



# ANALYTICAL CHEMISTRY OF THALLIUM

I. M. KORENMAN

Translated by ZVI LERMAN



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ANALYTICAL CHEMISTRY OF ELEMENTS

ANALYTICAL CHEMISTRY OF THALLIUM

# *Analytical Chemistry of Elements*

Series prepared by the Vernadskii Institute of Geochemistry and Analytical Chemistry  
USSR Academy of Sciences

A. P. VINOGRADOV, *Editor*

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ANALYTICAL CHEMISTRY OF BERYLLIUM  
ANALYTICAL CHEMISTRY OF BORON  
ANALYTICAL CHEMISTRY OF COBALT  
ANALYTICAL CHEMISTRY OF GALLIUM  
ANALYTICAL CHEMISTRY OF MOLYBDENUM  
ANALYTICAL CHEMISTRY OF NICKEL  
ANALYTICAL CHEMISTRY OF NIOBIUM AND TANTALUM  
ANALYTICAL CHEMISTRY OF PLUTONIUM  
ANALYTICAL CHEMISTRY OF POTASSIUM  
ANALYTICAL CHEMISTRY OF PROTACTINIUM  
ANALYTICAL CHEMISTRY OF RUTHENIUM  
ANALYTICAL CHEMISTRY OF TECHNETIUM, PROMETHIUM, ASTATINE  
AND FRANCIUM  
ANALYTICAL CHEMISTRY OF THALLIUM  
ANALYTICAL CHEMISTRY OF THORIUM  
ANALYTICAL CHEMISTRY OF URANIUM  
ANALYTICAL CHEMISTRY OF YTTRIUM AND THE LANTHANIDE ELEMENTS  
ANALYTICAL CHEMISTRY OF ZIRCONIUM AND HAFNIUM

## FOREWORD

The Vernadskii Institute of Geochemistry and Analytical Chemistry of the USSR Academy of Sciences has begun the publication of a series of monographs on the analytical chemistry of individual elements. This series, *Analytical Chemistry of Elements*, will include about fifty volumes, and it is planned to complete the publication during the coming five years. The necessity for such a project has been felt for a long time. We also have at our disposal the accumulated experience of numerous laboratories which now can (and should) be summarized. In this way the present series originated, the first of its kind. The analytical chemistry of any element with its different compounds is at present extremely varied; this is due to the complexity of the modern materials investigated and the wide range of concentrations determined, as well as to the variety of the methods employed.

With this in mind, a general plan has been worked out for the present series, both with respect to the contents and to the presentation of the material.

The monographs contain general information on the properties of the elements and their compounds, followed by a discussion of the chemical reactions which are the basis of the analytical work. The physical, physicochemical, and chemical methods for the quantitative determination of the element are given in the following order: first, the analysis of raw materials, next the analysis of the typical semi-manufactured products, and last, that of the finished products—metals or alloys, oxides, salts, and other compounds and materials. The underlying principles are always explained; whenever necessary, the exhaustive description of the entire analytical procedure is given. Due attention is paid to rapid analytical methods. A separate place is allotted to techniques for the determination of impurities in high purity materials.

Particular stress is placed on the accuracy and the sensitivity of the various methods, in view of the general tendency toward increased sensitivity of determination of traces of impurity elements.

The monographs contain an exhaustive and up-to-date bibliography. They are intended for a wide circle of chemists: in the first place, for the analysts of research institutes and industrial laboratories of various branches of the national economy, and also for teachers and students of chemistry in institutions of higher education.

Our most prominent experts participated in the preparation of the monographs, drawing upon their own extensive experience in the analytical chemistry of the element in question.

Each volume of the series will be published separately as soon as it has been made ready for publication. [A list of currently available volumes will be found facing the title page. Further titles are in preparation.]

We invite all our readers to send us their comments and criticisms on the monographs.

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## PREFACE

Thallium was discovered about 100 years ago. There is very extensive literature on this element, including numerous papers on the analytical chemistry of thallium. This monograph is an attempt to classify the available information on the qualitative reactions of thallium, and the methods for its quantitative determination. The author drew on Russian and non-Russian sources published up to 1958–1959. This book is intended for analysts working in plant laboratories, in scientific research institutes, and in educational institutions.

The author is grateful to Academician A. P. Vinogradov, Professor A. I. Busev, and Professor V. I. Kuznetsov for their valuable advice in the discussion on the manuscript.

*I. Korenman*



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## CHAPTER I

# Introduction

In 1861 W. Crookes [385, 388], during his observations on the spectra of slimes of the sulfuric acid industry, detected a green line ( $\lambda$  535 m $\mu$ ) which did not correspond to any of the previously known elements. Further study on this substance led to the discovery of a new element. The bright green line of its spectrum suggested to Crookes the name *thallium*, from the Greek *θαλλος* meaning *a young bough*, which has a color like that of the green thallium line. The date of the publication of the first paper on thallium, 30 March 1861, is considered as the date of the discovery of this element. At first, Crookes considered thallium to be a metalloid, an analog of sulfur, selenium, and tellurium. In 1862, A. Lamy [609, 612] isolated for the first time a fairly large quantity (14 g) of thallium from the slime of the sulfuric acid industry, and established its metallic nature and the similarity between its compounds and those of lead, silver, and the alkali metals. He obtained several thallium compounds, and gave a fairly accurate figure for its atomic weight (205.22). Even in 1863, the atomic weight of thallium was known with satisfactory accuracy, 204.0 [611, 898]. By that time Crookes [386, 387, 389] had also obtained metallic thallium. The isolation of metallic thallium led almost immediately to a dispute between Crookes and Lamy as to who was the first to discover the new element.\*

Thallium is a silvery-white soft metal with a fairly high density (11.85 g/cm<sup>3</sup> at 20°); m.p. 303°, b.p. 1457°. Thallium is readily soluble in nitric and sulfuric acids and somewhat less so in hydrochloric acid. It is readily soluble in mercury [858].

\* For the history of the discovery of thallium, see [143, 413, 525, 677, 841, 871, 912].

The content of thallium in the earth's crust is very low. According to A. P. Vinogradov [43], the average figure is  $6 \cdot 10^{-5}$  wt%. According to other sources, the content of thallium ranges from  $8 \cdot 10^{-7}$  to  $3 \cdot 10^{-4}$  wt% [41, 70, 152, 202, 233, 267, 483], or 0.3 to 0.6 g/ton [59, 503, 649]. At a superficial glance this content may appear exceptionally low; we must bear in mind, however, that some of the not so rare elements are found in even smaller quantities, e.g., lead [548], gold, silver, platinum, bismuth, cadmium, and others [41, 233, 649].

Unlike these elements, thallium forms almost no characteristic minerals. According to Vernadskii [41], thallium minerals are "extraordinary mineralogical rarities", and thus of no industrial value. There are, however, various natural materials and industrial products which contain thallium. The following minerals contain thallium: lorandite  $\text{TlAsS}_2$  [41], hutchinsonite  $(\text{Tl}, \text{Cu}, \text{Ag})_2\text{As}_2\text{S}_3 \cdot \text{PbAs}_2\text{S}_4$  [41, 481], crookesite (berzelianite)  $(\text{Tl}, \text{Cu}, \text{Ag})_2\text{Se}$  [143, 481], vrbaitite  $\text{Tl}_2\text{S} \cdot 3(\text{As}, \text{Sb})_2\text{S}_3$  [481].

Thallium is scattered in nature [18] and is present as an impurity in various minerals, namely, pyrite [659], chalcopyrite, zinc blende, carnallites, silvine, micas, feldspars, lepidolite, braunite, and others [4, 40, 143, 163, 183, 481]. Thallium is found together with lithium, potassium, rubidium and cesium, silver, lead, and other metals [41]. The usual thallium content of minerals does not exceed 0.001% [157].

In some minerals thallium is present in relatively large quantities. For instance in Halmeine pyrites (Poland) there is 0.3 to 0.5% of Tl [7], in Japanese minerals there is up to 0.1% of Tl [690], and in some zinc blendes there is about 0.01% of Tl [467]. Thallium has also been detected in meteorites [849].

When pyrites are roasted, various arsenic, selenium, and thallium oxides are evolved together with the sulfur dioxide and accumulate in varying amounts in the pipes and chambers (as slime). It is from this slime that thallium was first discovered. In the processing of other minerals, e.g., zinc blende, thallium concentrates in the wastes, which can then be used as a raw material for the production of thallium [1, 23, 31, 72, 88, 215, 548, 570].

For many years thallium had no industrial significance. In 1915, thallium was not mentioned among the elements used by man [41], and it is only recently that thallium has gained importance in the national economy [16, 630, 887]. It seems that thallium and its compounds have been used as a rodent poison since 1920 [521, 548]. According to other sources, the industrial application of thallium started in 1932 [42].

Pure thallium is used in relatively small quantities because of its poor mechanical properties; the element may, however, be introduced into alloys. The most important alloys of thallium with other elements are described in [128, 138, 160, 166, 202, 253, 361, 481, 524, 548, 790, 911]. For instance, thallium improves the hardness of lead, and its alloy with lead is corrosion resistant [89].

Alloys for bearings: 2 or 3% of Tl, the rest Cu; 1 to 34% of Tl, 1 to 34% of Pb, not less than 65% of Cu.  
Corrosion-resistant alloy: 20 to 65% of Tl, the rest Pb; used for the electrolytic coating of iron, steel, brass.

Alloys insoluble in mineral acids: 10% of Tl, 20% of Sn, 70% of Pb; 2% of Tl, 98% of Ag.  
 Antifriction alloy: 8% of Tl, 5% of Sn, 15% of Sb, 72% of Pb.

Some alloys containing thallium have a relatively low melting point [503, 548]:

Composition of alloy	m.p., °C
98.7% of Tl, the rest Ag . . . . .	289
83% of Tl, the rest Cd . . . . .	203
80% of Tl, the rest Sb . . . . .	195
52.5% of Tl, the rest Bi . . . . .	188
43.5% of Tl, the rest Sn . . . . .	170
73% of Tl, the rest Au . . . . .	131
11% of Tl, 55.2% of Bi, 33.8% of Pb . . . . .	90.8
8.9% of Tl, 11% of Cd, 35.8% of Pb, 44.3% of Bi . . . . .	81
40.5% of Tl, the rest Hg . . . . .	0.6

An alloy consisting of 8.5% of Tl and 91.5% of Hg is suitable for low-temperature thermometers (m.p.  $-60^{\circ}$ ). There is also a solid thallium amalgam containing 86% of Tl or more [164, 751].

Alloys of thallium with lithium, sodium, potassium [128], magnesium, calcium, zinc, cadmium, tin [256] are readily oxidized in the air; the alloys with gold, antimony, and bismuth are very brittle.

Thallium compounds have certain uses. Thallium oxide is employed as a catalyst in the syntheses of ammonia, in the chlorination of hydrocarbons, in reduction of nitrobenzene by hydrogen [143], and in the oxidation of aniline vapors [339]. Thallium (I) carbonate, bromide, and iodide are used in the manufacture of optical glass with a high refractive index [16, 18, 112], and also in the preparation of opaque black or brown glass [48]. Partially oxidized thallium sulfide is used for the production of photoelectric cells (thallofide photocells) with a maximum sensitivity at  $900\text{ m}\mu$  [51, 362, 523, 534]. The sensitivity of these photoelements decreases fairly rapidly [95, 96]. Thallofide photoresistors have analogous spectral characteristics [139, 242]. Thallium halides are also photoelectrically sensitive [175–178].

Thallium salts are used in the production of crystal phosphors. Of the many papers in the literature dealing with this problem we shall mention only those on the preparation, properties, and application of phosphors based on alkali halides [78, 91, 92, 102, 134, 170, 231, 244, 245, 260, 268, 320, 324, 337, 345, 370, 376, 531, 532, 569, 574, 594, 650, 695, 747, 748, 789, 907], on calcium iodide [809], and on magnesium oxide [343]; also phosphors based on the salts of silicic, phosphoric, and other acids [87, 376, 460, 635, 692].

No practical use has yet been made of the photosensitivity of thallium (I) halides [29, 297], although there is a possibility of employing these compounds for photographic purposes [143, 715]. Photographic developers containing thallium salts have been suggested [286].

A monochromatic green flame can be obtained from thallium salts.

Thallium salts are poisonous; they attack the nervous system, the gastric-intestinal tract, and the kidneys. The toxicity of thallium was reported soon after its discovery [390, 490, 613, 719]. Many publications are available on the toxic effects of thallium and of its compounds. We shall mention only the most important ones, and the reviews in this field [27, 193, 228, 251, 270, 365, 379, 425, 465, 525, 575, 644, 688, 720, 746, 845, 862, 904]. In view of the increase in the production and application of thallium, the element and its salts should be considered as industrial poisons [79, 130].

Thallium salts have some medicinal uses [133, 135, 172, 250, 525]; they are also employed as rodent poisons [112, 251, 705, 737].

Thallium salts are used for the detection and for the determination of various ions. Thallium (I) hydroxide is a suitable reagent for ozone [552, 614] and hydrogen peroxide [801]. With thallium (I) nitrate it is possible to detect alkali hydroxides in the presence of soluble sulfides [229], and iodides in the presence of bromides [550]. Soluble salts of thallium (I) are widely used as reagents in microcrystalloscopy [103]. Thallium (III) salts have recently been recommended for the same purpose [793]. Thallium (I) salts have been proposed for the identification of organic acids [480] and also for the determination of halogen in organic compounds [782], for example in ethyl iodide.

Phosphates and arsenates can be determined by weighing as  $\text{TlAg}_2\text{PO}_4$  and  $\text{TlAg}_2\text{AsO}_4$  [836].

Thallium carbonate has been proposed as the primary standard in the neutralization method [305, 494, 566, 712]. This salt can be readily purified by recrystallization; it is not hygroscopic, contains no water of crystallization, does not absorb atmospheric carbon dioxide, has a high gram-equivalent weight (234.4 g), and remains stable when heated up to  $230^\circ$  [760, 761].

Thallium (III) chloride is used as an indicator in the neutralization method [76, 77]. The effect of this indicator is based on the formation of the dark-brown sparingly soluble hydroxide  $\text{Tl}(\text{OH})_3$  between thallium (III) and hydroxyl ions; the hydroxide remains in the solution in the colloidal state coloring it yellow. The transition from a colorless to a yellow solution is fairly sharp. This indicator is suitable for the titration of solutions containing strong oxidants. A mixture of thallium (I) and thallium (III) salts in the presence of potassium iodide and starch has been proposed as an indicator for the titration of carbonates [756].

Solutions of thallium (I) sulfate are suitable for the titration of permanganate in the presence of dichromate, for example, in steel analysis [874].  $\text{TlNO}_3$  solutions can be used to titrate excess of sodium tetraphenylboron after the precipitation of the salts of potassium, ammonium, and organic bases [798]. Solutions of thallium acetate in glacial acetic acid are used in the visual (with neutral red or thionin as indicators) or potentiometric titration of lithium chloride or bromide [866].

Some thallium salts are present in heavy liquids used in mineralogical analysis [143, 238].

It must be emphasized that in some cases certain theoretical problems of analytical and physical chemistry, in particular the effect of common and noncommon ions on the solubility of sparingly soluble electrolytes, have often been studied with thallium salts [105, 108, 261, 263, 334, 426, 471, 549, 707, 842].

Thallium is used in the production of radioactive isotopes, not only of thallium,  $\text{Tl}^{204}$ , by the reactions  $\text{Tl}^{203} (n, \gamma)$  or  $\text{Tl}^{203} (d, p)$ , but also of some other elements, for example  $\text{Hg}^{203}$  by the reaction  $\text{Tl}^{203} (n, p)$  [195]. Radioactive thallium isotopes, especially  $\text{Tl}^{204}$ , are used in analytical chemistry [2, 5, 25, 26, 85, 107a, 117–119, 187], and also in other fields [85, 507, 740].

This brief survey shows that thallium is being employed to an increasing extent in various branches of the national economy and in science.

The chemical properties of thallium are similar, in some respects, to those of the heavy metals (lead, silver, gold), and in other respects to those of the alkali metals [41, 143, 145–148, 610]. The combination of these highly different properties in one element lead various authors to refer to thallium as an enigmatic [41] or even paradoxical metal [18, 504]. We would like to quote Dumas [84, 413] on this subject.

"Thallium is destined to be epoch-making in the history of chemistry by the remarkable contrast between its chemical nature and its physical properties. It is not an exaggeration if we state that from the point of view of the usual classification of metals, thallium exhibits contrasting properties, and so can justifiably be called a paradoxical metal-platypus". Should this diversity of properties in thallium be considered a paradox, an exception to the general rule dictated by the position of the element in Mendeleev's system? To answer this question, we shall consider mainly those properties of thallium which have some bearing on the nature of this element [104].

Thallium, like the elements of the third group, can combine with a maximum valency of +3. The  $\text{R}_2\text{O}_3$  oxides lose their acid properties and become basic when passing from boron to thallium. Thallium (III) hydroxide is a weak base which acts as an acid at very high concentrations of  $\text{NaOH}$  (50%) to form thallates. The following dirty-brown crystalline silver thallates have been described:  $\text{Ag}_3\text{TlO}_3$ ,  $\text{Ag}_4\text{Tl}_2\text{O}_5$ ,  $\text{AgTlO}_2$ ,  $\text{Ag}_2\text{Tl}_4\text{O}_7$ ,  $\text{Ag}_4\text{Tl}_6\text{O}_{11}$  [581]. The solubility of  $\text{R}(\text{OH})_3$  in water decreases when passing from boron to thallium.

Although there is a similarity between thallium and the other elements of group III, there are also essential differences shown mainly by the existence of compounds of thallium (I).

Many of the compounds of thallium (I) are analogous to the corresponding compounds of the alkali metals. This can be attributed to the fact that the alkali and the thallium cations have the same valency and very similar ionic radii. Thallium compounds are therefore isomorphous with the corresponding compounds of the alkali metals and often form mixed crystals with them. The similarity between thallium (I) and the alkali metals can be illustrated, for instance, by the considerable solubility of  $\text{TlOH}$  in water. Thallium forms precipitates with many of the reagents for  $\text{K}^+$ ,

## 6 INTRODUCTION

$\text{Rb}^+$ , and  $\text{Cs}^+$ , e.g., chloroplatinate, cobaltinitrite, hexanitrodiphenylamine, polynitrophenols.

It has been noted [8] that in two respects thallium (I) differs from the alkali metals, viz., as regards the low solubility of the sulfide and of the chloride. Thallium, a heavy element of group III, should obviously differ from the lighter elements of group I even in its monovalent state. Unlike the alkali metals, thallium forms other sparingly soluble compounds analogous to those of the monovalent cations of the heavy metals of group I ( $\text{Cu}^+$ ,  $\text{Ag}^+$ ,  $\text{Au}^+$ ) and to those of its nearest neighbors in the sixth period of Mendeleev's system ( $\text{Hg}_2^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ , and to some extent  $\text{Bi}^{3+}$  and  $\text{Po}$ ) [278]. Thallium and these elements form sulfides, iodides, chromates, molybdates, etc., which are sparingly soluble in water. Because the thallium (I) halides are photosensitive, there is a certain analogy between their properties and those of the corresponding salts of  $\text{Ag}^+$  and  $\text{Au}^+$ .

## CHAPTER II

# Qualitative Reactions of Thallium

There are many reagents suitable for the qualitative detection of thallium [32a]. For the sake of clarity, we shall divide all these reagents into several groups. The classification is based on the nature of the reagents employed and of the compounds formed, and also on the actual procedure used or the reaction product observed.

### REACTIONS OF THALLIUM (I)

#### Formation of compounds of the type $Tl_nA^{n-}$ \*

Thallium (I) forms sparingly soluble *halides* (except for  $TlF$ ):

$TlCl$  — white precipitate;  
 $TlBr$  — pale-yellow precipitate;  
 $TlI$  — yellow precipitate.

Due to the considerable solubility of  $TlA$ , and especially of  $TlCl$ , in water, most of these reactions are not sufficiently sensitive. Thallium (I) halides are photosensitive [29, 297], and so their colors gradually change when exposed to light. Thallium chloride turns violet [517] and then black [297]; thallium iodide turns green and then black [590, 718]. The least soluble of these compounds is the iodide, so that the reaction with  $KI$  is often used to detect thallium [533, 597, 875, 897, 899, 912]. The

\*  $A^{n-}$  is the anion.



## 8 QUALITATIVE REACTIONS OF THALLIUM

minimum detectable amount of  $0.6 \gamma$  of  $Tl^+$  in 0.5 ml of solution. The limiting concentration is 1:80,000 [229].

According to other sources, the minimum detectable amount is  $10.5 \gamma/ml$  of  $Tl_2SO_4$  [517], or  $13 \gamma/2 ml$  of  $Tl^+$ , and the limiting concentration is 1:150,000 [481]. The comparatively high sensitivity of this reaction is illustrated by the data in [326]. It is stated that the formation of  $TlI$  could be observed in a certain solution, although when two drops of this solution were evaporated the residue did not color a colorless flame (p. 48). The high sensitivity of this reaction has also been reported by other authors [710].

A yellow precipitate with potassium iodide is also produced by lead salts, but, in contrast to  $PbI_2$ , thallium iodide is insoluble in excess of  $KI$ . It is thus possible to detect thallium in the presence of lead, and also of mercury, salts.

Thallium (I) iodide, unlike  $PbI_2$ , is insoluble in ammonium acetate; this also makes it possible to detect thallium in the presence of lead [364].

To 1 ml of the solution being tested, 0.05 ml of concentrated acetic acid, 1.5 g of ammonium acetate, and water to 2.5 ml are added. The solution is heated to  $80^\circ$ , and 0.5 ml of 10% potassium iodide is added. In the presence of thallium (I) a yellow precipitate of  $TlI$  is formed. If the thallium content is low, the precipitate separates from the cooled solution.

Thus thallium can be detected in dilutions up to 1:50,000 ( $20 \gamma/ml$ ) in the presence of 2,400 times this amount of lead. The fact that  $AgI$  is soluble in thiosulfate solutions can be used to detect thallium in the presence of silver.  $TlCl$  is also precipitated from ammoniacal solutions (compare silver), and from alkaline solutions (compare lead).

The potassium iodide reaction for thallium (I) gives satisfactory results in the presence of ethylenediaminetetraacetic acid or of its disodium salt; the salts of  $Pb^{2+}$ ,  $Bi^{3+}$ ,  $Cu^{2+}$ , and  $Tl^{3+}$  do not react with  $KI$  under these conditions [743].

The reaction with  $KI$  can be carried out by a spot test on filter paper. The yellow spot of  $TlI$  is noticeable even in the presence of  $0.03 \gamma$  of  $Tl^+$  in 0.01 ml of solution; the limiting concentration is 1:330,000 [409]. The same reaction is recommended for the detection of thallium in minerals by trituration method [81].

The precipitation of thallium (I) halides is also used in chemical microscopic detection of the element [22, 103]. When a drop of 2N  $HCl$  or  $NaCl$  is added to a drop of a not too dilute solution of a thallium (I) salt, opaque cruciforms, three-ray asteroid, and small cubic crystals of the  $TlCl$  precipitate appear (Figure 1). In transmitted light the crystals appear black and in reflected light they are white [289]; their size is from 15 to  $100 \mu$ . The minimum detectable amount is  $0.15 \gamma$  of  $Tl^+$ , the limiting concentration is 1:7,000. The presence of mineral acids lowers the sensitivity of the reaction.

The precipitation reaction for yellow  $TlI$  cubes, which do not exceed  $20 \mu$  in size, is considerably more sensitive. The minimum detectable amount is  $0.03 \gamma Tl^+$ , the limiting concentration is 1:35,000. If the precipitation is carried out from hot con-