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Absolute Isotopic Abundance and the Atomic Weight of a Reference Sample of Thallium

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The accepted atomic weight of thallium has remained at a value of 204.37 ± 0.03 since 1962. At this level of uncertainty, however, the atomic weight becomes a limiting factor to high accuracy analysis.

The new mass spectrometric determination of the atomic weight of thallium has been completed. A high precision assay technique was developed so that accurately known quantities of the ^{203}Tl and ^{205}Tl separated isotopes could be mixed to produce standards for calibration of the mass spectrometer. This assay technique involved the gravimetric determination of 99.3 percent of the thallium as Tl_2CrO_4. The soluble thallium was then aliquoted and determined by isotope dilution mass spectrometry. Before making up the final solutions from which the assay and calibration samples would be withdrawn, the separated isotopes were purified by solvent extraction and electrodeposition.

A tungsten filament surface ionization technique was developed for the determination of precise isotopic abundance measurements for thallium. This technique allowed isotopic analysis of the separated isotopes, calibration standards, and a natural thallium reference standard with precisions of better than 0.1 percent. The ^{205}Tl/^{203}Tl absolute isotopic abundance ratio of the reference sample was found to be 2.38714 ± 0.00101, yielding an atomic weight of 204.38333 + 0.00018.

Key words: Absolute ratios; atomic weight; isotopic abundance; reference standard; thallium; thallium chromate.

1. Introduction

Since 1962, the Inorganic Analytical Research Division of the National Bureau of Standards has been conducting a long term program of absolute isotopic abundance ratios and atomic weight determinations using the mass spectrometric method. Previous atomic weight determinations include silver [1][1], chlorine [2], copper [3], bromine [4], chromium [5], magnesium [6], lead [7], boron [8], rubidium [9], rhenium [10], silicon [11], potassium [12], and strontium [13]. The present work extends the study to thallium.

The determination of the absolute isotopic abundance and atomic weight of any element to a high level of accuracy requires the development of highly precise chemical assay and mass spectrometric procedures. The mass spectrometers used for the isotopic abundance measurements are calibrated for bias by using synthetic mixes of known isotopic composition, prepared from nearly pure separated isotopes. Extensive research [14] has demonstrated that this bias is due primarily to mass dependent isotopic fractionation and to a lesser degree to non-linearities in the measurement circuit. The measured biases are used to calculate a calibration factor which is then applied to the observed isotopic ratio to yield the absolute isotopic abundance ratio of a reference sample. The atomic weight of the sample can then be calculated by summing the product of the nuclidic masses reported by Wapstra and Bos [15] and the corresponding atom fractions of the individual isotopes. For more general applications it is necessary to establish the limits of variation in nature and high purity commercial samples.

[1] Figures in brackets indicate literature references at the end of this paper.

The first thallium atomic weight determination was published in 1863 by Claude A. Lamy. [17] Since that time, at least fifteen independent determinations have been reported from either chemical or mass spectrometric data.

TABLE 1. *Chemically determined atomic weights of thallium ($C_{12} = 12$).*

Year	Investigator	Method	Atomic Weight
1863	Lamy [17]	$\frac{Tl_2SO_4}{BaSO_4} = 2.1692$	205.10
		$\frac{TlCl}{AgCl} = 1.669$	203.75
1865	Hebberling [18]	$\frac{Tl_2SO_4}{BaSO_4} = 2.167$	204.84
		$\frac{TlCl}{AgCl} = 1.664$	203.12
1864	Werther [19]	$\frac{TlI}{AgI} = 1.408$	203.71
1872	Crookes [20]	$\frac{Tl}{TlNO_3} = 0.7669$	204.02
1893	LePierre [21]	$\frac{2Tl}{Tl_2O_3} = 0.8948$	204.15
		$\frac{Tl_2O_3}{2TlNO_3} = 0.8571$	204.01
		$\frac{2Tl}{Tl_2SO_4} = 0.8095$	204.13
		$\frac{Tl_2O_3}{Tl_2SO_4} = 0.9046$	203.99
		$\frac{Tl_2O_3}{H_2O} = 8.448$	204.29
1894	Wells and Penfield [22]	$\frac{TlCl}{AgCl} = 1.673$	204.38
1922	Hönigschmid, Birckenback, and Kothe [23]	$\frac{TlCl}{Ag} = 2.2232$	204.36
		$\frac{TlCl}{AgCl} = 1.6733$	204.37
1930	Hönigschmid and Striebel [24]	$\frac{TlBr}{Ag} = 2.63539$	204.37
1931	Briscoe, Kikuchi, and Peel [25]	$\frac{TlCl}{Ag} = 2.22274$	204.31
1933	Baxter and Thomas [16]	$\frac{TlCl}{Ag} = 2.22336$	204.38
1960	Rodriquez and Magdalena [26]	Precision pycnometry of TlCl	204.45
		Average (overall)	204.21
		Average (since 1922)	204.37

Calculated using atomic weights recommended by the International Commission on Atomic Weights (1975) [27].

Most of the chemical determinations of the atomic weight of thallium were performed prior to 1934. In all cases, the atomic weight was determined by ratioing the weight of thallium or one of its compounds to an equivalent weight of another element or compound. The most common method involved the conversion of a known amount of thallium chloride to silver chloride. The weight of thallium chloride was then ratioed to the weight of silver consumed, and the atomic weight of thallium was calculated using the accepted atomic weights of silver and chlorine.

An example of one of the more accurate chemical atomic weight determinations is that of Baxter and Thomas [16]. In this experiment, thallous sulfate was recrystallized several times and converted to the chloride. The chloride was then recrystallized several times and prepared for weighing by distillation in nitrogen followed by refusion in nitrogen. The purified thallous chloride was weighed and dissolved in hot water. After dissolution was complete, a nearly equivalent amount of pure silver was added to precipitate the free chloride. The end point was determined nephelometrically through the addition of hundredth normal solutions of silver and chloride.

A history of the chemically determined atomic weight of thallium is given in table 1. The only determination after 1934 was that of Rodriques and Magdelena [26] in 1960. This group employed high precision density determinations of thallous chloride as the basis of their atomic weight determination.

Table 2 lists the atomic weight determinations based on mass spectrometric measurements of the relative isotopic abundance of natural thallium. A search of the literature yielded only five published isotope abundance measurements. The measurement made by White and Cameron [31] is still listed as the best measurement from a single natural source by the International Commission on Atomic Weights [27]. The present work marks the first time that calibrated mass spectrometry has been used for a determination of the atomic weight of thallium.

TABLE 2. *Calculation of the atomic weight of thallium from relative isotopic abundance measurements.*

Year	Investigator	$^{205}Tl/^{203}Tl$	Atomic Weight[a]
1931	Schüler and Keyston [28]	2.3	204.37
1931	Aston [29]	2.4	204.39
1938	Nier [30]	2.44	204.39
1948	White and Cameron [31]	2.394	204.38
1949	Hibbs [32]	2.394	204.38
		Average	204.38

[a] Calculated using nuclidic masses from Wapstra and Bos [25].

The accepted atomic weight of thallium was 204.39 from 1925 until 1962. In 1962, when the ^{12}C scale was adopted, the chemical combining weight ratios were recalculated as part of a general review of atomic weight data for all elements. The accepted atomic weight value of thallium has remained at 204.37 ± 0.03 since 1962. At this level of uncertainty the atomic weight becomes a limiting factor in high accuracy assay analyses.

2. Experimental Procedure

2.1 Mass Spectrometry

The isotope ratio measurements were made on two solid sample mass spectrometers. Both were nearly identical single stage 90°, 30 cm radius of curvature instruments equipped with a "Z" lens focusing source [33]. The collector was a deep bucket Faraday cup type equipped with a 50 percent transmission grid shadowing a series of suppression grids [33, 34, 35]. The measuring circuit consisted of two vibrating reed electrometers (VRE), a voltage to frequency converter, and a scaler-timer. Data acquisition was made by computer control. Prior to initiating the atomic weight ratio determinations, the digital measurement circuits of the mass spectrometers were calibrated and were found to be linear to within one part in 10^4 over a range of 20-100 percent of full scale for each VRE scale. Nonlinearities in the VRE and/or voltage to frequency converter can result in significant systematic biases in the correction factors unless the mixes closely bracket the isotopic ratio of the standard, and the signal intensities of the corresponding isotopes of the standard and mixes are measured at nearly the same point on the VRE scale. The linearities of the measurement electronics used in this work, combined with close matching of the isotopic ratio of the mixes to the standard, reduced the systematic biases introduced by the VRE and VF converter to less than a part in 10^5. Measurement circuits have been examined which exhibit nonlinear response approaching a part in 10^3. The use of such measurement systems combined with calibration mixes which differ in isotopic ratio significantly from the standard can result in errors in the correction factors which are larger than the precision of the ratio measurements.

The mass spectrometric procedure used in the determination of the thallium isotopic ratios employed a single filament tungsten ion source. The method was initially chosen based on the success of Gramlich and Machlan [36] in using a single filament tungsten approach for gallium, a member of the same periodic family. In addition, Huey et al. [37] had reported that the use of rhenium, a commonly used filament material for the analysis of thallium, opened up the possibility of interference from ReO^+ peaks at masses 201 to 205 with the thallium masses at 203 and 205. The potential interference of ReO^+ was examined using a bare rhenium filament ribbon at high temperatures (up to 2200 °C). Although no masses were found in the region from 201 to 205 at an ion current sensitivity of 2×10^{-16} A, the use of rhenium as a filament material was avoided since the potential for interference did exist.

To obtain highly precise ratios the fabrication and cleaning of the tungsten filaments had to be carefully controlled. The tungsten ribbon (0.025 × 0.76 mm) had to be mounted on the filament posts such that a nearly perfect square flat top filament surface was obtained. Filaments with either convex or concave surfaces affected the drying of the thallium on the filament and, thus the precision of the ratio measurement. The filament surface was cleaned by degassing at 3.0A for ½ h under a vacuum and in a potential field. The degassing parameters of current and time were especially critical to the precision of the thallium ratio measurements. If the degassing process was carried out at either higher currents or for longer periods of time, the $^{205}Tl/^{203}Tl$ ratio could be shifted as much as 0.15 percent.

A 10 μL drop containing 1 μg of thallium as $TlCl_3$ in (1 + 9, V/V) HNO_3 was loaded onto a tungsten filament ribbon. The thallium solutions were stored in (1 oz) 30 mL screw cap Teflon[2] PFA beakers. This container material was chosen after considerable testing indicated that prolonged storage in either polyethylene or glass containers yielded inconsistancies in the analytical procedure.

The sample mounting procedure was performed in two stages, hereafter referred to as the low temperature and the high temperature drying phases. The low temperature phase was carried out on a Class 100 clean air bench using a programmable sample dryer designed by Gramlich and Shideler [38] which permitted this phase of the drying to be accomplished with a high level of reproducibility. The low temperature drying utilized currents of 1A and 3A and an infrared heat lamp to dry the sample. The intensity of the lamp was controlled to yield a temperature of 50 °C at the filament surface. Failure to control this parameter could cause a shift in the measured thallium isotopic ratio by as much as 0.05 percent. The sample size was controlled by monitoring the length of time required for the drop to dry on the filament surface since a drop which was either too large or too small would affect the precision of the ratio measurement.

Another parameter which can greatly affect the precision of the ratio measurement is the air flow of the clean air bench where the low temperature drying was performed. A reduction in the air flow from 30 m/s to 12 m/s, which could

[2] Certain trade names and company products are identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the products are necessarily the best available for the purpose.

occur gradually over a long period of use was found to cause an upward shift in the ratio data of as much as 0.07 percent.

The high temperature drying was accomplished using a pyrometer to adjust the filament temperature to 860 °C. Since this temperature is at the low end of the pyrometer range, this stage of the drying had to be performed in a room where near darkness could be obtained. The use of the pyrometer for temperature control was believed to be a key factor in obtaining a highly precise isotopic ratio measurement. The dependency of the $^{205}Tl/^{203}Tl$ ratio on the filament temperature during the high temperature drying phase is shown in figure 1.

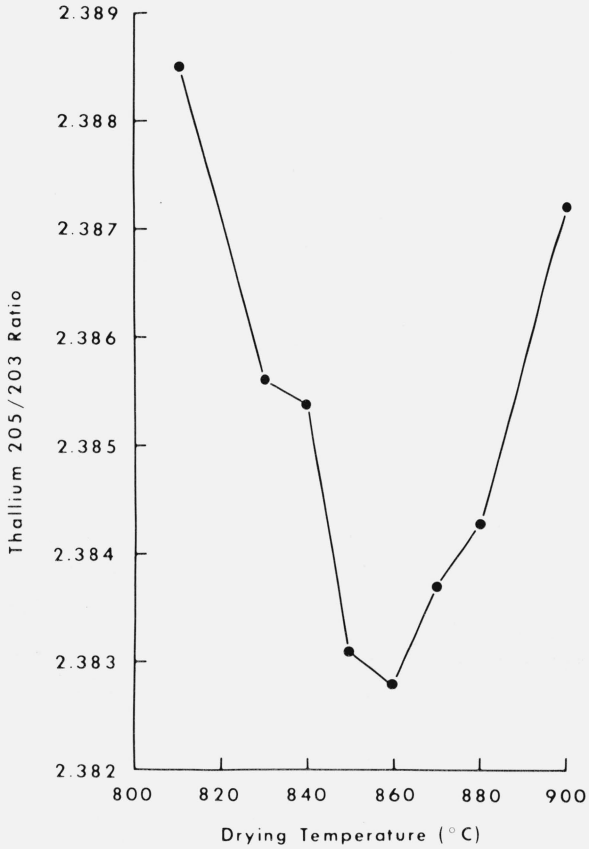

FIGURE 1. *Thallium 205/203 Ratio versus Drying Temperature*

The drying procedure was as follows: The thallium solution was dried on the filament using currents of 1A for 10 min. and 3A for 5 min. and a heat lamp. The filament was then transferred to a darkened room. A Class 100 clean air hood (airflow = 15 linear m/s) was set up over a drying box, which was designed for manual current adjustment, and the filament was mounted at a 45° angle to allow a better view of the filament surface. Using an optical pyrometer for temperature adjustment, the filament was heated at 860 °C for 1 min., producing a darkened filament containing a thin line of tungsten oxide along each edge.

After loading the sample into the source of the mass spectrometer the system was allowed to pump down to a pressure of 2×10^{-6} torr before starting the analysis. Liquid nitrogen was then added to a source cold finger which further reduced the pressure to less than 1×10^{-7} torr. Because the thallium ionizes at a very low temperature (about 700 °C) a pyrometer cannot be used to precisely set the filament temperature during the analysis, so instead, the filament current was increased until the intensity of the ^{205}Tl peak was approximately 2 mV (10^{11} Ω resistor). Through focusing of the ion beam and gradual increase of the filament current, the intensity of the ^{205}Tl peak was increased to 100 mV by 5 min. At t = 5 min., the intensity of the ^{205}Tl was increased to 250 mV. The signal was then allowed to grow until it reached 10 V. If the signal required less than 9½ min. or greater than 13 min. to reach 10 V, the run was aborted before any data was taken since, under these conditions data which was high by 0.05 percent had been observed. Upon reaching 10 V, the signal was reduced to 3 V and allowed to grow to 7 V which generally required 2 to 3 min. The signal intensity was then reduced to 2.5 V. After 2 min., the signal intensity was increased to 10 V and allowed to grow to 30 V over a period of 1 min. The signal intensity of the ^{205}Tl was then decreased to 2.5 V. At t = 30 min the ion beam was focused, and at t = 35 min. the ratio measurements were begun. Ratio sets are taken at t = 35, 40, 48, and 53 min. Each of the ratio sets described above consisted of five ratio pairs of data taken over a period of 5 min. The computer was programmed to delay 8 s after switching peaks and then to take 15 intensity measurements (one/s) on top of the peak before switching peaks again. At t = 45 min. additional baseline data were taken to ascertain that no baseline shifts had occurred during the measurement of the first two ratio sets. The average of the four ratio sets was recorded as the $^{205}Tl/^{203}Tl$ isotopic abundance ratio of the sample.

The rate of isotopic fractionation during the 25 min. over which ratio data was measured is very small, generally on the order of two to three parts in ten thousand. Even when the precision within an analysis is very high, the difference between successive analyses may be very large (approximately 0.3%). The traditional method of minimizing between run differences is strict parameter control. The procedure described herein was designed and tested to yield a high degree of internal and external precision; however, inconsistencies will result unless all parameters are rigidly controlled.

The data obtained during the analysis of some thallium minerals and high purity materials indicated that silica contamination could affect the observed isotopic ratio. The examination of a solution of Tl_2CO_3 which had been stored in a borosilicate glass flask for over a year, yielded $^{205}Tl/^{203}Tl$ ratios of 2.380 consistently until it was treated with HF.

After this treatment thallium ratios of approximately 2.382 were observed. This effect was not totally surprising since the silica gel technique for thallium had consistently yielded ratios 0.2 percent lower than the tungsten filament procedure. The addition of silica gel to the thallium on the tungsten filament yielded ratios of approximately 2.378.

The presence of the commonly found impurities sodium, potassium, and silicon were shown to have a detrimental effect upon the isotopic ratio measurement of thallium. Therefore, great care was taken to ensure that these impurities were not present in sufficient quantity to affect the ratio measurements.

Large amounts (1 μg) of sodium or potassium will shift the observed $^{205}Tl/^{203}Tl$ ratio to a higher value. However, the filament current required to ionize and volatilize the sample is much higher than normal (2.2A) or approximately 825 °C. In addition, the signal growth is abnormally sluggish. It is very important to monitor the filament current in this case because large sodium and potassium beams have been observed to sputter thallium off the source causing a dramatic memory effect, especially on small samples. If 1 μg each of sodium and potassium is loaded onto a tungsten filament and dried without thallium, peaks will still be seen at masses 203 and 205. The ratios of these peaks were found to reflect the composition of the samples which had been analyzed since the last source cleaning.

2.2 Purification of the Separated Isotopes

Electromagnetically separated ^{203}Tl and ^{205}Tl isotopes were obtained from the Isotopes Division, Oak Ridge National Laboratory of the Union Carbide Nuclear Company. The ^{203}Tl isotope was received in a sealed ampoule in the form of thallium metal, and the ^{205}Tl isotope was received in the form of thallous oxide. The ^{203}Tl was designated as series R and D, sample 000101 and the ^{205}Tl was designated as series 152102.

Included with each isotope was a certificate of analysis which contained a statement of isotopic purity as well as a semiquantitative spectrographic analysis. The chemical analysis indicated that most elemental impurities could be present at levels up to 0.1 percent and that silicon, which could interfere with the mass spectrometric analysis of thallium, was present at a level of 0.08 percent. The method used for the assay of the thallium separated isotope solutions depended upon the quantitative precipitation of thallium chromate, and thus a purification procedure was developed to reduce the levels of lead, barium, silver, zinc, copper, bismuth, and mercury which form insoluble chromates.

The techniques of solvent extraction, electrodeposition, and fusion under hydrogen gas were utilized to purify the thallium separated isotopes. Each isotope (about 1 g) was transferred to a covered Teflon beaker. Twenty grams of aqua regia were added to dissolve and oxidize the thallium to the trivalent oxidation state. After all of the thallium was dissolved, indicating that the oxidation was complete, the cover and the sides of the beaker were rinsed with about 5 ml of water and the solution was evaporated to dryness at approximately 80 °C to avoid reduction of the thallium to the more stable univalent oxidation state. Eleven grams of concentrated (9 M) HBr were added followed by dilution to 100 g with water. The thallium was extracted into two 50-mL portions of methyl isobutyl ketone (MIBK), and the organic layer was washed twice with 25 mL portions of 1N HBr. Since the thallium could not be quantitatively back extracted into an aqueous solution, the MIBK layer was transferred to a 150 mL quartz beaker and evaporated to dryness (quartz was used because of the eventual necessity of evaporating sulfuric acid). The residual organic material was destroyed by digestion with a mixture of 20 g of concentrated HNO_3, 5 g concentrated H_2SO_4, and 5 g concentrated $HClO_4$. Overnight digestion yielded a clear solution which was evaporated to dryness.

The thallium was reduced to the univalent state with H_2SO_3. Twenty grams of H_2SO_3 (V/V, 2 + 98) was added to dissolve the residue and H_2SO_3 was added until the odor of SO_2 could be detected. The solution was then evaporated to dryness.

The residue was taken up in 100 g of 0.05N $HClO_4$, and the thallium was plated anodically as Tl_2O_3 onto a large platinum gauze electrode using a single 0.75 mm platinum wire as the cathode at 2.0 V.

When the anodic deposition was complete, the Tl_2O_3 was stripped from the anode using concentrated HNO_3; 2 g of $HClO_4$ were added, and the solution was evaporated to dryness. Twenty grams of H_2SO_4 (V/V, 2 + 98) were added to the residue, the thallium was reduced with 4 mL H_2SO_3, and the solution was evaporated only to fumes of H_2SO_4. The solution was diluted to 20 g with water and thallium was plated cathodically onto high purity platinum wire. The metal was collected at intervals and stored under water to prevent air oxidation.

As a final step, the metal was kneaded into a lump under water and transferred to a tared quartz boat. The thallium metal was fused at 350–400 °C in a tube furnace under a flow of hydrogen gas for 2 h according to Brauer [39]. After cooling, the boat and the metal were weighed.

2.3 Preparation and Analysis of the Separated Isotope Solutions

The purified thallium isotopes, in the metallic form, were dissolved in 30 g of 8N HNO_3 and transferred to 200 mL quartz flasks. The solutions were diluted with water to yield a concentration of approximately 0.024 mmol thallium per

gram of solution for the ^{203}Tl isotope and 0.020 mmol per gram for the ^{205}Tl isotope. The solution of ^{203}Tl was designated "Tl 203" and the solution of ^{205}Tl as "Tl 205". Samples of the "Tl 203" and "Tl 205" were withdrawn for the analysis of impurities by isotope dilution spark source mass spectrometry (IDSSMS). Each sample was spiked with 3×10^{-7} g of each of the following separated isotopes: ^{206}Pb, ^{144}Nd, ^{137}Ba, ^{125}Te, ^{123}Sb, ^{117}Sn, ^{113}In, ^{111}Cd, ^{108}Pd, ^{107}Ag, ^{97}Mo, ^{91}Zr, ^{86}Sr, ^{69}Ga, ^{64}Cu, ^{58}Ni, ^{54}Fe, ^{52}Cr, ^{47}Ti, ^{40}Ca, ^{39}K, ^{24}Mg. The solution was blended to ensure equilibration of the spikes with the elements present in the sample, and the solution was evaporated to dryness. The thallium was oxidized with aqua regia and the solution was evaporated to dryness. Two grams of concentrated HBr were added to the sample, and following dissolution, water was added to increase the volume to 10 mL. The thallium was extracted into 10 mL of MIBK. The aqueous layer was drawn off and reserved, and the organic layer was washed with 10 g of 1N HBr. The aqueous fractions containing the impurities and separated isotopes were combined and evaporated to dryness for analysis by IDSSMS. Additional aliquots containing 2 mg of thallium were taken for the analysis of mercury and bismuth by atomic absorption spectrometry.

Table 3 shows the results of these analyses as well as that of a sample of doped thallium which had been purified by the same method used for the separated isotopes. This sample of pure thallium metal had been doped with 0.1 percent of 26 elements including Ag, Bi, Ba, Cu, Hg, and Pb to determine the efficiencies of the purification procedure.

TABLE 3. *Analysis of impurities in thallium separated isotopes*[a].

Element	203 Tl (ppm)	205 Tl (ppm)	Element	203 Tl (ppm)	205 Tl (ppm)
Pb[b]	80	16	Ga	0.2	0.5
Nd	1	2	Zn[b]	10	6
Ba[b]	1	1	Cu[b]	6	6
Te	0.3	2	Ni	1	1
Sn	28	30	Fe	27	50
In	9	1	Cr	4	0.4
Cd	1	5	Ca	20	6
Pd	1	4	K	160	70
Ag[b]	0.7	0.4	Mg	5	0.6
Mo	12	1	Al	9	21
Zr	0.3	3	Na	50	50
Sr	1	1	Bi[b]	N.D.[c]	N.D.[c]
Se	—	1	Hg[b]	2.3	5.7

[a] All elements analyzed by spark source isotope dilution except for Pb and Cu in ^{203}Tl (analyzed by thermal ionization isotope dilution) and Bi and Hg (analyzed by atomic absorption). In all cases concentrations are upper limit values.

[b] Elements which would interfere with the chemical assay.

[c] Not detected.

The only element that was detected at a level high enough to affect the thallium chromate assay procedure was lead at 80 ppm in the "Tl 203" solution. Two additional aliquots of the "Tl 203" were withdrawn and analyzed for lead by isotope dilution mass spectrometry [40]. Because lead chromate is much more insoluble than thallium chromate, a correction was applied to the "Tl 203" solution on the basis of quantitative precipitation of the lead.

2.4 Assay of the Separated Isotope Solution

The quartz flasks containing the purified separated isotopes were vigorously shaken to ensure thorough mixing of the solutions. Four weighed aliquots of about 30 g for the "Tl 203" solution and 37 g for the "Tl 205" solution, each containing approximately 0.7 mmol of thallium, were withdrawn by the following method. The polyethylene stopper which had been used to seal each flask was removed and replaced with a prepunctured stopper. An 18 gauge, 16 cm long platinum needle with a Kel-F hub was inserted into the solution. A 20-mL polyethylene hypodermic syringe was attached to the Kel-F hub of the needle. The plunger of the syringe had been covered with a 130 μm thick skived Teflon tape to prevent contamination. After withdrawing the desired amount of solution the syringe was disconnected from the hub and the tip was capped with a Kel-F hub. Any static charge that might be present on the plastic syringe was dissipated by wiping it with a damp lint-free cloth, and the syringe and contents were weighed on a semimicrobalance to $\pm$ 0.02 mg. The solution was then delivered to a 400-mL Teflon beaker and the syringe was again capped, wiped, and weighed. The weight of the sample was determined from the weights of the syringe before and after delivery of the sample. Since 30-mL or more of each solution were required to produce a 0.7 mmol sample, two loadings of the 20-mL syringe were weighed for each sample.

The aliquoting procedure involved the withdrawal of samples for the determination of isotopic composition, for assay of the solution concentration, and for the preparation of calibration standards. The entire process was carried out within five hours and the aliquoting pattern shown in table 4 was followed to ensure that the concentration and isotopic composition of the separated isotope solutions did not change during aliquoting. This process was carried out first for the "Tl 203" solution and then for the "Tl 205" solution. Nearly twice as much "Tl 205" was to be added to the mixes, and therefore the target ratio would be more easily achieved with the addition of a larger quantity of solution.

Each sample was assayed as follows: Ten grams of H_2SO_4 (V/V, 2 + 98) were added to each beaker and the solutions were evaporated until fumes of H_2SO_4 were observed. The solutions were cooled, diluted to 10 g with water, 4 mL of H_2SO_3 were added to each, and the solutions were again

TABLE 4. *Aliquoting procedure used for preparation of calibration standards.*

Aliquot No.	Sample Use
1	Isotopic Composition
2, 3	Assay
4 through 9	Mixes 1-6
10, 11	Assay
12	Isotopic Composition

evaporated until fumes of H_2SO_4 were visible. The solutions were diluted to 60 g with water, 1 mL of 10 percent K_2CO_3 was added to each, and the solutions were digested for ½ h. Glass stirring rods were placed in each beaker and the thallium was precipitated by adding 2 g of concentrated NH_4OH, followed by the dropwise addition of 1 g of 10 percent K_2CrO_4 to each with constant stirring.

The solutions were allowed to stand at room temperature for approximately 18 h. Each solution was then filtered through a tared 15-mL fine fritted glass crucible. The filtrate containing the soluble thallium was collected in a 100-mL Teflon beaker. After all the solution had been filtered, the Tl_2CrO_4 precipitate was washed three times with approximately 30-mL of 50 percent (v/v) ethanol-water mixture. The precipitate was dried for 2 h. at 125 °C and reweighed. Further drying at 125 °C yielded no change in weight of the Tl_2CrO_4 precipitate.

The crucibles were weighed to ± 0.002 mg on a microbalance. To eliminate any errors due to static charge, the crucibles and tares were reweighed cyclically until the reproducibility was within ± 0.005 mg. A buoyancy correction for the glass crucibles was made by averaging the change in weight of two empty tare crucibles. The air weight of the Tl_2CrO_4 was converted to vacuum weight using a measured value of 6.983 as the density of the precipitate at 22 °C. The millimoles of thallium present in the precipitate were determined using the calculated atomic weight for thallium and the 1975 atomic weight values for chromium and oxygen. The formula weights used were for $^{203}Tl_2CrO_4$ and for $^{205}Tl_2CrO_4$.

After filtration of Tl_2CrO_4 was complete, the soluble portion and washings were returned to the original 400 mL beaker and evaporated to a volume of approximately 10 mL. The solutions were made acidic with concentrated HNO_3 (color change from yellow to orange) and a small amount of ethanol was added to reduce Cr^{+6} to Cr^{+3}. The solutions were transferred to weighed polyethylene bottles, diluted to 80 to 100 g and aliquoted. The aliquots were spiked by weight with ^{203}Tl, and the resulting solutions were evaporated to dryness. One gram of aqua regia was added to oxidize the thallium and, after evaporation, the residues were taken up in 1N HBr. The thallium, as $HTlCl_4$, was extracted into methyl isobutyl ketone (MIBK) and evaporated to dryness. The organic matter was destroyed by digestion with a mixture of perchloric and nitric acids (1:5); and the solution was evaporated to dryness. The purified thallium was diluted to a concentration of 100 μg/mL with HNO_3 (1 + 49) for analysis by thermal ionization mass spectrometry. The thallium found in the soluble portion (in mmol) was added to the thallium determined gravimetrically to yield the total thallium in the sample. The results of this analysis are shown in table 5.

TABLE 5. *Concentration of thallium isotope solutions.*

Soln.	Sample No.	Wt. Soln. (g)	Total Thallium (mmol)	Conc. Soln. Tl/g Soln. (mmol)
Tl 203	1	30.42998	0.731881	0.02405131
	2	30.57911	.735270	.02404485
	3	30.74880	.739551	.02405138
	4	30.26530	.728017	.02405451
			Average	0.02405051[a]
Tl 205	1	37.19243	0.755083	0.02030206
	2	37.09542	.753115	.02030210
	3	37.79003	.767268	.02030345
	4	36.35100	.738048	.02030338
			Average	0.02030275[a]

[a] The standard error of the average is calculated to be 0.0000015 mmol Tl/g soln. and the uncertainty of the value of concentration at the 95 percent confidence level is 0.0000030 mmol Tl/g soln.

This method of determining the concentration of thallium solutions was previously tested on solutions containing a known amount of "natural" thallium. A thallium master solution was prepared from high purity (99.99%) thallium metal (SRM 997) and seven sets of four samples were withdrawn from this master solution, each on a different day over a period of one month. In addition, one more set of four was determined just before the assay work was begun on the separated isotope solutions. This extra set allowed the analyst to be certain that the experimental conditions were still under control. The final set which was completed 11 months after the first set was assayed, showed no evidence of any bias. The uncertainty (ts)[3] of 31 individual determinations is 0.029 percent and the ts of the set averages is 0.014 percent. Comparison of the calculated and measured concentrations indicated a positive bias of 0.028 percent which would have a negligible effect on the ratios.

Pooling the results of the analysis of the separated isotope solutions shown in table 5 with the results of the eight sets described above, yields a value of ± 0.0000030 mmol Tl/g solution for the standard deviation of an individual determination (7 deg of freedom). The standard error of the average of four determinations is ± 0.0000015 mmol Tl/g solution.

[3] Student T test at a 95 percent confidence limit.

2.5 Isotopic Analyses of the Separated Isotope Solutions

Each of the separated isotope solutions were analyzed four times on each of two mass spectrometers (#1 and #4) by Operators 1 and 2. The two aliquots of each isotope were analyzed in alternate fashion and no difference was seen between the solutions taken before and after the preparation of the calibration mixes. The mass spectrometer sources were cleaned between the analyses of the ^{203}Tl and ^{205}Tl as a precaution against the possibility of contamination from source parts, although back to back analyses of the two separated isotopes on the same source failed to yield any evidence of contamination. The corrected isotopic compositions of the two isotopes are shown in table 6. Although the measured uncertainties were less than 0.1 percent, an uncertainty of 0.2 percent was used for the statistical analysis of the ratio determination. This increased uncertainty was used to take into account any possible biases and non-linearities which might be encountered in the measurement of large ratios. The estimate of 0.2 percent was based on the mass spectrometric ratio measurements of uranium calibration standards.

TABLE 6. *Isotopic composition of the thallium separated isotopes.*

Separated Isotopes		Isotopic Composition (atom percent)
"Tl 203"	^{203}Tl	99.26333 ± 0.00140[a]
	^{205}Tl	0.73667 ± 0.00001
"Tl 205"	^{203}Tl	0.55758 ± 0.00001[a]
	^{205}Tl	99.44242 ± 0.00111

[a] Based on experience and results of MS work on uranium, the uncertainty of the ratio determinations is taken to be 0.2 percent, which is much larger than the calculated 95 percent confidence limit, to take into account bias and non-linear behavior for ratios as large as these.

2.6 Preparation of Calibration Samples

Six calibration samples were prepared by mixing weighed portions of the "Tl 203" and "Tl 205" solutions as described in sect. 2.4. The calibration standards were prepared so that three were higher and two were lower than the observed ^{205}Tl/^{203}Tl ratio of the standard. In addition, a sixth standard was prepared to yield a 1:1 ratio. The weighed aliquots were delivered into 33 mL screw cap Teflon PFA bottles.

The absolute isotopic compositions of the calibration standards are shown in table 7. The isotopic ratio of each calibration sample was calculated from the isotopic analysis of the separated isotopes and thallium concentration of each separated isotope solution. Each calibration sample was thoroughly mixed and evaporated to dryness on a hotplate. The thallium was oxidized to the trivalent state with aqua regia and the solutions were evaporated to dryness at a low temperature (about 80 °C) followed by dilution with (1 + 9) HNO_3 to produce a concentration of 1 mg of thalliun per gram of solution. Prior to the mass spectrometric analysis of the mixes, a 1:10 dilution was effected to produce solutions which were 100 μg/mL in thallium concentration.

2.7 Isotopic Analyses of the Calibration Mixes and the Standard Sample

Two complete sets of analyses of the calibration mixes and the standard samples were made (one by Operator 1 on Instrument #1 and one by Operator 2 on Instrument #4. Both analysts used the procedure outlined in section 2.1. Each set consisted of four analyses of each calibration mix and 24 analyses of the reference standard. The samples were run in a pattern alternating randomly selected mixes with the standard.

TABLE 7. *Thallium composition of calibration samples.*

Sample	Isotope Solution	Wt. Soln. (g)	^{203}Tl (mmol)	^{205}Tl (mmol)	^{205}Tl/^{203}Tl Ratio
1	Tl 203	1.21897	0.02910083	0.00021634	2.432950
	Tl 205	3.54447	0.00040125	0.07156125	
2	Tl 203	1.05205	0.02511590	0.00018639	2.365517
	Tl 205	2.97292	0.00033655	0.06002185	
3	Tl 203	1.09751	0.02620125	0.00019445	2.404896
	Tl 205	3.15388	0.00035703	0.06367537	
4	Tl 203	2.16573	0.05170319	0.00038371	1.002851
	Tl 205	2.56360	0.00029021	0.05175789	
5	Tl 203	1.08879	0.02599299	0.00019290	2.434939
	Tl 205	3.16857	0.00035870	0.06397200	
6	Tl 203	2.16484	0.05168195	0.00038355	2.378802
	Tl 205	6.15241	0.00069648	0.1242145	

As discussed in section 2.1, silica, if present, can depress the measured $^{205}Tl/^{203}Tl$ isotopic ratio by as much as 0.2 percent. To ensure that silicon did not interfere in the measurement of the calibration mixes, aliquots of the mixes were treated with 2 g concentrated HF and remeasured. In all cases, the remeasured isotopic ratios were within the uncertainty of the ratios measured during the determination of the atomic weight.

3. Results and Discussion

Table 8 summarizes the results for the six synthetic mixes. The calibration factors for each analyst varied over a range of only 0.022 percent for Operator 1 and 0.026 percent for Operator 2. In addition, the calibration factors obtained for the equal atom mix were within the range of the calibration factors determined from the other mixes, indicating an insignificant degree of nonlinearity.

Table 9 contains a summary of the observed and corrected $^{205}Tl/^{203}Tl$ values for the standard sample for Operators 1 and 2 as well as the absolute isotope abundance ratio for thallium and its associated uncertainty component.

Table 10 gives the summary calculations of the reference sample. The atomic weight is calculated from the absolute isotopic abundance by summing the product of the nuclidic masses obtained from Wapstra and Bos [15] and the corresponding atom fractions. The thallium reference standard used for the atomic weight measurements will become a new Standard Reference Material, SRM 997. This SRM will be certified for isotopic composition and chemical purity.

A limited survey of thallium minerals and high purity materials has failed to show any significant (±0.1%) isotopic variations. This indicates that the atomic weight determined for the thallium reference standard is, with an allowance for possible natural variations, applicable to other terrestrial thallium samples.

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TABLE 8. *Determination of calibration factors.*

Calibration Sample No.	Isotopic Ratio, $^{205}Tl/^{203}Tl$			Calibration Factor	
	Calculated	Operator 1	Operator 2	Operator 1	Operator 2
1	2.432950	2.428894	2.428315	1.001683	1.001896
2	2.365517	2.361285	2.361357	1.001805	1.001749
3	2.404896	2.400927	2.400032	1.001666	1.002014
4	1.002851	1.001271	1.000927	1.001584	1.001916
5	2.434939	2.431089	2.430200	1.001597	1.001937
6	2.378802	2.375074	2.374391	1.001582	1.001845
Mean Values of Calibration Factors				1.001653	1.001893

TABLE 9. *Determination of corrected isotopic ratios.*

	Observed $^{205}Tl/^{203}Tl$	Correction Factor	Corrected $^{205}Tl/^{203}Tl$
Operator 1	2.3832381	1.001653	2.387177
Operator 2	2.3825873	1.001893	2.387097
		MEAN	2.38714
		±	0.00101

Uncertainty Components:

95 percent confidence limits in ratio determination . . . . . ±0.00042

Bounds due to possible systematic error in composition of separated isotopes . . . . . ±0.00017

Bounds due to possible systematic error in chemical analysis . . . . . ±0.00042

TABLE 10. *Summary calculations of the atomic weight of thallium.*

Values	Uncertainty Components			
	Overall limit of error[a]	Mass spectrometric analytical error	Possible systematic error in composition of separated isotopes	Possible systematic error in chemical analysis
Atomic Weight = 204.38333	±0.000176	±0.000074	±0.000028	±0.000074
Nuclidic Masses ($^{12}C = 12$)				
$^{203}Tl = 202.972336$	±0.000006			
$^{205}Tl = 204.974410$	±0.000005			
Atom Percent				
$^{203}Tl = 29.524$	±0.0088	±0.0037	±0.0014	±0.0037
$^{205}Tl = 70.476$	±0.0088	±0.0037	±0.0014	±0.0037
Isotopic Ratio				
$^{205}Tl/^{203}Tl = 2.38714$	±0.00101	±0.00042	±0.00017	±0.00042

[a] The overall limit of error is the sum of the 95 percent confidence limits and the terms covering effects of known sources of possible systematic error.

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