1982

Application of Electroanalytical Techniques to Environmental Thallium Compounds.

Linda Katherine Hoeflich
Louisiana State University and Agricultural & Mechanical College

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APPLICATION OF ELECTROANALYTICAL TECHNIQUES TO ENVIRONMENTAL THALLIUM COMPOUNDS

The Louisiana State University and Agricultural and Mechanical Col.  PH.D.  1982

University Microfilms International  300 N. Zeeb Road, Ann Arbor, MI 48106
APPLICATION OF ELECTROANALYTICAL TECHNIQUES
TO ENVIRONMENTAL THALLIUM COMPOUNDS

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in
The Department of Chemistry

by
Linda Katherine Hoeflich
B.A., Goucher College, 1977
May 1982
To Mom and Dad,

with love and thanks
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ABSTRACT

Because of increasing concern over global pollution by the energy production industry, especially large, centralized utility complexes, the quantitation and speciation of heavy metals have taken on great importance. These metals are emitted with coal fly ash and may be subsequently deposited in natural waters. Complications arise when certain inorganic compounds undergo biomethylation by microbial action in these waters. Therefore, procedures must be developed to analyze and differentiate the mixture of inorganic and organometallic compounds present.

This work is a study of the electrochemical properties of inorganic and organothallium compounds. The toxicological significance of thallium compounds is known, and their presence in coal fly ash and natural waters indicates a need for study of their mixtures. Environmental concentrations are thought to be in the ppb range so that very sensitive quantitation procedures must be developed.

After discussions of the current literature and the theory pertinent to this work are presented, the experimental procedures for electrochemical analyses are described. Cyclic voltammetry experiments allowed the determination of the irreversible nature of the electron transfer reactions of organothallium compounds used, (CH$_3$)$_2$TI and (CH$_3$)$_2$TINO$_3$, and described the transfer coefficients and rate constants for them. The similarity of these respective coefficients as well as the diffusion coefficients found by normal pulse polarography confirmed
their ionic nature, appearing as \((\text{CH}_3)_2\text{Tl}^+\), in aqueous solutions. Also, it was shown that they undergo a three-electron reduction to \(\text{Tl}^0\).

Routine analytical methods were developed for mixtures of \(\text{TlNO}_3\) with \((\text{CH}_3)_2\text{TlI}\) and \((\text{CH}_3)_2\text{TlNO}_3\) using differential pulse polarography (DPP) and differential pulse anodic stripping voltammetry (DPASV). Direct speciation and quantitation of these solutions were accomplished with DPP at the ppm level. DPASV allows the same analyses at the ppb level by making use of the different electrolysis potentials of the compounds. This method is applicable to other metal systems and is adaptable to field analyses.
INTRODUCTION

The past twenty years have been characterized by an increasing awareness of the potential for global environmental pollution from a variety of sources. One of the major contributors is the energy production industry, particularly the large, centralized utility complexes. Problems of universal concern include the environmental impact of stack gas effluents and residual waste products. Recently, special emphasis has been given to the quantitation and speciation of heavy metals in environmental samples because of their emission with coal fly ash and subsequent deposition into natural waters. The problem is complicated by the fact that certain inorganic compounds have been shown to be biomethylated to organometallic forms by microbial action in these waters. Thus, analytical procedures must be designed which allow for the determination of total heavy metals and the subsequent differentiation of the chemical species present.

One of the heavy metals of interest is thallium because of its potential toxicological significance. This metal undergoes a series of bioenvironmental transformations and, although it is not present at concentrations as high as other heavy metals, its inorganic compounds are considerably more toxic than the corresponding species of other heavy metals. Environmental concentrations of thallium and thallium compounds are thought to be at the part-per-billion level so that any method chosen must be able to quantitate and speciate these materials at
these very low concentrations. In addition, for full utility the analytical methods must be adaptable to field use.

Electrochemical methods are obvious choices for the study of the speciation of metal compounds at low levels in environmental samples, as discrimination between various components is easily obtained. While organothallium moieties have been analyzed by some of these procedures, various constants and parameters have not been described that would allow comparison of the thallium system to others that are environmentally significant. In addition, no specific procedures have been developed which will allow routine analyses at the low levels expected in natural samples. Thus this study was undertaken to develop the background electrochemical parameters and the routine analytical procedures which could be applied to environmental thallium assessment. Emphasis has been placed on the speciation of the thallium systems and the environmental chemistry of the organothallium materials rather than on the description of absolute detection limits.

This report is organized to provide insight into the important questions surrounding environmental thallium. A survey of the literature describing the sources and toxicity of thallium is provided and some of the analytical methods already in use are described. This overview of the current status of the problem is followed by an outline of the theoretical considerations necessary for the understanding of the electroanalytical techniques to be developed. A discussion of the results obtained and the conclusions that can be substantiated from the work are summarized. Finally, recommendations for extensions of this study are provided.
LITERATURE SURVEY

Introduction

In 1861, Sir William Crookes noticed a definite, sharp green line emitted from a sample of metal obtained by the distillation of selenium. When compared to the emission of pure selenium, Crookes concluded that he had observed a new element, and named it thallium. It was independently discovered in France by Professor A. Lamy.¹

Thallium has found use in the electrical and electronic industries (photocells, semiconductors, scintillation counters), and as a catalyst in organic synthesis. It also has been used in rodenticides and depilatory agents for treatment of ringworm. Toxic doses were often given children who had ringworm and after many accidental, homicidal and suicidal poisonings, the use of thallium in rodenticides was banned in the U.S. in 1972.

Human exposure to thallium, therefore, is now limited to environmental and minor industrial sources. The toxicity of organothallium compounds is not known at this time, though analytical methods must be developed to detect the very low environmental levels. The purpose, then, of this research will be to characterize and develop detection methods for alkylthallium compounds, especially those suspected of being in the environment.
Environmental Presence of Thallium

Geochemical

Thallium is found in the very rare minerals lorandite, vrbaite, hutchinsonite, crookesite and avicennite, which form in the arsenic-antimony or lead-zinc deposits in the very last stages of the hydrothermal process. These deposits occur primarily in Switzerland, Yugoslavia, the Caucasus, and Soviet Central Asia.

Having an average crustal abundance of 1 ppm, nearly all the thallium is carried in potassium minerals. The thallous ion, Tl\(^+\), has a coordination number of at least eight in silicates, and is thus associated with alkali metals of large ionic radii. Tl\(^+\) (ionic radius \(= 1.49\AA\)) fits more readily into K\(^+\) (ionic radius \(= 1.33\AA\)) sites in minerals where potassium occurs in high coordination (octahedral or dioctahedral) rather than the low coordination (tetrahedral) configuration. Thallic ion, Tl\(^{3+}\), has an ionic radius of 0.95\(\AA\), and may substitute for Ca\(^{2+}\).

In most natural environments, thallium is present in univalent compounds as indicated by the high redox potential of the Tl\(^+\)-Tl\(^{3+}\) couple (+1.25V at pH 0, +0.82V at pH 7). However, under certain highly oxidizing aqueous conditions, Tl\(_2\)O\(_3\) may be formed and subsequently absorbed by MnO\(_2\) or may penetrate the Mn\(_2\)O\(_3\) lattice. This absorption explains the thallium enrichment of oceanic manganese nodules and certain US and USSR manganese oxide deposits.

Thallium is largely retained during rock weathering and may be enriched in clay, silt and loam from weathering granodiorite, andesite and shale. Ionic adsorption on clay sediments explains why eroded
thallium, like other large alkali ions, is impoverished in the oceans. Thallium becomes enriched in sediments in strong reducing environments where organic matter is accumulating under quiet, anaerobic conditions. In strongly oxidizing conditions, $\text{Tl}^+\text{ will be removed from solution as Tl}^{3+}$ by precipitation with manganese or iron. In general, then, it appears that $\text{Tl}^+$ will be the species transported by groundwater, although there is some argument for $\text{Tl}^{3+}$ transport. Humic acid and $\text{Ca}^{2+}$ have been shown to have no complexing effect on thallium in water at neutral pH's $^2$.

**Industrial Processes**

Thallium is produced commercially from $\text{H}_2\text{SO}_4$ plant materials (especially dusts collected to purify pyritic roasting gases used as a source of $\text{SO}_2$) and from dusts collected from the roasting and smelting of zinc, lead and copper sulfide concentrates. It has also been recovered in hydrometallurgical processes, including the purification of zinc sulfate solutions in electrolytic zinc refining and lithopone production.

The only US company to isolate pure $\text{Tl}$ or $\text{Tl}_2\text{SO}_4$ on a commercial basis within the past 50 years is the American Smelting and Refining Company, Inc. (ASARCO, Inc.). They recover the thallium products electrolytically at their cadmium refinery in Denver, where the intermittent production never exceeds five tons annually $^3$.

Because of thallium's association with sulfide minerals, the processing of these for zinc, cadmium, lead, copper, gold and other metals, as well as for sulfuric acid, is probably the largest potential source
of mobilized thallium, although not necessarily of environmental releases. Most of the wastes from these processes are held in tailings ponds, slag dumps and other confined areas, though leaching is possible. Production of materials such as iron and steel, manganese and ferro-alloys, mica and feldspar, and potash may produce significant thallium emissions due to the high thallium concentrations in at least some of the raw materials used.

Recovery in these processes is possible. The thallium compounds (probably \( \text{Tl}_2\text{S} \), \( \text{Tl}_2\text{SO}_4 \) and various oxides) are volatile and collect in the flue dusts from copper, lead and zinc smelting operations. The ASARCO thallium and cadmium recovery method recovers 75% of the thallium present, and uses the following process.\(^3\)

\[
\begin{align*}
\text{Raw material from} \\
\text{Smelting Pb and Zn} \\
\text{Sulfide ores} \\
(2-2,000 \text{ ppm Tl})
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{SO}_4 & \rightarrow \text{CdSO}_4 + \text{Tl}_2\text{SO}_4 \\
\text{electrolysis} & \rightarrow 5-20\% \text{Tl-Cd alloy}
\end{align*}
\]

\[
\begin{align*}
\text{Hot H}_2\text{O} & \rightarrow \text{TlOH} \\
\text{Cd(OH)}_2 & \rightarrow \text{CdCO}_3 + \text{TlOH} \\
\text{1) Filter-CdCO}_3 & \rightarrow \text{Tl}_2\text{S}
\end{align*}
\]

\[
\begin{align*}
\text{H}_2\text{SO}_4 & \rightarrow \text{Tl}_2\text{SO}_4 \\
\text{electrolysis} & \rightarrow \text{Pure Tl} \\
\text{Cryst. From} & \rightarrow \text{Commercial Tl}_2\text{SO}_4
\end{align*}
\]

**Thallium in Coal**

Thallium is present in coal as well as other mineral deposits, occurring almost entirely in the sulfide (pyritic) inclusions and not in the organic components. It is delivered to the coal basin during sedimentation or early diagenesis, when sediment is converted to rock. Almost equal concentrations of thallium in pyritic concretions in coal
and in bauxitic clay indicate that peat and clay have approximately the same capacity to adsorb thallium. During diagenesis it is easily desorbed, because the adsorption is only due to weak van der Waals forces. The concentration of thallium in the sulfides of the coal beds is determined entirely by the chemical composition of the rocks which supplied sediment to the deposition basins and by the distance of the basins from the source areas. For example, coal derived from granitic sources has a higher thallium content than that from carbonate sources.

Coal burning most probably provides the largest source of thallium release into the environment. Generally, there is about 0.7 ppm Tl in bituminous coal, anthracite coal having a negligible thallium content. Most of the thallium in U.S. coal is located in eastern deposits, although there is some in the western fields. In comparison, the thallium content in petroleum is approximately 0.5 ppb, and 0.9 to 25.8 ppm in U.S. oil shales.

Depending on the average thallium content of the coal used, between 0.8 and 1.6 tons of thallium may be released annually in some cities, indicating a daily human intake of 11 to 14 μg. This figure is derived in part by realizing that thallium, along with many other trace elements, is enriched on the smallest emitted particles. It is these particles (less than 1 μm) which are also deposited primarily in the alveolar regions of the lung, where the absorption efficiency of the trace elements into the bloodstream is between 50 and 80%. Larger particles deposit in the nasal, pharyngeal and bronchial regions of the respiratory system and are removed by ciliary action to the stomach, where the absorption efficiency is 5 to 15%. The natural size distribution of particles in ambient air indicates that about one-third of the
total particulate mass retained during respiration is deposited in the lung.\textsuperscript{3} Studies have also shown that pulmonary fluids are capable of leaching thallium compounds from the coal dust particles, greatly increasing the toxicity.\textsuperscript{6}

Natusch \textit{et al.}\textsuperscript{7} studied ten trace elements in coal fly ash, both in the fraction collected by the precipitators and in that present in the plant stacks. Thallium was shown to be present in the collected fly ash in the range from 7 \textmu g/g for particles greater than 74 \textmu m to 45 \textmu g/g for those less than 5 \textmu m. Similarly, it was present in concentrations of 20 \textmu g/g for airborne fly ash greater than 11.3 \textmu m to 76 \textmu g/g for particles 1.1 to 2.1 \textmu m.

One possible explanation of this trace element concentration on the smallest particles is that the element or one of its compounds volatilizes in the coal combustion zone (1300-1600°C) and either recondenses or is adsorbed preferentially onto the large available surface area per unit mass provided by small particles.\textsuperscript{7} Thallium and its compounds fit this description, as Tl\textsubscript{2}O, Tl\textsubscript{2}O\textsubscript{3} have boiling points of 1457°C, 1080°C, and 875°C, respectively. The sulfide, sulfate, halide and nitrate compounds either have lower boiling points or decompose on heating above their melting points, so that the thallium emitted would probably be as an oxide.\textsuperscript{3} The estimated average surface thickness of these compounds is 0.1\text{\AA}.\textsuperscript{8} However, sulfur may be present as the element, sulfide or, more importantly, sulfate,\textsuperscript{9} and recombination with thallium to form Tl\textsubscript{2}SO\textsubscript{4} is possible. This may be an even larger factor if the SO\textsubscript{2} emissions are considered. In the presence of atmospheric moisture the SO\textsubscript{2} may become SO\textsubscript{5}, and again could combine with Tl to form Tl\textsubscript{2}SO\textsubscript{4}.\textsuperscript{3}
Another explanation of the dependence of element concentration on particle size is that the ashing characteristics of pyritic inclusions, where thallium is found, predominantly give rise to small particles. Either explanation of concentration-size dependency may be shown by the following equation:

\[ \bar{C}_x = \bar{C}_0 + \frac{6\bar{C}_s}{\bar{p} \bar{D}} \]

where

- \( \bar{C}_x \) = average concentration of X
- \( \bar{C}_0 \) = average bulk concentration of X
- \( \bar{C}_s \) = average surface concentration of X
- \( \bar{p} \) = average particle density
- \( \bar{D} \) = average particle diameter

This relationship has been more simply expressed as:

\[ \bar{C}_x = \bar{C}_0 + \bar{C}_A \bar{D}^{-1} \]

where \( \bar{C}_A \) is the average surface concentration by adsorption or condensation.

Several environmentally significant points as outlined by Natusch et al. include the fact that the size distribution in ambient air is partly influenced by the particle size distribution in the source emission. Also the highest concentration of many very toxic elements is emitted in the smallest, lung-depositing particles, and the existing particle collection systems preferentially allow their emission.
Finally, estimates of toxic element emission based on analyses of undifferentiated fly ash collected from particle precipitators grossly underestimate the actual emissions.

An example of thallium emissions via coal fly ash was given by Carson and Smith. Using the average figure of 0.7 ppm thallium as given before, and the fact that between 1968 and 1972 U.S. coal consumption averaged 500 million tons annually, it may be seen that 350 tons of thallium were burned each year. An average of 60 ppm Tl is thus found in particulate emissions, with the breakdown being:

\[
\begin{align*}
\text{Coal, 10 tons} & \rightarrow (A) \text{ ash, } 10^5 \text{ tons} \\
0.67 \text{ ton Tl} & \rightarrow 6.7 \text{ ppm Tl} \\
& \rightarrow 0.67 \text{ ton Tl}
\end{align*}
\]

\[
\begin{align*}
\text{Collected ash "A", [10% "A"]} & \rightarrow 0.48 \text{ ppm Tl, 0.0048 ton Tl} \\
\text{Airborne ash, "A" [90% "A"]} & \rightarrow \text{average 7.3 ppm Tl}
\end{align*}
\]

\[
\begin{align*}
\text{Collected Ash} & \rightarrow \text{Airborne Ash} \\
85,500 \text{ tons} & \rightarrow 4,500 \text{ tons} \\
3.4 \text{ ppm Tl} & \rightarrow 82 \text{ ppm Tl if all in particulates} \\
0.29 \text{ ton Tl} & \rightarrow 0.37 \text{ ton Tl} \\
(44\% \text{ of Tl in coal}) & \rightarrow (55\% \text{ of Tl in coal})
\end{align*}
\]

In summary, there is an obvious problem with thallium emissions from coal-fired plants, which will increase as coal use does. Because of its volatility, thallium concentrates on respirable particles, and may in fact, combine with SO\textsubscript{2} emissions to form Tl\textsubscript{2}SO\textsubscript{4}. Other probable compounds include the oxides Tl\textsubscript{2}O and Tl\textsubscript{2}O\textsubscript{3}. Both of these fractions from coal burning (as well as other smelting processes) should be analyzed by surface, spectrophotometric and wet chemical techniques so that an accurate value of total thallium emissions may be calculated.
Biomethylation

As seen previously, coal fly ash is a potential source of environmental thallium pollution, and may contaminate natural waters in the vicinity of coal-fired power plants. Elevated thallium levels have also been detected in environmental samples and biota around copper smelters where much of the dust released is very fine and thus readily leachable. \( \text{Tl}^+ \) is the primary species in the runoff from the tailings. At higher pH's, \( \text{Tl}^+ \) may be removed from solution by ion exchange for \( \text{K}^+ \) in suspended clays, producing high thallium sediment levels with much lower water levels.

Because of the sulfide environment and the presence of microorganisms, biomethylation of thallium is possible. Biomethylation involves the transfer of a methyl group, often from methylcobalamin (MeB\(_{12}\)), a vitamin B\(_{12}\) derivative, to a metal cation such as \( \text{Tl}^+ \). Studies\(^{10}\) have shown that the \( \text{Tl}(\text{III}) \) salts, but not the \( \text{Tl}(\text{I}) \) salts, were capable of displacing the methyl group from MeB\(_{12}\) by a Lewis acid mechanism. This reaction has first order kinetics in both \( \text{Tl}(\text{III}) \) and MeB\(_{12}\), and occurs over a wide range of pH and in a variety of buffer media.

However, one experiment\(^{11}\) using a mixed anaerobic bacteria culture showed that \( \text{Tl}^+ \) may indeed be biomethylated to give products such as Me\(_2\text{TlX}\) (\( X = \) halogen). This indicates the oxidation of \( \text{Tl}^+ \) to \( \text{Tl}^{3+} \), which is postulated to occur simultaneously with the methyl transfer. A possible mechanism is:

\[
\text{Tl}^+ - 2e^- \rightarrow \text{Tl}^{3+} \tag{1}
\]

\[
\text{Tl}^{3+} + 2\text{MeB}_{12} \rightarrow \text{Me}_2\text{Tl}^+ + 2\text{B}_{12} \tag{2}
\]
Reaction (1) shows the oxidation of the thallous ion. Reaction (2) indicates an acid attack by the Tl$^{3+}$ on Me$_2$B$_{12}$, followed quickly by another methyl transfer to a good nucleophile such as Cl$^-$, Br$^-$, or X$^-$ (reaction (3)). While this final methyl transfer has been seen only under aerobic conditions in the laboratory, the initial methyl transfer in a biological system is thought to be enhanced by anaerobic conditions and by increasing numbers of bacteria capable of synthesizing alkylcobalamins such as Me$_2$B$_{12}$.

The biomethylation of Hg(II) has been of great concern for some time, and because Tl(III) has the same electronic structure, their analogous reactions have been studied. The alkylations, arylation and benzylations of Hg(II) and Tl(III) by organocobalt compounds [primarily organobis(dimethylglyoximato)cobalt(III) complexes] showed similar reaction rates that were consistent with a proposed $S_e^2$ mechanism. However, unlike the studies using microorganism-assisted reactions, only the first stage of alkylation or arylation could be detected with no indication of the formation of R$_2$Hg or R$_2$Tl$^+$ by further reactions of formed RHg$^+$ or RTl$^{2+}$ with the organocobalt complex. This was said to be consistent with the markedly reduced electrophilic characters of RHg$^+$ and RTl$^{2+}$ as compared with those of Hg$^{2+}$ and Tl$^{3+}$.

Another study of the alkylation of mercury used an anaerobic ecosystem and involved the evolution of methane. Both MeHg$^+$ and Me$_2$Hg were reaction products, with Me$_2$Hg the ultimate product being formed by both enzymatic and non-enzymatic reactions. This study combined with others would imply that Tl(III) could be biomethylated to both RTl$^{2+}$ and
R_2Tl^+, with R_2Tl^+ being the predominant product under anaerobic microbial conditions.

The work done on the biomethylation of Tl(I) compared the reactions to those of the analogous Pb(II), and while MeTl^2+ is a proposed intermediate, the final product is Me_2Tl^+. This is further indicated by studies showing that the MeTlX_2 compounds are unstable in aqueous systems while Me_2TlX compounds are very stable, so that even if the monomethyl species is formed it decomposes rapidly. Therefore, Me_2TlX appears to be the species of environmental consequence.

**Toxic Effects**

Thallium is present in unexposed humans only in very small amounts. When certain body parts were analyzed by mass spectrometry, it was found that hair, nail and colon wall samples contained 4.8-15.8, 0.72-4.93 and 0.56-5.40 µg/Kg, respectively. The mean body concentration is 1.2 µg/Kg, so that the thallium content in a 75 Kg person is on the order of 0.1 mg.

As discussed previously, thallium is released into the environment by human activities such as the burning of fossil fuels, roasting and smelting of ores, fertilizer use and glass manufacturing. The major forms of thallium are thought to be inorganic Tl_2O, Tl_2S, Tl_2SO_4, Tl_2Te, Tl_2Se, Tl-chromates and Tl-silicates. There is also the possibility of exposure to the trivalent Tl_2O_3 and other Tl^{3+} salts in the acidic smelter fumes from the pyrites used for phosphate fertilizer production.

These compounds may be inhaled, injected and absorbed through the skin and mucous membranes. Thallium is quickly demonstrated in the
urine after this absorption and, in fact, can be detected in rat urine within one hour of oral administration of Tl₂SO₄. Peak blood levels are reached two hours after oral dosing, indicating rapid equilibration with the tissues.¹⁵,¹⁷

After absorption, thallium compounds are widely distributed throughout the body, with the kidneys being the major organs of deposition. The central nervous system (CNS) and the skeletal bones are also sites of thallium accumulation.¹⁵,¹⁶

Excretion of thallium compounds occurs primarily through the feces and urine, with other routes being the hair and nails. Thallium also passes through the placenta into the fetus, and can be present in the milk in high enough concentrations to be toxic to the suckling.¹⁵,¹⁷ The biological half-life of these compounds is between three and eight days.¹⁵

It is thought that the oxidation state of thallium does not influence its metabolism in vivo. The similar biochemical behavior of the different species is probably related to a mechanism which transforms them to a single form, presumably reduction of Tl(III) to Tl(I).¹⁶,¹⁸ An indication of this is shown when rats are given inorganic Tl(I) and Tl(III) salts. The concentration of thallium found in the tissues is qualitatively and quantitatively similar.¹⁶ The relative organ concentration also remains constant whatever the route of administration.¹⁵

The biological handling of Tl⁺ and K⁺ ions seems to be interrelated, though once inside the cell Tl⁺ appears to be less readily released than K⁺. Thallium can also substitute for potassium in causing the activation of adenosine triphosphatase, indicating that the mechanism involved in the active transport of potassium cannot differentiate
between the two ions. The effect of thallium is also thought to be
due to its interference with the metabolism of sulfur-containing com-
ounds. This has been shown by feeding rats diets that are high in
cystine (a sulfur-containing amino acid), and noting that they are
protected against chronic thallium poisoning. The action of the B
vitamins and the metabolism of calcium and iron are also disrupted.

The valence state of thallium does not appear to have a significant
effect on the dose required for the lethal effect. The mean lethal
dose in an adult is about 1 g Tl$_2$SO$_4$, and single doses of 4 mg/Kg body
weight have caused toxic reactions in children. The LD$_{50}$ for inor-
ganic thallium salts is 5-70 mg/Kg for mammalian species in general.
One study showed LD$_{50}$'s for male mice by intraperitoneal injection for
Tl$_2$SO$_4$, Tl$_2$CO$_3$ and TlCl$_3$ to be 23.5, 21.0 and 23.7 mg/Kg, respectively,
again emphasizing the similarity of toxicity for different valences.

It is also interesting to note the synergistic effect of ethanol
and thallium. In a study performed by cutaneously dosing rats with
Tl$_2$CO$_3$ with oral administration of ethanol before, at the time of, or
after the thallium dose, the rat mortality was increased by 60-90%.
This is thought to be due to the formation of the more soluble thallium
ethoxide. It is generally thought that subacute and chronic intoxi-
cation is associated with the tissue retention of sparingly soluble
TlCl$_2$. The previous study also showed that the oral administration
of 0.0001 mg Tl$_2$CO$_3$/Kg showed specific mutation activity in male rats,
though this is the only indication of this effect in the present litera-
ture.

Acute poisoning will cause gastroenteritis, loss of kidney function
and joint pain, with the most unique manifestation being loss of hair.
Respiratory, circulatory and CNS involvement subsequently occur followed by death, usually in about three days. Chronic exposure causes milder forms of the acute symptoms, as well as fatigue, headache, limb pain, muscular atrophy and slowed responses. A metallic taste in the mouth may be noted and hypertension is also possible. Hair loss may occur within one to three weeks after initial exposure.

Recovery is usually complete, though some neurological defects may remain. Antidotes such as British Anti-Lewisite (BAL), calcium sodium edetate and penicillamine have little, if any, effect. Dithizone (diphenylthiocarbazone) offers good protection to rats by increasing fecal excretion, while diethyldithiocarbamate hastens both fecal and urinary elimination in dogs and rats, aiding recovery. The rate of thallium removal from rats and dogs is also increased by the elevation of dietary potassium. This is of some help in human poisoning cases, though the thallium toxicity symptoms may be aggravated at least temporarily.

Ferric cyanoferrate(II) (Prussian Blue) and similar coordination complexes with cobalt and nickel can bond thallium tenaciously and prevent its absorption from the gastrointestinal tract. Therefore, treatment of acute thallium poisoning with Prussian Blue has been recommended. The potassium associated with this molecule is replaced by thallium, though this capacity is partially dependent on the preparation method of Prussian Blue. The soluble form contains substantially more potassium than the insoluble product and therefore should adsorb thallium ions more effectively. Prussian Blue is not absorbed in the gut and is stable in the prevailing conditions of the
intestine; therefore, no toxicity is expected.\textsuperscript{21,23} It is either administered by a duodenal tube,\textsuperscript{21} or orally as a 2\% colloidal suspension within the first 24 hours after exposure. While this treatment has not been used for chronic poisoning cases, it should be successful, as is the vitamin B\textsubscript{12} treatment of chronic intoxication.\textsuperscript{24}

Comparatively little work has been done on the toxicity of organothallium compounds. One study did show that the administration of dimethylthallium bromide [(CH\textsubscript{3})\textsubscript{2}TlBr] showed tissue retention one to two orders of magnitude lower than in animals treated with inorganic species. It is thought that the organothalliums are converted to compounds similar to the Tl(I) inorganic salts \textit{in vivo}.\textsuperscript{16}

### Analytical Methods

Thallium may be determined both qualitatively and quantitatively by many analytical methods, including spectrophotometric, volumetric and gravimetric determinations. Other procedures are atomic absorption spectroscopy, inductively coupled plasma emission, activation analysis, X-ray fluorescence, and ion and electron spectroscopies. Electrochemical methods include conductometric studies, dc polarography, differential pulse polarography (DPP), anodic stripping voltammetry (ASV) and differential pulse anodic stripping voltammetry (DPASV).

Cheng and Bray\textsuperscript{25} used 1-(2-pyridylazo)-2-naphthol (PAN) as an indicator for metals in complexometric titrations with EDTA. Thallium(I) forms a red metal chelate, and the pH of the solution should be between 10.5 and 11.0 for maximum sensitivity. The amount of Me\textsubscript{2}Tl\textsuperscript{+} produced by biomethylation of Tl\textsuperscript{+} may also be determined by adding PAN
at pH 10-12 to complex the organothallium after the Tl\(^+\) has been masked with EDTA. The Me\(_2\)Tl\(^+\)-PAN complex is measured at 570 nm.\(^{11}\) Another spectrophotometric technique involves the reduction of any Tl(III) present with oxalic acid and subsequent titration of all Tl(I) present with Ce(SO\(_4\))\(_2\).\(^{26}\) Dithizone may also be used to complex thallium, with Beer's Law well obeyed.

A volumetric method involves the oxidation of Tl\(^+\) to Tl\(^{3+}\) with bromine and the addition of KI and starch-KI-phenol indicator. The solution is then titrated with sodium thiosulfate to remove the color. Bismuth, chromium and copper interfere.\(^{27}\)

Thallium may also be determined gravimetrically by saturating the test solution with SO\(_2\) which prevents the oxidation of Tl\(^+\) to Tl\(^{3+}\). The addition of HBr produces TlBr as a white flocculent precipitate which may be filtered, dried and weighed. Only silver interferes.\(^{27}\)

Total thallium is readily determined by atomic absorption spectroscopy (AAS), both with flame and graphite furnace atomization. Often it is extracted (along with other heavy metals) from the sample by a substance such as methylisobutyl ketone (MIBK), which is then injected directly into the flame or furnace. Aqueous solutions as well as biological and environmental samples may be tested, although matrix effects may be noted. The sensitivity for flame AAS procedures is 0.1 ppm and 100 ppb for non-flame atomization. One study by Morgan et al.\(^{28}\) used flame AAS to simultaneously determine inorganic thallium and dimethylthallium species. The inorganic thallium is reacted with bromine water to form TlBr, which is extracted into MIBK and determined. The organic thallium in the remaining aqueous phase is then extracted with sodium diethyldithiocarbamate into MIBK and determined.
Most activation analysis studies use gamma bombardment. The reaction $^{203}$Tl(Y,n)$^{202}$Tl is convenient in that the half-life of $^{202}$Tl is 12 days. This method has been used to determine thallium contents in sewage sludges. Sensitivities are 0.05-0.1 ppm, with the added advantage that no separation or complex sampling method is needed.

X-ray fluorescence has been used to detect thallium in aqueous samples. It first is extracted with ammonium pyrolidine dithiocarbonate. The fluorescence is measured after sample irradiation with a molybdenum target X-ray tube.

Thallium may be determined in solutions on the ppb level by ESCA. The metal is scavenged by chelating glass surfaces and thus detected. Ion microprobe mass spectrometry and Auger electron spectroscopy have been used to detect thallium in coal fly ash particles.

**Electrochemical Analyses**

Speciation, as well as quantification, of thallium compounds may be accomplished with electrochemical methods. Along with conductivity studies, polarography is often used. A common technique is conventional dc polarography, where a potential is applied between a dropping mercury electrode and a counter electrode, the resulting current being plotted versus the applied potential. Another method often used for trace analysis environmental samples is differential pulse polarography, in which a series of pulses of fixed amplitude is superimposed on a dc ramp. The current is measured before the pulse is applied and during the last few milliseconds of the pulse. The current difference is plotted versus the applied potential producing a peak or a series of peaks. The peak current is a quantitative measure of concentration and
peak potential is related (although not identical) to the half wave potential found in conventional dc polarography.\textsuperscript{34}

Still another electrochemical method is anodic stripping voltammetry (ASV) which may also be combined with a differential pulse technique (DPASV). In ASV, the analytical species is reduced (electrodeposited or plated) on or into the working electrode, resulting in concentration of the species to be analyzed on the stationary electrode or amalgam. When the potential is reversed, the material is stripped off and at the oxidation potential of each species, the faradaic current is measured. The stripping current is proportional to the concentration of that species in the sample solution. DPASV allows easy interpretation of polarograms of trace metals at sub-ppb levels with a very short deposition time.

Studies have been published in which thallium compounds have been determined in biological and environmental samples using ASV and DPASV.\textsuperscript{35-41} Some work has been done using DPP, though no comprehensive study of organothallium compounds has appeared. Work was published on some of these compounds using dc polarography in the late 1960's,\textsuperscript{42} although the emphasis was not environmental in nature.
THEORETICAL CONSIDERATIONS

Electrochemical methods have been an important part of analytical chemistry since 1801 when Cruikshank performed the first electrodeposition of copper and silver from their respective salts. However, it was not until Heyrovsky's first paper in 1922 that voltammetric processes at a dropping mercury electrode (DME), more commonly known as polarography, were described. Heyrovsky and his group at Charles University in Prague, Czechoslovakia then developed the quantitative interpretation of these processes, and by the 1930's the methods were well known outside of Eastern Europe.

While spectroscopic methods gained popularity, the use of polarography greatly declined in the U.S. and Western Europe in the 1950's and 1960's, although it was still widely used in the Eastern European countries. During this time, though, tremendous advances in the theory and instrumentation of alternating current (ac), pulse, linear sweep and other polarographic techniques were taking place. It is only recently that many of the new voltammetric methods have begun to gain practical acceptance in trace analysis work. The resurgence of interest may most probably be attributed to the use of solid state operational amplifier circuitry which, by lowering the cost, allowed many laboratories to buy commercial instruments. Also, environmental scientists realized the utility of electrochemical techniques for low concentration heavy metal and organic analyses.
Polarography

The first polarographic method at a DME was dc polarography. In this method, a linear potential ramp is applied through a DME to a solution containing one or more electroactive species. As may be seen in Figure 1, the resulting current is negligible until just before the reduction potential of the substance. At this point depletion of the species at the electrode surface is begun, and a concentration gradient is established between the DME and the bulk of the solution, and mass transfer of the reducible species is produced. As the potential is made more negative the rate of mass transfer is also increased, and is seen as a sharp increase in the current on the polarographic wave. When the rate of mass transfer becomes constant, the concentration of the electroreducible species at the electrode surface is essentially zero, and therefore a region of constant current is reached. This current plateau is known as the limiting or diffusion current, and because it is generally proportional to the bulk concentration of the electroactive species in solution it is used in quantitative polarographic analysis.

Although other electrodes may be used with the method known as voltammetry, mercury has several distinct advantages, perhaps the most important of which is its high hydrogen overpotential, allowing the analysis of many metallic ions. Both DME's and hanging mercury drop electrodes (HMDE) are continually renewed and have fresh, reproducible surfaces. As microelectrodes they generate very small currents, which leaves the bulk concentration of the solution virtually unaffected.

There are a number of different types of currents encountered in electrochemical analyses. Because the DME acts as a capacitor, charging
Figure 1: DC Polarography i-E Curve
currents result which add to the background or residual current; these currents, though small, become significant in trace analysis. Migration currents due to the movement of electroactive ions are usually suppressed by the addition of a large excess of supporting electrolyte. Convection currents are caused by vibrations or stirring ensuing from the release of the drop. They give rise to current maxima but may be eliminated by the addition of surfactants to the test solution.

Diffusion currents are the most important type as they give rise to the desired analytical data. These may be affected by the currents from kinetic, catalytic and adsorption processes if they occur in the electrochemical system being studied. The mathematical derivation for these currents begins with Fick's laws of diffusion. The first law relates the flux of the species, $J_{ox}$, through a plane of thickness $x$, to its concentration, $C_{ox}$:

$$J_{ox} = -D_{ox} \frac{\partial C_{ox}}{\partial x} \text{mol cm}^{-2} \text{sec}^{-1}$$

where $D_{ox}$ is the diffusion coefficient and is of the order of $10^{-5} \text{ cm}^2 \text{sec}^{-1}$. The second law is stated by

$$\frac{\partial C_{ox}}{\partial t} = D_{ox} \frac{\partial^2 C_{ox}}{\partial x^2}$$

and

$$i(t) = nF(J_{ox})_{x=0} = -nF D_{ox} \frac{\partial C_{ox}}{\partial x}_{x=0}$$
where \( i(t) \) is the current, \( n \) is the number of electrons involved in the reaction, and \( F \) is the Faraday constant equal to 96,485 C/equiv. A Laplace transformation converts it to:

\[
\frac{\partial^2 C(X,S)}{\partial x^2} - \frac{S}{D} \frac{\partial C(X,S)}{\partial S} + \frac{C^\infty}{D} = 0.
\]

where \( S \) is the surface area of the electrode in cm\(^2\). The current-time response for a planar electrode is then given by the Cottrell equation:

\[
i(t) = \frac{nFSD^{1/2}C^\infty}{\pi^{1/2}t^{1/2}}.
\]

For the semi-infinite spherical diffusion of a HMDE the equation is modified to:

\[
i(t) = nFSDC^\infty \left[ \frac{1}{(\pi Dt)^{1/2}} + \frac{1}{r_0} \right].
\]

Of primary importance in polarography is the current-potential relationship for a reversible process, such as

\[
0_x + ne^- \rightleftharpoons \text{Red}.
\]

If this reaction is assumed to be under isothermal, equilibrium and non-convective conditions, as well as in the presence of excess supporting electrolyte, the Nernst equation may be used. As shown by Bard and Faulkner, the form normally used in this case becomes

\[
E = E_{1/2} + \frac{RT}{nF} \ln \left( \frac{i_d - i(t)}{i(t)} \right).
\]
where

\[ E_{1/2} = E_0 - \frac{RT}{2nF} \ln \frac{[D_{ox}]}{[D_{red}]} \]

Other adjustments must be made in the Cottrell equation if it is to be applied to the DME case, because the drop's surface area changes with time. The expression for the surface area, \( S(t) \), may be written as:

\[ S(t) = 4\pi \left( \frac{3mt}{4\pi d_{Hg}} \right)^{2/3} \]

where \( m \) is the rate of mercury flow, \( d_{Hg} \) is the density of mercury and \( t \) is the time. When this is substituted into the Cottrell equation, the current-potential relationship becomes:

\[ i_d = \left[ 4\left( \frac{7\pi}{3} \right)^{1/2} F \left( \frac{3}{4\pi d_{Hg}} \right)^{2/3} \right] nD_0^{1/2} C_0^{*2/3} m^{2/3} t^{1/6} \]

After evaluation of the constant in the brackets to arrive at a numerical value, the familiar Ilkovic equation \(^{47,48}\) is obtained:

\[ i_d = 708nD_0^{1/2} C_0^{*2/3} m^{2/3} t^{1/6} \]

The value 708 becomes 607 when the average current is considered. The units of \( i_d \) are amperes, and \( D_0 \) is in cm\(^2\)sec\(^{-1}\), \( C_0^{*} \) is in mol cm\(^{-3}\), \( m \) is in mg sec\(^{-1}\) and \( t \) is in sec. Among the variations of the Ilkovic equation is the Koutecky equation, which allows for the curvature of the mercury drop. It is:

\[ i_d = 607nD_0^{1/2} C_0^{*2/3} m^{2/3} t^{1/6} \left[ 1 + 34.7D_0^{1/2} t^{1/6} m^{-1/3} + 100(D_0^{1/2} t^{1/6} m^{-1/3})^2 \right] \]
The currents calculated from this equation generally exceed those from the Ilkovic equation by 10%.

**Pulse Techniques**

Conventional dc polarography usually has a detection limit in the range of $10^{-5}$ M, so that methods that would lower this limit would be useful. Improved sensitivities may be obtained using pulse polarographic techniques, which had their beginnings in the 1950's as extensions of Barker and Gardner's work on alternating current (ac) methods. The advantages of fast (current-sampled dc), normal pulse (NPP) and differential pulse (DPP) polarography have their origin in an improved faradaic-to-charging current ratio, because the charging current's relative contribution to the measured current is reduced. These methods are directed toward concentration measurements and are not usually used for diagnostic purposes, so that a detailed knowledge of wave shapes is not often important.

In fast polarography the current is sampled just before the drop fall when the change in charging current is smallest. In practice, this is the last 5 to 20 msec of a drop, instead of the entire current-time curve for each drop. This value is then held electronically until the sampling of the next drop. The i-E curve of a conventional dc polarogram then appears without the non-faradaic spikes, allowing an increase in the detection limit to approximately $10^{-6}$ M. The sensitivity is limited because the potentiostat is on during the entire life of the drop. The faradaic current flow before the measurement is lost, and the concentration of the measured substance is depleted around the electrode.
Normal pulse polarography (NPP) eliminates this depletion effect by blocking electrolysis prior to the current measurement period. As shown in Figure 2, the electrode is held at a base potential $E_b$ from where no faradaic reaction ensues for most of the drop's lifetime. After a waiting period, $\tau$, the potential is abruptly increased in $E$ for a specified period of time (e.g., 50 msec) and then returned to $E_b$. The current is sampled near the end of the pulse, at $\tau'$, and a signal proportional to the value is stored in a recording device until the next signal is received. Just after the pulse ends, the drop is knocked off mechanically, and the entire process is repeated, though with each successive drop the pulse potential $E$ is increased by a few millivolts. Because $E_b$ is chosen when the faradaic current may be assumed to be zero, the current-potential curve for a reversible process may be expressed as

$$i_d = nFCS\left(\frac{D}{\pi t}\right)^{1/2}\left(\frac{1}{1 + P}\right)$$

where $t_m = \tau' - \tau$ and $P = \exp(nF/RT)(E - E_{1/2})$.

The sensitivity of NPP is increased over conventional dc polarography because the current is measured when the charging current has mostly decayed. Also, the measured current is larger because it is sampled for a shorter elapsed time when less depletion occurs. Quantitatively, this may be expressed by comparing the diffusion current of dc polarography, $(i_d)_{DC}$ by the familiar Ilkovic equation

$$(i_d)_{DC} = 708nD_o^{1/2}c_{ox}^{2/3}l^{1/6}$$

with a similar expression for $(i_d)_{NPP}$.
Figure 2: Plots of E-t and i-t Functions for Normal Pulse Polarography
PULSED ELECTROLYSIS

CURRENT SAMPLED

DROP REMOVED

\[ i \]

\[ E \]

\[ E_b \]
\[ (i_d)_{\text{NPP}} = \left(\frac{3}{7}\right)^{1/2} \frac{708nD_0^{1/2}c_o^{2/3}(\tau + \tau')^{2/3}}{\tau^{1/2}} \]

where, again, the \(\left(\frac{3}{7}\right)^{1/2}\) term is due to the expanding mercury drop. If \(\tau'\) is assumed to be negligible compared to \(\tau\) and equal to the time, \(t\), of the dc equation, the following ratio may be achieved:

\[ \frac{(i_d)_{\text{NPP}}}{(i_d)_{\text{DC}}} = \left(\frac{3}{7}\right)^{1/2} \frac{t^{2/3}}{\tau^{1/2}} \cdot \frac{1}{t^{1/6}} = \left(\frac{3}{7}\right)^{1/2} \frac{t^{1/2}}{\tau^{1/2}} \]

which, for example if \(t = 4\) sec and \(\tau' = 20\) msec are chosen,

\[ \frac{(i_d)_{\text{NPP}}}{(i_d)_{\text{DC}}} = 9 \]

Therefore, a nine-fold sensitivity over dc polarography may be obtained with NPP.

The NPP current-potential curve, as shown in Figure 3, has the same shape as the dc curve. Among the features preserved in the curve shape retention is that the limiting current is directly proportional to the concentration of the electroactive species. Also the proportionality constant is independent of the rate of the reaction.

A third method, differential pulse polarography (DPP), superimposes a small-amplitude pulse of approximately 50 mV onto a normal dc voltage ramp that is applied to the system. The current is sampled twice during the drop’s lifetime; once immediately before the pulse at time \(\tau\) and again near the end of the pulse and just before the drop is dislodged at time \(\tau'\), as shown in Figure 4. The data are recorded as a plot of the current difference \(i(\tau) - i(\tau')\) versus the base potential, and appear as peaks instead of the waveforms of dc and the normal pulse methods. This
Figure 3: Normal Pulse Polarography i-E Curve
Figure 4: Plots of E-t and i-t Functions for Differential Pulse Polarography
is because a DPP response can only be seen in potential regions where a small potential difference can make a sizable difference in the faradaic current flow, and for reversible systems this occurs in the region of $E^0'$, the formal potential of an electrode. Before this point the change in potential produced by the pulse is too small to stimulate the faradaic process, and after the $E^0'$ region the base potential is reducing the electroactive species at the maximum rate. Therefore, the rate of current change can no longer be increased by the pulse, and $i(t) - i(t')$ is small, producing a flat line response.

Osteryoung and Hasebe\textsuperscript{50} give the following quantitative view of the peak currents where the potential for the NPP wave may be written as a form of the Nernst equation:

$$E = E_{1/2} - \frac{RT}{nF} \ln \left( \frac{i}{i_d} \right)$$

which may be rewritten as

$$\frac{i}{i_d} = \frac{1}{1 + \varepsilon}$$

where

$$\varepsilon = \exp \frac{nF}{RT} (E - E_{1/2})$$

The difference current, $i(E + \Delta E) - i(E) = \Delta i(E)$ is given as

$$\frac{\Delta i(E)}{i_d} = \frac{\varepsilon (\sigma^2 - 1)}{(\sigma^2 + \varepsilon)(1 + \varepsilon)}$$

where
with a cathodic pulse implied by the negative sign. This equation gives a derivative of the current, while the DPP measurement is actually a differential. Agreement between theory and experiment results from the fact that the dc current contribution is small.

The maximum value of $\Delta i(E)$, $\Delta i(E_p) = i_p$ is found by differentiating equation 1:

$$\frac{i_p}{i_d} = \frac{(\sigma - 1)}{\sigma + 1}$$

which occurs at a peak potential, $E_p$, given by

$$E_p = E_{1/2} - \Delta E/2$$

The relationship between the peak difference current in DPP, $i_{DPP}$, and the diffusion current in NPP, $i_{NPP}$ is given by

$$i_{DPP} = i_{NPP} \frac{\sigma - 1}{\sigma + 1}$$

which is another form of equation 2.

Resolution of DPP peaks is important when simultaneous analysis of several species is performed. The peak half width, $W_{1/2}$, is given by

$$W_{1/2} = \frac{3.52RT}{nF}$$

which gives a value of $90.4/n$ mV at 25°C. For large pulse amplitudes, $W_{1/2}$ approaches $-\Delta E$.

A more rigorous mathematical expression for the current, $i_p$, is given by

$$\sigma = \exp\left(-\frac{nF}{RT} \Delta E/2\right)$$
\[ \Delta i_p = \frac{0.85nF m^{2/3}(\tau + \tau')^{2/3} D^{1/2}C_{ox}^*}{(\pi \tau')^{1/2}} \left\{ \frac{(1 - \sigma^2)E_1}{(1 + E_1)(1 + \sigma^2 E_1)} \right\} \]  

(3)

where

\[ \sigma^2 = \exp\left\{ \frac{nF \Delta E}{RT} \right\}, \quad e_1 = \exp\left\{ \frac{nF}{RT} (E_1 - E_{1/2}) \right\} \]  

and

\[ E_1 = \text{potential at time } t_1, \text{ before the pulse application} \]

Equation 3 thus shows that the peak current is a linear function of concentration. This is true not only of reversible processes but also of quasi-reversible and irreversible reactions. However, \( i_p \) is then also a function of \( k_s \) and the current per unit concentration is lower than for the reversible case.

The detection limits for DPP are about ten times lower than those for NPP, approximately \( 10^{-8} \text{ M} \). This results from a decrease in the capacitive background current because each pulse has the same amplitude. It may be stated that sample analyses are better accomplished by DPP, while NPP is more often used for the examination of complex reactions as well as adsorption and catalytic processes.

**Cyclic Voltammetry**

Cyclic voltammetry is a powerful electrochemical technique which is used to characterize the nature of overall electrochemical reactions and the nature of electron transfer processes by allowing the evaluation of certain kinetic parameters. The method uses a rapid linear sweep of the desired potential range. At a switching potential, \( E_{sw} \), the potential scan direction is reversed and the potential is returned to either the starting potential or, depending on the instrument used, another chosen
potential. This excitation is triangular in appearance, as shown in Figure 5. Sweep rates are generally in the range of 10 mV to 200 V/sec, with the use of X-Y recorders limiting the sweep rate to 1 V/sec. If the forward sweep is in the negative direction, the electroactive material will be reduced, and if the reduction product is electroactive, it may be oxidized on the return sweep. A diagram of this process is shown in Figure 6, and as in polarography, is a current-potential curve.

When the sweep begins, very little reaction occurs and little current flows. When a potential is reached at which an electroactive species is reduced, the diffusion current rises rapidly. Because the solution is not stirred, the species is depleted near the electrode surface and a drop in current is noted.

In 1948, Randles and Sevcik gave the magnitude of the cathodic and anodic peaks in a reversible system as:

$$i_p = (2.69 \times 10^5)n^{3/2}Sb^{1/2}C_o^{1/2}V^{1/2}$$

where $S$ is the area in cm$^2$, $C_o$ is the concentration in mol cm$^{-3}$, $V$ is the sweep rate in V sec$^{-1}$, $i_p$ is the peak current in A and $n$ is the number of electrons mole$^{-1}$. A rigorous numerical analysis of the Randles-Sevcik equation has been performed by Nicholson and Shain. From this equation it is clear that $i_p$ is directly proportional to both the species concentration and the sweep rate. Also, at 25°C, the peak potential $E_p$ is given as

$$E_p = E^{1/2} + 0.0285/n \ V$$
Figure 5: Cyclic Voltammetry Excitation Process
Figure 6: Cyclic Voltammetry i-E Curve
However, it is often difficult to determine $E_p$ because of the broadness of the peak, so $E_{p/2}$, the potential at $1/2i_p$, is often reported, where

$$E_{p/2} = E_{1/2} + 1.09RT/nF$$

or

$$E_{p/2} = E_{1/2} + 0.0280/n \text{ at } 25^\circ C$$

Criteria for reversibility at 25°C include the relationships

$$E_p - E_{p/2} = 0.0565/n \text{ V}$$

and

$$E_{p_c} - E_{p_a} = \frac{0.059}{n} \text{ V}$$

For a quasi-reversible reaction:

$$\text{Ox} + ne^- \frac{K_c}{K_a} \text{ Red,}$$

a shift in $E_p$ is noted with a change in sweep rate, $\nu$. In general, as described by Brown and Large, 54

$$E_{p_c} - E_{p_a} = \frac{0.060}{n} \nu$$

but this potential difference increases with increasing $\nu$. The quasi-reversible curves are a function of $\alpha$ and $\psi$, a parameter defined by Nicholson. 55
where \( \alpha \) is a transfer coefficient. Values of \( \psi \) are between 0.001 and 7, where the higher the \( \psi \) value, the more reversible the process.

Irreversible electrode processes, a representation being

\[
\begin{align*}
\text{Ox} + n\text{e}^- & \rightarrow \text{Red} \\
\kappa_s & \\
\end{align*}
\]

have \( i_p \) values calculated using the following equation:

\[
i_p = (2.99 \times 10^5)n(\alpha n_a)^{1/2}SC_{\text{ox}}^{1/2}D_{\text{ox}}^{1/2}V^{1/2}
\]

where \( n_a \) is the number of electrons in the rate determining step. Also,

\[
\frac{E_p - E_p/2}{\alpha n_a F} = \frac{47.7}{\alpha n_a} \text{ mV at 25°C}
\]

Therefore, \( i_p \) is proportional to \( C_{\text{ox}} \) and \( V^{1/2} \) for an irreversible wave, but \( E_p \) is a function of scan rate, shifting in the negative direction by 30/\( \alpha n_a \) mV at 25°C for each tenfold increase in \( V \).

To calculate \( k_s \), one of the following methods may be used. If \( E^0 \) is known, the equation is

\[
i_p = 0.227nFSC_{\text{ox}}^{1/2}k_s \exp\left[\frac{q_n F}{k_B} \cdot \left(\frac{\alpha n_a}{RT}\right)(E_p - E^0)\right]
\]

However, this is not often the case. Reinmuth\(^{56} \) has suggested that at the foot of the response wave the current is independent of the scan rate. Therefore, it may be related to the potential and the initial potential, \( E_i \), by

\[
\psi = \frac{D_{\text{ox}}^{1/2}}{D_{\text{red}}^{1/2}} \cdot \frac{k_s}{[D_{\text{ox}}^{1/2}nF(\alpha F/RT)]^{1/2}}
\]
\[ i = nFSC^*_{ox} k_b \exp\left(\frac{-onF}{RT}(E - E_1)\right) \]

and is valid for \( i < 0.1 \) \( \frac{a}{a} \). A graph of \( \ln i \) versus \( E - E_1 \) is made, where the slope is \( \frac{-onF}{RT} \) and the y-intercept is \( nFSC^*_{ox} k_b \).

Cyclic voltammetry is an excellent technique for investigating mechanisms, and Brown and Large\(^{54}\) have thoroughly discussed the diagnostic criteria for each basic type. Included in their discussion and expanded by Wopschall and Shain\(^{57,58}\) are the effects seen by adsorption processes. Figure 7 illustrates these. As can be seen, the strong adsorption of a product formed by the electrolysis gives a prewave and a strongly adsorbed reactant gives a postwave. A weak adsorption of a reactant will give an overall increase in the voltammogram, which may be distinguished from the normal reversible curve by a comparison of the curve variation with \( V^{1/2} \).

**Anodic Stripping Voltammetry**

Another form of voltammetry is stripping analysis, of which anodic stripping voltammetry (ASV) is the most commonly used. Detection limits in the part per trillion range have been reported.\(^{35-41}\) In general, the method involves three steps: preconcentration and deposition, a rest period, and stripping. The stripping is performed by a voltammetric procedure such as linear sweep, square-wave, pulse or differential pulse, where the applied potential is scanned in the positive direction. Different electrodes may be used, including solid metals and various carbon substrates, but hanging mercury drop electrodes (HMDE) and mercury thin film electrodes (MTFE) are preferred.
Figure 7: Adsorption Processes as shown by Cyclic Voltammetry

---- uncomplicated voltammogram
(a) Product strongly adsorbed

(b) Reactant strongly adsorbed
(c) Reactant weakly adsorbed
The preconcentration step makes use of a constant potential and an increase of the mass transfer of the species to the electrode by either spinning the electrode or stirring the solution to deposit the metals onto the electrode. Because complete electrolysis and removal of the substances is often lengthy it is more usual to use a fixed and reproducible time interval to electrolyze 2 to 3% of the total. Several different processes may take place at the electrode, including amalgam formation and the deposition of an insoluble compound onto the electrode.

A quiescent, or rest, period generally follows deposition, and allows the flux of the species to the electrode to decrease to the stationary diffusion current. In HMDE's, the distribution of the deposited substance becomes uniform. Because of the thin films involved, this rest period need not be used with MTFE's to obtain consistent results.

The stripping behavior of the species depends upon the type of electrode used. While a rigorous theoretical treatment is unnecessary because most analytical procedures employ relative methods such as calibration curves or standard additions rather than absolute measurements, certain basic equations must be discussed. For HMDE's and MTFE's, the concentration of metal in the amalgam, \( C_{B(Hg)} \), may be calculated using Faraday's law. In either case,

\[
C_{B(Hg)} = \frac{it}{nFV}
\]

where \( i \) is the reduction current, \( t \) is the electrolysis time, and \( V \) is the volume of mercury in the film or drop. The \( i-E \) behavior at a HMDE
is considered analogous to that of linear sweep voltammetry by Bond. For a reversible process, the Randles-Sevcik equation is used, giving:

\[
i_p = k m n^{3/2} D^{1/2} v^{1/2} C_B(Hg) t
\]

where \( m \) is the mass of the mercury and \( v \) is the scan rate of the dc potential. The peak potential, \( E_p \), is given by

\[
E_p = E_{1/2}^r + \frac{1.1RT}{nF}
\]

where \( E_{1/2}^r \) is the reversible polarographic half-wave potential. At high \( v \) and large mercury thickness, \( i_p \) is proportional to \( v^{1/2} \), because semi-infinite linear diffusion behavior predominates. For HMDE's differential pulse curves are easily understood by extrapolation from differential pulse and dc linear sweep results.

The theory for a linear dc sweep of potentials for the MTFE has been developed by de Vries and Van Dalen. The appropriate equations are:

\[
i_p = k n^2 A C_B(Hg) L v
\]

and

\[
E_p = E_{1/2}^r + \frac{2.3RT}{nF} \log \frac{\delta n F L v}{D R T}
\]

where \( \delta \) is the diffusion layer thickness and \( L \) is the mercury film thickness. In this case with small \( v \) and mercury thickness, depletion or thin-layer behavior predominates and \( i_p \) is proportional to \( v \). Pulsed stripping in this case has been solved by Osteryoung and Christie. Instead of considering a current-by-time term, \( Q_m \), a term for the total
charge passed for the deposition of the metal is used. This gives the expression

\[ Q_m = nF \Delta C_B(Hg) \cdot \]

An approximate result for the peak current at 25°C is given by

\[ i_p(\text{pulse}) = \frac{-0.138Q_m}{t_p} \]

where \( t_p \) is the pulse width or duration and the peak current is predicted to be dependent only on the amount of metal plated onto the electrode and on the pulse width.

While either a HMDE or a MTFE may be used in most cases, there are advantages and disadvantages of each. MTFE's suffer from intermetallic compound formation between two metals deposited into the mercury at the same time (Cu-Cd, Cu-Ni) because they yield fairly concentrated amalgams and a high ratio of substrate area-to-film volume. Also, there is at times a lack of reproducibility with some MTFE's, although in situ deposition of the mercury film during the initial analysis step instead of a separate plating step can overcome this. HMDE's are generally simpler, more economical and reproducible, although the peak resolution is decreased and the peaks are broadened because of the low surface area-to-volume ratio. Therefore, the decision as to which type of electrode to use must be made according to the samples to be analyzed.
EXPERIMENTAL

Apparatus

Several different instruments were used for the electrochemical studies described. A Princeton Applied Research Corporation (PAR) model 174A polarographic analyzer in conjunction with the PAR model 174/50 drop timer assembly was used to perform both normal and differential pulse polarography as well as differential pulse anodic stripping voltammetry. For cyclic voltammetry a PAR model 173 potentiostat/galvanostat, a PAR model 175 universal programmer and a PAR model 179 digital coulometer were interfaced. A Houston Instruments model 2000 X-Y recorder was used whenever any measurements were made with the PAR instruments.

The capillary column used for the dropping mercury electrode for the \((\text{CH}_3)_2\text{TlI}\) and \(\text{TlNO}_3\) analyses had a natural drop time of 4.7 sec, while that used for the analyses of \((\text{CH}_3)_2\text{TlNO}_3\) was 5.6 sec when the mercury column height was 76 cm. The response of the latter capillary was 60% of the former, so that the values obtained were multiplied by \(1/0.60\) in order to make accurate comparisons. By collecting several drops under the electrolyte and drying them by washing with acetone, the weight of each natural drop was found to be \(1.27 \times 10^{-2} \text{ g}\). For a drop time of 0.5 s, the weight for each drop was \(5.47 \times 10^{-4} \text{ g}\) and the surface area \(3.58 \times 10^{-3} \text{ cm}^2\). When a drop time of 1 s was selected, these values were \(1.36 \times 10^{-3} \text{ g}\) and \(1.04 \times 10^{-2} \text{ cm}\), respectively. A PAR model
9323 hanging mercury drop electrode was used for the cyclic voltammetry studies. A drop size of $3.22 \times 10^{-3}$ g and $1.85 \times 10^{-2}$ cm$^2$ was obtained by turning the 9323 head three units.

Differential pulse anodic stripping voltammetry was performed with a thin mercury film plated onto a rotating glassy carbon electrode (GCE). A simple rotator was assembled using a Sargent cone drive stirrer motor and is illustrated in Figure 8. The mercury film was plated onto the GCE (diameter of 0.32 cm) using the method described by Copeland et al. The mercury plating solution was placed in the cell and a potential of $-0.250$ V was applied to the GCE for 5 minutes while argon was bubbled through the solution. The electrolysis was then continued for an additional 10 minutes with bubbling and GCE rotation.

Chemicals and Solutions

Reagent grade chemicals were used throughout without further purification unless otherwise specified. Triply distilled mercury was obtained from Bethlehem Apparatus (Hellertown, Pa.). Inorganic thallium compounds were obtained from Alfa Products (Danvers, Mass.). Deionized and distilled water was used for all solutions.

Phosphate buffer solutions were made by combining the appropriate amounts of $\text{H}_3\text{PO}_4$, $\text{KH}_2\text{PO}_4$ and NaOH to obtain pH values of 4, 7 and 10. Acetate buffer was made by combining the correct quantities of $\text{CH}_3\text{COOH}$ and NaOH to give a pH value of 7. The thallium concentration reported refer to the thallium metal weight in ppm or ppb and not the compound weight.

The solution used in forming the thin mercury film electrode was made by combining a $\text{Hg(NO}_3)_2$ solution (elemental Hg dissolved in HNO$_3$)
Figure 8: Rotating Electrode Apparatus
Cone drive
Stirrer

To Drop Timer Circuit

Brass contact

Cu Strip

GCE

57
and an acetate buffer (pH 7) according to the procedure outlined by Copeland et al.\textsuperscript{38}

Lake water was collected from Campus Lake at LSU, acidified with HNO\textsubscript{3} so that the final concentration was 1\%, and stored in a polyethylene bottle for 6 months to allow the particulates to settle.

Coal fly ash leachates were obtained from an outside source. Fly ash from the Amos and Clinch River power plant furnaces of the Tennessee Valley Authority were leached with acid and shaking as outlined by the American Society for Testing and Materials (ASTM) standard method.\textsuperscript{62} The leachates, with pH values of 1, were stored in plastic screw-cap specimen jars until analysis.

**Synthesis Procedures**

Dimethylthallium iodide [(CH\textsubscript{3})\textsubscript{2}TlI] was synthesized following the procedure described by Gilman and Jones.\textsuperscript{63} The nitrogen used was passed over a copper coated catalyst (catalyst R3-11, Chemical Dynamics Corp., South Plainfield, N.J.) to remove O\textsubscript{2} and bubbled through H\textsubscript{2}SO\textsubscript{4}, KOH and Ascarite (Arthur H. Thomas, Phila., Pa.) to remove water, CO\textsubscript{2} and excess H\textsubscript{2}SO\textsubscript{4}, and CO\textsubscript{2}, respectively. A three-armed bubbler containing xylenes was the last one in line, and was used to monitor the nitrogen flow as well as reaction gas evolution. Anhydrous diethyl ether was dried overnight over lithium aluminum hydride under nitrogen and distilled immediately before use.

The (CH\textsubscript{3})\textsubscript{2}TlI was white and flaky after recrystallization from water, and an elemental analysis gave 6.44\% C (6.65\% calc.) and 1.67\% H (1.67\% calc.). Its infrared spectrum, shows strong absorption bands at 800 and 542 cm\textsuperscript{-1}, indicating the methyl rocking and C-Tl-C asymmetric
stretch, respectively. An ESCA spectrum was also run and is shown in Figure 9. The characteristic Tl and I peaks are evident and give the expected one-to-one ratio.

Dimethylthallium nitrate [(CH$_3$)$_2$TlNO$_3$] was synthesized from (CH$_3$)$_2$TlI following the procedure of Goddard.$^6$ The compound was re-crystallized from methanol, with an elemental analysis giving 4.75% N (4.74% calc.), 7.79% C (8.09% calc.) and 2.00% H (2.18% calc.). The infrared spectrum shows strong bands at 1385, 801 and 545 cm$^{-1}$, corresponding to methyl and nitrate stretches as well as the C-Tl-C asymmetric stretch. Other peaks were identified as indicative of (CH$_3$)$_2$TlNO$_3$ by comparison to data given by Deacon and Green.$^6$

**Experimental Procedures**

**Cyclic Voltammetry**

Cyclic voltammetry (CV) was used to determine the reaction mechanisms for the thallium compounds, as well as certain kinetic parameters. For this method, the proper connections were made between the PAR models 173, 175 and 179.

A HMDE was used and all solutions analyzed were made in pH 7 phosphate buffer. Appropriate dilutions were made from $10^{-3}$ M stock solutions, and each sample was deoxygenated before analysis. Also, each sample was run at various sweep rates. The instrument settings were:

- current range: 100 $\mu$A
- potential range: as applicable
- X-Y recorder: $x = 100$ mV/in, $y = 10$ or 100 mV/in
Figure 9: \((\text{CH}_3)_2\text{Tl}\) ESCA Spectrum

**Excitation:** 400 W Mg K\(_\alpha\)

**Pass Energy:** 100 eV

**RC:** 1 s

Peak a: \(I_{3p_{3/2}}\)

b: \(I_{3p_{3/2}}\)

c,d: O(KVV) & I(MNN)

e,f: \(I_{3d_{3/2,5/2}}\)

g: \(I_{4p_{3/2}}\)

h,j: \(Tl_{4d_{3/2,5/2}}\)

k: \(C_{1s}\)

l,m: \(Tl_{4f_{5/2,7/2}}\)

n: \(I_{4d}\)
Normal Pulse Polarography

The PAR model 174A was also used for normal pulse polarography (NPP). The information obtained from NPP studies included approximate half-wave potentials for the irreversible reactions and diffusion coefficients for the organothallium compounds. The instrument settings were:

- current range: 10 μA
- potential range: 1.5 V
- potential scan rate: 5 mV/s
- modulation amplitude: 50 mV
- drop time: 1 s

Stock solutions of the thallium compounds were made by dissolving the appropriate amount of solid in deionized water to give 100 mL of $10^{-3}$ M solution. Dilutions were made by adding the appropriate amount of stock solution to the buffer solution in the electrolysis cell. All samples were run in triplicate after deoxygenating as described in the previous section.

Differential Pulse Polarography

The calibration curves for the differential pulse polarography (DPP) analyses of the thallium compounds tested were obtained using the PAR model 174A and a DME. The instrument settings were:

- potential range: 3.0 V
- potential rate: 5 mV/s
- modulation amplitude: 50 mV
- drop time: 0.5 s

The current range was set at a convenient level.
A 50 mL aliquot of the buffer electrolyte was placed in the cell and bubbled with N₂ for 5 min. Also, N₂ was allowed to blanket the solution surface during analysis. After this deoxygenation, the DPP scan was begun at 0.0 V and continued in a negative direction until the final current rise was noted. This rise depended on the pH of the phosphate buffer and occurred at -1.4, -1.6 and -1.8 V for pH 4, 7 and 10, respectively.

Each concentration sample was made by diluting a 100 ppm stock solution with the appropriate amount of buffer in a 100 mL volumetric flask. For analysis, 50 mL of solution were used and deoxygenated as previously described. Each sample analysis was performed in triplicate. The remaining 50 mL of each solution were stored in the flask to test for possible sample loss to the container walls, and analyzed in the same manner after waiting the appropriate amount of time.

**Differential Pulse Anodic Stripping Voltammetry**

Differential pulse anodic stripping voltammetry (DPASV) was performed using the PAR model 174A and a rotating mercury thin film electrode (MTFE). The MTFE was produced as described previously and was stored in deionized water when not in use. The model 174A settings were

- potential range: 1.5 V
- potential scan rate: 2 mV/S
- modulation amplitude: 10 mV
- drop time: 1 s

The current range was set at a convenient value, usually 10 μA.

The analyses were made using the method of standard additions, with the correct amount of 100 ppm stock solution added via a microliter
syringe to the 50 mL of buffer solution in the cell. Argon was then bubbled through the solution to provide thorough mixing.

Before each analysis, the test solution was bubbled for 5 min. As the deoxygenation continued, the MTFE was stripped by electrolyzing at 0.0 V for 1 min while rotating the electrode. The cell was then switched off, the potential increased to the desired deposition potential, and the bubbling discontinued. With the electrode spinning, the cell was switched on again, and the deposition allowed to continue for the desired time. Then the cell was switched off, the rotation stopped, the initial potential for the the stripping scan set, the cell switched back on and the scan begun at the same time. Generally, the potential range for stripping was from -0.9 V to -0.4 V. Care was taken not to allow the potential to become greater than 0.0 V, as mercury dissolution would occur and the MTFE would be damaged.

Environmental samples, including tap water, lake water and coal fly ash leachates, were analyzed by diluting 25 mL of the sample with 25 mL of double-strength phosphate or acetate buffer. This allowed the acidic samples to be analyzed at a pH value of between 6 and 7. The presence of interfering metals is suppressed in phosphate buffer by the formation of their insoluble phosphates, which greatly simplifies the analysis for thallium compounds. When it was necessary to analyze thallium in the presence of other metals, acetate buffer was used. The subsequent quenching of interfering peaks was accomplished by the addition of EDTA which, with the considerations discussed below, left the thallium peaks untouched.
RESULTS AND DISCUSSION

Cyclic Voltammetry

A characterization of the electrochemical reactions of the organo-thallium compounds was necessary before an analytical method could be developed. Cyclic voltammetry is the method of choice as it allows both anodic and cathodic processes to be quickly studied on the same sample and reactions involving products formed by either pathway may be observed.

The cyclic voltammogram for (CH₃₂)₂Tl⁺ is shown in Figure 10. The initial cathodic sweep shows peaks at -0.1, -0.2 and -1.08 V. The first peaks are prewaves, and comparison with the scans given by Wopschall and Shain⁵⁷ indicates that there is strong adsorption of a product on the mercury electrode. In aqueous solution (CH₃₂)₂Tl⁺ is ionized and the I⁻ may combine with the mercury to form an insoluble iodide on the surface of the drop. This adsorption process was confirmed when the peak grew upon addition of a small amount of KI to the solution. This observation indicates that an interference from the halogen can cause problems in the development of an electrochemical analytical method.

The extended peak with its apex at -1.08 V is caused by the presence of (CH₃₂)₂Tl⁺. Its electrolysis is an irreversible process as indicated by the fact that there is no peak within 0.059/n V on the anodic sweep. The irreversible nature of this wave was also indicated
Figure 10: \((\text{CH}_3)_2\text{Tl}\) Cyclic Voltammogram, 
+0.15 \text{V} to -1.6 \text{ V}

scan rate = 200 \text{ mV/s}

(numbers indicate subsequent sweeps)
by DiGregorio$^{42}$ in his work on (CH$_3$)$_2$TIF. The extended tail is indicative of the presence of a hydrogen wave.

The initial anodic scan shows peaks at -0.12 and -0.44 V, the first voltage representative of the reversible electrochemical process with the mercury-iodine compounds. The peak at -0.44 V implies that Tl$^0$ is being formed after the electrolysis of the organothallium compound has been accomplished.

Subsequent voltammograms show the emergence of a peak at approximately -0.48 V which grows in height with each successive sweep. This is caused by the reversible oxidation of the Tl$^0$ (formed during the anodic electrolysis) to Tl$^+$. As more (CH$_3$)$_2$Tl releases Tl$^0$, larger amounts of Tl$^+$ are formed. When TlNO$_3$ was added to the solution these peaks grew accordingly.

When the switching potential is changed from -1.6 to -0.8 V, the organothallium reaction is not observed as shown in Figure 11. Also, no Tl$^0$ is formed on the reverse sweep, and as would be expected, the presence of Tl$^+$ is not indicated. Only the adsorption waves are shown.

The cyclic voltammogram of (CH$_3$)$_2$TlNO$_3$ is shown in Figure 12. It differs from the voltammogram of (CH$_3$)$_2$TIl in that there is no adsorption peak and the only significant peak seen on the anodic sweep is that for Tl$^0$. As before, the formation of Tl$^+$ is noted on subsequent sweeps. The same extended peak is seen with an apex of -1.08 V, indicating the (CH$_3$)$_2$Tl$^+$ ion.

The number of electrons transferred in the electrochemical process may be approximated by comparing the area under the cathodic process peak to that of the anodic process. It should be noted, however, that the quantity above the zero current level and the bottom of the extended
Figure 11: \((\text{CH}_3)_2\text{TI}1\) Cyclic Voltammogram, 
+0.15 V to -0.8 V

scan rate = 200 mV/s

(numbers indicate subsequent sweeps)
Figure 12: $(\text{CH}_3)_2\text{TlNO}_3$ Cyclic Voltammogram, 
$+0.15\text{V}$ to $-1.6\text{V}$

scan rate = 100 mV/s

(numbers indicate subsequent sweeps)
peak should be counted twice, as this represents a significant electrochemical quantity. When this comparison is made, the cathodic to anodic area ratio is 3 to 1, indicating that the organothallium compounds undergo a three electron change. This supports the suggested mechanism of DiGregorio, which will be discussed later.

As discussed previously, cyclic voltammetry is also a method by which certain kinetic parameters may be calculated. Using the procedure described by Reinmuth, the transfer coefficient, \( \alpha \), and the rate constant, \( k_s \), may be calculated using the foot of the cyclic wave. Figure 13 illustrates this process for \((CH_3)_2TlI\). As suggested by Reinmuth, as long as the current \( i \) is less than 10% of the peak current, the current is independent of scan rate for irreversible systems.

Table I gives the data obtained from Figure 13 for sweep rates of 20 and 50 mV/s, after choosing -0.8 V to be \( E_i \), the initial potential where no current is flowing. Plotting \( \ln i \) versus \( E - E_i \) (Figure 14) gives the expected linear relationship for each sweep rate. Using the values for the slopes and y-intercepts and substituting into the equation

\[
i = nFSC_{ox}k_s \exp\left[\frac{-\alpha nF}{RT}(E - E_i)\right]
\]

\( \pm \) confidence interval) for \((CH_3)_2TlI\) is found to be \( 0.410 \pm 0.025 \) and \( k_s \) to be \( 1.84 \times 10^{-3} \pm 5.4 \times 10^{-4} \) cm/s for an \( E_i \) of -0.8 V. Obviously the value of \( k_s \) is dependent on the choice of \( E_i \), although the slope of the line, and therefore \( \alpha \), is independent of the initial potential. Also, the kinetic parameters do seem to be independent of sweep rate as had been previously stated.
Figure 13: Foot-of-Wave Curves for $(\text{CH}_3)_2\text{TII}$

a: 10% point for 20 mV/s
b: 10% point for 50 mV/s
Table I

Foot-of-Wave Data for (CH₃)₂TlI

\[ E_1 = -0.8 \text{ V} \]

<table>
<thead>
<tr>
<th>Sweep Rate, mV/s</th>
<th>E, V</th>
<th>( E - E_1 ), V</th>
<th>i, µA</th>
<th>ln i</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.92</td>
<td>0.12</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>20</td>
<td>0.93</td>
<td>0.13</td>
<td>1.50</td>
<td>0.415</td>
</tr>
<tr>
<td>20</td>
<td>0.94</td>
<td>0.14</td>
<td>2.50</td>
<td>0.926</td>
</tr>
<tr>
<td>20</td>
<td>0.95</td>
<td>0.15</td>
<td>4.00</td>
<td>1.39</td>
</tr>
<tr>
<td>20</td>
<td>0.96</td>
<td>0.16</td>
<td>6.50</td>
<td>1.87</td>
</tr>
<tr>
<td>50</td>
<td>0.92</td>
<td>0.12</td>
<td>1.00</td>
<td>0.00</td>
</tr>
<tr>
<td>50</td>
<td>0.93</td>
<td>0.13</td>
<td>1.60</td>
<td>0.47</td>
</tr>
<tr>
<td>50</td>
<td>0.94</td>
<td>0.14</td>
<td>2.60</td>
<td>0.966</td>
</tr>
<tr>
<td>50</td>
<td>0.95</td>
<td>0.15</td>
<td>4.20</td>
<td>1.43</td>
</tr>
<tr>
<td>50</td>
<td>0.96</td>
<td>0.16</td>
<td>7.00</td>
<td>1.95</td>
</tr>
</tbody>
</table>
Figure 14: Graph of ln i vs E-E_0 from (CH₃)₂TlI Foot-of-Wave Data

0 - scan rate 20 mV/s
Δ - scan rate 50 mV/s
This independence is further illustrated when the same method is applied to \((CH_3)_2TLNO_3\). Figure 15 shows examples of the foot-of-wave plots for this compound and the ln \(i\) versus \(E - E^*\) data are found in Figure 16. For \(E^*\) of -0.8 V, the \(\alpha\) and \(k_s\) values obtained are shown in Table II and give \((CH_3)_2TLNO_3\) an average transfer coefficient (± confidence interval) of 0.368 ± 0.091 and an average rate constant of 4.05 x 10^{-3} ± 5.5 x 10^{-4} cm/s. The values have little dependence on sweep rates. Also, the values for both organothallium compounds are comparable, the variations due most probably to the different anions.

**Normal Pulse Polarography**

Normal pulse polarography (NPP) is used to determine the reversibility of an electrochemical system as well as provide information about the half-wave potential, \(E_{1/2}\), and the diffusion coefficient, \(D_0\). When a plot of \(E\) versus \(\ln(i_d - i)/i\) is made from NPP data, a straight line of slope \(RT/nF\) will result for a reversible process. The potential for which \(\ln(i_d - i)/i\) is equal to zero is then the half-wave potential for the reaction. By using the diffusion current, \(i_d\), obtained for a wave and the Ilkovic equation

\[i_d = 708nD_{0}^{1/2}C_{0}^{2/3}C_{0}^{2/3}t^{1/6}\]

the diffusion coefficient for the compound may be calculated.

Figure 17 is the normal pulse traces for various concentrations of \((CH_3)_2TII\). Three waves are apparent in each case. The first wave at approximately -0.25 V represents the adsorption process previously described by cyclic voltammetry. The next wave at -1.05 V does not appear to be a reversible system and this is confirmed by the nonlinear
Figure 15: Foot-of-Wave Curves for \((\text{CH}_3)_2\text{TlNO}_3\)

a: 10% point for 20 mV/s
b: 10% point for 50 mV/s
Figure 16: Graph of \( \ln i \) vs \( E-E_0 \) from \((\text{CH}_3)_2\text{TINO}_3\) Foot-of-Wave Data

- \( \bigcirc \) - scan rate 20 mV/s
- \( \Delta \) - scan rate 50 mV/s
Table II

Kinetic Parameters ($\alpha$, $k_x$) for $(\text{CH}_3)_2\text{TLNO}_3$

from Foot-of-Wave Data

$E_i = -0.8 \text{ V}$

<table>
<thead>
<tr>
<th>Sweep Rate, mV/s</th>
<th>Potential Range, V</th>
<th>$\alpha$</th>
<th>$k_x$, cm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>-0.92 to -0.98</td>
<td>0.295</td>
<td>$8.76 \times 10^{-3}$</td>
</tr>
<tr>
<td>20</td>
<td>-0.92 to -0.96</td>
<td>0.399</td>
<td>$2.18 \times 10^{-3}$</td>
</tr>
<tr>
<td>50</td>
<td>-0.92 to -0.98</td>
<td>0.425</td>
<td>$7.76 \times 10^{-4}$</td>
</tr>
<tr>
<td>50</td>
<td>-0.92 to -0.97</td>
<td>0.354</td>
<td>$4.48 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
Figure 17: Normal Pulse Traces for (CH₃)₂TlI

- Blank, 2μA
- - - - - 1 x 10⁻⁵ M, 2μA
- - - - - 5 x 10⁻⁵ M, 2μA
- - - - - 1 x 10⁻⁴ M, 5μA
- - - - - 5 x 10⁻⁴ M, 10μA
E versus ln\((i_d - i)/i\) plot, shown in Figure 18. A small indistinct wave occurs at higher concentrations at about -1.25 V, and is followed by a somewhat larger wave at -1.39 V. This last peak gives a fairly straight E versus ln\((i_d - i)/i\) plot, which is shown in Figure 19 and which indicates a reaction at least quasi-reversible in nature. While the potentials obtained from these NPP traces cannot be considered half-wave potentials as they are not derived from reversible systems, they may be used to identify reactions in this method as well as others.

The wave at -1.05 V appeared to increase upon addition of \((\text{CH}_3)_2\text{TlI}\), and was therefore thought to be diffusion controlled. Also, after comparison of these data to that obtained by cyclic voltammetry, this wave was determined to be from the \((\text{CH}_3)_2\text{Tl}^+\) ion and could consequently be used to calculate a diffusion coefficient for the cation. Table III gives the currents measured as a function of the concentration of \((\text{CH}_3)_2\text{TlI}\) used. Using the Ilkovic equation and a value of 3 for \(n\), the \(D_0\) values were obtained. For an electrochemical reaction which is diffusion controlled, the diffusion coefficient will be independent of concentration, and this fact is readily seen in these data. The average of the calculated values yields a diffusion coefficient of \(1.10 \times 10^{-7} \text{ cm}^2/\text{s}\). The \(D_0\) value for Tl\(^+\) is \(2.5 \times 10^{-5} \text{ cm}^2\), which is explained by the smaller size and more highly solvated nature of the ion.

Dimethylthallium nitrate may be treated in a similar manner. As shown in Figure 20 the NPP traces appear the same as for \((\text{CH}_3)_2\text{TlI}\) except that there is no adsorption wave. This difference was also noted in the cyclic studies. The waves again occurred at -1.05 and -1.39 V. When the data were analyzed, as seen in Table IV, the diffusion
Figure 18: E vs ln (i_d/i) Graph for (CH₃)₂TⅠ₂ (-1.08 V)
Figure 19: E vs ln (i_d/i) Graph for (CH₃₂)₂Tl⁺ (-1.39 V)
Table III
Diffusion Coefficient, $D_0$, for $(\text{CH}_3)_2\text{TlI}$ from NPP Data

\[ i_d = 708 \, nD_0^{1/2} C_0^{2/3} t^{1/6} \]

<table>
<thead>
<tr>
<th>$C_0^\star$, M</th>
<th>$\bar{i}_d$, A x $10^{-6}$</th>
<th>$D_0$, cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{-5}$</td>
<td>0.092</td>
<td>$1.24 \times 10^{-7}$</td>
</tr>
<tr>
<td>$5 \times 10^{-5}$</td>
<td>0.440</td>
<td>$1.13 \times 10^{-7}$</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>0.825</td>
<td>$9.97 \times 10^{-8}$</td>
</tr>
<tr>
<td>$5 \times 10^{-4}$</td>
<td>4.20</td>
<td>$1.03 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

$\bar{D}_o = 1.10 \times 10^{-7}$ cm$^2$/s

Table IV
Diffusion Coefficient, $D_0$ for $(\text{CH}_3)_2\text{TlNO}_3$ from NPP Data

\[ i_d = 708 \, nD_0^{1/2} C_0^{2/3} t^{1/6} \]

<table>
<thead>
<tr>
<th>$C_0^\star$, M</th>
<th>$\bar{i}_d$, A x $10^{-6}$</th>
<th>$D_0$, cm$^2$/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1 \times 10^{-5}$</td>
<td>0.090</td>
<td>$1.19 \times 10^{-7}$</td>
</tr>
<tr>
<td>$5 \times 10^{-5}$</td>
<td>0.400</td>
<td>$9.38 \times 10^{-7}$</td>
</tr>
<tr>
<td>$1 \times 10^{-4}$</td>
<td>0.900</td>
<td>$9.38 \times 10^{-7}$</td>
</tr>
<tr>
<td>$5 \times 10^{-4}$</td>
<td>4.00</td>
<td>$9.38 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

$\bar{D}_o = 1.06 \times 10^{-7}$ cm$^2$/s
Figure 20: Normal Pulse Traces for \((\text{CH}_3)_2\text{TlNO}_3\)

--- Blank, 2μA

-.-. 1 x 10^{-5} \text{ M}, 2μA

----- 5 x 10^{-5} \text{ M}, 2μA

.--- 1 x 10^{-4} \text{ M}, 5μA

----- 5 x 10^{-4} \text{ M}, 10μA
coefficient for \((CH_3)_2TlNO_3\) was calculated to be \(1.06 \times 10^{-7} \text{ cm}^2/\text{s}\). This value is indeed very close to that for \((CH_3)_2TlI\), verifying that the anion has little, if any, effect on the diffusion nature of the compound and that this type of organothallium moiety is ionic in dilute aqueous solutions.

**Differential Pulse Polarography**

The results of both the cyclic voltammetry and normal pulse polarography studies indicate that the electrochemical reactions of Tl(I) and organothallium compounds occur at different potentials. However, neither technique is useful for analysis of trace concentrations at the part-per-million (ppm) and part-per-billion (ppb) levels as may be found in environmental samples. Also, the wave shapes would not permit easy identification of a mixture of compounds. Because differential pulse polarography (DPP) data are peak-shaped and capable of detecting ppb levels, it was examined as a method by which mixtures of inorganic thallium and organothallium compounds could be analyzed and quantitatively determined.

Differential pulse polarography has been used to analyze environmental water samples without the aid of a supporting electrolyte. For this reason it was decided to study the thallium compounds at pH's of 4, 7 and 10 so that the spectrum of natural waters could be covered. As in the previous methods, phosphate buffer systems were used.

\(TlNO_3\)

The DPP study was begun with the gathering of calibration data for \(TlNO_3\) from 1 to 8 ppm. This concentration range allowed the analysis of
the compound well above the supposed detection limits so that artifacts caused by straining the method would not interfere. Also, the Tl⁺/Tl⁰ couple has often been studied by electrochemical methods, and is known to be reversible; thus the technique itself may be easily checked.

The TlNO₃ solutions were prepared and analyzed as previously described. Figure 21 is an example of the actual data obtained, showing well-defined peaks at -0.45 V; and Figure 22 gives the calibration curves for all three pH values studied. It is readily seen that the absolute current values resulting from the TlNO₃ concentrations are independent of pH. This is not surprising in that it is known that the Tl⁺/Tl⁰ couple is unaffected by changes in pH.

The next set of TlNO₃ calibration data was taken from 250 to 1000 ppb so that a closer approximation to environmental levels could be studied. This study necessitated increasing the current range setting from 2 μA to 0.2 μA, thus increasing the background noise level. Figure 23 illustrates the calibration curves, and again the lines are very similar. The larger amount of scatter is due to instrumental noise as well as to the interference peaks from the supporting electrolyte which become apparent at these sensitivity settings.

The detection limit was calculated using the method described by Osteryoung and Myers. After calculating the least squares line from the peak current \( i_p \) versus concentration \( C \) values:

\[
i_p = kC + b
\]

the current residual is determined:

\[
(\Delta i_p)_j = (i_p)_j - (kC_j + b)
\]
Figure 21: Differential Pulse Traces for TlNO₃, 1 to 8 ppm

--- Blank
.-.-.-  1 ppm
..-.--  2 ppm
......  4 ppm
.--.--  6 ppm
-----  8 ppm
Figure 22: Calibration Curves for 1 to 8 ppm TlNO$_3$ by DPP

0 - pH 4
Δ - pH 7
+ - pH 10
Figure 23: Calibration Curves for 250 to 1000 ppb TlNO₃ by DPP

- pH 4
- pH 7
- pH 10
The corresponding pooled standard deviation, $S$, is then calculated by:

$$ S = \sqrt{\frac{\sum_{j=1}^{n} [(\Delta i_p)_j]^2}{n - 1}} $$

where $n$ is the number of points. The detection limit, $d_l$, is then expressed by:

$$ d_l = st/k $$

where $k$ is the slope of the line and $t$ is the one-sided $t$ value at a stated confidence interval for $n - 2$ degrees of freedom. For this and all subsequent calculations the value of $t$ is 3.182. Using the calibration data for TlNO$_3$, the calculated values for $d_l$ are 88.1, 39.6 and 155.5 ppb for pH 4, 7 and 10, respectively.

**TlCl, Tl$_2$S**

To determine the effect of changing the anion of the Tl(I) salt, DPP data were taken on solutions of TlCl and Tl$_2$S. Both of these solutions were made as previously described. Unlike TlNO$_3$, TlCl and Tl$_2$S are rather insoluble in water (solubilities of 0.29 and 0.02 g/100 mL water respectively), and are very difficult to dissolve even with heat and stirring. When the compounds were analyzed in the same manner as TlNO$_3$, the only peak present was that due to the reduction of Tl$^+$ at -0.45 V. However, the peak heights for the compounds were lower than for the corresponding concentrations of TlNO$_3$. This is thought to result from the lower actual concentrations of the chloride and sulfide compounds in the standard solutions analyzed and not from an actual decrease in sensitivity. The latter consideration is based on the fact
that no other peaks appeared in their polarograms as would be expected if there were adsorption processes occurring on the mercury drops.

$$(\text{CH}_3)_2\text{TlI}$$

The next step in the development of this analysis method was to discover if organothallium compounds showed linear responses for current versus concentration experiments. The first compound to be tested was dimethylthallium iodide, $(\text{CH}_3)_2\text{TlI}$, which was synthesized as previously described. The test solutions were made and analyzed as reported in earlier sections.

So that the polarogram of $(\text{CH}_3)_2\text{TlI}$ could be observed with a minimum of instrumental noise, an initial calibration curve was derived from concentration data between 1 and 8 ppm at pH 4, 7 and 10 as before. Figure 24 gives a representative set of polarograms at pH 7. Three peaks are observed, with potentials of -0.36, -1.06 and -1.37 V, and they all appear to vary linearly with concentration. Using the information obtained from cyclic voltammetry and normal pulse polarography, these peaks were attributed to adsorption on the mercury by $I^-$, the reduction of $(\text{CH}_3)_2\text{Tl}^+$ to $\text{Tl}^0$ and a hydrogen wave, respectively. Although any peak could have been used, the one of -1.06 V was chosen as the analytical peak because it represented the diffusion-controlled process of the parent cation. Also, its potential was far enough removed from that of $\text{Tl(I)}$ that no interference was expected.

However, unlike the calibration curves of the inorganic salts, the current versus concentration data for $(\text{CH}_3)_2\text{TlI}$ are pH dependent. Figure 25 illustrates the change in peak heights and shapes, and the actual calibration curves are found in Figure 26. The final current
Figure 24: Differential Pulse Traces for $(CH_3)_2TI$, 1 to 8 ppm

- - - - - Blank
- - - - 1 ppm
- - - 2 ppm
- - 4 ppm
- - - 6 ppm
- - - - 8 ppm
Figure 25: DPP Peak Heights and Shapes for \( (\text{CH}_3)_2\text{Tl} \) at Different pH Values

(8 ppm)
Figure 26: Calibration Curves for 1 to 8 ppm \((CH_3)_2TI\) by DPP

0 - pH 4
Δ - pH 7
+ - pH 10
CONCENTRATION, PPM

i, µA

0 2.00 4.00 6.00 8.00

0.05 0.10 0.15 0.20
rise prevents the third peak from appearing at pH 4. At pH 10, an anomalous peak becomes evident at -1.2 V which does not affect the calibration data but which does seem to be involved in the reactions of \((\text{CH}_3)_2\text{Tl}^+\) and hydrogen. The pH dependency is consistent with the mechanism of the dialkylthallium(III) reduction asserted by DiGregorio: \(^{42}\)

\[
R-\text{Tl}^+-R + 3e^- + 2H^+ \rightarrow 2RH + \text{Tl}^0.
\]

Lower level calibration data were taken for \((\text{CH}_3)_2\text{TlI}\) at concentrations between 50 and 1000 ppb. These results are shown in Figure 27. The calculated detection limits for pH 4, 7 and 10 are 21.0, 35.0 and 114 ppb, respectively. Again, the problem of instrumental noise as well as trace contaminant peaks from the buffer seemed to be the limiting factors.

\(\text{TlNO}_3\) and \((\text{CH}_3)_2\text{TlI}\)

When inorganic thallium(I) salts enter an environment where they may be biomethylated it would be expected that mixtures of these salts with dimethylthallium(III) salts could result. Therefore, the DPP method was used to analyze synthetic mixtures of \(\text{TlNO}_3\) and \((\text{CH}_3)_2\text{TlI}\).

The solutions utilized and the analytical peak heights are given in Table V. Because of the iodide adsorption peak at -0.36 V, the measurement of the -0.45 V analytical peak for \(\text{TlNO}_3\) was hampered. As shown in Figure 28 the two peaks are discernible at pH 4, but have merged at pH 7 and 10. Also, there does not appear to be any change in the expected peak heights with the mixture. Figure 29 confirms this fact for the \((\text{CH}_3)_2\text{TlI}\) calibration data, which appear quite linear for all three pH values. However, the \(\text{TlNO}_3\) data are in doubt because of the peak...
Figure 27: Calibration Curves for 50 to 1000 ppb (CH$_3$)$_2$TI by DPP

0 - pH 4
Δ - pH 7
+ - pH 10
Table V

Peak Current versus Concentration Data for Mixtures of TlNO$_3$ and (CH$_3$)$_2$TlI

<table>
<thead>
<tr>
<th>Concentrations, ppm</th>
<th>Peak Currents, A x 10$^{-8}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 4</td>
</tr>
<tr>
<td>TlNO$_3$</td>
<td>(CH$_3$)$_2$TlI</td>
</tr>
<tr>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 28: Differential Pulse Traces for Mixtures of TlNO$_3$ and (CH$_3$)$_2$TlI

--- Blank
----- 5 ppm TlNO$_3$, 1 ppm (CH$_3$)$_2$TlI
..... 3 ppm TlNO$_3$, 3 ppm (CH$_3$)$_2$TlI
-.-- 1 ppm TlNO$_3$, 5 ppm (CH$_3$)$_2$TlI
Figure 29: Calibration Curves for (CH₃)₂TlI from Mixtures by DPP

0 - pH 4
Δ - pH 7
+ - pH 10
interference. The average calculated detection limits are 202 ppb for TlNO₃ and 194 ppb for (CH₃)₂TlI at the pH values studied.

\[(CH₃)₂TlNO₃\]

Although the halide salts of dialkythallium are expected to be the most common environmental form, the nitrate salt would also be anticipated. As has been shown by cyclic voltammetry and normal pulse polarography, \((CH₃)₂TlNO₃\) does not have any adsorption interferences with the mercury electrodes. The first step is to repeat the calibration curve procedures for this compound. Figure 30 illustrates one set of data curves for 1 to 8 ppm, and as was anticipated, no adsorption peak is seen, while the double peaks from the \((CH₃)₂Tl^+\) appear at the same potentials as for \((CH₃)₂TlI\). Figure 30 shows that, again, the calibration curves vary with pH.

When the calibration data were repeated for 50 to 1000 ppb, the current versus concentration curves were linear as seen in Figure 31. The calculated detection limits are 76.1, 22.2 and 135 ppb for pH 4, 7 and 10, respectively. For most purposes the detection limits for both organothallium compounds are the same.

\[TlNO₃ \text{ and } (CH₃)₂TlNO₃\]

Both nitrate compounds were mixed in the ppm ratios as before. The absence of an adsorption peak in the \((CH₃)₂TlNO₃\) would seem to aid the measurement of the TlNO₃ peaks. As is seen in Figure 32 this is apparent.

The calibration data are present in Figure 33, and are linear for both the inorganic and organometallic species. The average calculated
Figure 30: Calibration Curves for 1 to 8 ppm \((\text{CH}_3)_2\text{TINO}_3\) by DPP

- O - pH 4
- Δ - pH 7
- + - pH 10
Figure 31: Calibration Curves for 50 to 1000 ppb (CH₃)₂TLNO₃ by DPP

0 - pH 4
Δ - pH 7
+ - pH 10
Figure 32: Differential Pulse Traces for Mixtures of TlNO$_3$ and (CH$_3$)$_2$TlNO$_3$

--- Blank

----- 5 ppm TlNO$_3$, 1 ppm (CH$_3$)$_2$TlNO$_3$

***** 3 ppm TlNO$_3$, 3 ppm (CH$_3$)$_2$TlNO$_3$

-.--. 1 ppm TlNO$_3$, 5 ppm (CH$_3$)$_2$TlNO$_3$
Figure 33: Calibration Curves for TlNO₃ and (CH₃)₂TlNO₃ from Mixtures by DPP

- O - TlNO₃, pH 4
- Δ - TlNO₃, pH 7
- + - TlNO₃, pH 10
- x - (CH₃)₂TlNO₃, pH 4
- ◊ - (CH₃)₂TlNO₃, pH 7
- † - (CH₃)₂TlNO₃, pH 10
detection limits are 214 ppb and 419 ppb for TlNO₃ and (CH₃)₂TlNO₃, respectively.

When altered by the 0.60 factor, these values become 128 and 251 ppb, respectively. The decrease in the detection limit for TlNO₃ is notable and obviously results from an interference from an adsorption peak. The detection limit for (CH₃)₂TlNO₃ is higher than that for (CH₃)₂TlI but the reasons for this are not clear. The possibility exists that the iodide adsorption enhances the detection of that compound while the nitrate would not have that advantage.²⁵⁸

Sample Loss and Exchange

Whenever the thallium compounds were analyzed for concentrations of 1 to 8 ppm, 100 mL of each sample was prepared. The initial analysis used only 50 mL in each case, and the remaining 50 mL was stored in the glass volumetric flask for later analysis. Table VI shows that for the elapsed times, the specified concentrations and the container material, no sample loss was noted, indicating that both inorganic thallium and organothallium solutions may be stored without acidification.

To check for possible problems by having TlNO₃ and (CH₃)₂TlNO₃ mixed in low levels over a period of time, solutions containing 250 ppb of each substance were made in the three buffer solutions and stored in glass 250 mL volumetric flasks. The samples were analyzed at 0, 27, 48, 96 and 120 hours from mixing. Figure 34 shows that no trends of increase or decrease in either analytical peak were noted; the variation can be attributed to noise at a current range setting of 0.2 µA.
Table VI

Sample Loss over Time for TlNO\textsubscript{3}, (CH\textsubscript{3})\textsubscript{2}TII and (CH\textsubscript{3})\textsubscript{2}TlNO\textsubscript{3} in Glass Flasks

<table>
<thead>
<tr>
<th>A. TlNO\textsubscript{3}</th>
<th>Peak Current, A x 10\textsuperscript{-8}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 4</td>
</tr>
<tr>
<td>Conc, ppm</td>
<td>0 hr</td>
</tr>
<tr>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td>2</td>
<td>4.2</td>
</tr>
<tr>
<td>4</td>
<td>8.6</td>
</tr>
<tr>
<td>6</td>
<td>12.8</td>
</tr>
<tr>
<td>8</td>
<td>17.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B. (CH\textsubscript{3})\textsubscript{2}TII</th>
<th>Peak Current, A x 10\textsuperscript{-8}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 4</td>
</tr>
<tr>
<td></td>
<td>0 hr</td>
</tr>
<tr>
<td>1</td>
<td>1.9</td>
</tr>
<tr>
<td>2</td>
<td>3.8</td>
</tr>
<tr>
<td>4</td>
<td>8.0</td>
</tr>
<tr>
<td>6</td>
<td>12.2</td>
</tr>
<tr>
<td>8</td>
<td>16.6</td>
</tr>
<tr>
<td>Conc, ppb</td>
<td>pH 4</td>
</tr>
<tr>
<td>----------</td>
<td>-------</td>
</tr>
<tr>
<td></td>
<td>0 hr</td>
</tr>
<tr>
<td>50</td>
<td>0.8</td>
</tr>
<tr>
<td>250</td>
<td>3.9</td>
</tr>
<tr>
<td>500</td>
<td>7.1</td>
</tr>
<tr>
<td>750</td>
<td>10.3</td>
</tr>
<tr>
<td>1000</td>
<td>12.3</td>
</tr>
</tbody>
</table>

Table VI (continued)
Figure 34: Peak Current vs Time Graphs for 250 ppb Mixtures of TlNO$_3$ and (CH$_3$)$_2$TlNO$_3$ by DPP

- O - TlNO$_3$, pH 4
- Δ - TlNO$_3$, pH 7
- + - TlNO$_3$, pH 10
- X - (CH$_3$)$_2$TlNO$_3$, pH 4
- ◊ - (CH$_3$)$_2$TlNO$_3$, pH 7
- † - (CH$_3$)$_2$TlNO$_3$, pH 10
Interference Study

It would be anticipated that environmental samples would be mixtures of metals, including those that would interfere with the DPP determination of thallium compounds. Expected interferences would include Pb\(^{2+}\) (\(E_{1/2} = -0.43\) V), Cd\(^{2+}\) (\(E_{1/2} = -0.63\) V) and Zn\(^{2+}\) (\(E_{1/2} = -1.02\) V) as their presence in natural waters and coal fly ash would not be uncommon. Therefore, an analysis of a mixture of TlNO\(_3\) and (CH\(_3\))\(_2\)TlNO\(_3\) in a solution containing these three metals was undertaken.

The analysis was run in an acetate buffer so that the removal of the interferences by formation of their insoluble phosphates would not occur. The test solution was made 4 ppm in TlNO\(_3\) and (CH\(_3\))\(_2\)TlNO\(_3\) and a DPP scan was run as illustrated in Figure 35. The solution was then made approximately 4 ppm in lead, cadmium and zinc by adding the appropriate volumes of Pb(NO\(_3\))\(_2\), CdCl\(_2\) and ZnCl\(_2\), respectively. As is readily seen the peaks for Pb\(^{2+}\) and Zn\(^{2+}\) are at the same potentials as those for Tl\(^{+}\) and (CH\(_3\))\(_2\)Tl\(^{+}\), and that for Cd\(^{2+}\) would clearly interfere with the Tl\(^{+}\) peak at higher Cd\(^{2+}\) concentrations.

The most obvious method for removal of these interferences is by the addition of EDTA to the test solution, which would not be expected to alter the positions of the peaks of the thallium compounds. To accomplish this, 1 mL of 0.4 M EDTA solution was added to the solution. The peaks for Pb\(^{2+}\) and Cd\(^{2+}\) were shifted to more negative potentials so that they no longer interfered with the Tl\(^{+}\) peak, which remained at -0.45 V, as shown in Figure 35. However, these peaks along with that for Zn\(^{2+}\) appeared at potentials very close to that of the (CH\(_3\))\(_2\)Tl\(^{+}\) peak (-1.1 V) and, in fact, obscured it. Also, a peak that originally appeared at -0.1 V was shifted to -0.3 V upon the addition of EDTA, and by
Figure 35: Differential Pulse Traces for TlNO₃ and (CH₃)₂TlNO₃ in the Presence of Interfering Metals and EDTA

Line 1 (-----): Blank
  Peak 1a: Cu²⁺

Line 2 (-----): 4 ppm TlNO₃,
  4 ppm (CH₃)₂TlNO₃ added
  Peak 2a: Cu²⁺
  2b: Tl⁺
  2c: (CH₃)₂Tl⁺

Line 3 (-----): 4 ppm Pb²⁺, Cd²⁺,
  Zn²⁺ added
  Peak 3a: Cu²⁺
  3b: Tl⁺, Pb²⁺
  3c: Cd²⁺
  3d: (CH₃)₂Tl⁺, Zn²⁺

Line 4 (-----): solution made 0.01 M EDTA
  Peak 4a: Cu²⁺
  4b: Tl⁺
  4c: (CH₃)₂Tl⁺, Pb²⁺,
       Cd²⁺, Zn²⁺
comparison to table values, this peak is attributable to small amounts of copper in the solution.

Obviously, then, both inorganic and organothallium compounds may be quantified by DPP in the presence of interfering metals with certain considerations. The detection of Tl\(^+\) is facilitated by the addition of EDTA as long as excessive quantities of Cu\(^{2+}\) are not present. The fact that the addition of EDTA may obscure the (CH\(_3\))\(_2\)Tl\(^+\) peak is disturbing but the ability of computers to separate peaks would enable the unraveling of the contaminant contributions. This same process would also be of use when the determination of Tl\(^+\) in the presence of excess Cu\(^{2+}\) is desired. This procedure is greatly simplified by the numerous compilations of half-wave potentials in various media.

Differential Pulse Anodic Stripping Voltammetry

The detection limits achieved with DPP were, for the most part, in the 100 to 200 ppb range. Also, the problem of interfering peaks both with and without the addition of EDTA indicated that the method might not be suitable for analysis of complex environmental mixtures unless extensive data analysis was performed on the DPP scans. Furthermore, environmental levels of thallium compounds would most probably be in the lower part-per-billion or upper part-per-trillion range, suggesting the inspection of differential pulse anodic stripping voltammetry (DPASV) as a method to determine these compounds at lower concentrations.

A previously described, the rotating electrode equipment was rather crude. Non-uniform rotation of the GCE resulted in a wobbling action, so that a "worst-case analysis" is what may be safely presented.
However, on the basis of this study recommendations on equipment and method improvements can be made.

Perhaps the most difficult part of the DPASV procedure is the formation of a uniform thin mercury film on the GCE. Because the effect of mixing organothallium compounds with mercury salts was not known, the plating of the film was performed separately from the sample deposition step instead of an in situ deposition of the film and the compound of interest. Also, the two-step method allowed the inspection of the film. Changes in film thickness and uniformity could be noted by a change in peak height and potential. Generally, the potential at which metals reduce is more negative for thin films than for mercury drops. A pertinent example is the Tl⁺ reduction occurs at -0.45 V on DME's or HMDE's, whereas the same electrochemical process occurs at -0.67 V for a MTFE. DPASV peaks appear at an intermediate potential and also vary within the same standard additions curve when the film is thick or beaded.

Analysis in Phosphate Buffer

All DPASV studies were performed in pH 7 phosphate buffer, except as noted. As mentioned earlier the analyses were carried out by the standard additions method, so that solution variability could be kept to a minimum. The procedure for an analysis of TlNO₃ was as outlined previously, with -0.9 V chosen as the electrolysis potential. This voltage has been selected by several authors and allows a complete electrolysis of the thallium salt and, at the same time, does not cause compounds of higher potentials to be plated onto the electrode which would interfere in the stripping step. Figure 36 shows the resulting DPASV curves for 100 to 500 ppb TlNO₃, with the deposition time of 3 min.
Figure 36: DPASV Traces for TlNO$_3$, 100 to 500 ppb

--- Blank
••••• 100 ppb
•••• 200 ppb
•••• 300 ppb
•••• 400 ppb
••••• 500 ppb
used for each run. The peak potential was -0.665 V for the Tl\(^+\)/Tl\(^0\) reaction. The calibration curve obtained from these data is shown in Figure 37, and is quite linear.

Because of the great sensitivity of this method, new calibration data were collected between 20 and 100 ppb for TlNO\(_3\). For these analyses, the deposition time was 3 min and the current range 10 \(\mu\)A. The actual DPASV curves appeared very similar to that from the higher concentrations, and the resulting current versus potential curve is shown in Figure 38. Using this low level data, the calculated detection limit for TlNO\(_3\) is found to be 3.2 ppb.

A similar procedure was used to analyze (CH\(_3\))\(_2\)TlNO\(_3\), although the electrolysis potential was -1.2 V. However, the stripping scan was begun at -0.9 V as for the TlNO\(_3\) determinations since the peak potential and height are time dependent. Figure 39 illustrates a 20 to 100 ppb standard additions procedure for (CH\(_3\))\(_2\)TlNO\(_3\), and, as may be seen, the stripping peak appears at the same potential as that of TlNO\(_3\). This is not surprising, as earlier studies by cyclic voltammetry showed that organothallium(III) salts reduce to Tl\(^0\). A straight line is obtained from the data and is shown in Figure 40. The detection limit for (CH\(_3\))\(_2\)TlNO\(_3\) by DPASV was calculated using analyses of concentrations between 20 and 100 ppb, and was found to be 3.4 ppb.

Now that DPASV has been shown to be a method to detect lower ppb levels of thallium compounds separately, the utility of the procedure for mixtures must be shown. The mixture analyzed was 20 ppb of both TlNO\(_3\) and (CH\(_3\))\(_2\)TlNO\(_3\). Figure 41 shows the stripping peaks obtained. There was no peak obtained when only (CH\(_3\))\(_2\)TlNO\(_3\) was electrolyzed at -0.9 V, but one did result when the potential was set at -1.2 V. When
Figure 37: Standard Additions Curves for 100 to 500 ppb TlNO₃ by DPASV
Figure 38: DPASV Traces for TlNO$_3$, 20 to 100 ppb

- Blank
- `.---` 20 ppb
- `..--` 40 ppb
- `....` 60 ppb
- `--.--` 80 ppb
- `-----` 100 ppb
i, $\mu$A vs E, -V vs SCE
Figure 39: DPASV Traces for $\text{(CH}_3\text{)}_2\text{TLNO}_3$, 20 to 100 ppb

--- Blank

.-.-.- 20 ppb

..--.. 40 ppb

-----.. 60 ppb

.-.-- 80 ppb

------ 100 ppb
Figure 40: Standard Additions Curve for 100 to 500 ppb (CH$_3$)$_2$TlNO$_3$ by DPASV
Figure 41: DPASV Traces for TlNO$_3$-(CH$_3$)$_2$TlNO$_3$ Mixture (20 ppb) with and without EDTA Addition

--- Blank and 50 ppb (CH$_3$)$_2$TlNO$_3$, -0.9 V

・・・・・ 50 ppb (CH$_3$)$_2$TlNO$_3$, -1.2 V

----- 50 ppb (CH$_3$)$_2$TlNO$_3$ and 50 ppb TlNO$_3$, -0.9 V

---- 50 ppb (CH$_3$)$_2$TlNO$_3$ and 50 ppb TlNO$_3$, -1.2 V

..-. 50 ppb (CH$_3$)$_2$TlNO$_3$ and 50 ppb TlNO$_3$, -0.9 V, 0.01 M EDTA

.-.-.- 50 ppb (CH$_3$)$_2$TlNO$_3$ and 50 ppb TlNO$_3$, -1.2 V, 0.01 M EDTA
the TlNO₃ was added and the solution electrolyzed at -0.9 V, a peak did appear, giving a quantitative measure for the inorganic species only. Electrolysis at -1.2 V then gave a peak whose height was the sum of that obtained from TlNO₃ and (CH₃)₂TlNO₃. Therefore, the method is capable of analyzing both species in the same solution by changing only the electrolysis potential. From these results it was assumed that if the deposition times were lengthened and the sensitivity increased that almost any desired concentrations of thallium compounds could be determined.

The effect of adding EDTA to a solution to be analyzed by DPASV was observed by the introduction of 1 mL of 0.4 M EDTA solution to a sample containing a mixture of TlNO₃ and (CH₃)₂TlNO₃. As shown in Figure 41 the peaks obtained were shifted to slightly more negative potentials and the peak current decreased. However, the difference between the peak representing TlNO₃ alone and that representing both TlNO₃ and (CH₃)₂TlNO₃ was equal to that in the absence of EDTA. This indicated that the peak current attributable to (CH₃)₂TlNO₃, which is equivalent to this difference, is unaffected by EDTA, while the same cannot be said for the current for TlNO₃. Several references in the electrochemical literature make no mention of this effect, although EDTA has been used to mask Tl⁺ in colorimetric determinations of Me₂Tl⁺.

To investigate this phenomenon in greater detail 0.4 M EDTA was added by standard additions to a 50 ppb TlNO₃ solution. Figure 42 illustrates the decrease in peak potential versus the EDTA addition and Figure 43 shows the corresponding peak potential shift. The magnitude of the decrease in peak current becomes insignificant after 1 mL of the
Figure 42: Graph of Peak Height vs Volume of EDTA Added for TlNO$_3$ and (CH$_3$)$_2$TlNO$_3$ by DPASV

0 - 50 ppb TlNO$_3$

Δ - 50 ppb (CH$_3$)$_2$TlNO$_3$
VOLUME 0.04 M EDTA ADDED, ML
Figure 43: Graph of Peak Potential vs Volume of EDTA
Added for TlNO$_3$ and (CH$_3$)$_2$TlNO$_3$ by DPASV

$0 - 50$ ppb TlNO$_3$

$\Delta - 50$ ppb (CH$_3$)$_2$TlNO$_3$
solution is added (a solution concentration of approximately $1 \times 10^{-2}$ M EDTA), so this would be a recommended EDTA concentration to use for interference removal.

The effects of EDTA addition to a sample containing 50 ppb $(\text{CH}_3)_2\text{TlNO}_3$ was also studied. As expected, the peak current showed no increase as illustrated in Figure 42 although the peak potential showed a shift of -0.030 much like that noted for TlNO$_3$ (Figure 43).

The potential shift for the thallium peak does not affect the analysis of these compounds. The cathodic shift of the peak potential upon addition of EDTA is related to the lowering of the free energy of dissociation by complex formation. This implies that the reduction of the Tl-EDTA complex proceeds with greater difficulty than that of the uncomplexed thallium compounds.$^{59,66}$ The significant decrease in the current for the Tl$^+$ peak is an important consideration in its quantitation by DPASV in the presence of EDTA. However because the procedure presented in this work is a relative rather than an absolute one, the only requirement implied by these results is that an equal amount of EDTA must be used in each solution containing TlNO$_3$.

**Analyses in Environmental Matrices**

The utility of this DPASV method for the analysis of thallium compounds in a "pristine" system has been demonstrated. The next step was to repeat the procedure in nonideal solutions including tap water, lake water and coal fly ash leachates where interferences from other metals in solution are to be expected.
**Tap Water**

Samples of tap water were analyzed by the same procedure outlined above using three different media: without the addition of any supporting electrolyte, with NaCl added to make the solution 0.1 M NaCl, and 50% tap water and 50% double-strength phosphate buffer. The pH value of the water alone was 6. Also, Baton Rouge water is soft (i.e., has a low level of CaCO₃), so that the amount of interfering metals is expected to be low. As shown in Figure 44 the standard addition of TlNO₃ to tap water without any supporting electrolyte did not give a straight line, curving over at higher added concentrations of TlNO₃. This phenomena is easily explained by realizing that without a supporting electrolyte, the addition of even the small amounts of thallium salt are enough the change the ionic strength of the sample appreciably.

When NaCl was added to a sample of tap water, the ionic strength of the solution was not affected by sample addition and as illustrated in Figure 44, yielded a straight line current versus concentration curve. The same effect was noted for the tap water/phosphate buffer system, with the absolute peak magnitudes being almost identical. No Tl⁺ was noted in the sample before the first addition, and the calculated detection limit was 1.5 ppb. Therefore, it was apparent from this study that some sort of supporting electrolyte must be used for the analysis of water samples and that a one-to-one dilution with a buffer solution caused no unforeseen problems.

The same procedure was used to analyze tap water in the presence of (CH₃)₂TlNO₃, except that the plating voltage was -1.2 V as before. Again, no (CH₃)₂TlNO₃ was noted before any addition, and when the solution was diluted with phosphate buffer as in the TlNO₃ analysis, yielded...
Figure 44: Standard Additions Curve for 20 to 100 ppb Tl(NO₃)₂ in Tap Water by DPASV

0 - without NaCl

Δ - with NaCl
a straight current versus concentration curve, as shown in Figure 45. The DPASV scan for this analysis is shown in Figure 46 with a contaminant peak noted at -0.22 V. This is attributable to Cu\(^{2+}\) but its presence did not interfere with the analysis of either thallium compound. The calculated detection limit in this case was 5.2 ppb.

Also, as described in the previous section, a mixed solution of 20 ppb of both TINO\(_3\) and (CH\(_3\))\(_2\)TINO\(_3\) was analyzed. As seen in Figure 47 the peaks derived from the electrolysis of the solution at the appropriate potentials are additive. This reconfirms the utility of the selective electrolysis procedure to determine the amounts of both inorganic and organothallium compounds in the same solution.

Lake Water

The lake water used for analysis has been described previously. It was expected to contain contaminant metals as well as various forms of biota so it presented an interesting matrix in which to study thallium compounds. Also, if a similar method was to be adapted to field investigation the ability to analyze this type of sample without pretreatment would be necessary.

In each case, 25 mL of lake water were added to 25 mL of phosphate buffer, the final pH value of the sample being approximately 6. No thallium peak was seen in the initial DPASV scan but peaks at -0.47 V and -0.22 V were noted and indicated the presence of Pb\(^{2+}\) and Cu\(^{2+}\) in the lake water as shown in Figure 48. While the copper peak presented potentially little hindrance in the analysis the same could not be said for the lead peak, as its potential was close to the thallium potential of -0.610 V.
Figure 45: Standard Additions Curve for 20 to 100 ppb \((\text{CH}_3)_2\text{TlNO}_3\) in Tap Water by DPASV
Figure 46: DPASV Traces for \((\text{CH}_3)_2\text{TlNO}_3\) in Tap Water, 20 to 100 ppb

- - - - - - Blank, \(\text{Cu}^{2+}\) peak (without EDTA)
- - - - - 20 ppb (with EDTA)
- - - - - 40 ppb (with EDTA)
- - - - - - - 60 ppb (with EDTA)
- - - - - 80 ppb (with EDTA)
- - - - - - - - 100 ppb (with EDTA)
Figure 47: DPASV Traces for TlNO$_3$-(CH$_3$)$_2$TlNO$_3$
Mixture (20 ppb) in Tap Water

--- Blank and 20 ppb (CH$_3$)$_2$TlNO$_3$, 
-0.9 V

--- 20 ppb (CH$_3$)$_2$TlNO$_3$, -1.2 V

...... 20 ppb (CH$_3$)$_2$TlNO$_3$ and 
20 ppb TlNO$_3$, -0.9 V

------- 20 ppb (CH$_3$)$_2$TlNO$_3$ and 
20 ppb TlNO$_3$, -1.2 V
E, -V vs SCE

i, μA

0.1 μA
Figure 48: DPASV Traces for TlNO$_3$ in Lake Water, 20 to 100 ppb

- - - - - - Blank ($\text{Pb}^{2+}$ peak)
- - - - - 20 ppb
- - - - - 40 ppb
- - - - - 60 ppb
- - - - - 80 ppb
- - - - - 100 ppb
Figure 48 illustrates a series of standard additions DPASV scans for TlNO₃ and Figure 49 is a graph of the current versus concentration data obtained. One interesting observation made in this experiment was that an addition of Tl⁺ also caused an apparent increase in the Pb²⁺ peak. No definitive explanation will be attempted in this work, although it may be postulated that the lead and thallium may be involved in competing equilibria with the humic acid in the lake water samples. The calculated detection limit for TlNO₃ in this matrix was 3.7 ppb, and while this value is approximately the same as that for other matrices, the slope of the standard additions curve was 0.91 as opposed to an average of 0.65 for the other curves. Again, this difference is probably caused by some component in the lake water that remains undefined.

Dimethylthallium nitrate was likewise analyzed in lake water/phosphate buffer. The same increase in the lead peak was noted. In this case, the calculated detection limit was 3.4 ppb, and, again, the slope of the standard additions curve was 0.45 as compared to 0.34 for the other matrices. A more thorough comparison of detection limits and curve slopes for this method will be made later in this work.

Again, a mixture of 20 ppb of both TlNO₃ and (CH₃)₂TlNO₃ was analyzed as previously described. As illustrated in Figure 50, the peaks are additive, reinforcing the utility of the method for successive quantitation of inorganic and organothallium compounds.

The quantitation of Pb²⁺ was attempted by the dilution of lake water with acetate buffer and the subsequent addition of incremental amounts of Pb(NO₃)₂. This data was not reproducible over time and it was concluded that the lake water was affecting the MTFE in such a way as to change the electrical double layer. When analyzed by
Figure 49: Standard Additions Curve for 20 to 100 ppb TlNO$_3$ in Lake Water by DPASV
Figure 50: DPASV Traces for TlNO$_3$-(CH$_3$)$_2$TlNO$_3$ Mixture (20 ppb) in Lake Water

- Blank (Pb$^{2+}$ peak) and
- 20 ppb (CH$_3$)$_2$TlNO$_3$, -0.9 V
- 20 ppb (CH$_3$)$_2$TlNO$_3$, -1.2 V
- 20 ppb (CH$_3$)$_2$TlNO$_3$ and
  20 ppb TlNO$_3$, -0.9 V
- 20 ppb (CH$_3$)$_2$TlNO$_3$ and
  20 ppb TlNO$_3$, -1.2 V
potentiometric stripping analysis, however, the lead concentration of the lake water was found to be 20 ppb. Also, the lead peak potential shifted to -0.55 V in the presence of acetate buffer, a potential cause of hindrance in the analysis of thallium. However, as depicted in Figure 48, the addition of 1 mL 0.4 M EDTA solution completely removed the lead peak, leaving only that attributable to thallium. Therefore, thallium compounds may be analyzed in this more complex matrix and metal interferences may be masked with the addition of EDTA.

Coal Fly Ash Leachates

This research was undertaken in part because of the possibility of thallium emissions in coal fly ash and their leachates; thus, samples of leachate were analyzed by the DPASV procedure developed. The samples were prepared and stored as discussed previously and were from two different sources. When analyzed before the addition of any thallium compound, the only metals noted were lead and copper, with peak potentials at -0.55 and -0.14 V, respectively. The sample from the Clinch River furnace appeared to have substantially more Pb\(^{2+}\) than that from the Amos furnace. As it was necessary to preserve the integrity of these samples, the Pb\(^{2+}\) peak could not be masked by EDTA and the sample had to be diluted with acetate buffer. Also, because neither leachate showed any thallium present and both samples appeared to contain the same metals at the electrolysis times and potentials chosen, only the sample leached from the Amos fly ash was used.

Figure 51 is an illustration of the analysis of the leachate sample by differential electrolysis for a mixture of 20 ppb TlNO\(_3\) and
Figure 51: DPASV Traces for TlNO$_3$-(CH$_3$)$_2$TlNO$_3$ Mixture (20 ppb) in Coal Fly Ash Leachate

--- Blank (Pb$^{2+}$ and Cu$^{2+}$ peaks) and
20 ppb (CH$_3$)$_2$TlNO$_3$, -0.9 V

-.-- 20 ppb (CH$_3$)$_2$TlNO$_3$, -1.2 V

----- 20 ppb (CH$_3$)$_2$TlNO$_3$ and
20 ppb TlNO$_3$, -0.9 V

----- 20 ppb (CH$_3$)$_2$TlNO$_3$ and
20 ppb TlNO$_3$, -1.2 V
(CH$_3$)$_2$TlNO$_3$. Clearly, this type of analysis is applicable to the leachate matrix as it was in the others studied.

Unless the electrolysis potential in the DPASV analysis is -1.2 V, the (CH$_3$)$_2$TlNO$_3$ present in the leachate sample would not contribute to the thallium peak. Therefore, the standard addition procedure for TlNO$_3$ was straightforward, and as seen in Figure 52 showed a linear relationship. The calculated detection limit for TlNO$_3$ was 3.2 ppb, which is in the same range as for the analyses in other matrices. The slope was 0.65, as was the case for deionized and tap water analyses.

The same sample was used for a standard addition of (CH$_3$)$_2$TlNO$_3$, which allowed a check on the concentration of thallium already present. The calculated detection limit was 5.3 ppb, and the extrapolated original thallium concentration, as may be derived from Figure 53, was 128 ppb. This is acceptable considering the high background levels as well as the interference from the Pb$^{2+}$ peak, and would definitely improve if EDTA were used as a masking agent. Also, the slope of the curve, 0.19, was somewhat lower than that for deionized and tap water analyses.

Table VII is a summary of the calculated detection limits and standard additions curve slope obtained by the DPASV procedure developed. The only significant difference may be seen in the slope values for analyses in lake water and, as stated before, the reason for this is not clear. However, the analysis of thallium compounds is not hindered and may be accomplished in the presence of interfering metals or after their masking. The pH values of these matrices was between 6 and 7, and, as was seen in DPP studies, the electrochemical response of Tl$^+$ compounds is unaffected by pH while that for Me$_2$Tl$^+$ is decreased with
Figure 52: Standard Additions Curve for 20 to 100 ppb TlNO₃ in Coal Fly Ash Leachate by DPASV
Figure 53: Standard Additions Curve for 20 to 100 ppb \((\text{CH}_3)_2\text{TlNO}_3\) in Coal Fly Ash Leachate by DPASV
### Table VII

Detection Limits (D.L.) Obtained with DPASV

<table>
<thead>
<tr>
<th>Compound</th>
<th>Matrixa</th>
<th>D.L., ppb</th>
<th>Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tl(NO₃)₂</td>
<td>Deionized Water/PO₄³⁻</td>
<td>3.2</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>Tap Water/PO₄³⁻</td>
<td>1.5</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>Lake Water/PO₄³⁻</td>
<td>3.7</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>CFAL/Ac⁻</td>
<td>3.2</td>
<td>0.65</td>
</tr>
<tr>
<td>(CH₃)₂Tl(NO₃)₂</td>
<td>Deionized Water/PO₄³⁻</td>
<td>3.4</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>Tap Water/PO₄³⁻</td>
<td>5.2</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>Lake Water/PO₄³⁻</td>
<td>3.4</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>CFAL/Ac⁻</td>
<td>5.3</td>
<td>0.19</td>
</tr>
</tbody>
</table>

aAbbreviations: PO₄³⁻ - phosphate buffer, pH 7  
Ac⁻ - acetate buffer, pH 7  
CFAL - coal fly ash leachate (Amos)
increasing pH value. Therefore, the analysis of any sample for these compounds should be done in a buffer system, and comparison of the data obtained may only be made with the pH of the sample considered.
Several conclusions may be drawn from the results obtained by the electroanalytical methods described in this work. The mechanism for organothallium reduction proposed by DiGregorio was supported by cyclic voltammetry and normal pulse polarography; these compounds undergo an irreversible three electron reduction to \( \text{Tl}^0 \) with the reaction being pH dependent. The similarity of the values of the transfer coefficients, rate constants and diffusion coefficients for \((\text{CH}_3)_2\text{TlI}\) and \((\text{CH}_3)_2\text{TlNO}_3\) serve to establish the ionic nature of these compounds in solution. Also, the observation of an adsorption prewave in the cyclic voltamogram of \((\text{CH}_3)_2\text{TlI}\) foreshadowed an interference problem in the other electrochemical methods used.

Differential pulse polarography is best used to perform survey scans so that a sample's total metal content may be seen in one analysis step. The direct observation of the species present is a clear advantage of this technique, with the analyses of ppm levels of thallium compounds being easily attainable. However, the quantitation of ppb amounts, as would be expected in environmental samples, is not readily accomplished. Although interfering metal peaks are easily shifted away from the \( \text{Tl}^+ \) peak by the addition of EDTA, the addition of this masking agent obscures the \((\text{CH}_3)_2\text{Tl}^+\) peak. Finally, the presence of an organothallium halide produces an interference with the \( \text{Tl}^+ \) peak which subsequently increases its detection limit.
From this study it is apparent that differential pulse anodic stripping voltammetry is the electroanalytical method of choice for the analysis and speciation of thallium compounds in the environment. Using the fact that the electrolysis potentials of the moieties are different, their quantitation is straightforward and part-per-billion and part-per-trillion detection limits are achieved. Generally, environmental matrices do not affect the procedure although the presence of compounds such as humic acid may require certain adjustments in the method. The electroanalysis of \( \text{(CH}_3\text{)}_2\text{Tl}^+ \) is unaffected by EDTA, although there is a decrease in the \( \text{Tl}^+ \) peak height upon this addition. However, as long as the same concentration of EDTA is used in each solution, this effect is unimportant. Interferences are also suppressed by the use of phosphate buffers, and in DPASV the choice of electrolysis potential also aids in the selectivity of the method.

The limitations of the techniques described revolve around the use of mercury electrodes, although their advantages are felt to exceed their disadvantages. The DPASV method would also be improved with more robust equipment; i.e., a commercial rotating electrode would not have the wobble that was present in the analyses described. After determining the appropriate electrolysis potentials this procedure would be applicable to other inorganic-organometallic systems such as those of lead and tin. In fact, with certain refinements, mixtures of various metal systems could be quantitated in this manner.

Other extensions of this work could include the study of the kinetic breakdown of organothalliums in natural waters by sunlight. This would necessitate the identification of interfering components such as humic acid in these waters and the subsequent unravelling of their
effects on the environmental chemistry of thallium and other heavy metal compounds. In addition, potentiometric stripping analysis could be applied to these systems, and a field monitoring device could be developed to enable on-site quantitation of metal species.
REFERENCES


VITA

Linda Katherine Hoeflich was born in Baltimore, Maryland on August 14, 1955. While residing in Baldwin, Maryland, she attended Baltimore County Public Schools, and graduated from Dulaney Senior High in 1973. Subsequently she attended Goucher College in Towson, Maryland where she received a B.A. in Chemistry in May, 1977.

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Major Field: Analytical Chemistry

Title of Thesis: Application Of Electroanalytical Techniques To Environmental Thallium Compounds

Approved:

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