Thallium

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Not to be confused with Thulium or Thorium.

Thallium ( /ˈθæliəm/ /ˈθæli-əm/ THAL-ee-əm) is a chemical element with the symbol Tl and atomic number 81. This soft gray poor metal resembles tin but discolors when exposed to air. The two chemists William Crookes and Claude-Auguste Lamy discovered thallium independently in 1861 by the newly developed method of flame spectroscopy. Both discovered the new element in residues of sulfuric acid production.

Approximately 60–70% of thallium production is used in the electronics industry, and the remainder is used in the pharmaceutical industry and in glass manufacturing. [2] It was also used in infrared detectors. Thallium is highly toxic and was used in rat poisons and insecticides. Its use has been reduced or eliminated in many countries because of its nonselective toxicity. Because of its use for murder, thallium has gained the nicknames "The Poisoner's Poison" and "Inheritance Powder" (alongside arsenic). [3]

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### Characteristics

Thallium is extremely soft and malleable and can be cut with a knife at room temperature. It has a metallic luster, but when exposed to air, it quickly tarnishes with a bluish-gray tinge that resembles lead. It may be preserved by immersing it in oil. A heavy layer of oxide builds up on thallium if left in air. In the presence of water, thallium hydroxide is formed. Sulfuric and nitric acid dissolve thallium rapidly to make the sulfate and nitrate salts, while hydrochloric acid forms an insoluble thallium(I) chloride layer. Its standard electrode potential is -0.34, slightly higher than the potential for iron (at -0.44).

### Isotopes

Main article: Isotopes of thallium

Thallium has 25 isotopes which have atomic masses that range from 184 to 210. 203Tl and 205Tl are the only stable isotopes, and 204Tl is the most stable radiodisotope, with a half-life of 3.78 years. [5]

202Tl (half-life 12.23 days) can be made in a cyclotron, [6] while 204Tl is made by the neutron activation of stable thallium in a nuclear reactor. [5] [7]

201Tl (half-life 73 hrs), decays by electron capture, emitting Hg X-rays (~70–80 keV), and photons of 135 and 167 keV in 10% total abundance; therefore it has good imaging characteristics without excessive patient radiation dose. It is the most popular isotope used for thallium nuclear cardiac stress tests. [8] [5]

### Chemical properties

See also Category: Thallium compounds. The two main oxidation states of thallium are +1 and +3. In the oxidation state +3 many compounds closely resemble the corresponding potassium or silver compounds (The ionic radius of thallium(I) is 1.47 Å while that of potassium is 1.33 Å and that of silver is 1.26 Å. For example, the water-soluble and very basic thallium(I) hydroxide reacts with carbon dioxide forming water-soluble thallium carbonate. This carbonate is the only water soluble heavy metal carbonate. The similarity

### General properties

- **Name, symbol, number**: thallium, Tl, 81
- **Pronunciation**: /θæliəm/ /θæli-əm/
- **Element category**: post-transition metal
- **Group, period, block**: 13, 6, p
- **Standard atomic weight**: 204.3833
- **Electron configuration**: [Kr] 4d¹ 5s²
- **Electrons per shell**: 1, 2, 8, 18, 18, 3
- **1st: 589.4 kJ·mol⁻¹, 1473 °C, 579 °F**
- **2nd: 1971 kJ·mol⁻¹, 1473 °C, 2683 °F**
- **3rd: 3087 kJ·mol⁻¹, 2683 °F**
- **43 GPa, 2.8 GPa**
- **Phase**: solid
- **Density (near r.t.)**: 11.85 g cm⁻³
- **Liquid density at m.p.**: 11.22 g cm⁻³
- **Melting point**: 877 K, 304 °C, 579 °F
- **Boiling point**: 1746 K, 1473 °C, 2683 °F
- **Heat of fusion**: 4.14 kJ mol⁻¹
- **Heat of vaporization**: 165 kJ mol⁻¹
- **Molar heat capacity**: 26.32 J·mol⁻¹·K⁻¹
- **Vapor pressure**: P (Pa) 1 10 100 1 k 10 k 100 k at T (K) 862 977 1097 1252 1461 1758
- **Atomic properties**:
  - **Oxidation states**: 3, 1 (mildly basic oxide)
  - **Electronegativity**: 1.62 (Pauling scale)
  - **Ionization energies**: 1st: 588.4 kJ mol⁻¹, 2nd: 1971 kJ mol⁻¹, 3rd: 3087 kJ mol⁻¹
  - **Atomic radius**: 170 pm
  - **Covalent radius**: 170 pm
  - **Van der Waals radius**: 196 pm
- **Miscellanea**:
  - **Crystal structure**: hexagonal
  - **Magnetic ordering**: diamagnetic
  - **Electrical resistivity**: (20 °C) 0.18 µΩ m
  - **Thermal conductivity**: 46.1 W m⁻¹ K⁻¹
  - **Thermal expansion**: (25 °C) 29.9 µm m⁻¹ K⁻¹
  - **Speed of sound (thin rod)**: (20 °C) 818 m s⁻¹
  - **Young's modulus**: 8 GPa
  - **Shear modulus**: 2.8 GPa
  - **Bulk modulus**: 43 GPa
  - **Poisson ratio**: 0.45
Thallium is a metallic lustrous silver-white element with atomic number 81, symbol Tl. It is highly toxic and its compounds are corrosive to the skin and eyes.

### History

**Greek** ἂνθέλλος (thalmos, meaning "a green shoot or twig")[^8] was discovered by flame spectroscopy in 1861.[^10] The name comes from thallium's bright green spectral emission lines.[^11]

After the publication of the improved method of flame spectroscopy by Robert Bunsen and Gustav Kirchhoff[^12] and the discovery of caesium and rubidium in the years 1859 to 1860, flame spectroscopy became an approved method to determine the composition of minerals and chemical products. William Crookes and Claude-Auguste Lamy both started to use this new method. William Crookes used it to make spectroscopic determinations for tellurium on selenium compounds deposited in the lead chamber of a sulfuric acid production plant near Tükerode in the Harz mountains. He had obtained the samples for his research on selenium cyanide from August Hofmann years earlier.[^13][^14] By 1862, Crookes was able to isolate small quantities of the new element and determine the properties of a few compounds.[^15] Claude-Auguste Lamy used a similar spectrometer to Crookes' to determine the composition of a selenium-containing substance which was deposited during the production of sulfuric acid from pyrite. He also noticed the new green line in the spectra and concluded that a new element was present. Lamy had received this material from the sulfuric acid plant of his friend Fried Kuhlmann and this by-product was available in large quantities. Lamy started to isolate the new element from that source.[^16] The fact that Crookes was able to work ample quantities of thallium enabled him to determine the properties of several compounds and in addition he prepared a small ingot of metallic thallium which he prepared by remelting thallium he had obtained by electrolysis of thallium salts.

As both scientists discovered thallium independently and a large part of the work, especially the isolation of the metallic thallium was done by Lamy, Crookes tried to secure his priority on the work. Lamy was awarded a medal at the International Exhibition in London 1862. For the discovery of a new and abundant source of thallium and after heavy protest Crookes also received a medal: thallium, for the discovery of the new element. The controversy between both scientists continued through 1862 and 1863. Most of the discussion ended after Crookes was elected Fellow of the Royal Society in June 1863.[^17][^18]

The dominant use of thallium was the use as poison for rodents. After several accidents the use as poison was banned in the United States by the Presidential Executive Order 11643 in February 1972. In the subsequent years several other countries also banned the use.[^19]

### Occurrence and production

Although thallium is a modestly abundant element in the Earth's crust, with a concentration estimated to be about 0.7 mg/kg, mostly in association with potassium-based minerals in clays, soils, and granites, thallium is not generally economically recoverable from these sources. The major source of thallium for practical purposes is the trace amount that is found in copper, lead, zinc, and other heavy-metal-sulfide ores.[^21][^22]

Thallium is found in the minerals crookesite TlCu₇Se₄, hutchinsonite TlPbAs₂S₄, and lorandite TlAs₂S₄. Thallium also occurs as a trace element in iron pyrite, and thallium is extracted as a by-product of roasting this mineral for the production of sulfuric acid.[^23]

Thallium can also be obtained from the smelting of lead and zinc ores. Manganese nodules found on the ocean floor also contain some thallium, but the collection of these nodules has been and continues to be prohibitively expensive. There is also the potential for damaging the environment of the oceans.[^25] In addition, several other thallium minerals, containing 16% to 60% thallium, occur in nature as complexes of sulfides or selenides that primarily contain antimony, arsenic, copper, lead, and/or silver. However, these minerals are rare, and they have had no commercial importance as sources of thallium.[^20] The Alchitr deposit in southern Macedonia was the only area where thallium was ever actively mined. This deposit still contains a loosely estimated 500 tonnes of thallium, and it is a source for several rare thallium minerals, for example lorandite.[^23]

The United States Geological Survey (USGS) estimates that the annual worldwide production of thallium is about 10 metric tonnes as a by-product from the smelting of copper, zinc, and lead ores.[^23] Thallium is either extracted from the dusts from the smelter fly ashes or from residues such as slag that are collected at the end of the smelting process.[^23] The raw materials used for thallium production contain large amounts of other materials and therefore a purification is the first step. The thallium is leached either by the use of a base or sulfuric acid from the material. The thallium is several times precipitated from the solution and to remove further impurities. At the end it is converted to thallium sulfate and the thallium is extracted by electrolysis on platinum or stainless steel plates.[^24] The production of thallium decreased by about 33% in the period from 1995 to 2009 – from about 15 metric tonnes to about 10 tonnes. Since there are several small deposits or ores with relatively high thallium content, it would be possible to increase the production of it if a new application, such as a hypothetical thallium-containing high-temperature superconductor, becomes practical for widespread use outside of the laboratory.[^23]

### Applications

#### Historic uses

The odorless and tasteless thallium sulfate was once widely used as rat poison and ant killer. Since 1972 this use has been prohibited in the United States due to safety concerns.[^19] Many other countries followed this example in the following years.[^2] Thallium salts were used in the treatment of ringworm, other skin infections, and to reduce the night sweating of tuberculosis patients. However this use has been limited due to their narrow therapeutic index, and the development of more-advanced medicines for these conditions.[[^27][^28][^29]}

[^8]: Name origin.
[^10]: William Crookes.
[^12]: Robert Bunsen.
[^13]: Claude-Auguste Lamy.
[^14]: August Hofmann.
[^15]: Crookes.
[^16]: Lamy.
[^17]: Crookes.
[^18]: Lamy.
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[^24]: Lamy.
[^25]: Crookes.
[^26]: Lamy.
[^27]: Crookes.
[^28]: Lamy.
[^29]: Crookes.
Optics

Thallium(II) bromide and thallium(II) iodide crystals have been used as infrared optical materials, because they are harder than other common infrared optical materials, and because they have transmission at significantly longer wavelengths. The trade name KRS-5 refers to this material. \[30\] Thallium oxide has been used to manufacture glasses that have a high index of refraction. Combined with sulfur or selenium and arsenic, thallium has been used in the production of high-density glasses that have low melting points in the range of 125 and 150 °C. These glasses have room temperature properties that are similar to ordinary glasses and are durable, insoluble in water and have unique refractive indices. \[31\]

Electronics

Thallium(I) sulfide's electrical conductivity changes with exposure to infrared light therefore making this compound useful in photoresistors. \[27\] Thallium selenide has been used in a bolometer for infrared detection. \[32\] Doping selenium semiconductors with thallium improves their performance, and therefore it is used in trace amounts in selenium rectifiers. \[27\] Another application of thallium doping is the sodium iodide crystals in gamma radiation detection devices. In these, the sodium iodide crystals are doped with a small amount of thallium to improve their efficiency as scintillation generators. \[33\] Some of the electrodes in dissolved oxygen analyzers contain thallium. \[2\]

High-temperature superconductivity

Research activity with thallium is ongoing to develop high-temperature superconducting materials for such applications as magnetic resonance imaging, storage of magnetic energy, magnetic propulsion, and electric power generation and transmission. The research in applications started after the discovery of the first thallium barium calcium copper oxide superconductor in 1988. \[34\]

Medical

Before the widespread application of technetium-99m in nuclear medicine, the radioactive isotope thallium-201, with a half-life of 73 hours, was the main substance for nuclear cardiology. The nuclide is still used for stress tests for risk stratification in patients with coronary artery disease (CAD). \[35\] This isotope of thallium can be generated using a transportable generator which is similar to the technetium-99m generator. \[36\] The generator contains lead-201 (half-life 9.33 hours) which decays by electron capture to the thallium-201. The lead-201 can be produced in a cyclotron by the bombardment of thallium with protons or deuterons by the (p,3n) and (d,4n) reactions. \[37\][38]

Thallium stress test

A thallium stress test is a form of scintigraphy, where amount of thallium in tissues correlates with tissue blood supply. Viable cardiac cells have normal Na+/K+ ion exchange pumps. The Tl⁺ cation binds the K⁺ pumps and is transported into the cells. Exercise or dipyridamole induces widening (vasodilation) of normal coronary arteries. This produces coronary steal from areas where arteries are maximally dilated. Areas of infarct or ischemic tissue will remain "cold". Pre- and post-stress thallium may indicate areas which will benefit from myocardial revascularization. Redistribution indicates the existence of coronary steal and the presence of ischemic coronary artery disease. \[39\]

Other uses

A mercury-thallium alloy, which forms a eutectic at 8.5% thallium, is reported to freeze at −60 °C, some 20 °C below the freezing point of mercury. This alloy is used in thermostats and low-temperature switches. \[27\] In organic synthesis thallium(III) salts, as thallium trinitrate or trisacetaate, are useful reagents performing different transformations in aromatics, ketones, olefins, among others. \[2\] Thallium is a constituent of the alloy in the anode plates in magnesium seawater batteries. \[27\] Soluble thallium salts are added to gold plating baths to increase the speed of plating and to reduce grain size within the gold layer. \[41\]

The saturated solution of equal parts of thallium(II) formate (Tl(HCOO)₂) and thallium(II) malonate (Tl(C₃H₂O₄)₂) in water is known as Clerici solution. It is a mobile odorless liquid whose color changes from yellowish to clear upon reducing the concentration of the thallium salts. With the density of 4.25 g/cm³ at 20 °C, Clerici solution is one of the heaviest aqueous solutions known. It was used in the 20th century for measuring density of minerals by the flotation method, but the use is discontinued due to the high toxicity and corrosiveness of the solution. \[42\][43]

Toxicity

Main article: Thallium poisoning

Thallium and its compounds are extremely toxic, and should be handled with great care. There are numerous recorded cases of fatal thallium poisoning. \[44\] Contact with skin is dangerous, and adequate ventilation should be provided when melting this metal. Thallium(II) compounds have a high aqueous solubility and are readily absorbed through the skin. Exposure to them should not exceed 0.1 mg per m³ of skin in an 8-hour time-weighted average (40-hour work week).

Thallium is a suspected human carcinogen. \[45\] For a long time thallium compounds were easily available as rat poison. This fact and that it is water soluble and nearly tasteless led to frequent intoxications caused by accident or criminal intent. \[18\]

Treatment and internal decontamination

One of the main methods of removing thallium (both radioactive and normal) from humans is to use Prussian blue, which is a material which absorbs thallium. \[46\] Up to 20 g per day of Prussian blue is fed by mouth to the person, and it passes through their digestive system and comes out in the stool. Hemodialysis and hemoperfusion are also used to remove thallium from the blood serum. At later stage of the treatment additional potassium is used to mobilize thallium from the tissues. \[47\][48]

Thallium pollution

According to the United States Environmental Protection Agency (EPA), man-made sources of thallium pollution include gaseous emission of cement factories, coal burning power plants, and metal sewers. The main source of elevated thallium concentrations in water is the leaching of thallium from ore processing operations. \[23\][49]

See also
External links

- Toxicity, thallium
- NLM hazardous substances databank – Thallium
- ATSDR - ToxFAQs
- NLM hazardous substances databank – Thallium, elemental
- Toxicity, thallium
- Thallium-201 production from Harvard Medical School Joint Program in Nuclear Medicine
- Thallium-201 production from Harvard Medical School’s Joint Program in Nuclear Medicine

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