THALLIUM AND THALLIUM COMPOUNDS

1. Introduction

1.1. History. Thallium was discovered spectroscopically in 1861 by Sir William Crookes by an intense green color imparted to a flame by the element while examining residues from a sulfuric acid plant (1). Thallium was named after this spectral emission from the Greek *thallos* (a green shoot or twig). The metal was isolated by Crookes and Claude-Auguste Lamy independently in 1862.

1.2. Occurrence. The abundance of thallium in the earths crust is estimated at 0.7 mg/kg (ppm). Thallium has been found to exist in conjunction with potassium minerals in clays, granites, etc. These are not considered to be commercially viable sources. Over 40 thallium-containing minerals have been identified with the most notable being crooksite ($Cu_7Tl_{0.75}Ag_{0.25}Se_4$) and lorandite ($TlAsS_2$).

While thallium does occur in oxide minerals, it is primarily found as a chalcophile complexed as sulfides or selenides with antimony, arsenic, copper, lead, zinc. Because of this, thallium is most often extracted from the flue dust and residues produced during the processing of these ores. It has also been obtained as a by-product from the roasting of pyrite ore in the production of sulfuric acid.

2. Thallium Metal

2.1. Properties. Thallium [7440-28-0] is grayish white metal, similar to tin in appearance. The metal has a close-packed hexagonal lattice $< 230°C$, at which it transforms to a body-centered cubic (bcc) lattice. It resembles lead in that it is both heavy and soft and can be easily cut with a knife. When first exposed to air, freshly cut thallium metal has a metallic luster that is quickly dulled to a blue-gray color by the formation of a film of thallium(I) oxide [1314-12-1]. When submersed in water, the oxide film is rapidly dissolved as thallium(I) hydroxide [12026-06-1] and the metal reassumes its metallic appearance. Prolonged exposure to air results in the formation of a dark brown crust of thallium(III) oxide [1314-32-5]. Thallium is dissolved readily in nitric acid. Dilute sulfuric acid attacks thallium considerably slower than nitric. The metal is only sparingly soluble in hydrochloric acid due to the low solubility of the salt. The physical properties of thallium metal are summarized in Table 1.

2.2. Production. Commercial thallium is obtained as a by-product in the processing of zinc, copper, and lead ores. The thallium is collected in the flue dust in the form of an oxide or sulfate along with other by-product metals, such as cadmium, indium, germanium, selenium, and tellurium. One process used in the extraction of thallium is that the flue dust is treated with boiling sulfuric acid to convert the metals to their soluble sulfate salts and precipitate lead sulfate. The solution is filtered and treated with hydrochloric acid to precipitate thallium(I) chloride [7791-12-0]. The TlCl is then heated to dryness with sulfuric acid then leached with boiling water then further acidified with sulfuric acid. This is necessary to avoid cathodic separation of zinc and deposition of thalliu-

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m(III) oxide [1314-32-5] at the anode. Electrolysis of the thallium sulfate [7446-18-6] solution yields a relatively pure thallium metal. The deposited metal is removed from the cathode, dried, melted under hydrogen, and cast into rods (2−7).

After the United States banned the use of thallium sulfate in pest control in 1975, the demand for thallium has decreased significantly. Wherever possible, substitute materials are used due to its high toxicity. World thallium production totaled 15,000 kg in 2002, whereas domestic consumption in the same year was estimated at only 500 kg. Imports in 2002 accounted for 307 kg and were obtained from Belgium, 93%; France, 4%; Russia, 3%; and United Kingdom, < 1%. Domestic sources of thallium in the form of flue dust and residues from base-metal smelters are being exported to Canada, France, the United Kingdom, and other countries (8). Thallium metal has not been recovered in the United States since 1981 and the price of thallium has risen significantly from $18/kg in 1981 to > $1000/kg at present for 99.9% pure metal. The steady increase in the price of thallium is the result of inflation coinciding with the demand for a higher purity metal as more technologically advanced applications are being developed (8). Thallium metal is sold in various shapes from granules to rods or ingots and in purities from 99.9 to 99.999%. The principal domestic supplier of thallium metal is NOAH Technologies Corporation, Chemical Division.

2.3. Uses.   Thallium has limited commercial applications because of its toxic nature. Thallium readily forms alloys with many metals and some of these alloys have unique properties. A number of binary, ternary, and quaternary eutectic alloys are known and have properties, such as very low coefficients of friction and acid resistance (9). Alloys, such as Ag−Tl and Au−Al−Tl have been used in bearings and contact points. An alloy of Pb−Sn−Tl has been used in the production of specific anodes. Another important alloy of thallium is the mercury−thallium amalgam with forms a eutectic at 8.7% and has a freezing point of $-60°C$ versus $-38°C$ for mercury alone. This alloy can be used in switches and seals for equipment in the polar region, stratosphere or space program.

2.4. Isotopes of Thallium.   Thallium occurs in nature as two stable isotopes, ^{203}Tl and ^{205}Tl. The natural abundance of these isotopes is 29.5% ^{203}Tl and 70.5% ^{205}Tl. Thallium has 25 recognized isotopes having atomic masses ranging from 184 to 210. The only relatively stable radioisotope is ^{204}Tl with a half-life of

Table 2.   **Isotopes of Thallium**

Isotope	Half-life
^{200}Tl	1.1 days
^{201}Tl	3.0 days
^{202}Tl	12.2 days
^{203}Tl	stable
^{204}Tl	3.8 years
^{205}Tl	stable
^{206}Tl	4.2 min
^{207}Tl	4.8 min
^{208}Tl	3.1 min
^{209}Tl	2.2 min
^{210}Tl	1.3 min

3.8 years (see Radioisotopes). The half-lives of some of the other isotopes of thallium are listed in Table 2.

Radioisotopes of thallium have been utilized in the medical field in cardiovascular imaging. The so-called thallium stress test is a myocardial perfusion imaging test used to show how well blood flows to the muscles of the heart. This is typically done in conjunction with an exercise stress test on a treadmill or bicycle. When the patient reaches a maximum level of exercise, a small amount of enriched thallium (^{201}Tl) is injected into the bloodstream. Because thallium has similarities to potassium in the body, it is taken up by the heart muscle. A gamma camera is used to collect images of the heart as it takes up the radioactive thallium while under stress and at rest. These images can be used in determining the location and extent of coronary artery blockages and scar tissue resulting from a previous heart attack.

3. Thallium Compounds

3.1. Introduction.   Thallium resides on the periodic table in Group IIIA along with aluminum, gallium and indium. Atomic properties of thallium are outlined in Table 3. While the primary oxidation state of the Group IIIA elements is M^{3+} with several stable compounds containing M^{2+}, thallium is most often found in the Tl^+ (thallous) state rather than the Tl^{3+} (thallic). This is due to the electronic configuration of thallium, more specifically the bonding orbitals, $6s^2 6p^1$. The two $6s$ electrons are quite stable in their orbitals and often resist loss via ionization or taking part in bond formation. Thus the monovalent thallium is most often observed as the $6p$ electron is lost or takes part in covalent bond formation. This is referred to as the *inert pair* effect, which also accounts for the relatively low reactivity of mercury and becomes even more evident in Groups IVA and VA.

Because of this, the thallium(I) ion resembles alkali metal ions and the silver ion in its properties. In this respect, like the alkali metal ions it forms a soluble, strongly basic hydroxide and a soluble carbonate, oxide, and cyanide. However, like the silver ion, it forms a very soluble fluoride while the other halides are insoluble. The thallium(III) ion more resembles aluminum, gallium and indium ions in its properties.

Thallium(III) salts are readily reduced to the thallium(I) salts by common reducing agents. Thallium(I) salts are oxidized only by very powerful oxidizing agents (eg, MnO_4^- or Cl_2) in acidic solutions. The properties of the more common thallium compounds are listed in Table 4. The Tl^+ ion is not very dependent on the pH of its environment. The Tl^{3+} ion is readily hydrolyzed to $Tl(OH)^{2+}$ and can begin to form the colloidal oxide at pH values as low as 1. The presence of certain anions, such as Cl^- can stabilize Tl^{3+} by the formation of soluble complexes.

Thallium compounds and salts are manufactured in both research and production quantities by NOAH Technologies Corporation, Chemical Division. Other suppliers include Aldrich, Alfa-Aesar, and Fisher Scientific.

3.2. Carbonates.   Thallium forms only Thallium(I) carbonate and bicarbonate. Thallium(I) carbonate, Tl_2CO_3 [29809-42-5] is a convenient precursor to other thallium compounds and is prepared by saturating an aqueous solution of

thallium hydroxide with carbon dioxide. The carbonate precipitates upon concentration and cooling of the solution. It dissolves in water yielding a basic solution due to hydrolysis. It is stable to $175°C$ in air, but looses CO_2 with further heating. Thallium(I) bicarbonate, $TlHCO_3$ can be prepared by the reaction of CO_2 on a dilute aqueous solution of Tl_2CO_3.

3.3. Carboxylates.   Thallium forms a large number of carboxylate derivatives as both Tl^+ and Tl^{3+}. The thallium(I) carboxylic salts can be prepared from the corresponding acid and thallium(I) hydroxide or carbonate. Thus, thallium(I) formate, TlOOCH, is prepared by treating Tl_2CO_3 or TlOH with formic acid followed by evaporation of the solution in a vacuum. Thallium(I) acetate is prepared in a similar process or can be obtained by adding acetic acid to a solution of thallium(I) ethoxide in ethanol. These carboxylates are colorless and hygroscopic. A saturated aqueous solution of 1:1 thallium(I) formate–thallium(I) malonate is called Clerici's solution, having a density of 4.32 g/mL at $20°C$ has been used in sink-float separation of minerals on a laboratory scale (see Flotation; Mineral Recovery and Processing).

Thallium(III) salts of formic, acetic, and trifluoroacetic acids are prepared from the corresponding acid and thallium(III) oxide (10). Other thallium(III) carboxylates can be obtained from the metatheses of thallium(III) acetate and the carboxylic acid (11). They are colorless, hygroscopic solids.

3.4. Halides.   Thallium(I) halides are air-stable, light sensitive salts (12). The water-soluble thallium(I) fluoride [7789-27-7] is made by dissolving Tl_2CO_3 in hydrofluoric acid. The salt is obtained by concentrating and cooling the solution. Thallium(I) chloride, bromide and iodide are prepared via precipitation from an aqueous solution (eg, Tl_2SO_4, $TlNO_3$) by adding a solution containing the corresponding anion. Thallium(I) chloride [7791-12-0], upon precipitation is similar to silver chloride physically as well as being photosensitive (darkens upon exposure to light) and can be purified by recrystallization from hot water. Thallium(I) bromide [7789-40-0] may also be further purified by digesting in boiling water and recrystallizing. Thallium(I) halides form many double salts and complexes with nitrogen, oxygen and sulfur ligands.

Thallium(III) fluoride [7783-57-5] has been prepared by the reaction of gaseous fluorine or bromine trifluoride on thallium(III) oxide at $300°C$. It is stable to $500°C$, but is extremely sensitive to moisture. Thallium(III) chloride [13453-32-2] can be obtained as the tetrahydrate [13453-33-3] by passing chlorine through a boiling suspension of thallium(I) chloride in water. It can be dehydrated with thionyl chloride. Thallium(III) bromide, tetrahydrate [13453-37-7] is prepared in a similar manner, whereas the iodide yields thallium(I) triiodide [13453-37-7] $Tl^+I_3^-$.

A large number of halide complexes of thallium(III) have been prepared by precipitation of the complexes from solution with a suitable cation, eg, Tl^+, $(C_2H_5)_4N^+$, $(C_6H_5)_4As^+$, K^+. Both four-coordinated $[TlX_4]^-$ and six-coordinated $[TlX_6]^{3-}$ ions exist in solutions and in solid states.

3.5. Hydrides.   Unlike boron and aluminum, which form many stable and useful hydrides, there is very little evidence for the existence of TlH and TlH_3 (13). Lithium tetrahydridothallate(III) [82374-47-8], $LiTlH_4$, has been obtained from $TlCl_3$ and LiH in ether at $-15°C$ (14). However, it decomposes rapidly $> 30°C$ to hydrogen, thallium, and lithium hydride (12).

Thallium(I) salts of tetrahydridoborate and aluminate are obtained from a thallium(I) compound (ie, ethoxide, perchlorate or nitrate) and $LiBH_4$ or $LiAlH_4$ in ether. Thallium(I) tetrahydridoborate [61204-71-5], $TlBH_4$, is unstable at $40°C$ evolving diborane. Thallium(I) tetrahydridoaluminate [82391-12-6], $TlAlH_4$, is extremely unstable that decomposes to yield H_2 and Tl at $-80°C$.

3.6. Oxides and Hydroxides.

Thallium(I) oxide [1314-12-1] is most readily obtained by dehydration of TlOH in high vacuum at $50°C$. It is black, crystalline and hygroscopic. It reacts with water to form the hydroxide and dissolves in ethanol to yield the ethoxide (12).

Thallium(III) oxide [1314-32-5] can be prepared by the reaction of thallium metal and oxygen or hydrogen peroxide and an alkaline thallium(I) solution. However, it is more easily made from the oxidation of thallium(I) nitrate by chlorine in an aqueous solution of potassium hydroxide. It is insoluble in water but dissolves in carboxylic acids to give carboxylates.

There is no evidence for the existence of thallium(III) hydroxide by isolation. Addition of a hydroxide to an aqueous solution of a thallium(III) salt yields Tl_2O_3. Thallium(I) hydroxide [1310-83-4] can be isolated as yellow needles by the hydrolysis of thallium(I) ethoxide [20398-06-5], which is prepared by the oxidation with O_2 of thallium metal in ethanol vapor (12). Thallium (I) hydroxide darkens at room temperature and decomposes to Tl_2O and H_2O upon warming.

3.7. Nitrates.

Thallium(I) nitrate [10102-45-1] is prepared from the reaction of the pure metal with dilute nitric acid (12). The solid is stable to $300°C$ and decomposes at $800°C$ to Tl_2O, NO and NO_2. Thallium(III) nitrate is obtained as a trihydrate [13453-38-8] by dissolving Tl_2O_3 in cold nitric acid. It decomposes to Tl_2O_3 on heating to $100°C$ or by hydrolysis. Thallium(III) nitrate is soluble in alcohols and ethers of polyethylene glycols and is often used as an oxidizing agent in organic syntheses.

3.8. Sulfates.

Thallium(I) sulfate [7446-18-6] is produced by the reaction of the metal with sulfuric acid and concentrating the solution until crystallization begins (12). Its solubility is increased in the presence of excess sulfuric acid and it reacts with SO_3 to form the pyrosulfate $Tl_2S_2O_7$ [82391-11-5]. Thallium(III) sulfate is extremely unstable, and therefore cannot be isolated. Reaction of thallium(III) oxide with dilute sulfuric acid results in $TlHSO_4$ or $Tl(OH)SO_4$ depending on the ratio and concentration of sulfuric acid used.

3.9. Organometallics.

Organothallium compounds have attracted interest mostly because of the applications of these compounds in organic synthesis. Stable compounds occur in both the Tl^+ and Tl^{3+} oxidation states. Only the cyclopentadienyl ligand is known to stabilize the thallium(I) ion, and the parent compound, cyclopentadienylthallium(I) [34822-90-7] is prepared from freshly distilled cyclopentadiene and thallium(I) hydroxide (15). It is a yellow, air stable solid that is insoluble in most common organic solvents. X-ray and microwave spectroscopic studies in the gas phase indicate C_{5v} symmetry consistent with the half-sandwich structure. The crystal has a polymeric structure with zigzag chains of alternating C_5H_5 units and Tl atoms. A number of alkylated derivatives of cyclopentadienylthallium, $(RC_5H_4)Tl$ where $R=CH_3$ [34034-67-8], C_2H_5 [28553-52-8], and C_4H_9 [28553-53-9], can also be prepared by the same procedure.

Organothallium(III) derivatives can be classified into three types: R_3Tl, R_2TlX, and $RTlX_2$. The trialkyl derivatives are reactive, unstable compounds whereas the dialkyl derivatives are among the most stable and least reactive organometallic compounds. The monoalkyl compounds are rather unstable and often cannot be isolated. They are important intermediates in some Tl(III)- promoted organic reactions.

The R_3Tl compounds, ie, methyl, ethyl, isobutyl, and phenyl thallium(III) are usually prepared by the reaction between a dialkyl or diarylthallium halide and an organolithium reagent in ether (16):

$$R_2TlX + LiR \rightarrow R_3Tl + LiX \qquad (1)$$

or a Grignard reagent in tetrahydrofuran (17):

$$R_2TlX + RMgX \rightarrow R_3Tl + MgX_2 \qquad (2)$$

However, the most convenient method of preparation is from the reaction of thallium(I) iodide and organolithium:

$$TlI + 2\ CH_3Li + CH_3I \rightarrow (CH_3)_3Tl + 2\ LiI \qquad (3)$$
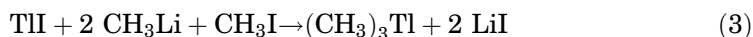
The intermediate involved in this reaction is thought to be CH_3Tl.

The R_3Tl compounds react readily with acids, halocarbons, or sulfur dioxide to form R_2TlX. They also form neutral complexes ($R_3Tl \cdot L$) with Lewis bases (L) (eg, amines and phosphenes), in a similar manner as the gallium and indium analogues.

The R_2TlX compounds are best prepared from thallium(III) halides and an excess of Grignard reagent (18):

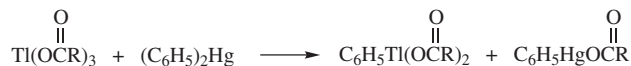$$TlX_3 + 2\ RMgX \rightarrow R_2TlX + 2\ MgX_2 \qquad (4)$$
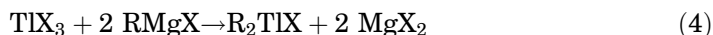
However, the yields are usually poor because of the oxidation of the Grignard reagent by thallium(III). The reaction of R_3Tl with acids also affords a convenient route to this type of compound.

Dialkyl and diarylthallium(III) derivatives are stable, crystalline solids that melt at $180-300°C$. The dimethylthallium derivatives of CN^-, ClO_4^-, BF_4^- and NO_3^- contain linear $(CH_3)_2Tl$ cations and the free anions (19). In aqueous solutions they ionize to the $(CH_3)_2Tl(H_2O)_x{}^+$ ions, except those derivatives containing alkoxide, mercaptide, or amide anions which yield dimeric structures (20,21).

The $RTlX_2$ compounds (eg, dichlorophenylthallium(III) [19628-33-2]), can be obtained from the reaction of a thallium(III) halide or carboxylate with an organoboron compound (22):

$$TlCl_3 + C_6H_5B(OH)_2 + H_2O \rightarrow C_6H_5TlCl_2 + B(OH)_3 + HCl \qquad (5)$$
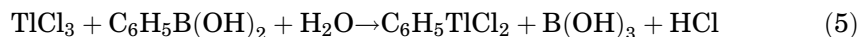
or with an organomercury compound (23):

$$Tl(OCR)_3 \ + \ (C_6H_5)_2Hg \ \longrightarrow \ C_6H_5Tl(OCR)_2 \ + \ C_6H_5HgOCR$$

They can also be prepared by thallation (24), eg, thallium(III) trifluoroacetate, which yields di(trifluoroacetato)phenylthallium(III) [23586-54-1]:

$$C_6H_6 \ + \ Tl(OCCF_3)_3 \ \longrightarrow \ C_6H_5Tl(OOCCF_3)_2 \ + \ CF_3COH$$
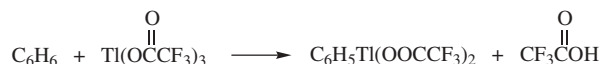
Or oxythallation (25), eg, thallium(III) acetate and vinylbenzene, which yields diaceto-2-methoxy-2-phenylethane thallium(III) [37011-27-1]:

$$C_6H_5CH{=}CH_2 \ + \ Tl(OCCH_3)_3 \ + \ CH_3OH \ \longrightarrow \ C_6H_5CHCH_2Tl(OCCH_3)_2$$
$$OCH_3$$
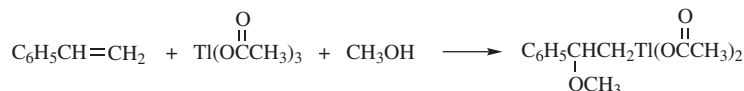
The $RTlX_2$ derivatives are covalent compounds, generally soluble in organic solvents. The aryl and vinyl derivatives are more stable than the corresponding alkyl compounds. This type of compound has been postulated to be an intermediate in many organic syntheses involving thallium(III) species.

4. Uses in Organic Reactions

4.1. Thallium(I) Compounds.   Carboxylic anhydrides can be prepared by the reaction of acyl or aroyl halides in ether with thallium(I) carboxylates (26):

$$R'CCl \ + \ TlOCR \ \longrightarrow \ R'COCR \ + \ TlCl$$
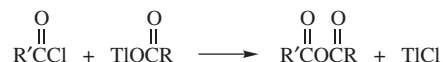
Thallium(I) carboxylates also react with alkyl iodides to form the esters (27):

$$R'I \ + \ TlOCR \ \longrightarrow \ RCOR' \ + \ TlI$$
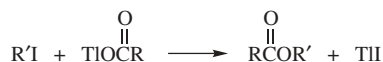
Thallium(I) acetate reacts with iodine and an alkene to give the *trans*-iodoacetate derivatives in 90% yield (28):
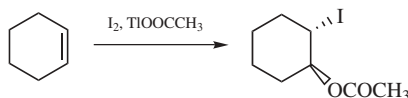

Cyclopentadienylthallium and its alkylated derivatives are used in the synthesis of metallocenes and other transition-metal cyclopentadienyl complexes (29).

4.2. Thallium(III) Compounds. Thallium (III) derivatives have been used extensively as oxidants in organic synthesis. In particular, thallium(III) acetate and trifluoroacetate are extremely effective as electrophiles in oxythallation and thallation reactions. For example, ketones can be prepared from terminal acetylenes by means of $Tl(OOCCH_3)_3$ in acetic acid (oxythallation) (30):
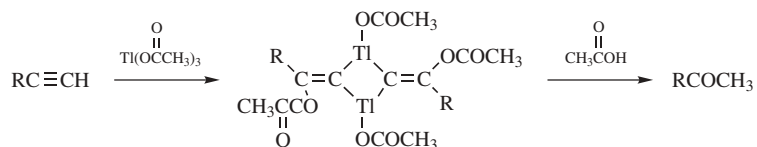

Oxythallation reactions of olefins provide useful synthetic routes to products, eg, glycols, aldehydes, and ketones (31):
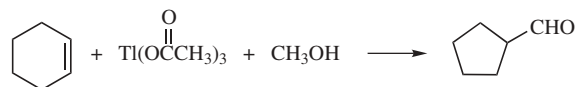
Thallium(III) nitrate in nitric acid and thallium(III) sulfate in sulfuric acid are also effective.

The enhancement of the electrophilic properties of thallium(III) trifluoroacetate makes it a very important thallation reagent. The products of thallation, eg, arylthallium bis(trifluoroacetate), undergo a variety of substitution reactions yielding iodides, fluorides, nitriles, thiophenols and biaryls.
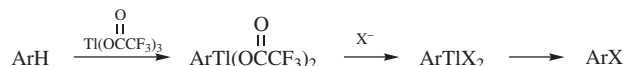
Thallium(III) trifluoroacetate promotes olefin cyclization reactions and intramolecular coupling reactions (32,33).

The highly ionic thallium(III) nitrate, which is soluble in alcohols, ethers and carboxylic acids, is also a very useful synthetic reagent. Oxidation of olefins, α, β-unsaturated carbonyl compounds, β-carbonyl sulfides, and α-nitrato ketones can all be conveniently carried out with good yields (31,34−37).

4.3. Uses. Thallium(I) sulfate was once a widely used rodenticide and ant killer. It is an odorless, tasteless poison that gives no warning to its presence. The use of thallium for household pest control was banned in the United States in 1975. Thallium halides have been used in lenses, prisms and windows for infrared (ir) detection and transmission equipment. Thallium is also used as a dopant in sodium iodide crystals for gamma radiation detection equipment (scintillation counter). In medicine, thallium has been used to treat ringworm and other skin infections but this has declined rapidly due to the narrow margin between therapeutic benefits and toxicity. In combination with selenium and arsenic, thallium has been used in formulating specialty high density, low melting point (125−150°C) glasses that exhibit unique refractive indices. The electrical conductivity of thallium sulfide changes with exposure to specific wavelengths of light making it useful in photoelectric cells (see PHOTOVOLTAIC

CELLS). Thallium(I) nitrate has been used as an analytical reagent for the measurement of iodine in the presence of bromine and chlorine. Other applications include catalysts for organic synthesis as detailed in the previous section or as an intermediate for the manufacture of inorganic acetates.

More recent applications for thallium compounds have included the development of high temperature superconductive (HTS) wires, tapes and films for applications, such as magnetic energy storage, magnetic imaging, magnetic propulsion and more efficient electrical motors as well as power generation and transmission. A material containing a mixture of thallium, mercury, copper, barium, and calcium has attained superconductivity at a temperature of $138\,K$ $(-135°C)$. Materials are considered HTS if they have a transition to superconductivity $>77\,K$ $(-196°C)$, the temperature of liquid nitrogen. Thallium has also found uses in the ongoing development of thin films and coating technologies in the automotive and aerospace industries.

5. Analytical Methods

Traditional complexometric determinations have been reported, almost exclusively involving the titration of thallium(III) with ethylenediaminetetraacetic acid (EDTA) due to the lower stability of the Thallium(I)−EDTA complex. One such method involves the precipitation of the thallium ion from an aqueous solution with KI. The thallium iodide is filtered, washed and dissolved in hot aqua regia to oxidize the thallium ion to Tl^{3+}. The solution is then neutralized, buffered then titrated using EDTA (38).

More modern methods of analysis involving optical emissions spectroscopy (ie, Atomic Absorption (AA), Inductively Coupled Plasma−Optical Emissions Spectrometer (ICP−OES), and ICP−Mass Spectrometer (ICP−MS) are most commonly used. Parameters for these methods are shown in Table 5.

6. Shipment

All thallium compounds are regulated for shipment either by specific name or by generic term (ie, Thallium compound, n.o.s.) according to the Department of Transportation, International Air Transport Association, International Civil Aviation Organization and the International Maritime Organization. Certain restrictions apply to all modes of transportation.

7. Toxicology

Thallium is considered more toxic to mammals than cadmium, lead, and mercury and has been implicated in many accidental, deliberate, occupational and therapeutic poisonings (39). In fact, thallium intoxication is considered one of the most frequent causes, on a world wide scale, of purposeful or accidental human poisoning (40).

The relative toxicities of thallium compounds depend on their solubilities and valence states. Soluble monovalent thallium compounds [eg, thallium(I) sulfate, acetate, and carbonate] are especially toxic. Insoluble compounds [eg, thallium(I) sulfide and iodide] are poorly absorbed by any route and are less toxic. The water-insoluble thallium(III) oxide shows a somewhat lower acute toxicity by oral or parenteral administration than thallium(I) salts. Thallium is rapidly and efficiently taken-up through the gastrointestinal tract and the skin. Thallium is also rapidly absorbed from the mucous membranes of the respiratory tract, mouth, and lungs following inhalation of soluble thallium salts. It is rapidly distributed to all organs and passes the placenta and the blood–brain barrier. Rapid absorption in organs may cause the concentration in whole blood to be nonreflective of the levels in tissues. Urine analysis has been the most widely used biological indicator of thallium exposure.

Thallium, which is only detected in trace amounts in normal tissue, is not essential to mammals but does accumulate in the human body. Thallium has been found to accumulate primarily in the kidneys followed by the heart, brain, bone, skin and blood. Levels as low as 0.5 mg/100 g of tissue may suggest thallium intoxication. Based on industrial experience, 0.10 mg/m^3 of thallium in air has been established by the American Conference of Governmental Industrial Hygienists (ACGIH) as a threshold limit value (TLV) and the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) on a time-weighted average (TWA) for a 40-h work week (41). The lethal dose for humans is not definitely known, but typically an adult oral intake of 20–60 mg thallium/kg body weight is lethal within 1 week although 10 mg thallium/kg body weight has been fatal to children. The usual symptoms of human thallium poisoning resulting from acute, subacute, or chronic intoxication are generally the same.

Chronic intoxication symptoms, irrespective of the route of entry, normally occur after 2–5 days. Thallium compounds can affect the liver, kidneys, and respiratory, cardiovascular, gastrointestinal, and male reproductive systems. Symptoms are often protracted and include metallic taste, salivation, nausea, vomiting, anorexia, abdominal pain and sometimes gastrointestinal hemorrhage. Although common, alopecia (hair loss) does not always occur, especially in cases of acute intoxication and low resistance where the patient may die before the occurrence of hair loss. Constipation commonly develops and may be resistant to treatment, causing interference in antidotal treatment. Effects on the central nervous system (CNS) vary, but a characteristic symptom is extreme sensitivity of the legs, followed by a burning sensation in the feet and paresthesia covering the body.

The symptoms of acute intoxication generally appear originally with anorexia, vomiting and depression, then diarrhea, and skin effects (eg, inflammation at body orifices, skin furuncles, alopecia). Dyspnea and nervous disorders commonly follow. Finally, respiratory, renal, CNS or cardiac failure most commonly leads to death within 10–12 days, but death occurring within 8–10 h or several weeks has also been reported. Neurological damage was evident in most cases of death by intoxication; however, the cause of death was most commonly attributed to respiratory or cardiac failure.

In thallium poisonings that do not occur in death, recovery may take several months and can be interrupted by relapses. The CNS and myocardial damage, electrocardiographic changes and intellectual function impairment as well as blindness can sometimes remain after physical recovery. Persons with preexisting neurological and renal disease, or liver and kidney damage may be more susceptible to the effects of thallium exposure.

No human studies were located regarding the reproductive or carcinogenic effects of thallium exposure. A retrospective study of children of pregnant women who were chronically exposed to thallium, showed no increase of congenital abnormalities compared to the general population. Some evidence of testicular toxicity has been observed. The potential for thallium to cause cancer cannot be determined in light of the absence of epidemiological studies.

A variety of therapies for thallium poisoning have been suggested including neutralizing thallium in the intestinal tract, hastening excretion after resorption, or decreasing absorption. Hemoperfusion with activated carbon and hemodialysis has been shown to be successful if used within 48 h and most commonly in cases of extreme intoxication. Oral administration of Prussian blue (potassium ferric hexacyanoferrate(II)), has been shown to be a very effective oral antidote in cases of oral thallium administration. Potassium ions in this compound are exchanged with the thallium and passed out of the body as the compound cannot be absorbed. Activated carbon given orally has been shown to adsorb thallium in the gastrointestinal tract and facilitate removal. Potassium, as potassium chloride, has been shown to increase renal excretion and decrease degenerative effects of thallium intoxication although it has also been shown to increase the death rate in animals when used in conjunction with the administration of large doses of a thallium compound.

8. Environmental Concerns

Thallium is a nonvolatile heavy metal that exists naturally in the environment combined with other elements in naturally occurring minerals (see the section Occurrence). Thallium as an element cannot be biodegraded or transformed. Disposal of thallium bearing wastes is controlled by a number of federal, state and local regulations. All thallium compounds are regulated for transportation and some specifically for storage limits either by name or by generic classification.

The major source of thallium releases into the environment have occurred from processes, such as coal burning and the smelting of zinc, copper, and lead ores where thallium is a minor contaminant rather than from facilities using or producing thallium compounds. Environmental atmospheric releases of thallium in the mid-1980s were estimated at 127 metric tons/year from coal burning power plants and from iron and steel production facilities in the United States. Raw or treated waste waters from various mining, refining and ore-processing industries have contributed considerable amounts of thallium to urban waste waters. Thallium contamination of soil could be expected to occur in the vicinity of processing plants from flu dusts but direct soil releases are expected to be small given that thallium containing wastes are subject to EPA land disposal restrictions;

although, prior to 1987, disposal of industrial wastes and pesticides containing thallium were allowed in municipal and industrial landfills.

Compounds of thallium are generally soluble in water and can accumulate in soils and sediments, and bioconcentrate in aquatic fish, invertebrates and plants as well as terrestrial plants. Many cases of thallium intoxication have been attributed to consumption of plants and vegetables grown in gardens in the vicinity of environmental releases of thallium. The dietary intake of food is probably the major source of thallium exposure in the general population.

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BOB BLUMENTHAL
KELLY SELLERS
MATTHEW KOVAL
NOAH Technologies Corporation

Table 1. **Physical Properties of Thallium**

Property	Value
atomic weight	204.37
melting point, °C	303
boiling point, °C	1457
density, g/cm^3	11.85
thermal conductance, W/(cm·K)	0.39
specific heat, 20°C, J/g^a	0.13
heat of fusion, J/g^a	21.1
heat of vaporization, J/g^a	795
Brinell hardness	2
linear coefficient of expansion, cm/°K	28×10^{-6}
electrical resistivity, μΩ·cm	18
tensile strength, MPa	9

^{a}To convert J to cal, divide by 4.184.
^{b}To convert MPa to psi, multiply by 145.

Table 3. **Atomic Properties of Thallium**

Property	Value
atomic number	81
electronic configuration	[Xe]$4f^{14}5d^{10}6s^26p^1$
ionization enthalpies, kJ/mol	
1st	589.0
2nd	1958.7
3rd	2862.8
$E°$ $Tl^+ + e^- \rightarrow Tl°$	-0.34
$E°$ $Tl^{3+} + 3e^- \rightarrow Tl°$	0.72
atomic radius, Å	2.08
ionic radius Tl^+, Å	1.54
ionic radius Tl^{3+}, Å	0.95
nuclear spin, $\hbar$	
^{203}Tl	0.5
^{205}Tl	0.5
nuclear magnetic moment, J/T^a	
^{203}Tl	1.495×10^{-23}
^{205}Tl	1.509×10^{-23}

^{a}To convert from J/T to Bohr magneton, divide by 9.274×10^{-24}.

Table 4. **Properties of Selected Thallium Compounds**

Compound	CAS Registry Number	Formula	Molecular weight	Density, g/cm^3	Melting point, °C	Boiling point, °C	Color	Solubility in H$_2$O, g/L
Thallium(I) acetate	[563-68-8]	$TlC_2H_3O_2$	263.43	3.77	131		white	very soluble
Thallium(I) bromide	[7789-40-4]	$TlBr$	284.29	7.56	480	815	pale yellow	0.05 at 20°C
Thallium(I) carbonate	[29809-42-5]	Tl_2CO_3	468.78	7.11	273		white	40.3 at 15.5°C
Thallium(I) chloride	[7791-12-0]	$TlCl$	239.84	7.00	430	720	white	2.9 at 15.6°C
Thallium(III) chloride	[13453-32-2]	$TlCl_3$	310.74	4.7	25	dec.	colorless	very soluble
Thallium(I) fluoride	[7789-27-7]	TlF	223.38	8.23	327	655	colorless	786 at 15°C
Thallium(III) fluoride	[7783-57-5]	TlF_3	261.38	8.36	550 dec.		olive green	dec.
Thallium(I) hydroxide	[12026-06-1]	$TlOH$	221.39		139 dec.		pale yellow	259 at 0°C
Thallium(I) iodide	[7790-30-9]	TlI	331.29	7.29	440	823	yellow	6×10^{-3} at 20°C
Thallium(I) nitrate	[10102-45-1]	$TlNO_3$	266.39	5.56	206	430	white	95.5 at 20°C
Thallium(I) oxide	[1314-12-1]	Tl_2O	424.77	9.52	300	1080	black	dec. to TlOH
Thallium(III) oxide	[1314-32-5]	Tl_2O_3	456.76	10.19	720	875 (-O$_2$)	black/brown	insoluble^a
Thallium(I) sulfate	[7446-18-6]	Tl_2SO_4	504.82	6.77	632	dec.	white	48.7 at 30°C
Thallium(I) sulfide	[1314-97-2]	Tl_2S	440.85	8.46	448	dec.	blue/black	insoluble^a

^{a}Tl$_2$O$_3$ − K_{sp} for Tl(OH)$_3$ = 1.7×10^{-44}, Tl$_2$S − K_{sp} = 6.0×10^{-22}

Table 5. **Parameters for Thallium Analysis**

Method	Line	Interferences
ICP–OES	190.864 nm	V, Ti
ICP–OES	276.787 nm	Ta, V, Fe, Cr
ICP–OES	351.924 nm	Th, Ce, Zr
ICP–MS	205 amu	