CHAPTER 1

INTRODUCTION

The elements of group III A studied in this thesis are
gallium, indium and thallium. They were all discovered through
spectroscopic means between 1860 - 1875 (1). The name thallium refers
to its green spectrum, and the name indium, to its indigo-blue spectral
lines. However, gallium is named in honor to France. These three
elements are extremely rare. Gallium, indium and thallium are on the
borderline between ionic and covalent character in their compounds.
The trivalent state is important for these three elements, but the
univalent state becomes progressively more stable as the element
descended in the group (2). In spite of the higher positive charge on
their ions, they do not show as great tendencies to form "coordination
compounds" or "complexes" as zinc, cadmium and mercury do (1).

Gallium is normally trivalent and forms compounds as Ga_2O_3,
Ga_2S_3, $Ga(OH)_3$, $GaCl_3$, GaN, GaAs, etc. Gallic ion, Ga (III), in the
presence of carbonate is completely hydrolyzed, leading to the pre-
cipitation of the hydroxide (1). The sulfates, nitrates and halides
are soluble, but the solutions are highly hydrolyzed and precipitated
as basic salts upon boiling (1). Ga (III) in perchlorate solution,
the aquo ion, $\left[Ga(H_2O)_6\right]^{3+}$, appears to be the main species and the
hydrolysis, which is exceedingly slow at $25^{\circ}C$, gives only white
crystalline GaOOH (2).

Indium is normally trivalent and forms compounds as In_2S_3,
$In(OH)_3$, $InCl_3$, In_2O_3, InN, etc. The hydroxide is soluble to a

very small extent in strong alkali hydroxide (but not in dilute
ammonia solution), probably forming indate ion, InO_2^- (1). The
carbonate is slightly soluble and hydrolyzed. It is soluble in
excess of ammonium carbonate but not in excess of sodium carbonate.
The nitrates, sulfates, alums and halides are soluble (1). Indium
aquo ion, $\left[In\ (H_2O)_6\right]^{3+}$, is known in perchlorate solution, but in
the presence of halide and other complexing anions the complex species
such as $InSO_4^+$ is formed (2).

For thallium, the unipositive state is quite stable. In
aquous solution Tl (I) is distinctly more stable than Tl (III) by
its reduction potential (2);

$$Tl^{3+} + 2e = Tl^+ \quad E^o = +1.25\ V\ (+0.78\ V\ in\ 1\,M\,HCl,\ +1.26\ V\ in\,1M\ HClO_4)$$

Thallic ion, Tl (III), is a strong oxidizing agent, and is reduced to
thallous ion, Tl (I). Thallous ion is not very sensitive to pH,
although the thallic ion is extensively hydrolyzed to $TlOH^{2+}$ and
the colloidal oxide Tl_2O_3, even at pH 1 - 2.5 (2). The redox potential
is hence very dependent on pH as well as on the presence of com-
plexing anions. Thus, as indicated by the above potentials, the pre-
sence of chloride stabilizes Tl (III) more than Tl (I) by the formation
of complexes, and the potential is thereby lowered (2). Thallic
compounds decompose in general, upon heating, with the formation of
the thallous compounds, e.g. $TlCl_3 = TlCl + Cl_2$. TlOH is fairly
soluble and is a strong base while $Tl\ (OH)_3$ is extremely insoluble.
Thallous sulfate, nitrate and acetate are moderately soluble in water,
the halides are sparingly soluble and the solubility is decreased
by the presence of excess halide ion except for the very soluble TlF.

Thallic sulfate and nitrate are soluble and highly hydrolyzed.
Thallic chloride, $TlCl_3$, forms complex ions with excess chloride,
and a complex thallous chlorthallate exists, $Tl^+(Tl^{3+}Cl_4)$ (1).
$TlBr_3$ is quite similar to the chloride, but the iodide, TlI_3, is
probably thallous triiodide. The sulfide, Tl_2S_3, is very unstable,
and form thallous sulfide and sulfur. With the exception of those
with halide, oxygen and sulfur ligands, Tl (I) gives rather few
complexes such as dithiocarbamates, which are useful reagents for
the synthesis of other metal dithiocarbamates (1, 2).

Gallium, indium and thallium can form organometallic compounds
but are unstable . The important one is that thallium can form
organomethallic compounds, such as TlC_5H_5 which is a very useful
reagent for preparation of other metal cyclopentadienyl compounds (2).

Some physical properties of gallium, indium and thallium
are listed in Table 1.1 (3), and their standard reduction potentials
are summarized in Table 1.2 (4).

These three elements are markedly used in the recent years.
Gallium, the only metal except mercury, cesium and rubidium, which
can be a liquid near room temperature, which makes it possible to be used in
high temperature thermometers. Its most important use is in inter-
metallic compounds (particularly with As, Sb or P) for use in
semiconductors and producing solid-state devices, such as transistors.
Gallium arsenide diodes which convert electrical energy into modulated
infrared radiation can be used for multichannel line-of-sight com-
munications. Magnesium gallate containing divalent impurities, such
as Mn^{2+}, is found using in commercial ultraviolet activated powder

Table 1.1 Physical properties of gallium, indium and thallium (3)

	Gallium	Indium	Thallium
Symbol	Ga	In	Tl
Abundance in Earth's crust (mass %)	1.5×10^{-3}	1×10^{-5}	3×10^{-5}
(atom %)	4×10^{-4}	1.5×10^{-6}	3×10^{-6}
Abundance in sea water (g/ton)	5×10^{-4}	-	present (organic)
Atomic number	31	49	81
Electronconfiguration	$[\text{Ar}]\,3d^{10}\,4s^2\,4p^1$	$[\text{Kr}]\,4d^{10}\,5s^2\,5p^1$	$[\text{Xe}]\,4f^{14}\,5d^{10}\,6s^2\,6p^1$
Atomic weight	69.72	114.52	204.37
Isotope, natural, abundance (%)	^{69}Ga (60.2)	^{113}In (4.23)	^{203}Tl (29.50)
	^{71}Ga (39.8)	^{115}In (95.77)	^{205}Tl (70.50)
Atomic radius	1.30	1.55	1.90

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Table 1.1 (continued)

	Gallium	Indium	Thallium
Melting point (^{o}C)	29.780 ± 0.005	156.17 ± 0.05	302.4
Boiling point (^{o}C)	ca 2250	2070	1453
Crystal structure	orthorhombic	tetragonal	α hexagonal, β cubic
Density (g/cm^3) at 20°C	5.907	7.31	α 11.85, β 11.86 – 11.87
Ionization energies, eV (and kcal/g-atom)			
1st	6.00 (138.4)	5.785 (133.4)	6.106 (140.8)
2nd	20.51 (473.0)	18.86 (434.2)	20.42 (470.9)
3rd	30.70 (705.6)	28.03 (643.4)	29.8 (685)
4th	64.2 (1471)	54.4 (1333)	50.7 (1165)

Table 1.2 Standard reduction potentials of gallium, indium and
thallium vs standard hydrogen electrode (SHE) (4).

Reaction	Volts
$Ga^{3+} + 3e = Ga$	-0.560
$H_2GaO_3^- + H_2O + 3e = Ga + 4OH^-$	-1.22
$In^{2+} + e = In^+$	-0.40
$In^{3+} + e = In^{2+}$	-0.49
$In^{3+} + 2e = In^+$	-0.40
$In^{3+} + 3e = In$	-0.338
$Tl^+ + e = Tl$	-0.3363
$Tl^+ + e = Tl(Hg)$	-0.3338
$Tl^{3+} + e = Tl^{2+}$	-0.37
$Tl^{3+} + 2e = Tl^+$	1.247
$Tl^{3+} + 2e = Tl^+$ (1 F HCl)	0.783
$TlBr + e = Tl(Hg) + Br^-$	-0.606
$TlCl + e = Tl(Hg) + Cl^-$	-0.555
$TlI + e = Tl(Hg) + I^-$	-0.769
$Tl_2O_3 + 3H_2O + 4e = 2Tl^+ + 6OH^-$	0.02
$TlOH + e = Tl + OH^-$	-0.3445
$Tl(OH)_3 + 2e = TlOH + 2OH^-$	-0.05
$Tl_2SO_4 + 2e = Tl(Hg) + SO_4^{2-}$	-0.4360

phosphors (4, 5). In addition, gallium has the unique property of being concentrated in the bones, because of this selective action, the radioactive gallium has been used in the diagnosis of bone cancer (6). Indium has found an application in making low-melting alloys. It is used in making bearing alloys, germanium transistors, rectifiers, thermisters and photoconductors (4). It can be plated onto metal and evaporated onto glass, forming a mirror as good as that made with silver but with more resistance to atmospheric corrosion (4). While thallium with sulfur or selenium and arsenic produced low melting glass, thallium oxide has been used to produced glasses with a high index of refraction. Thallium bromide-iodide crystal has been used as infrared detectors, as well as thallium sulfide whose electrical conductivity changes with an exposure to infrared light are used in photocells (4, 5).

The toxicity of compounds due to gallium or indium content is low, it depends upon the type of compounds and the means of administration. Individuals exposed to gallium or indium compounds during the production of metal suffer from tooth decay, pain in joints and bones, nervous and gastrointestinal disorders, heart pain , and general debility (3). For oral administration, lethal doses for gallium and indium nitrates are 3.28 and 4.2 grams per kilogram, respectively (3). There is some disagreement over the fatal dose for subcutaneous or intramuscular injection of ionic indium. However, gallium and indium are both linked to tumor formation (7).

Thallium compounds are toxic, especially thallous solution. Many serious or fatal poisonings have resulted from accidental or

therapeutic ingestion or external application of materials containing thallium. The human lethal dose of thallium sulfate is about 1.75 grams. Thallium is readily absorbed following ingestion, it is also absorbed by the skin. It can associate with potassium, accumulate in erythrocytes, agglutinate and lyse erythrocytes, and also accumulate in kidney, bone and soft tissue (7). Moreover, it is a cumulative poison (only 3.2% of body burden is excreted per day (3). It has a lethal dose of 0.026 gram per kilogram (7). It causes gastrointestinal and nervous system disorder and also causes loss of hair. Evidence of acute poisoning appears in 1 - 5 days. Radiographic studies of thallium poisoned human beings reveal hepatic opacity due to the presence of thallium in the liver. The recommended maximum atmospheric concentration (8 hours per day)is 0.1 milligram thallium per cubic meter (3).

Gallium, indium, and thallium have been found in trace level in minerals, ores, rocks, natural water, blood, urine, biological tissues, etc. The significant uses of gallium, indium and thallium in modern tools as well as the tremendous toxicity of their compounds to human being enthuse the author to search for methods that will give more sensitivity and selectivity in analyzing and recovering them. In addition, the anodic stripping voltammetry, ASV, was chosen for this study because of its ability to simultaneously determine several elements at concentration level ranging down to the fraction part per billion range with relatively

inexpensive instrumentation. Moreover, the technique clearly offers capabilities for solving of numerous difficult trace analysis problems (8).

The fundamental of an ASV measurement involves two discrete steps. The deposition step, the analytical species is firstly reduced (electrodeposited, plated) onto or into the working electrode; and is secondly oxidized (stripped, electrolyzed) back into the electrolyte solution, which is known as stripping step. For the deposition step, a suitable electrode is maintained at a potential cathodic of the reduction potential of the element (s) to be determined. The metals to be deposited arrive at the electrode surface at rates determined by their respective concentrations, the diffusion property of the electrolyte solution, and the area of the electrode used. The deposition time is consequently carefully measured. The deposition results in preconcentration of the analyte (s) into a small (surface) volume. To strip this material from the electrode, the potential is systematically changed back in the direction required for oxidation. At the oxidation potential of each analytical species, the faradaic current produced by its oxidation is measured.

For a single metal ion species (M^{n+}) being reduced at an electrode surface, it can be shown that the current flow (the deposition current at time t) is reasonably approximated by the Levich equation (8):

$$i(t)_{dep} = 0.62 \, nFAD^{2/3} \omega^{1/2} \mu^{-1/6} C(t)$$

where $i(t)_{dep}$ = limiting current of deposition time t, ma

n = number of electrons transfer

F = the Faraday constant, 96,494 coulombs

A = the electrode surface area, cm^2

D = diffusion coefficient, $cm^2 sec^{-1}$

ω = the rate of electrode rotation or solution stirring ($\omega = 2\pi N$, with N = rps)

μ = the kinematic viscosity of the solution, $cm^2 sec^{-1}$

C(t) = the ion concentration of deposition time t, mole cm^{-3}

The stripping current due to oxidation of each analyte is proportional to the concentration of the analyte on or in the electrode and, thus, in the analytical solution. The oxidation potentials have the same qualitative meaning as their half wave potentials in polarography (9). Several different current-potential curves may be used to strip the deposited analyte from the electrode and obtain the quantitative parameter, the stripping peak current, i_p, which is given by Randles-Sevick equation (10):

for reversible process

$$i_p(rev) = 602 \, n^{3/2} A D^{1/2} v^{1/2} C^b \quad (X')$$

and for irreversible process

$$i_p(irr) = 602 \, n(\propto n_a)^{1/2} A D^{1/2} v^{1/2} C^b \quad (X'')$$

where i_p = stripping peak current, ma

D = diffusion coefficient, $cm^2 sec^{-1}$

V = rate of potential change or scan rate, volt sec^{-1}

C^b = concentration of oxidizable species in bulk

solution, mole cm^{-3}

α = electron transfer coefficient

n_a = number of electrons in the rate determining step

X' = a current function for the reversible process

with the maximum value = 0.4463

X'' = a current function for the irreversible process

with the maximum value = 0.4958

Thus, the value of i_p is seen to be directly proportional to C^b and $V^{1/2}$.

If the rate of the electron transfer reaction is very rapid compared to the mass transport, the electrode reaction is called reversible process. On the other hand, if the electron transfer rate is relatively slow, such reaction is called irreversible process (10).

The simplest instrumentation required for ASV includes a three electrode potentiostat and voltage ramp generator, current measuring circuitry; a cell with working, reference and counter electrodes; and a recorder or other readout device. Instruments designed for dc, ac or pulse polarographic measurements are generally quite adequate for stripping application (8).

Materials applied as working electrodes for ASV are in a wide range such as Hg, Pt, Au, Ag, Bi, B_4C and C. Some of the noble metals have a mutual tendency for the formation of intermetallic

compounds, i.e., AgHg. To avoid this, a carbon electrode is often used (8, 10). Thus, a glassy carbon (vitreous carbon) is used in this research, because of its special physical and chemical properties which were previously described in reference 11.

In the present study, the condition for Ga (III), In (III) and Tl (I) ions to electrodeposit at the glassy carbon electrode are investigated. The optimum conditions involving type and concentration of electrolyte, pH of the test solution, and deposition potential can be obtained by performing its cathodic voltammetry. The deposition time and stripping conditions (range of potentials for ASV) for the element determined are tested by its anodic stripping voltammogram. The sensitivity of each condition is examined by the stripping current. In addition, the mixtures of these three elements are also studied by ASV technique.