute to a suitable volume with water in a volumetric flask. The above steps for the determination of aluminum with morin and SDS in water was applied to determine aluminum content in alloys.

Results and Discussion

Fluorescence Spectra

The excitation and emission spectra of the fluorescent system aluminum-morin at optimum experimental conditions were found to occur at 421 and 495 nm, respectively as shown in Fig.1 (curves 1 and 2). Whereas, in the presence of anionic surfactant SDS, the wavelength maxima of excitation and emission were 425 and 495 nm, respectively (curves 3 and 4). The addition of SDS was enhanced the fluorescence intensity of aluminum-morin complex.

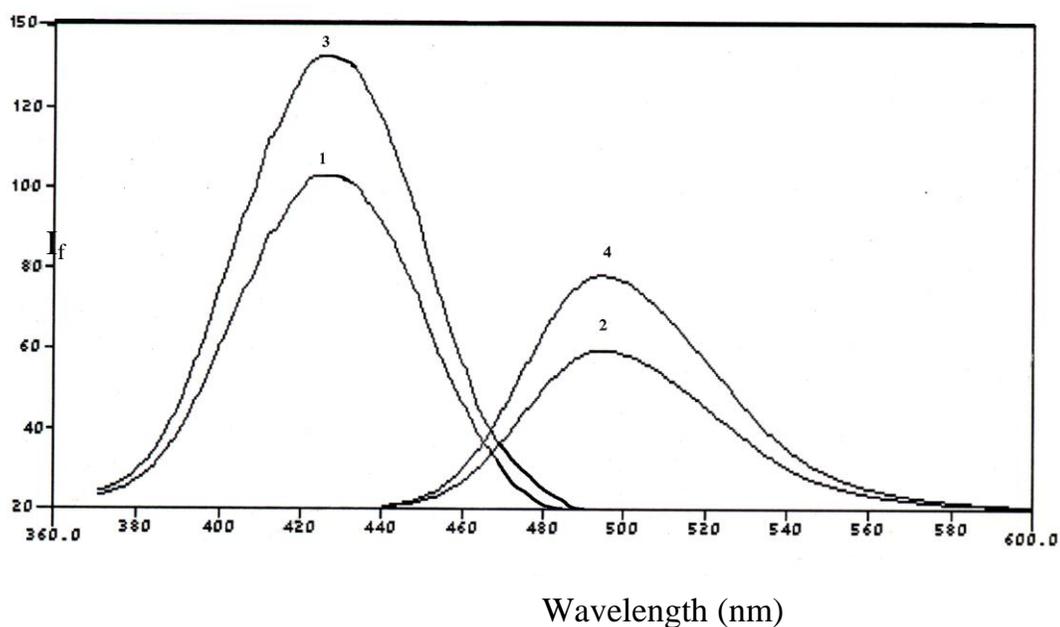


Fig. (1): Fluorescence spectra of aluminum-morin complex in the absence and presence of SDS; curves 1 and 3, excitation spectra in absence and presence of SDS; curves 2 and 4, emission spectra in the absence and presence of SDS; scale x 10 for curves 1 and 2.

Effect of pH

The effect of pH on the fluorescence of aluminum-morin-SDS system was carried out in the pH range 2.6-5.4. The maximum fluorescence intensity was observed when the pH maintained between 3.2 and 4.0 by the addition of acetate buffer solution. Therefore, pH 3.5 was selected for aluminum determination

using acetate buffer solution.

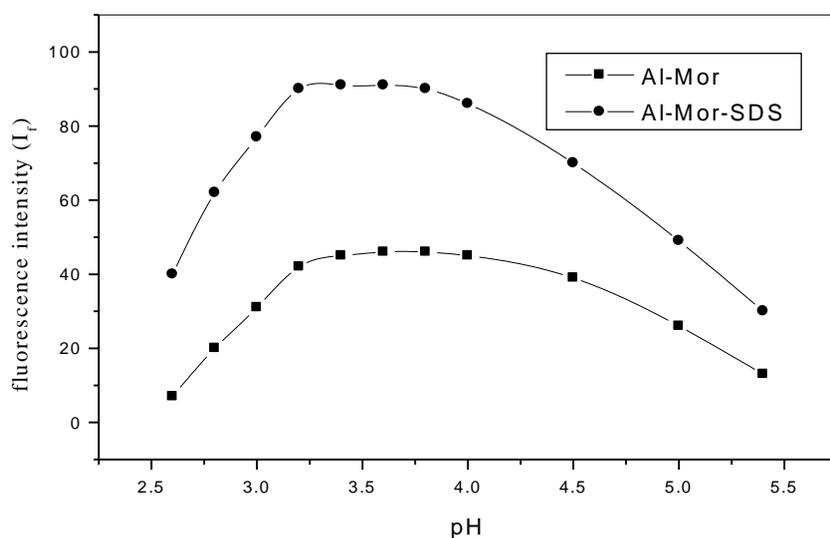


Fig. (2): Effect of pH on the fluorescence intensity of Al-morin complexes

Effect of Surfactants and Protective Colloids

In an attempt to enhance the fluorescence of the binary aluminum-morin complex, some surfactants and protective colloids were investigated. The utilized surfactants were CTAB, CPB, CPC, Zephiramine, Triton X-100, Emulsifier S, Tween 20, Tween 40, Tween 60, Tween 80, SLS, SDBS and SAS; as well as PVA, PVP, Gelatin and Arabic Gum as protective colloids.

The cationic surfactant Zephiramine and most of the nonionic surfactants Tween 20, Tween 40, Tween 60 and Tween 80 exerted precipitation. However, the protective colloids PVA, PVP, Gelatin and Arabic gum caused slight

sensitization of the colour reaction, whereas the anionic surfactants SLS, SDS and SDBS exerted a significant sensitization. Maximum enhancement of the complex fluorescence was obtained in an micellar solution of SDS and was used in the procedure.

Effect of Ethanol

Ethanol has an important influence on the morin fluorescence⁽¹²⁾. The influence of the ethanol content on the binary and ternary aluminum complexes over the range 1-40% v/v is shown in Fig. 3. The binary complex was exhibited maximum fluorescence intensity in the range 1-25% v/v whereas, the ternary complex in the range 2-20% v/v. Hence, the suitable ethanol content for that study was 5% v/v.

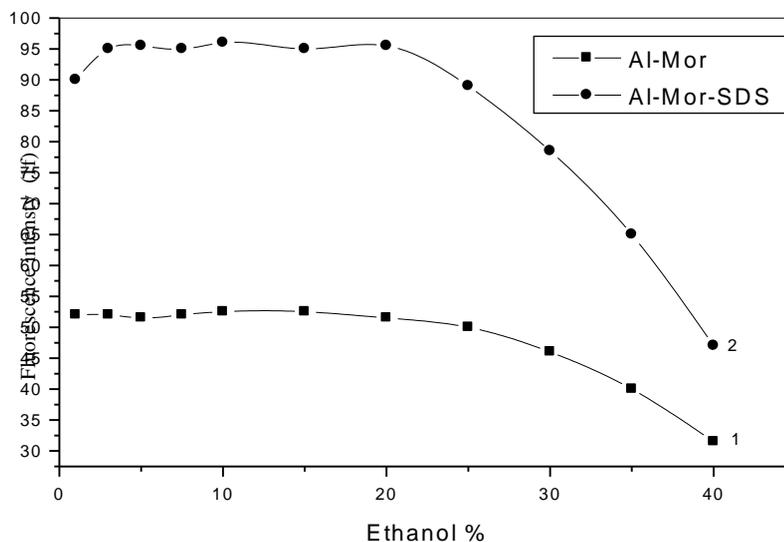


Fig.(3): Effect of ethanol concentration on the fluorescence intensity of Al-morin complexes

Effect of Morin Concentration

The effect of morin concentration on the fluorescence intensity of aluminum in absence and presence of SDS were carried out at the optimum pH value, using reagent concentration varied between 2×10^{-5} M and 1×10^{-3} M. The yellow fluorescent of the ethanolic solution of morin was intensified and remained constant over the range 1.6×10^{-5} M and 1×10^{-3} M.

Effect of SDS Concentration

The dependence of fluorescence intensity of the sensitized complex on SDS concentration was examined using SDS concentration ranged between 4×10^{-4} M

and 2×10^{-2} M throughout the study. Sensitization of the binary aluminum-morin complex required $\geq 2.4 \times 10^{-3}$ M of SDS.

Effect of Time

The effect of time on the fluorescence intensity of Al-morin and Al-morin-SDS complexes were investigated using the above optimum experimental conditions. The fluorescence intensity reached a maximum immediately after mixing to the final volume and remained stable up to 5 and 15 minutes, for both aqueous and sensitized complexes, respectively after which the fluorescent intensity of the two complexes started to decrease gradually. Consequently, no standing time required in the recommended procedure for the determination of Al-morin complexes.

Calibration Graphs and Limits of Detection

The calibration graphs of Al-morin and Al-morin-SDS complexes passing through the origin were linear over the most ranges of aluminum concentrations up to 1.9 and 2.2 ng/ml, respectively as shown in Fig. 4. The detection limit was 0.01 ng/ml of aluminum for both two complexes. The standard deviation calculated for 12 determinations of a solution containing 1.5 ng/ml of aluminum were 6.56 and 9.80, respectively and their coefficients of variation were 0.69% and 0.41%, respectively.

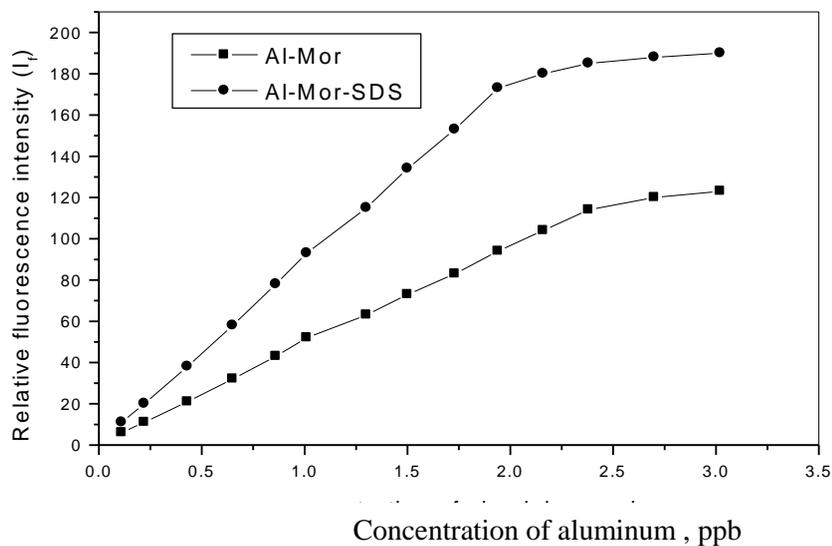


Fig.(4): Fluorescence calibration graphs for Al-morin complexes

Composition of the Fluorescent Complex

Job's method of continuous variation and the molar-ratio method were applied to ascertain the stoichiometric composition of the fluorescent complex under the experimental conditions for maximum emission. Both methods showed that the compositions were 1:2 and 1:2:1 for Al-morin and Al-morin-SDS complexes, respectively.

Interference Study

The influence of various ions on the fluorescence intensity of the Al-morin-SDS complex were examined. The tested ions and tolerance levels found were illustrated in

Table 1. The tolerance level was taken as the amount that cause change $\pm 3\%$ unit in the fluorescence intensity. The study was carried out to investigate the selectivity of the proposed method by adding 1.5 ng/ml of aluminum with variable amounts of a foreign ions, and the procedure for aluminum was followed. Complexing agents such as oxalate and EDTA were interfered.

Table 1: Influence of foreign ions on the determination of aluminum with morin and SDS.

Foreign ions	Tolerance level (ng/ml)
Cl ⁻ , F ⁻ , HCO ₃ ⁻ , HPO ₄ ²⁻ , NO ₂ ⁻ , NO ₃ ⁻ , SiO ₃ ²⁻ , SCN ⁻ , SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , thiourea, Na ⁺ , K ⁺ , Ag ⁺ , Ba ²⁺ and NH ₄ ⁺ .	> 10000
Br ⁻ , formate, perchlorate, ethanolamine, diethanolamine, triethanolamine, Cd ²⁺ , Ni ²⁺ , Sr ³⁺ , Cr ³⁺ and Cr(VI).	> 1000
succinate, B ³ , Ca ²⁺ , Co ²⁺ , Fe ²⁺ , Fe ³⁺ , Mg ²⁺ , Pb ²⁺ , Zn ²⁺ , Sn ²⁺ and Sn ⁴ .	> 500
Be ²⁺ , Bi ³⁺ , Cu ²⁺ , Hg ²⁺ , Mo(VI), Ti(IV), U(VI), V(V), W(VI), Zr(IV), acetylacetone, malonate and	> 100

tartrate.	
-----------	--

Application of the Method

The recommended procedure has been used for the determination of aluminum in water. Most of the water samples were obtained from River Nile and water plant in Shoubra El-Kheima power station and West Cairo power station.

A fixed volume of each water sample containing ≥ 2.2 ng/ml of aluminum has been transferred into 25 ml volumetric flask, and the procedure for aluminum determination was followed. The results obtained were illustrated in Table 2, and in good agreement with the spectrophotometric method utilizing Eriochrome Cyanin R reagent⁽¹³⁾.

On the other hand, at the concentration levels encountered in steel alloys, aluminum cannot be determined directly in presence of large number of interfering metal ions in the analyzed alloy. However, an ion exchange column has been used to separate the undesired metal ions with good efficiency. The developed method has been successfully used to determine aluminum in steel alloys in the concentration range 0.002-0.02% and the results obtained were in good accordance with the certified values given in Table 3.

Table 2: Determination of aluminum in water samples using morin and SDS

Sample	Source	Aluminum (ng/25 ml)			
		*This method	S.D.	**ECR method	S.D.
Raw water in clarifier A	Water plant in Shoubra El-Kheima power station	12.5	0.005	12.2	0.01
Raw water in clarifier B	Water plant in Shoubra El-Kheima power station	10.8	0.007	10.5	0.008
Filtered water in clear water sump	Water plant in Shoubra El-Kheima power station	3.0	0.002	2.8	0.005
Wastewater in clarifier A	Water plant in Shoubra El-Kheima power station	11.2	0.009	11.0	0.012

Wastewater in clarifier B	Water plant in Shoubra Kheima El-power station	13.8	0.013	14.0	0.015
Wastewater in retentation basin	Water plant in Shoubra Kheima El-power station	10.2	0.008	10.5	0.009
River Nile	Water plant in Shoubra Kheima El-power station	2.5	0.004	2.7	0.006
Drinking water unit	Water plant in Shoubra Kheima El-power station	1.1	0.003	1.2	0.007
Raw water	Water plant in west Cairo Power station	9.5	0.007	9.4	0.005
Wastewater	Water plant in west Cairo Power station	6.9	0.011	7.2	0.008

* Mean of five readings

** Standard method using spectrophotometric method

Table 3: Determination of aluminum in alloys using morin and SDS

Sample No.	Aluminum , %		Diff., %
	Present	Found	
Ni-Mo steel 111B	0.043	0.044	+0.001

		0.042	-0.001
		0.042	-0.001
		0.045	+0.002
Mn-Al bronze 164	6.21	6.10	-0.11
		6.19	-0.02
		6.20	+0.08
		6.30	+0.09

References

1. M. Gallego; M. Valcarcel; M. Garcia-Vargas, *Analyst*, 108, 92-8 (1983).
2. De Pablos, Fernando; Gomez Ariza, Jose Luis; Pino, Francisco., *Analyst*, 111, (10), 1159-162 (1986).
3. M. Genteno, Gallego; M. Callejon Mochon; M. Ternero Rodriguez; A. Guiraum Perez , *Mikrochim. Acta*, 109 (5-6), 301-9 (1992).
4. F. Sanchez Rojas; A. Garcia de Torres; C. Bosch Ojeda; J. M. Cano Pavon, *Analyst*, 113 (8), 1287-290 (1988).
5. M. P. Manuel-Vez; M. Garcia-Vargas, *Talanta*, 41 (9), 1553-59 (1994).
6. Jiang, Chongqiu; Tang, Bo; Wang, Rongying; Yen, Jianchong, *Talanta*, 44 (2), 197-202 (1997).
7. You, Jinmao; Sun, Xuejun; Zheng, Geng Xiu, *Huxue Shiji*, 18 (3), 162-67 (1996).
8. Cui, Wancang; Wang, Jinling; Shi, Huiming., *Fenxi Huaxue*, 11 (12), 900-904 (1983).
9. Chen, Lanhua; Shi, Guojiang., *Fenxi Huaxue*, 20 (8), 942-44 (1992).

10. Obata, Hajime; Nozaki, Yoshiyuki; Okamura, Kei; Maruo, Masahiro; Nakayama, Eiichiro. *Field Anal. Chem. Technol.*, 4(6), 274-82 (2000).
11. Ren, Jing; Zhang, Jing; Luo, Jing Qing; Pei, Xiao Kun; Jiang, Zhen Xi, *Analyst*, 126 (5), 698-702 (2001).
12. American Standards of Testing Materials, "*Annual Book of ASTM Standards*", Philadelphia, Vol. 3 (1983).
13. "*Standard Methods for the Examination of Water and Wastewater*", Sixteenth Ed., ASTM, (1985), pp 162.