Spectrophotometric Determination of Nano Amounts of Gallium (III) using 2-(5-Bromo-2-Pyridylazo)-5-Diethylaminophenol Reagent in Water Samples

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ABSTRACT

The aim of the present work is to develop a simple and sensitive spectrophotometric method for determination of nano amounts of Ga(III) using 2-(5-Bromo-2-Pyridylazo)-5-Diethylaminophenol (5-Br-PADAP) reagent. The factors affecting the determination procedure including absorption spectra, pH value, surfactant type and dye reagent concentration were studied and optimized. Interferences had also been evaluated. Maximum absorbance was obtained at 573 nm at pH 2.75, after 5 minutes mixing time. The proposed method was valid for Ga(III) concentration determination ranging from 0.005 to 1.25 µg ml\(^{-1}\) in aqueous solution. However, the detection limit was decreased up to 0.001 µg ml\(^{-1}\) in the presence of methanol. The ratio between Ga(III) and 5-Br-PADAP was found to be 1:1 with apparent molar absorptivity 1.12 \(\times\) 10\(^5\) 1 mol\(^{-1}\) cm\(^{-1}\) and coefficient of variation 0.44%. The elucidation of the complex composition was proved using FTIR technique. The method was applied for the determination of Ga(III) in some polluted water samples from different sources.

Keywords: Spectrophotometry / Gallium / 5-Br-PADAP complexing agent.

INTRODUCTION

Gallium in the earth crust is rather limited. It does not exist in free form in nature, and its abundance in the earth's crust is approximately 16.9 µg m\(^{-1}\). It is found and extracted as a trace component in bauxite and in small extent from sphalerite, germanite ores processing. In soil, gallium has a median value of 13.8 mg kg\(^{-1}\) in subsoil and 13.5 mg kg\(^{-1}\) in topsoil and in stream water, it has a median value of 0.01 µg l\(^{-1}\).

In recent years, the increasing demand of gallium is due to use in widespread industrial applications. It has a variety of uses such as quartz thermometers, lighting tubes, infrared transmitters, semiconductors, photoelectric cells and electron tubes. Moreover, it is found a useful application in the nuclear field as alloying element with plutonium \(^{(1)}\). So increasing interest and importance of this element in different fields has made it necessary to develop a simple and accurate method for its determination.

Several techniques have been used for the determination of gallium \(^{(2-8)}\). Spectrophotometric methods of analysis are widely used due to their simplicity and low cost. Several procedures have been reported for spectrophotometric determination of Ga(III) ions using different reagents such as Rhodamine B \(^{(9)}\), Erichrome Cyanine R C \(^{(10)}\), Chrome Azurol S \(^{(11)}\), Pontachrome Azure Blue B \(^{(12)}\), Chromal Blue G \(^{(13)}\), Xylenol Orange \(^{(14)}\), 4-(2-pyridylazo)- resorcinol (PAR) \(^{(15,16)}\), 1-(2-pyridylazo)-2-naphthol (PAN) \(^{(17)}\), Bromopyrogallol Red \(^{(18)}\), phenylfluorone \(^{(19)}\) (PF) and 2-[2-(3,5-Dibromopyridyl)-azo]-5-diethylaminobenzoic acid \(^{(20)}\).
2-(5-bromo-2-pyridylazo)-5-diethylaminophenol complexing agent (5-Br-PADAP) has recently attached much attention as a spectrophotometric reagent due to its high sensitivity and good selectivity. It has been applied successfully as a new and metalochromic indicator for complexmetric determination of metal ions\(^{(21-25)}\). Survey of the literature showed that little work has been published regarding the use of 5-Br-PADAP for the spectrophotometric determination of gallium.

The reagent has been reported for derivative spectrophotometric determination of gallium and indium in synthetic mixture at \(\lambda_{\text{max}}\) 553 nm and pH 4.0 and also in the presence of surfactants at pH 3.8 and \(\lambda_{\text{max}}\) 575 nm\(^{(26,27)}\). The present study is an extension of the reported studies. It aims to examine the different variables required to direct determination of Ga(III) in aqueous solutions. It includes acidity, reagent concentration, medium of the measurements, etc.

**EXPERIMENTAL**

1. Materials

1.1. Reagents:

All chemicals and reagents used in this study were of analytical grade. It included stock of gallium solution (AAS standard solution 1000 \(\mu\)g ml\(^{-1}\), Merck), reagent 5-Br-PADAP (Merck) were used. Its structure is shown in Fig. (1). The surfactants sodium dodecyl sulfate (SDS), cetylpyridinium chloride (CPC) were obtained from (Sigma-Aldrich). Cetyltrimethylammonium bromide (CTAB) and triton X-100 (TX-100) were obtained from (Buchem bv), (Fluka) respectively. Double distilled water was used to prepare the aqueous solutions.

![Fig. (1): Structure of of 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol.](image)

1.2. Solutions:

5-Br-PADAP reagent was prepared by dissolving 0.05 g in 100 ml ethanol. Sodium dodecylsulfate, cetyltrimethylammonium bromide, cetylpyridinium chloride and triton X-100 surfactants were prepared by dissolving 1g from the reagents in 100 ml of double distilled water. The phthalate-hydrochloric acid buffer solution (Dop), pH 2.75 was prepared from 0.2 M potassium acid phthalate and 0.2 M hydrochloric acid. Water samples were collected from Talkha and Beni Suef canal.

2. Apparatus:

UNICAM UV-visible spectrophotometer was used for recording absorption spectra and absorbance measurements. The pH value of solutions was measured using Digimed, DM-21 pH-meter.

3. Procedure:

To an aliquot solution containing up to 1.25 \(\mu\)g ml\(^{-1}\) of Ga(III), 1 ml of methanol, 2.5 ml of phthalate buffer and 1ml of 0.05% (5-Br-PADAP) were added in 25 ml volumetric flask then diluted up to volume with double distilled water. The absorbance of the solution was measured at 573 nm against its blank solution that prepared in the same manner. The time for the absorbance to reach stable value was 5 minutes after mixing at room temperature and the absorbance was stable for at least 24hr. The concentration of Ga(III) present in sample was determined from calibration curve prepared under the same experimental conditions.
RESULTS AND DISCUSSION

1. Absorption Spectra:

The absorption spectra of the formed chelate [Ga(III)-5-Br-PADAP] against the blank was recorded as given in Fig. (2). Maximum absorbance of the formed Ga(III)-5-Br-PADAP chelate was achieved at 573 nm. Therefore, all the absorbance measurements of the formed complexes have been carried out at 573 nm.

Fig. (2): Absorption spectra of Ga(III) -5-Br-PADAP complex.

2. Effect of pH:

The influence of acidity on the formation of Ga(III)-5-Br-PADAP complex was investigated in the pH range from 1.0 to 4.5 using 0.05% 5-Br-PADAP at 573 nm. The results were illustrated in Fig. (3) where the maximum absorbance was attained at pH 2.75. The absorbance intensity diminished at both lower and higher pH values.

Fig. (3): Effect of pH on the absorbance of Ga(III)- 5-Br-PADAP complex at 573nm.
2. Effect of 5-Br-PADAP Concentration:

The effect of varying 5-Br-PADAP concentrations on color intensity of the formed complex was examined from 0.01 to 0.08% at pH 2.75. The maximum absorbance was observed at 0.05% 5-Br-PADAP as indicated in Fig. (4). The absorbance of a series of solution containing 0.4 µg ml⁻¹ Ga(III) and various amounts of 0.05% Br-PADAP reagent solution were measured. It was found that 1 ml of 0.05% Br-PADAP is sufficient to complex 0.4 µg ml⁻¹ Ga(III). The ratio between the Ga(III) and 5-Br-PADAP was found 1:1 and representative structure for the formed complex was shown in Fig. (5). As reported by different authors (28) the stoichiometry ratio of 1:1 is indicative of square planer and tetrahedral complexes with three donor atoms from Br-PADAP being involved of the pyridine nitrogen, β-azo nitrogen and the O-hydroxy oxygen atom and a monodentate ligand such as H₂O from water.

![Graph showing absorbance vs dye concentration](image)

Fig. (4): Effect of dye concentration on the formed complex at pH 2.75, 573 nm.

![Proposed structure of Ga(III) loaded Br-PADAP](image)

Fig. (5): The proposed structure of Ga(III) loaded Br-PADAP.

4. Effect of Surfactant Type:

Surfactants have found wide use in spectrophotometric metals analyses due to their great effect on the solubilization of metal chelates, increase the molar absorptivity of these chelates as a result of ternary complex formation and change in ionization equilibria of the ligand (29).

In the presence of anionic surfactant sodium dodecylsulfate (SDS) and cationic surfactants cetyltrimethylammonium bromide (CTAB) and cetylpyridinum chloride (CPC), the Ga(III) chelate
showed low absorbance whereas in the presence of nonionic surfactant Triton X-100 (TX-100) the absorption of the complex increased as shown in Fig. (6).

This observation is attributed to the presence of an aromatic nucleus in the hydrophobic group which increase the adsorption of the surfactant onto polar surfaces and decrease its biodegradability. Moreover, nonionic surfactants are considered better solubilizing agents than ionic due to their lower critical micelle concentration (30).

![Fig. (6): Effect of surfactants on the absorbance of the formed complex at pH 2.75, 573 nm.](image)

5. **Effect of Organic Solvents:**

The effect of organic solvents (acetone, methanol, ethanol and propanol) on the intensity of absorption spectra of Ga(III)-5-Br-PADAP complex was studied under the optimum conditions. The results in Table (1) indicates that the absorbance increase in the following sequence methanol > ethanol > isopropanol > acetone. The polarity of (methanol, ethanol, propanol, acetone) is 0.762, 0.654, 0.546, 0.355 respectively. It was clear that the color intensity of the formed complex increased as the polarity of the solvent increased (31). A series of experiments were performed to investigate the effect of the concentration of methanol on the color development. Results in Fig. (7) demonstrated that methanol contents of 5% (v/v) was suitable and chosen for further experiments.

![Table (1): Effect of organic solvents on the color intensity of the formed complex.](image)
6. Calibration Graph:

Under the optimum conditions outlined in the recommended procedure there is a satisfactory linear relationship between absorbance and Ga(III) concentration in the range (0.005-1.25) µg ml⁻¹. The detection limit decreased to 0.001 µg ml⁻¹ in presence of methanol as shown in Fig. (8). The apparent molar absorptivity estimated at 573 nm was $1.12 \times 10^5$ mol⁻¹ cm⁻¹. The calibration sensitivity which is the slope of the analytical curve was 1.69 ml µg⁻¹. The precision of the procedure was checked by calculating the coefficient of variation after eight replicate determinations of 0.4 µg ml⁻¹ of Ga(III) standard solution and it was found 0.44%.
7. Infra Red Spectra of the dye and the formed complex:

Fourier Transformation infra red (FTIR) spectra before and after Ga(III) complexation with Br-PADAP were carried out as shown in Fig. (9). The changes in the functional group between the two spectra were confirmed. It clearly shows the presence of some new bands and shifts of the characteristic bands for metal chelate. The peak appeared at 1651 cm\(^{-1}\) due to C=N stretching vibration for Br-PADAP was shifted to 1643 cm\(^{-1}\) for Ga(III)-Br-PADAP chelate. Also the peak appeared at 1396.4 cm\(^{-1}\) due to N=N stretching vibration of Br-PADAP was shifted to 1377 cm\(^{-1}\) for Ga (III)-Br-PADAP chelate. All these results were proved and confirmed that Br-PADAP chelates with Ga (III). On the other hand the broad band which observed at 3417.6 cm\(^{-1}\) was attributed to O-H stretching vibration arising from two hydroxyl group, one from Br-PADAP and the other for ethanol. The shift obtained for this band in Ga(III)-Br-PADAP complex to 3301.9 cm\(^{-1}\) is due to hydroxyl group of Br-PADAP share in the reaction \(^{33,34}\). Therefore, IR spectra confirms that 5-Br-PADAP reacts with Ga (III) to form the previous suggested complex in Fig. (5).

8. Effect of Diverse ions:

The effect of some foreign ions were examined by carrying out determination of 0.4 µg ml\(^{-1}\) of Ga (III) with a known amount of foreign ions solutions and the proposed procedure was followed. The tolerance limit of various foreign ions were given in Table (2). A large number of ions such as Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), NH\(_4\)\(^+\), Th\(^{4+}\) and Tl\(^{3+}\) did not interfere. Among the tested anions sulfate, nitrate, chloride and PO\(_4\)\(^{3-}\) had no interference effect. However, fluoride ions up to 5 µg ml\(^{-1}\) decreased the absorbance intensity. Ferric ions, Fe\(^{3+}\), Al\(^{3+}\), Cu\(^{2+}\), Ni\(^{2+}\), Co\(^{2+}\) and Cr\(^{3+}\) ions had a great effect. Manganese ions have a negative effect but uranium and indium ions had no interference up to 0.1 µg ml\(^{-1}\) and 0.05 µg ml\(^{-1}\) receptively however, Ba\(^{2+}\) ions was tolerated up to 100 µg ml\(^{-1}\).

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**Fig. (9):** The IR spectra of (A) the dye, (B) the formed complex with Ga(III).
Table (2): Effect of diverse ions on the determination of Ga(III).

<table>
<thead>
<tr>
<th>Foreign ions</th>
<th>Tolerated limit, µg ml⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al³⁺</td>
<td>15.00</td>
</tr>
<tr>
<td>Cr⁶⁺</td>
<td>10.00</td>
</tr>
<tr>
<td>Th⁴⁺</td>
<td>Up to 50</td>
</tr>
<tr>
<td>Co²⁺, Fe³⁺, Fe²⁺, In³⁺</td>
<td>0.05</td>
</tr>
<tr>
<td>Ba²⁺, NH₄⁺</td>
<td>Up to 100</td>
</tr>
<tr>
<td>La³⁺, Nd³⁺, Tl³⁺</td>
<td>Up to 10</td>
</tr>
<tr>
<td>UO₂²⁺, Cu²⁺, Ni²⁺, Mn²⁺</td>
<td>0.10</td>
</tr>
<tr>
<td>Na⁺, K⁺, Ca²⁺, Mg²⁺</td>
<td>Up to 1000</td>
</tr>
<tr>
<td>SO₄²⁻, NO₃⁻, Cl⁻, PO₄³⁻</td>
<td>Up to 1000</td>
</tr>
<tr>
<td>F⁻</td>
<td>5.00</td>
</tr>
<tr>
<td>Si⁴⁺</td>
<td>20.00</td>
</tr>
</tbody>
</table>

9. Application:

A portion of preconcentrated H₂O (5ml) was taken into 25 ml graduated flask, the proposed procedure was followed then the absorbance of solution was measured. The quantitative chemical analysis of Ga(III) in H₂O samples is presented in Table (3). As can be seen this suggested procedure can deal directly for determination of nano amounts of Ga(III) ions. The data were in reasonable agreement with those obtained by atomic absorption analysis.

Table (3): Determination of Ga(III) in real water samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Presented work, Ga(III) µg ml⁻¹</th>
<th>Spectrophotometer</th>
<th>AAS</th>
<th>RSD%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap water</td>
<td>N.d</td>
<td>N.d</td>
<td>N.d</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>0.003</td>
<td>0.0029</td>
<td>3.4</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.007</td>
<td>0.0067</td>
<td>4.4</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0.005</td>
<td>0.0048</td>
<td>4.1</td>
<td></td>
</tr>
</tbody>
</table>

N.d : not detected

CONCLUSION

5-Br-PADAP is proposed as a successful reagent for spectrophotometric determination of nano amounts of Ga(III) ions in aqueous solutions. Various parameters affect on the determination of Ga(III) ions have been evaluated and optimized. The reagent react with Ga(III) forming red complex with absorption maximum at λ_max 573 nm and pH of 2.75 with molar absorptivity of 1.12 × 10⁵ l mol⁻¹ cm⁻¹. Beer’s law obeyed for 0.005-1.25 Ga(III) µg ml⁻¹. Under the optimum conditions, Ga(III) : reagent ratio was found to be 1:1. The suggested method is useful for determination of ultra trace concentration of Ga(III) in water samples due to simplicity and high sensitivity.
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