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

S. L. C. Ferreira,* A. C. S. Costa,* and H. A. S. Andrade†

*Department of Analytical Chemistry, Federal University of Bahia Salvador, Bahia, Brazil; and †Department of Chemistry, PUC of Rio de Janeiro, Rio de Janeiro, Brazil

Received November 18, 1990; accepted March 16, 1991

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 × 10⁴ 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 × 10⁴)‡ arsenazo I (2) (a = 5.80 × 10⁴), 4-(2 pyridilazo) resorcinol (3) (a = 4.3 × 10⁴), xylene orange (4) (a = 1.8 × 10⁴), and stilbazo (5) (1.6 × 10⁴). 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 × 10⁴) and bromooxine (3) (a = 0.88 × 10⁴), 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 × 10⁴ 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

‡ a, apparent molar absorptivity (liters · mol⁻¹ · cm⁻¹).

To whom correspondence should be addressed.

0026-265X/91 $1.50
Copyright © 1991 by Academic Press, Inc.
All rights of reproduction in any form reserved.
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 \( \mu \text{g} \) 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 \( \mu \text{g} \) 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

\[
A = 0.366 \text{ concentration Ind}(\text{III}) (\mu\text{g/ml}) + 0.016, \quad r = 0.9995
\]

\[
A = 0.104 \text{ concentration Ind}(\text{III}) (\mu\text{g/ml}) + 0.008, \quad r = 0.9998.
\]

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

<table>
<thead>
<tr>
<th>TABLE 1</th>
<th>Determination of Indium in the Presence of Various Cations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cation</td>
<td>Reagent used</td>
</tr>
<tr>
<td></td>
<td>100 × 1</td>
</tr>
<tr>
<td>Mg(II)</td>
<td>MgSO₄ · 7H₂O</td>
</tr>
<tr>
<td>Ca(II)</td>
<td>Ca(NO₃)₂</td>
</tr>
<tr>
<td>Ba(II)</td>
<td>Ba(NO₃)₂</td>
</tr>
<tr>
<td>Sr(II)</td>
<td>Sr(NO₃)₂</td>
</tr>
<tr>
<td>Al(III)</td>
<td>KAI(SO₄)₂ · 7H₂O</td>
</tr>
<tr>
<td>Ti(III)</td>
<td>Ti(NO₃)₃</td>
</tr>
<tr>
<td>V(V)</td>
<td>NH₄VO₃</td>
</tr>
<tr>
<td>La(III)</td>
<td>LaCl₃ · 7H₂O</td>
</tr>
<tr>
<td>Mn(II)</td>
<td>MnSO₄</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>Cd(CH₃COO⁻)₂ · 2H₂O</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>Pb(NO₃)₂</td>
</tr>
<tr>
<td>Y(III)</td>
<td>Y₂O₅/HCl</td>
</tr>
<tr>
<td>Fe(III)</td>
<td>FeNH₄(SO₄)₂ · 12H₂O</td>
</tr>
<tr>
<td>Ga(III)</td>
<td>Ga₂O₃/HCl</td>
</tr>
<tr>
<td>Zr(IV)</td>
<td>ZrOCl₂ · 8H₂O/HCl</td>
</tr>
<tr>
<td>Pt(IV)</td>
<td>Pt/HCl–HNO₃</td>
</tr>
<tr>
<td>Au(III)</td>
<td>AuCl₃ · 3H₂O/HCl</td>
</tr>
<tr>
<td>Fe(II)</td>
<td>FeSO₄ · 7H₂O</td>
</tr>
<tr>
<td>Ti(IV)</td>
<td>TiO₂/H₂SO₄NH₄H₂SO₄</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>ZnSO₄ · 7H₂O</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>CuSO₄ · 5H₂O</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>NiSO₄ · 7H₂O</td>
</tr>
<tr>
<td>Co(II)</td>
<td>CoSO₄ · 7H₂O</td>
</tr>
</tbody>
</table>

*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 Catalysta

<table>
<thead>
<tr>
<th>Method</th>
<th>% In foundb</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>TAC</td>
<td>0.30 ± 0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>ICP</td>
<td>0.33 ± 0.02</td>
<td>0.01</td>
</tr>
</tbody>
</table>

a Composition of catalyst: Al₂O₃, 85.30%; Sn, 0.50%; Pt, 0.50%; In, 0.33%; SiO₂ + Na₂O + K₂O, 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), xylanol orange (4), oxine (3), bromooxine (3), and stilbazo (5).

REFERENCES