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2-(2-Thiazolylazo)-*p*-Cresol (TAC) as a Reagent for the Spectrophotometric Determination of Indium(III)

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The reaction between indium(III) and the 2-(2-thiazolylazo)-*p*-cresol (TAC) in aqueous methanol media at apparent pH 5.0–6.0 results in an intensely colored complex which is stable for at least 2 h. The composition is 1:2 cation: TAC and the log of the formation constant is 10.78 ± 0.64. Beer's law is obeyed up to 8.0 μg · ml^{-1} of indium(III) at 580 nm. The apparent molar absorptivity at 580 nm is 1.21 × 10^4 liter · mol^{-1} · cm^{-1} and the detection limit was obtained as 10.0 ng · ml^{-1} of indium(III). The method is applied to the determination of indium in a catalyst.

INTRODUCTION

The main reagents used for spectrophotometric determinations of indium are dithizone (*1*) (a = 6.12 × 10^4)‡ arsenazo I (*2*) (a = 5.80 × 10^4), 4-(2 pyridilazo) resorcinol (*3*) (a = 4.3 × 10^4), xylenol orange (*4*) (a = 1.8 × 10^4), and stilbazo (*5*) (1.6 × 10^4). The dithizone provides one of the most sensitive methods, but it has some disadvantages such as low selectivity, photodecomposition, and insolubility of the complex in aqueous media. The oxine (*3*) (a = 0.67 × 10^4) and bromooxine (*3*) (a = 0.88 × 10^4), also commonly used, have low sensitivity and selectivity.

The 2-(2-thiazolylazo)-*p*-cresol (TAC) reacts with many metal ions with the formation of colored complexes. It has been used for the spectrophotometric determinations of zinc(II) (*6*), cadmium(II) (*6*), iron(II) (*7*), yttrium(III) (*8*), bismuth(III) (*9*), rhodium(III) (*10*), nickel(II) (*11*), and zirconium(IV) (*12*). It and its chelates have low solubility in water; therefore it cannot be used in aqueous media. Methods proposed include extractions using an organic solvent (*6, 7*) in the presence of surfactants (*8–10*) or in aqueous–ethanol systems (*11, 12*).

The present work describes the reaction of TAC with indium(III) in aqueous–methanol media, which gave a system with an apparent molar absorptivity of 1.21 × 10^4 liter · mol^{-1} · cm^{-1}.

EXPERIMENTAL

Reagents

TAC solution, 0.1 g in 100 ml of methanol; standard indium solution, prepared from indium oxide in 0.30 *M* hydrochloric acid; buffer solution, prepared by

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‡ a, apparent molar absorptivity (liters · mol^{-1} · cm^{-1}).

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mixing 1.0 *M* sodium acetate and 1.0 *M* acetic acid in appropriate ratios; stock solution of other elements, prepared by dissolving suitable salts in water, nitric acid solution (1%), or hydrochloric acid solution (1%).

Equipment

Spectrophotometer, Varian DMS-100; pH meter, Fisher-600; analytical balance, Mettler-H20.

Procedure

Into a 25-ml standard flask transfer a portion of solution containing up to 100.00 μg of indium(III). Add 5.0 ml of acetate buffer (pH 5.5), 5 ml of methanol, and 1 ml of a 0.1% methanolic solution of TAC. Dilute to the mark with water, mix, and after 5 min measure the absorbance at 580 nm in a 2-cm cell versus an appropriate prepared blank.

RESULTS AND DISCUSSION

Reagent Solubility

2-(2-Thiazolylazo)-*p*-cresol is slightly soluble in water but the addition of organic solvents like methanol, ethanol, isopropanol, propanone, dioxane, and ethylene glycol, among others, provides for the solubilization of the reagent. The complex is formed with all the solvents above, but methanol and ethylene glycol are preferred, due to the higher absorbances.

Complex Stability and Influence of Solvent

The solvent effect on the complex stability was studied by measuring the absorbance of the system for 1 h in 5-min intervals. The best results were obtained with the systems containing methanol and ethylene glycol because the absorbances were practically stable during such periods of time.

Amount of Reagent (TAC)

Maximal and constant absorbance is obtained for 80.00 μg of indium(III) with 0.50 ml of 0.1% TAC solution per 25 ml, so 1.00 ml of TAC solution was selected as optimal.

pH Effect on Complex Formation

It was observed that formation of the complex is greatly influenced by pH. The results showed that the best pH range is between 5.0 and 5.8.

Effect of the Amount of Acetate Buffer

The indium(III)–TAC reaction was conducted in the presence of the acetate buffer. The amount of buffer affects complex formation. The results show that when the buffer concentration increases the absorbance signal is reduced.

Order of Addition of the Reagents

The order of addition was studied and the results demonstrated that complex formation was not significantly affected.

Composition and Conditional Constant

The complex composition and its conditional constant were determined by the molar ratio method. The results show that the complex has a molar ratio of 1:2 indium(III)–TAC and the log of the formation constant is 10.78 ± 0.64 (95% confidence level).

Calibration Curve

Calibration curves were made for the determination of indium(III) in the ranges 0.00 to 2.50 and 0.00 to 8.00 μg/ml, with 4- and 1-cm cells, respectively. Lambert–Beer's law is followed in these ranges. The curves had the equation

$$A = 0.366 \text{ concentration In(III) } (\mu g/ml) + 0.016, \quad r = 0.9995$$
$$A = 0.104 \text{ concentration In(III) } (\mu g/ml) + 0.008, \quad r = 0.9998.$$

Molar absorptivity and sensitivity for the system were determined as being 1.20×10^4 liter · mol^{-1} · cm^{-1} and 9.62 ng/cm^2, respectively.

TABLE 1
Determination of Indium in the Presence of Various Cations

Cation	Reagent used	100 × 1	10 × 1	1 × 1	0.1 × 1
Mg(II)	$MgSO_4 \cdot 7H_2O$	n	n	n	n
Ca(II)	$Ca(NO_3)_2$	n	n	n	n
Ba(II)	$Ba(NO_3)_2$	n	n	n	n
Sr(II)	$Sr(NO_3)_2$	n	n	n	n
Al(III)	$KAI(SO_4)_2 \cdot 7H_2O$	n	n	n	n
Tl(III)	$Tl(NO_3)_3$	n	n	n	n
V(V)	NH_4VO_3	i	n	n	n
La(III)	$LaCl_3 \cdot 7H_2O$	i	n	n	n
Mn(II)	$MnSO_4$	i	i	n	n
Cd(II)	$Cd(CH_3COO^-)_2 \cdot 2H_2O$	i	i	n	n
Pb(II)	$Pb(NO_3)_2$	i	i	n	n
Y(III)	Y_2O_3/HCl	i	i	n	n
Fe(III)	$FeNH_4(SO_4)_2 \cdot 12H_2O$	i	i	n	n
Ga(III)	Ga_2O_3/HCl	i	i	n	n
Zr(IV)	$ZrOCl_2 \cdot 8H_2O$/HCl	i	i	n	n
Pt(IV)	Pt/HCl–HNO_3	i	i	n	n
Au(III)	$AuCl_3 \cdot 3H_2O$/HCl	i	i	n	n
Fe(II)	$FeSO_4 \cdot 7H_2O$	i	i	i	i
Ti(IV)	$TiO_2/H_2SO_4NH_4)_2SO_4$	i	i	i	i
Zn(II)	$ZnSO_4 \cdot 7H_2O$	i	i	i	i
Cu(II)	$CuSO_4 \cdot 5H_2O$	i	i	i	i
Ni(II)	$NiSO_4 \cdot 7H_2O$	i	i	i	i
Co(II)	$CoSO_4 \cdot 7H_2O$	i	i	i	i

Note. Indium present, 25.00 μg per 25 ml of solution; i, interference; n, no interference.

TABLE 2
Analysis of Indium in a Sample of Catalyst[a]

Method	% In found[b]	Standard deviation
TAC	0.30 ± 0.01	0.01
ICP	0.33 ± 0.02	0.01

[a] Composition of catalyst: Al_2O_3, 85.30%; Sn, 0.50%; Pt, 0.50%; In, 0.33%; SiO_2 + Na_2O + K_2O, 13.37%.
[b] Results of three determinations.

Interferences

The selectivity of reaction between the TAC and the indium(III) cation was investigated by determination of 25.00 μg indium(III) per 25 ml in the presence of various proportions of other ions (Table 1).

The interference limit of an ion was defined as that proportion at which a change of ±5% in absorbance of the chelate is observed.

It was found that copper(II), nickel(II), iron(II), cobalt(II), and titanium(IV) interfere at all proportions.

Determination of Indium in a Catalyst

Results obtained by applying the method proposed under Experimental to a sample agree well with the results obtained by applying of analysis by ICP (Table 2).

CONCLUSION

The system indium(III)–TAC has sensitivity and selectivity comparable to the other reagents used for spectrophotometric determination of indium.

In comparison with oxine and bromooxine, both commonly used reagents, TAC shows better sensitivity.

The main advantage of this reagent is that it does not show interference from aluminum(III) as commonly found in methods using 4-(2-pyridilazo)-resorcinol (*3*), xylenol orange (*4*), oxine (*3*), bromooxine (*3*), and stilbazo (*5*).

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