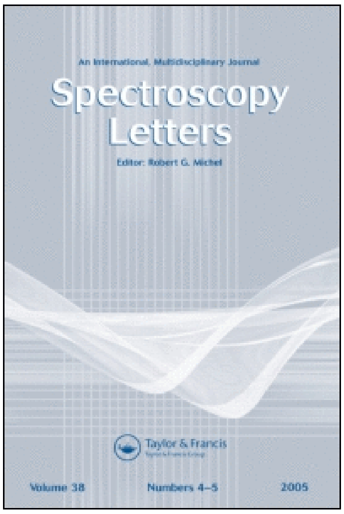

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Spectrofluorimetric Determination Of Indium with 1,2,4-Trihydroxyanthraquinone

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SPECTROFLUORIMETRIC DETERMINATION OF INDIUM WITH 1,2,4-TRIHYDROXYANTHRAQUINONE

Key words: 1,2,4-Trihydroxyanthraquinone, indium, spectrofluorimetry, alloys, determination.

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Abstract. A new method for the spectrofluorimetric determination of indium by formation of a fluorescent 1:1 complex with 1,2,4-trihydroxyanthraquinone is proposed. The complex is formed in a mixed, 60:40 v/v acetone-water medium

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at pH 3.8 provided by an acetic acid–sodium acetate buffer. The calibration graph is linear between 10 and 600 ng/ml. The effect of potential interferents on the determination was assessed and the proposed method was applied to the determination of indium in synthetic samples.

INTRODUCTION

Notwithstanding the fact that indium is scarce in nature, some of its compounds are widely used, not only for industrial, but also for metallurgical, electronic and nuclear technological applications, among others[1]. In the medical field, it is employed as an antitumour agent[2]. The toxic effects of this element have been the subject of a number of publications which were reviewed by Izrael *et al.*[3] and Smith *et al.*[4].

Indium can be determined by using a host of methods, chiefly spectrophotometric[5,6] or atomic emission spectrometric[7,8], many of which entail extraction of the element into some solvent. On the other hand, there are few spectrofluorimetric methods available for the determination of indium[9-10], which led us to develop one based on the use of 1,2,4 trihydroxyanthraquinone (1,2,4-THAn) as reagent.

EXPERIMENTAL

Apparatus

Fluorescence measurements were made on a Perkin-Elmer MPF-44A spectro-fluorimeter furnished with an Osram 150-w xenon lamp, quartz cuvettes of 1 cm pathlength and a Perkin-Elmer 056 recorder. The instrument was calibrated by using a standard fluorescence band equivalent to that yielded by a 10^{-5} M ovalene solution. All reported spectra are in uncorrected form.

A PHM 84 pH-meter furnished with a combined glass-calomel electrode was used for pH measurements. All reported pH values were measured in 60:40 v/v acetone -water and are also given in uncorrected form, so they must be considered apparent in nature.

The experimental setup included an Ander 182 electronic balance and a Selecta thermostatic bath with a built-in compressor.

Reagents

Analytical reagent-grade chemicals, pure solvents and de-ionized water were used throughout. The solutions employed included the following:

——An In(III) standard containing 1.0004 g/ml of the metal (Aldrich) in 2% HNO_3.

——A 10^{-3}M solution of 1,2,4-THAn (Merck, R.A.) in acetone (Panreac, R.A.).

——HAcO/NaAcO (Merck, R.A.) buffers of C_t = 1.5 M and pH 2.6-5.1.

Working strength solutions were made from the above three stocks as required by dilution with de-ionized water.

Procedure

Determination of In(III) in aqueous solutions and alloys

In a 25-ml flask, place a volume of unknown solution containing between 0.25 and 15.00 μg of In(III). Add 2 ml of 10^{-3} M 1,2,4-THAn, 1 ml of buffer at pH 3.8(C_t = 1.5M) and 15 ml ——30% of the overall volume ——of acetone. Make to the mark and thermostat the mixture at 20 °C for 10 min. Then, measure the fluorescence at 608 nm (λ_{exc} = 545 nm) and subtract the blank signal from the readout.

The amount of In(III) is read off a calibration curve constructed for an indium standard prepared under the same experimental conditions as the samples.

RESULTS AND DISCUSSION

The excitation and emission spectra of the complex formed between 1,2,4-THAn and In(III) in a weakly acidic 50:50 acetone -water medium showed qualitative signs of fluorescence emission. The solutions used to record the spectra contained 2×10^{-4} M reagent and 2×10^{-5} M indium, and their pH was adjusted to 4.8 by adding 0.5 ml of HAcO/NaAcO buffer (C_t = 1.5 M).

Figure 1A and 1B shows the excitation and emission spectra for the complex and reagent. The complex yields two excitation maxima at 468 and 545 nm, respectively, and one emission maximum at 608 nm. The excitation maximum at 545 nm is only observed in the presence of acetate ion. On the other hand, the reagent yields an excitation maximum at 468 nm and is only weakly fluorescent on excitation with longer wavelengths. Thus, 545 and 608 nm were chosen as the optimal excitation and emission wavelength, respectively, because they resulted in the largest possible difference between the emission intensity of the complex and the reagent (Fig. 1B).

The effect of the medium acidity on the complex formation was investigated by using solutions containing 50% acetone that were pH-adjusted with 1.0 M HCl. No fluorescence was produced under these conditions, which confirmed that the concurrence of acetate ion was required in order that any fluorescence emission may be observed. This is consisting with previous findings for the thioxine -In(III) complex, the fluorescence intensity of which is doubled in the presence of acetate [11]. We thus carried out a new set of experiments in which the medium acidity was adjusted by using various HAcO/NaAcO buffers of pH between 2.5 and 5.1. The maximum fluorescence intensity was obtained at pH 3.4-4.0, over which it remained virtually constant (Fig. 2A). A pH of 3.8, equivalent to an apparent pH of 5.2, was thus chosen for subsequent experiments.

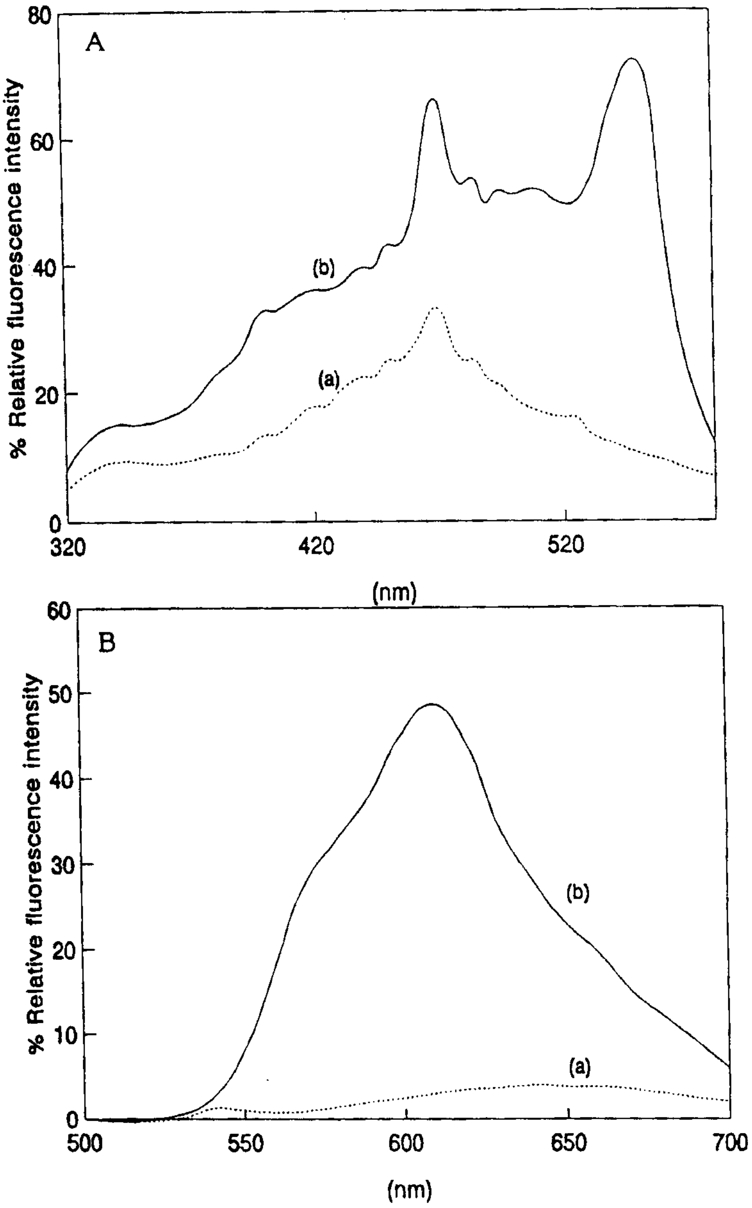

Figure 1.- A, Excitation and B, emission spectra of (a) THAn and (b) THAn-In(III) complex in 50% v/v acetone-water. [THAn]= 2.0 10^{-4} M; [In^{3+}]= 2.0.10^{-5}M λ_{exc} = 468 nm; λ_{em} = 608 nm. 10 coarse, 0 fine, slits 6 nm.

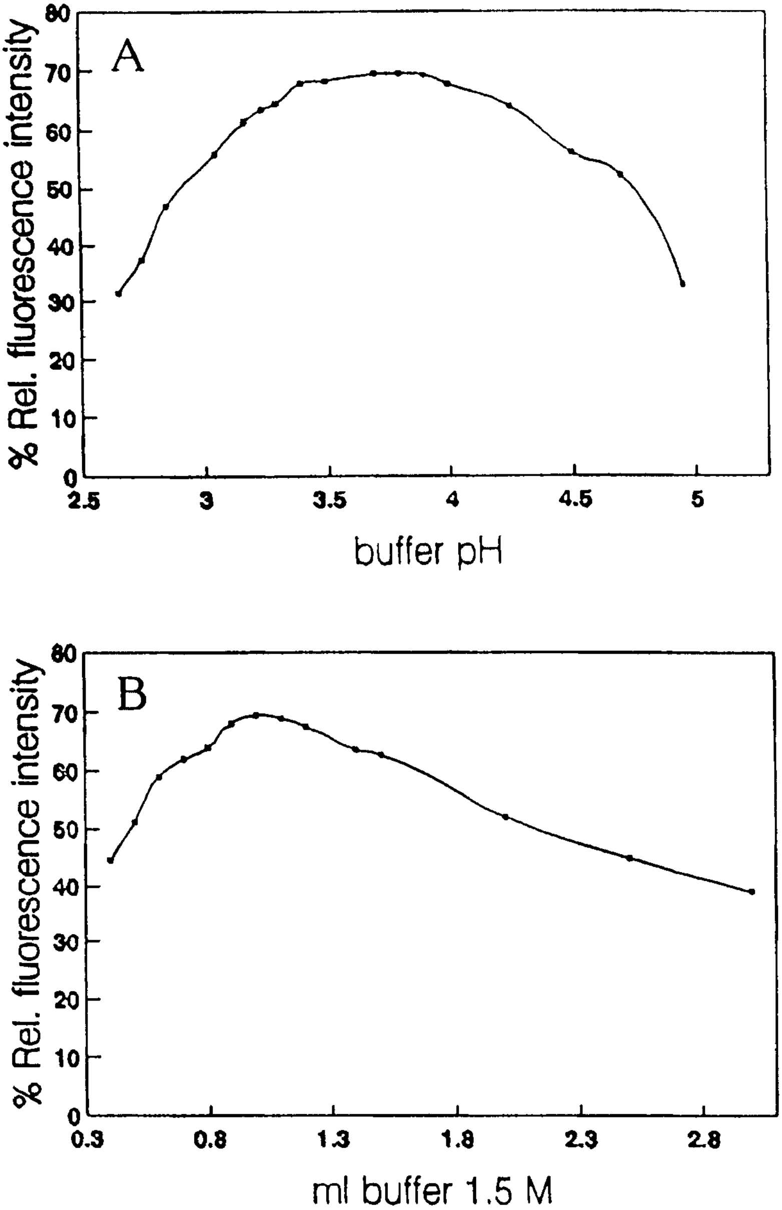

Figure 2.- (A), pH, (B) Buffer concentration; on the fluorescence of In(III)-1,2,4-THAn complex, sensitivity 10 coarse, 0 fine, slits 6 nm.

A similar experiment was conducted in order to find the optimal concentration of buffer. As can be seen in Fig. 2B, buffer concentrations over the range 2.4 × 10^{-2} M to 0.18 M resulted in a virtually constant fluorescence intensity, so 3 × 10^{-2} M, obtained by making 1 ml of the 1.5 M HAcO/NaAcO to 25 ml, was selected as optimal (Fig. 2B).

As far as the solvent is concerned, the maximum fluorescence intensity was obtained at acetone contents between 60 and 70% (Fig. 3A). The latter was thus chosen in order to have as much water as possible to dissolve the samples.

Under the above-described conditions, the fluorescence intensity was found to decrease by less than 1% during the first 5 min, after which it remained constant for over 24 h.

Increasing temperatures resulted in decreasing fluorescence intensity, so all subsequent measurements were made at 20°C (Fig. 3B).

Figure 4 shows the influence of the 1,2,4-THAn concentration on the fluorescence signal emitted by a solution containing 4.36 × 10^{-6} M In(III). As can be seen, the maximum fluorescence intensity was obtained at a reagent concentration between 6.4 × 10^{-5} and 1.12 × 10^{-4} M. Above this range, the fluorescence started to decay, probably through inversion produced by excess reagent. A 1,2,4-THAn concentration of 8 × 10^{-5}M was chosen as optimal.

The fluorescence intensity was found to increase linearly with increasing In(III) concentrations above 5.2 × 10^{-6} M in a 8 × 10^{-5} M 1,2,4-THAn solution.

The order of addition of the reactants was found to have no effect on the measured fluorescence intensity.

Finally, the stoichiometry of the In(III)-1,2,4-THAn complex was calculated to be 1:1, both by the continuous-variation and by the molar-ratio method.

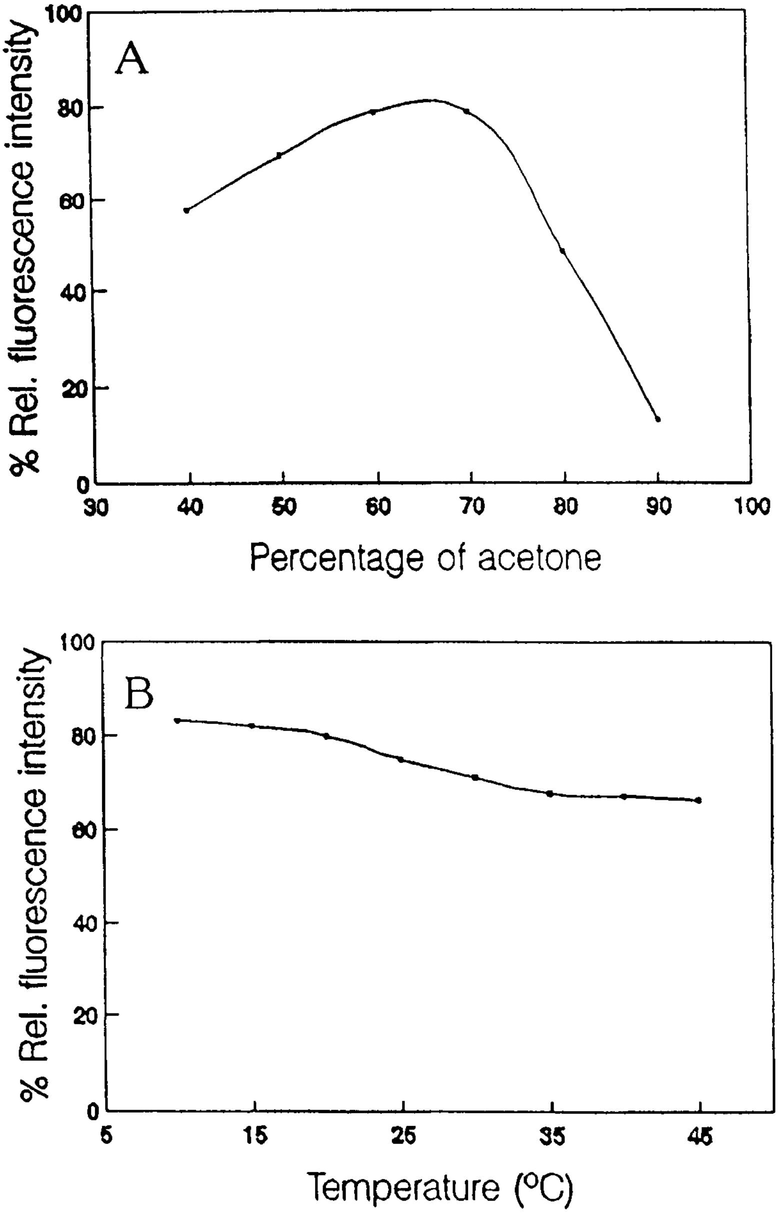

Figure 3.- (A), percentage of acetone, (B) temperature; on the fluorescence of In(III)-1,2,4-THAn complex, sensitivity 10 coarse, 0 fine, slits 6 nm.

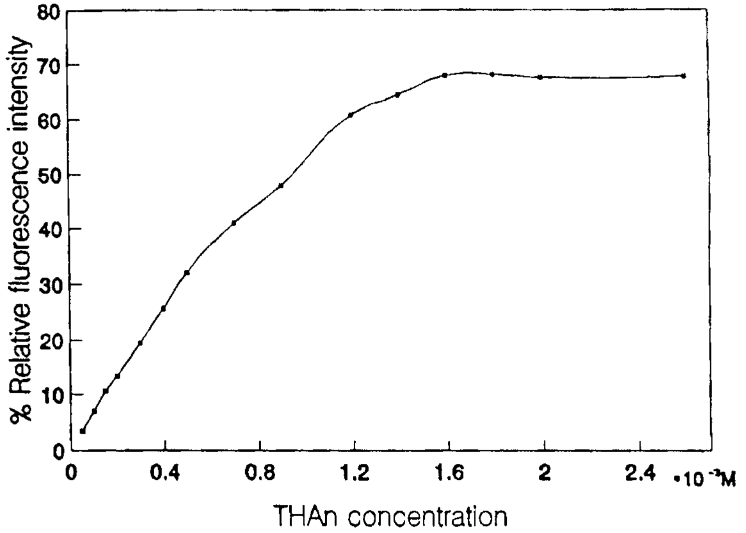

Figure 4.- Influence of 1,2,4-THAn concentration on the fluorescence of In(III)-1,2,4-THAn complex, sensitivity 10 coarse, 0 fine slits 6 nm.

Analytical figures of merit

Under the above-described experimental conditions, the emitted fluorescence intensity varied linearly with the indium concentration over the range 10–600 ng/ml. The equation for the calibration curve as determined by least-squares regression was

$$y = 0.378 + 0.127\,[\mathrm{In(III)}] \qquad (r = 0.9998)$$

The detection limit was 1,29 ng/ml, and the relative standard deviation obtained by analysing two sets of 11 samples containing 100 and 300 ng/ml In(III) was 0.35 and 0.29%, respectively ($p < 0.05$).

TABLE 1

Effect of foreign species on the determination of 300 ppb of In (III)

[Specie]/[Mg(II)]	Specie Added
100/1	Na(I), K(I), Ag(I), CO_3^{2-}, IO_3^-, ClO_3^-, BrO_3^-, $S_2O_3^{2-}$, Glucose, Tartrate, Thiourea.
50/1	Urea, Li(I), Cd(II).
10/1	Zn(II), Mg(II).
1/1	Ascorbic Acid, Oxalate, Sn(II), Pb(II),
0.5/1	Cu(II), Al(III), Fe(III), Mo(VI), La(III), EDTA.

TABLE 2

Determination of indium in synthetic mixtures.

Sample	Comp. Cert.	$In(III)_{present}$ (ppb)	$In(III)_{found}$ (ppb)	% E. rel.
Nuclear Control Rod Alloy	15% Ag; 5% In; 80% Cd	300	301.7	0.56
Cerro-seal	50% Cd; 50% In	300	302.0	0.67
Indalloy	75% Pb; 25% In	300	305.0	1.60

I Nuclear control Rod alloy
II Cerro-seal 25 (Cerro Corporation)
III Indalloy-10 (Indium Corporation of America)

Effect of interferents

The selectivity of the proposed method and its applicability to the determination of In(III) in various types of samples were assessed by investigating the effect of some potentially interfering ions on the determination of 300 ppb of the analyte. Foreign ions were added in a 100:1 ratio with respect to In(III). If any interference was observed, then the initial ratio was gradually lowered until the effect disappeared. A given species was considered to interfere if it gave rise to a deviation greater than ± 5% from the added In(III) concentration. The results obtained in this respect are listed in Table 1. As can be seen, the most serious interferences were posed by those species reacting with 1,2,4-THAn (Al^{3+}, La^{3+}, Mo^{6+}) and those forming fairly stable complexes with In(III).

Determination of indium in synthetic samples

The proposed method was validated by applying it to the determination of In(III) in synthetic mixtures. Since no standards containing the analyte were available, synthetic samples with In(III) contents similar to those typically found in some industrial alloys[12] were prepared. As can be seen in Table 2, the results obtained were highly consistent with the added amounts.

ACKNOWLEDGEMENT

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REFERENCES

1 B.A.Fowler, Handbook on the Toxicology of Metals. 2nd edition. Elsevier Science Publishers B.V. 1986.

2 H. Olkkonen, S. Suonio, T. Lahtinen, and I.M. Penttila, Int. J. Nucl. Med. Biol., 4, 179 (1977).

3 Z.I. Izrael'son, Problems of Industrial Hygiene and Occupational Pathology in Work with Rare Metals,pp 206-218, Izrael'son,Z.I., Mogilevskaja, O. J. and Suvorov, S.V.(Eds), Medicine. Moscow (1973).

4 I.C. Smith, B.L. Carson, and F. Hoffmeister, Trace elements in Environment, Vol 5.Indium.Ann Arbor Science Publishers, Ann Arbor, Michigan (1978).

5 Z. Marczenko. Spectrophotometric Determination of elements. Ellis Horwood Limited. Chichester, England, (1976).

6 Z. Holzbecher et al. Handbook of Organic Reagents in Inorganic Analysis. Ellis Horwood Limited. Chichester, England, (1976).

7 H. Armannsson, P.J. Ovenden, Int. J. Environ. Anal. Chem., 8, 127 (1980).

8 M. S. Cresser, Solvent Extraction in Flame Spectroscopic Analysis, Butterworths, London, (1978).

9 A. M. Afonso, J.J. Santana, M.P. González, F. García Montelongo, Quim. Anal. 6, 151 (1987).

10 F. Capitán, A. Navalón, J.L. Vilchez, L.F. Capitán-Vallvey Mikrochim. Acta I, 301 (1991).

11 K. Watanabe, A. Fujiwara, and K. Kawagaki, Bull. Chem. Soc. Jpn. 50(6), 1460 (1977).

12 F.D. Snell, and L.S. Ettre, Eds., Encyclopedia of Industrial Chemical Analysis.Interscience, Vol. 14, 518 (1971).

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