

The Absolute Isotopic Abundance and Atomic Weight of a Reference Sample of Silver

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August 12, 1981

The atomic weight of a reference sample of silver has been determined by mass spectrometry, with an uncertainty of one part in 10^6 , using a single filament silica gel procedure. Accurately known quantities of chemically pure ^{107}Ag and ^{109}Ag were mixed to produce standards of known isotopic composition for calibration of the mass spectrometer. The absolute isotopic ratio of the reference sample of silver is $^{107}\text{Ag}/^{109}\text{Ag} = 1.07638 \pm 0.00022$ yielding an atomic weight of 107.86815 ± 0.00011 . The indicated uncertainties represent an overall limit of error at the 95 percent confidence level which is the sum of the uncertainty components for the ratio determined and the components covering effects of known sources of possible systematic error.

Key words: Absolute ratios; atomic weight; Faraday Constant; isotopic abundance; mass spectrometry; silica gel; silver; silver iodide.

1. Introduction

The inorganic mass spectrometry group of the National Bureau of Standards has been conducting a long term program of absolute isotopic abundance ratio and atomic weight determinations using high precision isotope ratio mass spectrometry. 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], thallium [13], and strontium [14].

The present work, a redetermination of the atomic weight of silver, was undertaken in conjunction with the calculation of a more accurate Faraday constant. The Faraday is directly related to other physical constants including the Avogadro constant, the proton gyromagnetic ratio, the magnetic moment of the proton in nuclear magnets, and the ratio of the NBS as-maintained ampere to the absolute or SI ampere. Over the years a problem arose in assigning a recommended value for the Faraday due to apparent discrepancies between the Faraday determined from electrochemical experiments and the Faraday calculated from other fundamental constants. Unfortunately, earlier electrochemical experiments were not sufficiently precise (6.8 ppm, one standard deviation, for the best silver determination) to either prove or disprove the existence of this discrepancy. As a result, the Faraday was excluded from the most recent (1973) least squares adjustment of the fundamental constants [28].

In 1980, Bower and Davis [15], using the same source of silver as was analyzed in this work, NBS Standard Reference Material (SRM) 748, published a new value for the electrochemical equivalent of silver with an accuracy of 1.28 ppm (one standard deviation). The calculation of the Faraday using this value and the 1962 atomic weight of silver [1], indicated that significant differences between the various Faraday calculations might indeed exist. In order to assess the significance of these differences, however, it became necessary to significantly reduce the uncertainty in the atomic weight of silver.

The method used for the determination of atomic weights at NBS, which has been briefly described in previous publications [1-14], and may be described as calibrated mass spectrometry, combines the techniques of high precision chemical assay with high precision mass spectrometry. The mass spectrometers to be used for the isotopic abundance measurements are calibrated for bias using synthetic mixes of known isotopic composition, prepared from nearly pure separated isotopes. Extensive research has demonstrated that this bias is due to non-linearities in the measurement circuit and mass-dependent isotopic fractionation [16]. In the case of ratios near one, this bias reduces to isotopic fractionation. These measured biases are then used to calculate the absolute isotopic abundance ratio and, ultimately, the atomic weight of the reference sample. A block diagram characterizing the atomic weight method is shown in figure 1.

The chemical research requires the development of an assay procedure for the pure element or reference sample precise to at least one part in 10^4 , which will ultimately be used to assay the separated isotope solutions. In addition, a

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

Mass Spectrometric Atomic Weight Method

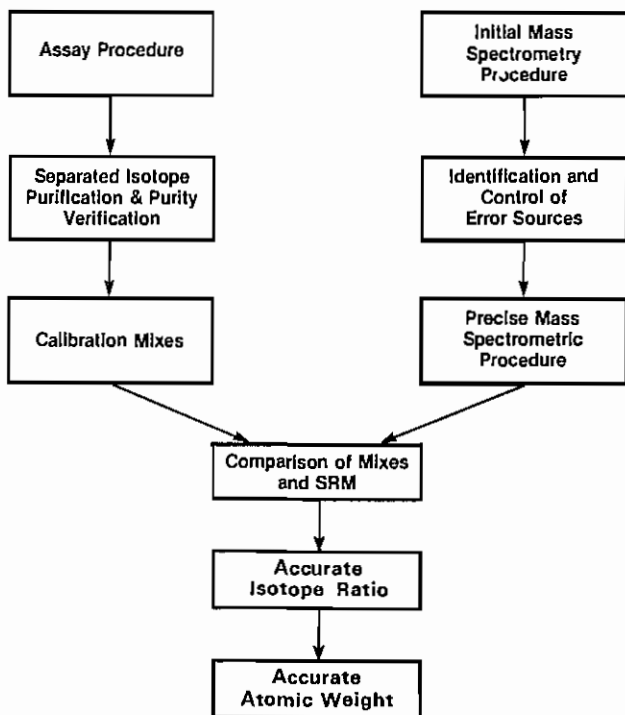


FIGURE 1.

procedure must be developed to purify the separated isotopes to eliminate impurities which could interfere with either the chemical or mass spectrometric procedures. Once these methods have been thoroughly tested using the reference sample, the separated isotopes are purified and dissolved. Aliquots of each isotope are then taken to produce calibration mixes which are blended to bracket the natural isotopic abundance ratio of the element. In addition, aliquots of each isotope are taken for assay so that accurate solution concentrations can be ascertained. A knowledge of the solution concentrations combined with aliquoting data allows the actual ratios of the calibration mixes to be calculated.

The mass spectrometric research involves the development of a high precision method for the analysis of the relative isotopic abundance ratios of the reference sample, followed by a comprehensive study to identify and control any sources of bias which could affect the final measurements.

After the above tasks have been accomplished, two complete sets of analyses of the calibration mixes and the SRM are made by two different operators using different mass spectrometers. The calibration mixes are randomly selected and are analyzed in an alternating pattern with the reference sample. A comparison of the relative isotopic abundance ratios obtained for the calibration mixes with the calculated or true value produces a calibration factor. This factor is applied to the relative isotopic ratio obtained for the SRM to produce

the absolute isotopic abundance ratio. The atomic weight is then obtained by multiplying the fractional abundance of each isotope by its nuclidic mass² and summing the resultant products.

2. Experimental Procedure³

2.1 Mass Spectrometry

The isotopic ratio measurements were made using two nearly identical 90°, 30 cm radius of curvature solid sample mass spectrometers equipped with a "Z" lens focusing source [18]. The collector was a deep bucket Faraday cup equipped with a 50 percent transmission grid shadowing a series of suppression grids [18–20]. The measuring circuit consisted of two vibrating reed electrometers (VRE) and a voltage-to-frequency conversion system which transmits data to a computer for data acquisition. Prior to initiating the atomic weight ratio determinations, the measuring circuits of the mass spectrometers were calibrated and found to be linear to within one part in 10⁴ over a range of 30–80 percent of full scale for each VRE scale. However, the linearity of the measurement electronics becomes insignificant because of the equal atom composition of the standard and most of the mixes. Under these conditions any non-linearities in the ratio measurement will cancel, and any possible effects would be indicated by the endpoint calibration mixes.

The relative isotopic composition of the calibration mixes and the reference sample were determined by surface ionization mass spectrometry using a platinum single filament silica gel technique.

The filaments used in this work were fabricated from 99.9 percent pure platinum ribbon (0.025 × 0.76 mm) and were cleaned by heating at 2.5 A for 1 h(r) in a vacuum and under a potential field.

The sample mounting was carried out in two stages, hereafter referred to as the low temperature drying stage and the high temperature drying stage. The low temperature drying stage was similar to the lead-silica gel method described by Barnes *et al.*, [21]. A 5 µL drop of silica gel suspension was placed on the filament surface and dried at 1.0 A for 5 min. A second drop of silica gel was added and the drying repeated. A 5 µL drop of silver as AgNO₃ in (1 + 9)⁴ HNO₃ was placed

² Nuclidic masses, as published in Wapstra and Bos [17] are known to parts per billion accuracies.

³ In order to describe adequately materials, instruments, equipment, and procedures, it was occasionally necessary to identify commercial products by manufacturer's name or label. In no instance does such identification imply endorsement by the National Bureau of Standards nor does it imply that the particular product or equipment is necessarily the best available for that purpose.

⁴ A reagent dilution of (1 + 9) indicates 1 volume of concentrated reagent diluted with 9 volumes of pure water. If no dilution is specified, use of the concentrated reagent is implied. The acids and water used for these dilutions were produced at NBS by sub-boiling distillation [23].

on top of the silica gel and dried at 1.0 A for 5 min. A drop of 0.75 N H_3PO_4 was then added and dried at 1.5 A for 5 min then at 2.0 A for 5 min. This drying procedure was carried out in a class 100 clean air hood with an airflow of 100 linear ft/s per s using a programmable sample drier designed by Gramlich and Shideler [22]. Throughout the procedure a heat lamp, whose intensity was adjusted to yield a temperature of 70 °C at the filament surface, was used to aid the drying process.

The high temperature drying stage was accomplished using pyrometer adjustment of the filament temperature. This method was first used for the determination of the atomic weight of thallium [13] and has since proved to be an important key to controlling the reproducibility of isotopic ratios of a number of elements. The filament was covered with a bell jar and purged with nitrogen gas for 5 min. The nitrogen flow was stopped and the filament was adjusted to a temperature of 1040 °C for 60 s.

After loading the sample into the source of the mass spectrometer, the system was allowed to pump down to a pressure of at least 2×10^{-6} torr (300 μPa) before starting the analysis. Liquid nitrogen was then added to the source cold finger to reduce the pressure to less than 1×10^{-7} torr (10 μPa). At $t = 0$ min, the temperature of the filament was increased to 760 °C. This yielded a ^{107}Ag ion beam intensity $1 - 2 \times 10^{-12}$ A. At $t = 25$ min, the temperature of the filament was increased to 790 °C. At this temperature the intensity of the ^{107}Ag ion beam was between 5×10^{-12} A and 1×10^{-11} A. If the intensity of the ^{107}Ag ion beam was outside of these limits, the analysis was rejected. Baseline data were taken and ratio data were collected between $t = 30$ and 50 min.

2.2 Purification of Separated Silver Samples

Electromagnetically separated ^{107}Ag and ^{109}Ag isotopes in the form of silver metal powder were obtained from the Nuclear Division, Oak Ridge National Laboratory of the Union Carbide Nuclear Company. The ^{107}Ag was designated series R&D, sample 000101 and the ^{109}Ag was designated series R&D, sample 000201. The certificate which accompanied each sample showed enrichment to better than 99.9 percent for the major isotope. No information on chemical purity was given.

Since the method developed for the assay of silver was based on the precipitation of AgI from ammonical solution, it was necessary to develop a purification procedure that would reduce possible impurities to a level low enough so they would not cause a significant error.

Elements that form relatively insoluble iodides or hydroxides could possibly interfere. Included are Pb, and Tl which form insoluble iodides, and Al, Cr, Fe, Ga, In, Ti, Zr, and the rare earths which form insoluble hydroxides.

Each separated silver isotope was purified as follows: The

silver isotope, as powdered silver metal (about 1g) was transferred to a 150 mL Teflon-FEP beaker, dissolved in 20 mL of (1 + 4) HNO_3 , and the resulting solution evaporated to dryness. The residue was taken up in 50 mL of water and enough concentrated NH_4OH solution to dissolve the precipitated AgOH . The solution was digested on a warm hot plate for about one hour, allowed to cool, and filtered through a close textured paper. After washing the filter paper with dilute (1 + 49) NH_4OH the filtrate was heated to drive most of the NH_3 from the solution. The solution was made acidic with dilute (1 + 9) HNO_3 and 25 mL of (1 + 9) HCl was added to precipitate silver chloride. The solution and precipitate were digested on a hot plate for three hours in darkness and allowed to stand overnight at room temperature, also in darkness. Most of the supernatant solution was removed from the precipitated silver chloride by decantation and the last 10–15 mL was withdrawn by means of a plastic syringe equipped with a platinum needle. The precipitated AgCl was washed three times with a few mL of H_2O and the washings were removed with the syringe and needle.

The precipitated AgCl was then dissolved in 15 mL of NH_4OH and diluted with about 50 mL of water. The solution was heated to drive off excess NH_3 and made acid with (1 + 9) HNO_3 to reprecipitate AgCl . A few drops of (1 + 9) HCl were added and the solution was allowed to stand overnight in darkness. The supernatant liquid was then removed in the manner previously described. The precipitated AgCl was then dissolved in 20 mL of NH_4OH and transferred to a 350 mL platinum dish. A solution prepared by reacting 25 mL of (1 + 4) HNO_3 with 50 mL of (1 + 4) NH_4OH yielding NH_4NO_3 , was added as an electrolyte and the resulting solution was diluted to approximately 250 mL. The platinum dish was placed on aluminum foil which was connected to the cathode of a de-power source. The dish was covered with a Teflon-TFE cover fitted with a platinum rod through the middle which reached to within 1 cm of the dish bottom. This rod was connected to the anode of the dc-power source. Silver was then electrodeposited onto the dish by plating with a potential of 1.0 V for 24 h.

The electrolyte was then poured from the dish into a Teflon beaker and the electrodeposited silver in the dish was washed with dilute (1 + 9) NH_4OH .

The electrodeposited silver was dissolved with (1 + 4) HNO_3 diluted to about 150 mL and the solution was made ammonical with concentrated NH_4OH . Additional NH_4NO_3 electrolyte was added and the silver was again electrodeposited by plating at 1.0 V for 24 h.

The electrolyte was then poured into the Teflon beaker, and the silver was washed with water. The dish and contents were then dried and weighed. The electrodeposited silver was then dissolved with (1 + 4) HNO_3 and transferred to a Teflon beaker. The dish was washed with water, dried, and weighed to obtain the approximate weight of purified silver.

Calculations based on the starting weight of silver, and the weight of purified silver showed that more than 99 percent of the silver was recovered in each case.

The effectiveness of this purification procedure was first tested by purifying a solution of natural silver which had been doped at the 1000 $\mu\text{g/g}$ level with each of thirty common impurity elements. The results of the analysis of this purified silver are shown in table 1. All of the impurity elements were reduced to 10 $\mu\text{g/g}$ or less (the analytical method will also be described later).

Since the method was effective in purifying grossly contaminated silver, it was applied to each of the silver separated isotopes, which were of much higher initial purity.

The acids and water used in these purifications were produced at NBS by sub-boiling distillation [23] and have been shown to be extremely low in trace metal contamination. The NH_4OH was produced by saturating high purity cold water with high-purity NH_3 gas and allowing the resulting solution to warm to room temperature. Apparatus such as beakers and filters were cleaned with ACS Reagent Grade acids and rinsed with high purity water before use.

TABLE 1. Analysis of impurities in silver separated isotopes.

Element	Spike Isotope	Ag Doped* and Purified ($\mu\text{g/g}$)	^{107}Ag ($\mu\text{g/g}$)	^{109}Ag ($\mu\text{g/g}$)
Al	^{26}Mg	4	<14	<20
As	^{82}Se	0.3	— ^b	—
Ba	^{137}Ba	0.1	3.1	0.9
Bi	^{203}Tl	0.05	—	—
Ca	^{44}Ca	2.6	1.5	1
Cd	^{111}Cd	0.4	0.3	1.2
Co	^{62}Ni	0.5	—	—
Cr	^{52}Cr	0.2	0.2	0.1
Cu	^{65}Cu	1.2	2.2	0.7
Fe	^{54}Fe	5	6	6
Ga	^{71}Ga	0.2	<1.1	<1.6
K	^{41}K	2.7	5	1.2
Mg	^{26}Mg	1.8	0.8	1.2
Mn	^{54}Fe	0.03	—	—
Mo	^{97}Mo	0.01	0.06	0.06
Na	^{41}K	9	<50	<60
Nd	^{145}Nd	0.2	0.6	0.4
Ni	^{62}Ni	0.4	2	0.4
Pb	^{206}Pb	1.6	1.5	1.6
Pd	^{110}Pd	0.2	0.8	0.2
Sb	^{117}Sn	0.6	—	—
Se	^{82}Se	0.2	0.3	0.4
Sn	^{117}Sn	0.07	0.3	0.4
Sr	^{86}Sr	0.03	0.1	0.1
Te	^{125}Te	0.002	0.1	0.07
Tl	^{203}Tl	0.1	0.5	0.5
V	^{52}Cr	0.03	—	—
Zn	^{67}Zn	1	0.3	0.6
Zr	^{91}Zr	0.06	0.5	0.6

* Original concentration—1000 $\mu\text{g/g}$ each.

^b — denotes data not reported.

2.3 Preparation and Analysis of Separated Isotope Solutions

Each isotope (^{107}Ag and ^{109}Ag) was transferred to a specially constructed and tared 500 mL quartz flask. These flasks were constructed from a standard taper joint 500 mL quartz flask by cutting the neck of the flask about 1 cm from the body and tooling the neck to fit a number zero polyethylene stopper and a standard aluminum serum cap. Final solutions were diluted to about 350 mL and final acidity was about 0.5 N HNO_3 . The solution of ^{107}Ag was labeled "Ag-107" and the solution of ^{109}Ag was labeled "Ag-109".

Portions of each separated isotope solution, equivalent to about 40 mg of silver, were taken for determination of impurities. Each sample was spiked with 10^{-7} g of ^{44}Ca , ^{111}Cd , ^{53}Cr , ^{65}Cu , ^{54}Fe , ^{71}Ga , ^{26}Mg , ^{97}Mo , ^{145}Nd , ^{62}Ni , ^{206}Pb , ^{110}Pd , ^{82}Se , ^{117}Sn , ^{86}Sr , ^{125}Te , ^{203}Tl , ^{67}Zn , and ^{91}Zr . Each spiked solution was then treated as follows: the solution was diluted to about 40 mL with H_2O and a slight excess of HCl was added to precipitate AgCl . The beaker and contents were allowed to stand in the dark overnight. Most of the supernatant liquid was removed from the precipitated AgCl by decantation into a second Teflon beaker. The last approximately 10 mL was removed by means of a plastic syringe and platinum needle and added to the decanted solution. The precipitate was washed with a few mL of (1 + 9) HNO_3 which was also combined with the decanted solution by use of the syringe. This solution was then evaporated to a few mL, removed from any remaining AgCl with the syringe and transferred to another beaker. This solution was evaporated to a large drop and transferred to specially prepared gold wire electrodes for analysis by spark source mass spectrometry using a peak switching electronic detection system.

The results of the analysis of the purified separated silver isotopes are shown in table 1. In addition to the spiked elements, the concentrations of other elements were estimated by comparison to spiked nuclides using the assumption that the sensitivity of the natural element and spike nuclides are the same. The results show that most elements are at the low ppm level or less. The only elements found at concentrations of greater than 10 ppm were Al and Na. These contaminants may have resulted from the Pyrex glass flask used to store the spike isotopes. Even if they were present in the amounts indicated, the effect would be negligible since sodium would not interfere with the analysis at this level, and aluminum, as $\text{Al}(\text{OH})_3$, would cause an error of only 0.001 percent in the assay of each isotope.

2.4 Assay of the Separated Isotope Solutions

The method developed for the high-precision assay of the silver solutions was based on a combination of gravimetry for the determination of most of the silver (greater than 99.5

percent) as AgI and isotope dilution mass spectrometry (IDMS) for the remainder. Silver iodide was selected as the gravimetric form since, of all the silver halides it is the least light sensitive, least soluble, and has the highest gravimetric factor. In fact, it was found that dry stoichiometric silver iodide was not detectably sensitive to fluorescent lighting since the material remained lemon yellow and no change in weight could be detected on prolonged exposure. The material was also found to be non-hygroscopic up to relative humidities of 90 percent.

The "Ag-107" solution and the "Ag-109" solution were each sampled for assay of silver in the following manner: four weighed portions of about 35 g, containing about 0.25 mmol Ag were withdrawn from each flask. A 10 cm platinum needle which had been inserted through a No. 0 polyethylene stopper was used to replace the stopper on the quartz flask. A 20 mL polyethylene hypodermic syringe, the plunger of which had been covered with a sheet of Teflon-FEP, was attached to the Kel-F hub of the needle and the desired amount of solution was withdrawn. The syringe was then disconnected from the hub and the tip was capped with a Kel-F cap. The syringe and contents were then weighed on a semi-micro balance to ± 0.02 mg. (Any static charge on the syringe was dissipated by placing the syringe on the balance pan which was surrounded by several polonium anti-static sources and waiting 2 min before taking a weight.) The solution was then delivered to a 100 mL Pyrex beaker with a Teflon coated rim and the syringe was again capped and weighed. The weight of the sample taken was determined from the weight of the syringe before and after delivery of the sample. A second weighed portion was taken in the same manner and combined with the first portion for each assay sample. Two assay samples were withdrawn from each solution before and after withdrawing the calibration samples to ensure that no change in concentration had occurred during the time interval of withdrawing samples (about 6h).

Each sample was then assayed as follows: 20 mL of concentrated high-purity NH_4OH was added and approximately a 1 percent excess of 0.5 N NH_4I was added slowly from a small wash bottle. The solution was heated covered on a hot plate.

Precipitation from ammoniacal solution resulted in the formation of a white precipitate, $\text{AgI} \cdot 1/2 \text{NH}_3$ [24]. Heating the solution drives off ammonia and results in the conversion of this white compound into yellow AgI. The AgI formed in this manner is composed of relatively large, easily filterable crystals that do not pass into the colloidal state when washed with water. The fact that AgI is slightly soluble in dilute NH_4OH also contributes to the formation of larger crystals.

After digesting overnight, the cover was removed and the solution was evaporated to a volume of 20 mL. Removal of NH_3 was tested by holding moist p-Hydriion paper over the hot solutions. If the paper indicated NH_3 in the vapor the

solution was heated until NH_3 was no longer detected. The beaker was then removed from the hot plate, covered, and allowed to stand overnight.

The solution was then filtered through a tared platinum-Munroe crucible and the precipitated AgI was caught on the platinum mat. The beaker and precipitate were washed with several small increments of water. The filtrate and washings were transferred back to the original beaker and reserved for the determination of dissolved and untransferred silver. The crucible and contents were dried for 3 h at 200 °C. Pure AgI is only very slightly reduced by light when wet. To guard against any possible decomposition, the precipitation, filtration, and drying were carried out in orange light or darkness. (The pure compound is lemon yellow and even slight decomposition causes the AgI to darken.)

After heating, the crucible was cooled in a desiccator and transferred to the ease of a micro-balance and allowed to stand for at least 2 h. The crucible and contents were then weighed on a micro-balance to ± 0.002 mg. An effective buoyancy and adsorption correction for the platinum crucible was made by averaging three empty tare crucibles. (The drying, cooling, and weighing were repeated to ensure constant weight.) The apparent mass of the AgI was then determined and converted to true mass using a $5.66 \text{ g} \cdot \text{cm}^{-3}$ for the density of ^{107}AgI and $5.71 \text{ g} \cdot \text{cm}^{-3}$ for the density of ^{109}AgI . These densities were calculated by assuming that they are proportional to the density of natural αAgI , $D^{30} = 5.68 \text{ g} \cdot \text{cm}^{-3}$, in the same ratio as their molecular weights. The vacuum weight of the silver iodide was converted to millimoles of silver using the calculated atomic weight for silver and 120.9045 for iodine. The formula weights used were 233.8909 for ^{107}AgI and 235.8087 for ^{109}AgI .

To determine the soluble and untransferred silver, the filtrate and washings, which had been reserved in the original beaker, were spiked with 1 to 2 μmol of either ^{107}Ag or ^{109}Ag . Five mL of ammonium hydroxide solution and 0.25 g of potassium cyanide (ACS Reagent Grade) were added to dissolve silver iodide and the solution was well mixed by stirring with a magnetic stirring bar for a few hours. Silver was then separated electrolytically by plating overnight with a potential of 2.6 V onto a platinum wire anode. Silver was then dissolved from the electrode with a few mL of (1 + 1) HNO_3 and the resulting solution was evaporated to dryness. The residue was taken up in (1 + 49) HNO_3 and the 107/109 ratio was determined by surface ionization mass spectrometry. The amount of silver as μmol of Ag was then calculated and added to the silver from the gravimetric determination to yield the total silver in the sample.

This method of assaying silver solutions was first tested on solutions containing known amounts of silver. The material was SRM 748 which is 99.999 + percent silver. The solutions were prepared in the approximate concentration range of 0.10 to 0.16 mmol AgI. Four portions containing from 0.9 to 1.1

mmol Ag were withdrawn from each solution and silver was determined as described above. Nine sets of four samples were analyzed in this manner.

Statistical analysis of the data from these nine sets showed that the standard error of the mean of four values was 5.2×10^{-6} mmol/g and that the coefficient of variation (standard error/mean) for a set of four was 0.003 percent. Comparison of calculated to measured concentrations showed a small positive bias of about 0.005 percent, but this would have a negligible effect on the ratio of two assays.

The results of the assay of the separated isotope solutions are shown in table 2. Pooling the results of the assay of the separated isotope solutions and the nine sets of natural solutions, yields a value of 0.0000009 mmol Ag/g for the standard error of the average concentration of each separated isotope solution. The uncertainty associated with this value at the 95 percent confidence level is 1.8×10^{-6} mmol Ag/g.

2.5 Isotopic Analyses of the Separated Isotope Solutions

Each of the separated isotope solutions was analyzed eight times on each of two mass spectrometers, MS #1 and MS #5, by Operators 1 and 2, respectively. The mass spectrom-

eter sources were cleaned between the analyses of the ^{107}Ag and ^{109}Ag 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 3.

The measured imprecision of the ratio measurements for each of the separated isotope solutions was less than 3 percent (2 standard deviations), however an uncertainty of 7 percent was placed on the ratios for the separated isotopes to cover possible measurement system nonlinearities and isobaric interferences. Several possible species have a potential for producing isobaric interferences in the silver mass region. These include CaPO_2^+ , SiPO_3^+ , and AsS^+ . Any interferences from CaPO_2^+ can be detected by monitoring mass 103 which results from the major isotope of calcium (^{40}Ca : 96.9 percent abundant). However, the major isotopes of silicon and sulfur would produce SiPO_3^+ and AsS^+ interferences at mass 107. Thus extremely small quantities of either of these species could not be detected by examining other masses in the silver spectral region. A SiPO_3^+ species has not been reported or observed in a thermal ionization-silica gel analysis but is included herein because of the nearly infinite supply of these elements on the filament, and the fact that an intense and

TABLE 2. Concentration of silver separated isotope solution

Solution	Sample No.	Weight Ag I (g)	Ag from Ag I (mmol)	Ag from Filtrate (mmol)	Total Ag (mmol)	Weight Sample (g)	Concentration (mmol Ag/g)
"Ag 107"	1	0.223445	0.955668	0.002583	0.958251	34.00905	0.0281760
	2	0.231677	0.990876	0.002358	0.993234	35.25092	0.0281761
	3	0.234055	1.001047	0.001176	1.002223	35.56893	0.0281769
	4	0.228265	0.976283	0.001211	0.977493	34.69020	0.0281778
Average							0.0281767
"Ag 109"	1	0.229478	0.973153	0.003956	0.977109	35.78498	0.0273050
	2	0.228795	0.970257	0.002316	0.972573	35.62279	0.0273020
	3	0.226974	0.962534	0.001029	0.963563	35.28974	0.0273044
	4	0.231376	0.981202	0.001614	0.982814	35.99738	0.0273024
Average							0.0273034

TABLE 3. Isotopic composition of the silver separated isotopes

Separated Isotope	Isotopic Composition (atom percent)
"Ag 107"	^{107}Ag 99.97136 \pm 0.00206*
	^{109}Ag 0.02863 \pm 0.00206
"Ag 109"	^{107}Ag 0.02865 \pm 0.00203*
	^{109}Ag 99.97135 \pm 0.00203

* The uncertainty of the ratio determination is taken to be 7 percent, which is much larger than the 95 percent confidence limit, to take into account possible biases and non-linear instrumental behavior for ratios as large as these.

sustained PO_3^- ion beam is observed in the negative ion spectra under the analytical conditions reported in this paper.

Kelly and Wasserburg [25] reported the existence of AsS^+ which, if present, would enhance the measured 107/109 ratio. The measurement of the ^{109}Ag separated isotope is particularly sensitive to this interference because AsS^+ would produce a 107/109 ratio of 22. Efforts to generate an AsS^+ ion beam by loading As_2S_3 and H_2SO_4 onto the filament using the procedure described in section 2 were unsuccessful. Since the silver was loaded in (1 + 9) HNO_3 , it is felt that the nitric acid allowed oxidation of the sulfur to sulfate, thus reducing any AsS^+ to an undetectable level.

Analysis under identical conditions of ^{109}Ag samples ranging in amount from 4 μg to 0.005 μg indicated a possible mass-107 isobaric interference at a level of $1 (\pm 1) \times 10^{-16}$ A. This level of interference is below the direct measurement detection limit of the instrument but can be inferred from the slight decrease in the observed 109/107 ratio with decreasing sample size. This suspected interference would produce a bias of approximately 2 percent to the observed ratios of the ^{109}Ag separated isotope and a bias of approximately 0.002 percent to the observed ratios of the reference sample and the calibration mixes.

2.6 Preparation of Calibration Samples

Eight calibration mixes were prepared by blending weighed portions of the "Ag-107" and the "Ag-109" solutions to pro-

duce 107/109 ratios ranging from 0.5 to 2.0. Six of the calibration mixes were within a few percent of the natural ratio 107/109 of 1.076.

The portions for mixing were withdrawn from the flasks and weighed in the manner previously described for the assay of each solution. Each portion weighed about 10 g and was weighed to ± 0.05 mg. It is therefore estimated that the weighing error for each mix should not exceed one part in 10^5 . To minimize any significant possibility of change in concentration of the isotope solutions with time, the portions for the calibration mixes were withdrawn from the flasks between the samples taken for assay, over a period of about 6 h.

Each calibration mix was thoroughly mixed, the sides of the beaker were washed with water, and the solution was evaporated to dryness. The residue was taken up with dilute (1 + 9) HNO_3 and the mixing, washing, and evaporation were repeated. The calibration mixes were then taken up in (1 + 9) HNO_3 to a concentration of 0.8 mg Ag/mL and transferred to small Teflon bottles. The isotopic compositions of the calibration mixes are given in table 4.

2.7 Isotopic Analyses of the Calibration Mixes and the Standard Sample

Two complete sets of analyses of the calibration mixes and reference sample were performed by Operator 1 on MS #1 and Operator 2 on MS #5. Operator 1 performed three anal-

TABLE 4. Isotopic composition of calibration mixes

Solution No.	Isotope Solution	Weight Solution (g)	Ag from Solution (mmol)	^{107}Ag from Solution (mmol)	^{109}Ag from Solution (mmol)	Total ^{107}Ag (mmol)	Total ^{109}Ag (mmol)	Ratio 107/109																																																																																														
1	"Ag 107"	10.02135	0.282369	0.282288	0.000081	0.282364	0.263439	0.07184																																																																																														
	"Ag 109"	9.64836	0.263433	0.000076	0.263358				2	"Ag 107"	8.95832	0.252416	0.252344	0.000072	0.252412	0.237226	1.06402	"Ag 109"	8.68835	0.237222	0.000068	0.237154	3	"Ag 107"	9.24458	0.260482	0.260407	0.000075	0.260477	0.243049	1.07171	"Ag 109"	8.90162	0.243044	0.000070	0.242974	4	"Ag 107"	9.75636	0.274902	0.274823	0.000079	0.274897	0.257233	0.06867	"Ag 109"	9.42110	0.257228	0.000074	0.257154	5	"Ag 107"	9.59357	0.270315	0.270237	0.000078	0.270309	0.248906	1.08599	"Ag 109"	9.11603	0.248899	0.000071	0.248828	6	"Ag 107"	10.11275	0.284944	0.284862	0.000082	0.284940	0.269592	1.05693	"Ag 109"	9.87378	0.269588	0.000078	0.269511	7	"Ag 107"	10.01824	0.282281	0.282200	0.000081	0.282348	0.517264	0.545849	"Ag 109"	18.94756	0.517333	0.000148	0.517185	8	"Ag 107"	18.47706	0.520623	0.520474	0.000149	0.520552	0.270624	1.92353	"Ag 109"
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yses of each calibration mix and 24 analyses of the reference sample. Operator 2 performed four analyses of each calibration mix and 32 analyses of the reference sample. The samples were run in a pattern alternating randomly selected mixes with the reference sample.

3. Results and Discussion

The results of the measurement of the eight calibration mixes are shown in table 5. The calibration factors for each analyst varied over a range of 0.011 percent for Operator 1 and 0.019 percent for Operator 2. In addition, the calibration factors for those mixes with a $107/109 = 2$ and $107/109 = 0.5$ were indistinguishable from those bracketing the reference sample, indicating an insignificant degree of nonlinearity over the measured range.

Table 6 summarizes the observed and corrected $^{107}\text{Ag}/^{109}\text{Ag}$ values for the SRM for Operators 1 and 2 as well as the absolute isotopic abundance ratio for silver and its uncertainty.

Table 7 gives 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 [17] and the corresponding atom fractions.

The atomic weight of silver, 107.868 ± 0.001 , as recommended by the IUPAC Commission on Atomic Weights, is based on the isotopic abundance measurements reported by Shields, Garner, and Dibeler [1] in 1962. This ratio is, in fact, the average of their isotopic abundance measurements published in 1960 [26] and the results of the mineral survey described in the 1962 publication.

A reanalysis of sample C-140, a nugget of native silver from Ontario, Canada, which had yielded anomalous data in the 1962 study [1], was undertaken. One section of this nugget, referred to as position 1, had yielded a ratio of $^{107}\text{Ag}/^{109}\text{Ag}$ which was 0.3 percent higher than three other sections, designated positions 2, 3, and 4; all of which mirrored the $^{107}\text{Ag}/^{109}\text{Ag}$ ratio of the natural silver reference sample (SRM 948). At the time, little or no chemistry was performed to purify the samples prior to analysis, and it was believed that the "anomaly" might be due to natural differences or chemical impurities. A reanalysis of the four sections of C-140, confirmed that position 1 yielded a $^{107}\text{Ag}/^{109}\text{Ag}$ ratio that was higher than the ratios for positions 2, 3, and 4, which again yielded ratios indistinguishable from the natural silver reference standard. Subsequent analyses indicated the major impurity at position 1 was mercury. Following purification by electrodeposition and ion exchange chromatography, the $^{107}\text{Ag}/^{109}\text{Ag}$ ratio for position 1 matched the ratios obtained for

TABLE 5. Determination of correction factors

Calibration Sample No.	Isotopic Ratio, $^{107}\text{Ag}/^{109}\text{Ag}$			Correction Factors	
	Calculated	Operator 1	Operator 2	Operator 1	Operator 2
1	1.071840	1.081566	1.081420	0.99100367	0.99114511
2	1.064016	1.073622	1.073579	0.99104924	0.99109658
3	1.071705	1.081345	1.081214	0.99108175	0.99120936
4	1.068671	1.078304	1.078236	0.99106309	0.99113312
5	1.085996	1.095850	1.095681	0.99100465	0.99116505
6	1.056931	1.066516	1.066407	0.99100878	0.99111770
7	0.5458493	0.5507895	0.5506505	0.99102567	0.99128580
8	1.923532	1.941050	1.940748	0.99097136	0.99113254
Mean Values of Calibration Factors				0.9910261	0.9911607

TABLE 6. Determination of corrected isotopic ratios

	Observed $^{107}\text{Ag}/^{109}\text{Ag}$	Correction Factor	Corrected $^{107}\text{Ag}/^{109}\text{Ag}$
Operator 1	1.0861089	0.9910261	1.076362
Operator 2	1.0859898	0.9911607	1.076390
		MEAN	1.07638
		\pm	0.00022

Uncertainty components:

95 percent confidence limits in ratio determination	± 0.00003
Bounds due to possible systematic error in composition of separated isotopes	± 0.00009
Bounds due to possible systematic error in chemical analysis	± 0.00010

TABLE 7. Summary calculations of the atomic weight of silver

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 = 107.86815	± 0.00011 ^b	± 0.0000137	± 0.0000408	± 0.0000466
Nuclidic Masses (¹² C = 12)				
¹⁰⁷ Ag = 106.905095	± 0.000012			
¹⁰⁹ Ag = 108.904754	± 0.000010			
Atom Percent				
¹⁰⁷ Ag = 51.839170	± 0.005057	± 0.000687	± 0.00204	± 0.00233
¹⁰⁹ Ag = 48.160830	± 0.005057	± 0.000687	± 0.00204	± 0.00233
Isotopic Ratio				
¹⁰⁷ Ag/ ¹⁰⁹ Ag = 1.07638	± 0.00022	± 0.0000296	± 0.0000880	± 0.0001006

^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.

^b Includes a component for uncertainty in nuclidic masses.

positions 2, 3, and 4, and thus, the reference standard. This experiment clearly documents the critical importance of chemical purification in the determination of accurate isotopic ratios and in establishing the limits for natural isotopic variations. The data reflecting the effects of purification on sample C-140 are shown in table 8.

TABLE 8. Effect of Purification on C-140

Chemical Procedure	Corrected ^a ¹⁰⁷ Ag/ ¹⁰⁹ Ag
Initial Electrodeposition	1.07686
Additional Electrodeposition	1.07676
Anion Exchange, Precipitation and Electrodeposition	1.07634

^a All ratios have been placed on an absolute basis using the absolute isotopic abundance ratio for silver from Table 7 (¹⁰⁷Ag/¹⁰⁹Ag = 1.07638).

In an attempt to establish the limits of isotopic variability among commercially available silver, a series of analyses were performed on silver metal samples of varying purity, which had been obtained from refineries throughout the world. The results are shown in table 9. With the exception of the marz grade silver from Materials Research Corporation, all samples yielded isotopic ratios which were in excellent agreement with the natural reference standard. Although a deviation of 7.6 parts in 10⁴ is small, it is not known whether the difference is real or an artifact due to a chemical impurity. Additional testing of this material will be done in conjunction with a more thorough mineral survey in the future.

The effect of this isotopic survey of commercial silver on the atomic weight is small. A recalculation of the atomic weight of silver based on the isotope ratios of these materials yields a value of 107.86816 ± 0.00032 at the 95 percent confidence level, which is nearly identical to the atomic weight

of the reference sample (107.86815) as given in table 7, the major difference existing in the uncertainty.

The reference sample used in this atomic weight determination will be issued as both an isotopic and assay Standard Reference Material (SRM) and will be designated as SRM 978a. Its isotopic analysis was found to be experimentally

TABLE 9. Isotope Ratios of Commercial Silver

Description ^a	Corrected ^b ¹⁰⁷ Ag/ ¹⁰⁹ Ag
Needle Ag, 99.995%, Engelhard, Indiana, USA	1.07650
AgNO ₃ , 99.999%, Engelhard, Indiana, USA	1.07633
Ag, Marz Grade, Materials Research Corp., USA	1.07557
Ag, Single Crystal, Marz Grade, USA	1.07622
Refined Ag, Port Pirie, Australia	1.07634
Ag, Normal Purity, Johnson Mathey, Canada	1.07640
Ag, High Purity, Cominco, TADANAC, Canada	1.07648
Refined Ag, Mixture of Swedish Ores	1.07646
Electrolytic Ag, Boliden Mine, Sweden	1.07670
Ag, Crystalline, Mexico	1.07638
Ag, 99.99 + %, Lima, Peru	1.07653
Ag, Plata Fina, Granalla, Mexico	1.07656
	Average 1.07637
	Standard Deviation 0.000282

^a All descriptions are as stated by the producer. No further purity verification was made.

^b All ratios have been placed on an absolute basis using the absolute isotopic abundance ratio for silver from table 7 (¹⁰⁷Ag/¹⁰⁹Ag = 1.07638).

identical to SRM 978, the major difference existing in the uncertainty placed on the measurement.

The redetermination of the atomic weight of silver has allowed the recalculation of the Faraday from the electrochemical equivalent of silver as determined by Bower and Davis [5], yielding a value of $96486.18 \pm 0.13 A_{\text{NBS}} \cdot \text{s} \cdot \text{mol}^{-1}$ (one standard deviation). Further details of the calculation of this constant are given elsewhere in this issue of the *Journal of Research* [27].

The reduction of the overall uncertainty in the Faraday constant has allowed discernment of the discrepancies which existed between the Faraday determined from electrochemical experiments, and the Faraday calculated from other fundamental constants. It is expected that the new NBS value of the Faraday will be included in the 1981 CODATA least squares adjustment of the fundamental constants.

We are indebted to: Keith R. Eberhardt for statistical analysis; Paul J. Paulsen for analysis of the separated isotopes; Karen A. Brletic for isotope dilution analysis of many of the assay samples; William A. Bowman III for instrumental maintenance support; Joy J. Shoemaker and Theresa Sperow for skillful manuscript preparation; and our colleagues in the mass spectrometry group of the Inorganic Analytical Research Division for their helpful discussions.

We also wish to express our gratitude to Richard Davies, Executive Director of the Silver Institute for his assistance in gathering the high purity silver metal samples and to the following companies for their contributions: Boliden Metall AB, Sweden; The Broken Hill Associated Smelters Proprietary Limited, Australia; Met-Mex Peñales, S. A. de C. V., Mexico; Empresa Minera Del Centra Del Peru; Johnson-Matthey, Ltd., Canada.

We also wish to thank Oak Ridge National Laboratory for their special efforts to produce the high purity ^{107}Ag and ^{109}Ag isotopes which were so necessary for this work.

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