CHAPTER VII

RAPID SEQUENTIAL SOLVENT EXTRACTION, SEPARATION AND DETERMINATION OF ALUMINIUM(III), GALLIUM(III), INDIUM(III) AND THALLIUM(III) BY n-OCTYLANILINE IN TOLUENE AS AN EXTRACTANT FROM WEAK ORGANIC ACID MEDIA
Chapter - 7

Rapid sequential solvent extraction, separation and determination of aluminium(III), gallium(III), indium(III) and thallium(III) by n-octylaniline in toluene as an extractant from weak organic acid media.

Aluminium and its congeners, Ga, In and Tl are considerably larger than boron and hence they are much more metallic and ionic in their character [1]. Aluminium is the most abundant metal and the third most abundant element by weight in the earth's crust (83000 ppm). Gallium (5-15 ppm) is twice as abundant as boron, but indium (0.24 ppm) and thallium (0.5 ppm) are much less common [2]. All three elements, Ga, In and Tl occur as sulphides. World production of bauxite was 100 million tones, whereas that of aluminium was 17.6 million tones in 1988. Production of indium is about 52 tonnes per year and of gallium and thallium about 10 tonnes per year. Small amounts of gallium are found in the ores of the elements adjacent to it in the periodic table (Al, Zn and Ge). Traces of indium and thallium are found in ZnS and PbS ores.

There are many uses of aluminium and its alloys (industry, domestic and pharmaceutical). Traces of gallium are found in bauxite and the ratio of gallium to aluminium is about 1/5000. This ratio can gradually increased to about 1/250 during purification of alumina by Bayer's process. Gallium is used to dope crystals to make transitors. Gallium arsenide (Ga As) is iso-electronic with germanium, is used light emitting diodes and laser diodes, indium is used to dope crystals to make p-n-p transitors and in thermistors (In As and In Sb).
7.1 Summary of methods for solvent extraction of aluminium(II), gallium(III), indium(III) and thallium(III)

The literature survey reveals that very few extraction methods are devoted to the extraction of either two, three or four elements from the group III. The optimum extraction conditions for indium(III) and thallium(III) have been established by using trioctylamine (TOA) and methyl trioctylammonium salt in benzene from sodium succinate at pH 7.0 [3]. Method has been developed for separation from associated elements. The extraction and mutual separation of trivalent aluminium and gallium from sodium hydroxide solutions containing tartaric acid were investigated by using trioctylmethyl ammonium chloride in benzene [4]. Solvent extraction equilibrium of gallium(III) and indium(III) were studied from aqueous nitrate media with acidic organophosphorus extractants and 2-bromododecanoic acid in toluene at 303 K [5]. The selectivity to indium(III) over gallium(III) increases with the increase of the acidity of the extractants. Similar study has been carried out using bis (2-ethylhexyl) phosphoric acid (D2EHPA) [6,7]. The extraction of aluminium(III) and gallium(III) with liquid cation exchangers di-n-butylidithiophosphoric acid (DBTPA) and di(2-ethylhexyl) dithiophosphoric acid (DETPA) in kerosene in the presence and absence of alcohols and TBP has been studied. Both gallium(III) and aluminium(III) extracted in the form of neutral complexes MA₃. The distribution coefficient of gallium(III) was higher than that of distribution coefficient of aluminium(III) [8]. The synergistic extraction of gallium(III) and indium(III) with 2,4-pentendione (Hacac) in heptane and carbon tetrachloride has been studied using 3,5-dichlorophenol (DCP) as a synergist [9]. It was found that the present synergism caused by outersphere complexation improved not only the extraction efficiency but also the
separation efficiency of these metals. Extraction of gallium(III) and indium(III) with LIX®-984 dissolved in n-heptane was studied [10].

A simple and rapid method was proposed for extraction and separation of trivalent gallium, indium and thallium with N-benzylaniline in chloroform[11]. Thallium and gallium were extracted from hydrochloric acid while indium from hydriodic acid. Extraction of gallium(III), indium(III) and thallium(III) with n-octylaniline in chloroform at various concentrations of hydrogen halide acids (HCl, HBr, HI) has been studied and scheme for their separation was proposed [12]. The procedure has been applied to the separation and determination of these metal ions from associated elements. Selective solvent extraction of trivalent aluminium, gallium and indium with tripod quadridentate phenolic ligand, tris (2-hydroxy-3,5-dimethylbenzyl) amine was investigated as fundamental study for their mutual separation [18]. Gallium(III) was extracted almost quantitatively, whereas aluminium(III) and indium(III) were hardly extracted due to steric hindrance. The extraction of trivalent gallium, indium and thallium from aqueous solution containing hydrochloric acid [14] and/or lithium chloride [15] by tributyl phosphate (TBP) and thioctylamine (TOA) in benzene has been investigated. The extraction efficiency of the extractants towards the metal ions have been studied. The extraction of gallium(III), indium(III) and thallium(III) from hydrochloric acid solution and lithium chloride by trioctyl phosphate oxide (TOPO) and tributyl phosphate (TBP) in benzene has been examined under different conditions [16]. The extraction efficiency and various species involved have been calculated. Triocetylphosphine oxide was used as a synergist with 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP) [17]. A method was proposed for the extraction and individual separation trivalent gallium, indium and thallium from
salicylate media using triphenylarsine oxide (TPASO) dissolved in toluene as an extractant [18]. A method permits rapid and precise individual separation of gallium(III), indium(III) and thallium(III) and was applicable to the analysis of alloy samples. A method for the estimation of gallium(III), indium(III) and thallium(III) in geological materials (bauxite, zinc slags) by solvent extraction in to methyl isobutyl ketone (MIBK) in hydrobromic acid medium has been developed [19]. The effect of temperature and hydrochloric acid concentration on extraction of trivalent gallium, indium and thallium by α-hydroxyoxime was studied [20]. The distribution coefficient of gallium(III) and indium(III) decreased, while that of thallium(III) increased with temperature. Synergistic extraction of aluminium(III), gallium(III) and indium(III) with 8-quinolinol (Hq) in chloroform has been studied using 3,5-dichlorophenol (DCP) as the synergist [21].

Aluminium, gallium, indium and thallium are industrially important metals and hence their separation and purification is desired. However, the methods reported in literature are very few for the separation and determination of these metals. Solvent extraction of trivalent aluminium, gallium, indium and thallium from hydrochloric acid solution by acid organophosphorus compounds D2EHPA and EHEHPA was studied [22]. The extraction efficiency of the metals varied as a function of hydrochloric acid concentration. The distribution coefficients for aluminium(III) and gallium(III) increased, while for indium(III) and thallium(III) decreased with increasing temperature in the range 10-50°C. The extent of extraction of aluminium(III), gallium(III), indium(III) and thallium(III) was shown to be dependent on the solvent, the acidity of the aqueous phase and ion pairing reagents such as chlorpromazine or prochlorperazine [23] and promethazine [24]. The effects of time, agitation rate
and the mechanism of extraction were used for separation and determination of these metals.

n-Octylaniline has been employed successfully in this analytical chemistry laboratory for solvent extraction separation of many metals [25-27]. Therefore, it is desirable to have a versatile scheme of analysis for the separation and determination of aluminium(III), gallium(III), indium(III) and thallium(III). In the present work we report on a novel extractant n-octylaniline, which can exhibit specific extraction behaviour for these metal ions from weak organic acid media.

7.2 Extraction scheme for separation of aluminium(III), gallium(III), indium(III) and thallium(III) and its application to synthetic mixture.

The extraction shows that it is possible to separate aluminium(III), gallium(III), indium(III) and thallium(III) from one another. The separation of these metals was based upon use of weak organic acid, masking agent and strippant. The extraction scheme-I is presented in the form of flow sheet, while the results of analysis of synthetic mixtures containing these metals are given in Table 7.1.
Separation Scheme - I (Flow Sheet)

Al(III) + Ga(III) + In(III) + Tl(I) (1mg each)
Adjust the acidity to 0.005 sodium succinate in a total volume of 25 mL and pH 4.0, add 75 mg oxalate as masking agent (to mask Al, In, Tl) extract with 7% n-octylaniline in toluene for one min

Aqueous phase
Al(III) + In(III) + Tl(I) Demask with concentrated hydrochloric acid, adjust succinate concentration to 0.005M, pH 5.0, and 40mg oxalate to mask Al and Tl, extract with 4% n-octylaniline in toluene for one min

Organic phase
Ga(III)
Strip with water (2x25mL)
Determine Ga(III) complexometrically [28]

Aqueous phase
Al(III) + Tl(I)
Demask with concentrated hydrochloric acid, adjust succinate concentration to 0.04M, pH 6.0, extract with 2% n-octylaniline in toluene for one min.

Organic phase
In(III)
Strip with water (2x25mL)
Determine In(III) complexometrically [28]

Aqueous phase
Tl(I)
Decompose succinate, oxidize Tl(I) To Tl(III) by bromine water, adjust salicylate concentration to 0.03M, pH 2.5, extract with 2% n-octylaniline in toluene for 2 min.

Organic phase
Al(III)
Strip with 0.1M E.D.T.A. (2 x 10 mL)
Determine Al(III) complexometrically [28]

Aqueous phase
Rejected

Organic phase
Tl(III)
Strip with Acetate buffer (pH 4.7) (2 x 25 mL)
Determine Tl(III) complexometrically [28]
Separation Scheme –I (Flow Sheet)

**Al(III) + Ga(III) + In(III) + Tl(I) (1mg each)**

Adjust the acidity to 0.005M sodium succinate in a total volume of 25 mL, add 75 mg oxalate as masking agent (to mask Al, In & Tl) and pH 4.0, extract with 7%, n-octylaniline in toluene for one min.

**Organic Phase:** Ga(III); strip with water (2 x 25 mL) and determine Ga(III) complexometrically

**Aqueous phase:** Al(III) + In(III) + Tl(I); demask with concentrated hydrochloric acid, adjust succinate concentration to 0.005M, pH 5.0, add 40 mg oxalate to mask Al and Tl, extract with 4% n-octylaniline in toluene for one min.

**Organic phase:** In(III); strip with water (2 x 25 mL) and determine In(III) complexometrically.

**Aqueous phase:** Al(III) + Tl(I), demask with concentrated hydrochloric acid, adjust succinate concentration to 0.04M, pH 6.0, extract with 2% n-octylaniline in toluene for one min.

**Organic phase:** Al(III), strip with 0.1M E.D.T.A. (2 x 10 mL) and determine Al(III) complexometrically.

**Aqueous phase:** Tl(I), decompose succinate, oxidize Tl(I) to Tl(III) by bromine water, adjust salicylate concentration to 0.03M, pH 2.5, extract with 2% n-octylaniline in toluene for 2 min.

**Organic phase:** Tl(III), strip with acetate buffer (pH 4.7) (2 x 25 mL) and determine Tl(III) complexometrically.
Table - 7.1

Separation of aluminium(III), gallium(III), indium(III) and thallium(III) from their synthetic mixture (1 mg each)

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Aqueous phase (25mL)</th>
<th>Organic phase (10 mL)</th>
<th>Stripping agent</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga(III)</td>
<td>0.005 succinate, pH = 4.0</td>
<td>Toluene</td>
<td>Water (2 x 25 mL)</td>
<td>99.9</td>
</tr>
<tr>
<td>In(III)</td>
<td>0.005 M succinate, pH = 5.0</td>
<td>Toluene</td>
<td>Water (2 x 25 mL)</td>
<td>99.8</td>
</tr>
<tr>
<td>Al(III)</td>
<td>0.04 M succinate, pH = 6.0</td>
<td>Toluene</td>
<td>0.1 M E.D.T.A. (2 x 10 mL)</td>
<td>99.9</td>
</tr>
<tr>
<td>Tl(III)</td>
<td>0.03 M salicylate, pH = 2.5</td>
<td>Toluene</td>
<td>Acetate buffer (pH 4.7) (2 x 25 mL)</td>
<td>99.8</td>
</tr>
</tbody>
</table>
Reference


