Electrolytic production of thallium metal and its oxide from Tl(I) and Tl(III) nitrates

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The cathodic and anodic deposition of thallium as a pure metal or its oxide from different baths containing Tl(I) or Tl(III) nitrates with some suitable additives has been investigated. The quantity and quality of the metal and its oxide have been found to be dependent on the type of the bath used. The effect of different parameters such as pH (1-12), current density (0.01-4.0 A dm\(^{-2}\)), temperature (20-60°C), electrode type (platinum and graphite), metal and additives concentration on the cathodic and anodic efficiencies and on the quality of deposit has been studied. The interfering effect of some cations and anions has also been studied. Spectrophotometric, polarographic, AAS and X-ray diffraction techniques revealed the purity of separated deposit to be 99.9%. A suitable mechanism for the formation of the element and its oxide is suggested. An analytical application for preconcentration and separation of thallium from its natural ores and alloys using the proposed electrolytic method has been found to be satisfactory and successful.

Thallium and its salts are extremely toxic, hazardous, skin contact ingestion and inhalation are all dangerous, also have great effect on plants, animals and human. Its compounds are used for destroying vermin, lice worm and ant. The thallium(II) and OH free radical induce damage to DNA and trypsin as complex in individual biomols. Since TIBr and TII are transparent to long wavelength, there are possibilities for their use in photosensitive diode and infrared detector.

Few electrochemical methods were found in literature about thallium and Tl\(_2\)O\(_3\) production. Cathodic deposition of thallium was studied by Fouda\(^2\) from aqueous baths containing some additives such as Cl\(^-\), F\(^-\) and SO\(_4\)\(^{2-}\) at current density of 0.4 A dm\(^{-2}\) and pH = 9. Toney et al.\(^5\) deposited thallium on Ag and Au as a monolayer. Under controlled potential thallium was deposited on polycrystalline Ag and Au substrate. The co-deposition under controlled potential of Pb and Tl (1:2) on polycrystalline Ag was also investigated.\(^8\)

In the present investigation, efforts have been made to determine the optimum conditions for production of highly pure Tl and Tl\(_2\)O\(_3\), by electrodeposition, and to develop a simple and rapid electrolytic preconcentration and separation of Tl from its natural ores and minerals.

**Experimental Procedure**

A standard solution of Tl(I) and Tl(III) nitrate was prepared by dissolving the required amounts of AR grade product in bidistilled water. The Tl(III) content was determined by titration with standard Na\(_2\)EDTA solution using xylenol orange indicator, whereas Tl(I) was analysed gravimetrically as Tl I. All other chemicals used were of AR quality and used without further purification.

A double wall electrolytic cell with two compartments separated by a porous diaphragm and connected to an ultrathermostate (± 0.05°C), was used. The catholyte was provided with a platinum sheet electrode or cylindrical graphite electrode, whereas the anode was a platinum wire, and vice-versa during anodic deposition. The electric current was supplied from a constant current device and a digital multimeter (PM-2517X). All the electrode potentials were measured with reference to SCE at 25 ± 0.05°C.

The metal deposit or its oxide was dissolved in 5 mL hot nitric acid and made up to 25 mL by bidistilled water and was analysed spectrophotometrically, after quantitative oxidation to Tl(III) by Br\(_2\)-water, using semi-xylenol orange in acetate buffer (pH = 4, I = 0.1 (KNO\(_3\)), at \(\lambda = 520\) nm).\(^{13}\)

The average current-voltage curves were recorded by polarograph model E-506 (Metrohm Herisau Switzerland) in acetate buffer, pH = 4. Perkin-Elmer model 2380 AAS was used with Pye Unicam hollow cathode lamp for thallium estimation, \(\lambda = 276.8\) nm.
Moreover, the metal deposit and its oxide were subjected to X-ray diffraction measurements using a method described earlier (PW 1846· Philips· PW generator, 2θ range 10-90°, with CuKα, λ = 1.542 Å and Cu filter). Analysis gave purity of Tl metal 99.99% on the cathode. The metal has a hexagonal close packed crystal with 2θ, 32.0°, 32.5° and 68.2°. The process of crushing, grinding (100 mesh), decomposition by different fusion mixtures and dissolution of various ores samples were carried out as described in literature. For each sample = 0.5 g was dissolved in aqua regia. In order to remove the interferences of other cations, selective precipitation of thallium as TlII followed by dissolution was carried out. Thallium (III) ion (formed by the action of aqua regia), was reduced by 1 g sodium sulphite, adjusting the pH to 4 and filtering any precipitate formed. To the clear solution 0.5 g of Na2EDTA and 5 mL of 1M KCN were added and heated to about 80°C in fuming cupboard. Finally, 0.3 g KI was added to the hot solution with constant stirring until the formation of yellow precipitate. After 1 h Tl(I) iodide was separated and dissolved in aqua regia and subjected to the electrolysis using thiosulphate bath.

Results and Discussion

The effect of different parameters which play an important role in the deposition process was extensively studied in order to determine the optimum conditions necessary for the electrolytic production of the metal and its oxide.

Effect of different baths—The baths were arranged according to the current efficiency (cathodic or anodic). The maximum current efficiency (percentage) was found to be 48% in case of Tl+ nitrate using MeOH bath and 98.1% for Tl3+ nitrate from thiosulphate bath. The stoichiometry of Tl+ and Tl3+ complexes was confirmed by conductometric titration of both Tl+ and Tl3+ nitrates solutions.

Effect of pH—The effect of pH on cathodic and anodic current efficiency of some selected baths was studied at pH values varied from 1 to 12 under certain specific conditions. It has been observed that the best efficiency was obtained in the pH range of 6-8. This range was decreased to a value of 4 during deposition of metal from Tl+ using thiourea (TU) bath. No deposition occurred below pH of 2 for most baths. This may be due to the attack of the deposit by hydrogen ions resulting in its dissolution (Fig. 1). On the other hand, at higher pH values a decrease in current efficiency was observed, which may be due to: (i) hydroxide formation, (ii) non-adherent nature of deposit and (iii) higher polarization at higher pH.

Cathodic efficiency (CE %)—Fig. 2 reveals a gradual increase in CE % (except TU bath) with increasing current density during deposition of metal from Tl3+ or Tl+ on a Pt-electrode until a maximum value was found to be 95-99% (according to bath type) at 0.4 A dm⁻² in case of Tl3+ and 55-79% at 0.2 A dm⁻² for Tl+. Such increment may be attributed to the increase of positive
charge on the metal ion. Above these current densities, a continuous decrease in CE % was observed and then tend to flatten out with rising current density.

A minimum value of 7.5-4.9% for Tl⁺ and 13.5-7.5% for Tl³⁺ was obtained at a current density of 4 A dm⁻². This is due to the competition of hydrogen evolution with metal deposition at cathode. At current density < 0.02 A dm⁻² a very thin film of metal was obtained from most baths which may be attributed to the low rate of cathodic reduction. On the other hand, at current density > 0.5 A dm⁻² a randomly oriented, large crystals deposit was found. The use of graphite electrode lead to the increase in AE % by 8% (at 0.4 A dm⁻², DMA and EDA). This may be attributed to higher value of oxygen overvoltage on Pt than graphite. On using glycerol bath a large decrease of ~ 53% (at 0.4 A dm⁻²) was observed, which may be due to the blocking of active centres on the graphite electrode by glycerol.

**Anodic efficiency (AE %)**—The percentage anodic efficiency as a function of current density for Tl₂O₃ deposition on Pt-electrode from Tl⁺ using different baths was determined. As expected from anodic polarization curve, the current efficiency curves fall sharply at first and then tend to flatten out with rising current density (Fig. 2). This is due to the competition of oxygen evolution with Tl₂O₃ deposition. The maximum values of AE % range from 92-99% (according to the bath used) were found below 0.1 A dm⁻². At current density > 0.4 A dm⁻², a non-adherent randomly oriented deposit was obtained. The most suitable CD ranges from 0.2-0.4 A dm⁻². The use of graphite electrode led to the decrease in AE % by 8% (at 0.4 A dm⁻², DMA and EDA). This may be attributed to higher value of oxygen overvoltage on Pt than graphite. On using glycerol bath a large decrease of ~ 53% (at 0.4 A dm⁻²) was observed, which may be due to the blocking of active centres on the graphite electrode by glycerol.

**Effect of metal ion (Tl⁺, Tl³⁺) concentration**—The effect of thallium ion concentration in the catholyte on CE % was studied in the range from 0.1-200 mg/L, at constant ligand concentration. It was found that the CE % increased sharply at first on increasing the thallium ion concentration in the concentration range 0.5-25 mg/L, then reached a maximum value of 100% and 90% for TU and MeOH on using Tl⁺. In case of Tl³⁺ using S₂O₅²⁻ and alizarin yellow (AY), the maximum value of CE % (100%) was obtained at ~ 25 mg/L of Tl³⁺. Also the anodic current efficiency was reached 100% at metal ion concentration = 25 mg/L for glycerol and methanol baths. At lower value of thallium ion concentration < 0.5 mg/L, no cathodic and anodic depositions were occurred from any used bath.
KENAWY et al.: ELECTROLYTIC PRODUCTION OF THALLIUM METAL

Table I—Analytical results of thallium separation from different samples

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Sample name and occurrence</th>
<th>Tl found</th>
<th>S_2</th>
<th>Tl (standard), AAS method, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(a) Synthetical sample:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tl 10%, Cu 50%, Zn 10%, Al 10%, Ni 10%, Fe 10%</td>
<td>9.90</td>
<td>1.01</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>Tl 10%, Zn 50%, Ag 10%, Cd 10%, Pb 10%, Se 8%, Te 2%</td>
<td>9.90</td>
<td>0.92</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Tl 10%, In 10%, Pb 45%, CO 5%, Ni 15%, Cr 15%</td>
<td>9.95</td>
<td>0.95</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Tl 10%, In 30%, Al 40%, Ga 5%, Ni 15%, Cr 15%</td>
<td>10.10</td>
<td>0.5</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>Tl 5%, Cd 90%, Cu 5%</td>
<td>4.95</td>
<td>0.40</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>Tl 1%, Fe 30%, As 10%, Se 10%, Te 10%, Cd 30%, Zn 9%</td>
<td>1.02</td>
<td>0.35</td>
<td>1.0</td>
</tr>
</tbody>
</table>

(b) (Ore sample & alloy)*

1. Crookes, Te mineral
2. Hutchinsonite mineral
3. Marcasite mineral
4. Lorandite mineral
5. Urbaitite mineral
6. Cassiterite ore
7. Aluminium alloy

Duba, Dubal factory.

*Average of three weighed samples (0.5-1 g)/100 mL.
S_2, is the relative standard derivation.
n is the number of repetition of experiment.

Effect of complexing agent (ligand) concentration—It has been found that the maximum efficiency of thallium metal and thallium oxide deposition occurred at certain concentration range of ligand. For thallium (III) nitrate ten milligrams per litre of TU and sodium thiosulphate were necessary. For the anodic deposition of thallium (III) oxide from Tl^+*, 20 mg/L of DMA and 50 mg/L of glycerol were found to give maximum efficiency.

Effect of temperature and time—Increasing the bath temperature from 30 to 60°C favoured the deposition of metal or its oxide and led to the rise in the recovery percentage (R%) from 60 to 80% for Tl^+ (TU bath); 80-90% for Tl^3+ (S_2O_3^- bath) and 57-72% for Tl_2O_3 (glycerol bath). This was attributed to the acceleration of deposition, ionic migration and fast evolution of H_2 or O_2 gases adsorbed on the electrode surface.

Also the effect of deposition time was studied in the range 2-40 min. (Pt. electrode CD = 0.4 A dm^-2 and T = 25°C). At time < 5 min a very thin film of cathodic or anodic deposit was obtained. Increasing the deposition time led to a sharp increase in recovery, R%, till ~ 10 min, then a gradual rise of recovery, R%, was observed. This may be due to: (i) decrease of metal ions concentration which causes a lower rate of deposition; (ii) change of electrode surface and pH during deposition which change metal over voltage.

Analytical Application for Separation of Thallium

A simple method for quantitative separation of thallium as a pure metal is based on masking all interfering ions, which may be present with it in synthetic alloys or natural ores by the strongest complex-forming agents such as Na_2EDTA and/or CN^- according to the cations present. Following this method thallium (I) was precipitated as Tl_2S (K_sp = 6.8 x 10^-8) which was dissolved in aqua-regia. The resulting solution was subjected to electrolysis conditions in order to obtain a pure metal.

It was found experimentally, using the proposed method that it was possible to separate Tl from a large number of samples containing; Pb^2+, Cu^2+, As^3+, Fe^3+, Se^4+, Te^6+, Sb^3+, Cd^2+, Ag^+, Zn^2+, In^3+, Al^3+, Ga^3+, Ni^2+, Co^2+ and Cr^3+.

The analytical results of determination of Tl^3+ in a series of synthetic samples and naturally occurring ores containing thallium with another metals are shown in Table 1. These results (average of two determinations for three different weighed samples) are in good agreement with the value obtained by the standard classical method. The
relative standard deviation as calculated by the range method\(^{19}\), was found to be 0.35-1.30% (AAS method). From the analytical result, it is clear that the preconcentration by electrodeposition for thallium in ore alloys and synthetical samples are simple, reliable and can be applied with good reproducibility.

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References