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Absolute Isotopic Abundance Ratio And Atomic Weight Of a Reference Sample of Gallium

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An absolute value has been obtained for the isotopic abundance ratio of a reference sample of gallium (Standard Reference Material 994), using thermal ionization mass spectrometry. Samples of known isotopic composition, prepared from nearly isotopically pure separated gallium isotopes, were used to calibrate the mass spectrometers. The resulting absolute ^{69}Ga/^{71}Ga ratio is 1.50676±0.00039, which yields atom percents of ^{69}Ga=60.1079±0.0062 and ^{71}Ga=39.8921±0.0062. The atomic weight calculated from this isotopic composition is 69.72307±0.00013. The indicated uncertainties are overall limits of error based on two standard deviations of the mean and allowances for the effects of known sources of possible systematic error.

Key words: absolute ratio; assay; atomic weight; gallium; isotopic abundance; mass spectrometry; tetraphenylarsonium chloride.

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1. Introduction

The Inorganic Analytical Research Division 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 [1,2][1], chlorine [3], copper [4], bromine [5], chromium [6], magnesium [7], lead [8], boron [9], rubidium [10], rhenium [11], silicon [12], potassium [13], thallium [14], and strontium [15]. The present work extends the study to gallium.

To obtain absolute isotopic ratios from the observed or relative measurements made on a mass spectrometer, it is necessary to calibrate the instrument using samples of accurately known isotopic ratios of the element under study. These synthetic isotopic standards, assayed and gravimetrically prepared from chemically pure and nearly isotopically pure isotopes, provide a bias correction (calculated isotopic ratio/observed isotopic ratio) which, when applied to the observed isotopic ratio of the reference sample being calibrated, allows an absolute ratio to be calculated for the sample. The atomic weight is then obtained by multiplying the fractional abundance of each isotope by its nuclidic mass [16] and summing the resultant products. A more detailed description of the method used for the determination of isotopic abundance ratios and atomic weights at NBS is given elsewhere [2].

In 1961, the IUPAC Commission on Atomic Weights recommended a value of 69.72 for the atomic weight of gallium, based on chemical determinations by Richards and Craig [17] and Lundell and Hoffman [18], as well as isotopic measurements by Inghram et al. [19]. Two more recent determi-

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[1] Figures in brackets indicate literature references.

nations, by coulometric assay of gallium and arsenic [20] and by calibrated isotope ratio mass spectrometry [21], have yielded values of 69.737 and 69.724, respectively. The currently recommended value [22] for the atomic weight of gallium is 69.723±0.004 based on the more recent mass spectrometric measurement [21].

Isotopic fractionation of gallium by more than 10 percent has been reported when a continuous electrical current is passed through a capillary column of liquid gallium [23,24]. Recent work in this laboratory has demonstrated that gallium isotopic fractionation approaching 1 percent is possible with ion exchange chromatography [25]. A survey of commercial high-purity gallium shows a range of approximately 0.25 percent in the ^{69}Ga/^{71}Ga ratio for the samples investigated [26]. The origin of these variations in commercial high-purity gallium is likely the result of isotopic fractionation during the multiple recrystallization steps used for purification. Little information is available in the literature regarding isotopic variations of gallium in nature. Values reported during the past 35 years for the isotopic composition of gallium range over 3 percent; however this spread is probably due to measurement imprecision. DeLaeter [27] reports a maximum deviation of 0.11 percent in six meteorites relative to the isotopic composition of his terrestrial standard.

A relatively large discrepancy between the two recently published values for the atomic weight of gallium, combined with evidence for isotopic variations among commercial materials, provided impetus for the certification of a Standard Reference Material (SRM 994) of known isotopic composition and atomic weight.

2. Experimental Procedure[2]

2.1 Mass Spectrometry

Isotope ratio measurements were made on two NBS designed thermal ionization mass spectrometers equipped with 30 cm radius of curvature, 90° magnetic sectors. Each instrument contained a thin lens "Z" focussing ion source and a deep bucket Faraday cage collector [28,29]. One collector (Inst. #5) was equipped with a 50 percent transmission grid shadowing a series of suppression grids, while the other collector (Inst. #1) was of a new design, eliminating the pre-slit transmission and suppression grids but containing a double slit collimator before the Faraday cage. The remainder of the measurement circuitry consisted of a vibrating reed electrometer, precision voltmeter, and computer. Timing, magnetic field switching, and data acquisition were controlled by computer.

Gallium was thermally ionized from a tungsten filament fabricated from 0.001 in × 0.030 in (0.0025 cm×0.076 cm) high purity tungsten ribbon. After fabrication, the filaments were degassed for 45 min by passing a current of 4.5 A through them in a vacuum. Filaments cleaned in this manner generally exhibited no detectable gallium signal or isobaric interferences in the gallium spectral region. Occasionally, analyses have shown small interfering peaks (presumably hydrocarbons) which can be resolved from the ^{69}Ga and ^{71}Ga mass positions. Even if not resolved, their contribution to an error in the ratio measurement of natural gallium would be less than 1 part in 10^5. Possible isobaric interferences could produce a significant systematic bias in the measurement of the isotopic composition of the separated isotopes. This possible systematic error has been incorporated into the statistical evaluation of the experimental data and will be discussed in more detail in section 2.5 of this paper.

All sample loading was conducted in a Class 100 clean air hood. Pipets made from fused silica tubing were used to transfer the samples from their containers to the filaments. The tubing was cleaned by heating in 8M HNO_3 for 48 hours, followed by several rinsings with ultra-high purity water. Approximately 5 μL of the sample solution (500 ng Ga) was placed on the tungsten filament and dried by passing a current of 1 A through the filament for 10 min followed by a current of 3 A for 5 min. Drying was aided by a heat lamp placed 20 cm above the filament. Because the rate and degree of isotopic fractionation during the mass spectrometric analysis may be affected by variations in the sample loading procedure, all samples were loaded on a programmable sample dryer [30] which automatically and reproducibly controls the timing and currents to the filament during the sample drying procedure. After the initial drying, the filaments were transferred to a separate Class 100 clean air hood and heated for 15 s at 900 °C, using an optical pyrometer for temperature adjustment (temperature not corrected for emissivity). This final step was to ensure conversion of the sample to the most stable cyrstalline form of gallium oxide, β-Ga_2O_3 [31]. During this high temperature drying step, the air flow through the hood was turned off so that reproducible temperature settings could be obtained.

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[2] Certain commerical equipment, instruments, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Gallium ion currents were measured with a constant accelerating potential of 9.8 kV. The ions of each isotope were brought into alignment with the collector slit by computer controlled stepping of the magnetic field. The filament current was initially set at 2.15 A, corresponding to an optical pyrometer temperature reading of approximately 700 °C. Initially no gallium signal was observed; however, after 2–3 min, the Ga^+ would rapidly increase, reaching a total Ga^+ ion current at the collector of approximately 2×10^{-11} A at 5 min into the analysis. The filament current was adjusted at 5, 10, and 15 min into the analysis to produce gallium ion currents of 2×10^{-11} A, 4×10^{-11} A, and 6×10^{-11} A,[3] and baseline measurements were taken on each side of both isotopes. Data were collected between 20 and 50 min into the analysis. Ten 1-second integrations of the ion current were made for each isotope before magnetic field switching, with an 8 s time delay between isotopes to allow for magnetic field stabilization and settling of RC time constants in the measurement circuitry.

2.2 Purification of Separated Gallium Isotopes

Electromagnetically separated ^{69}Ga and ^{71}Ga isotopes in the form of gallium oxide were obtained from the Nuclear Division, Oak Ridge National Laboratory. The ^{69}Ga was designated sample 121201 and the ^{71}Ga was designated sample 121301. The certificate which accompanied each sample showed enrichment to approximately 99.8 percent for the major isotope. The certificates included a semi-quantitative spectrographic analysis which showed that the principal impurities were sodium, magnesium, and zirconium at the 0.1 percent level or higher; and calcium, iron, potassium, lithium, rubidium, and silicon at the 0.01 to 0.05 percent level. While only the element iron was at a level where it would interfere with the assay method for gallium, several other elements, which were reported as less than 0.05 percent, could interfere if they were, in fact, near that level. Among these elements were chromium, copper, molybdenum, lead, tin, cadmium, and platinum, which could interfere with the gallium assay procedure by forming insoluble compounds with tetraphenylarsonium chloride [32].

To reduce these impurities to a level low enough so that they would not cause a significant error in the assay procedure, the separated isotopes were purified by a combination of chloride precipitation to remove insoluble chlorides, anion exchange chromatography in the thiosulfate form to reduce the iron concentration, and then, sequentially, cation exchange and anion exchange chromatography to remove other potentially interfering impurities.

Each separated isotope was treated as follows: The gallium oxide (about 1.2 g of $^{69}Ga_2O_3$ and 0.9 g of $^{71}Ga_2O_3$) was dissolved in 100 mL of HCl (1+3).[4] The resulting solution was evaporated to constant volume at about 50 °C. The residue was dissolved in 20 g of H_2O and filtered through fine textured filter paper. The filtrate was evaporated to 50 g and then 10 g of 0.5M HCl and 4.5 g of 0.2M KSCN were added. This solution was passed through an anion exchange column (6.4×0.8 cm filled with 2 mL of AG1×8, 100–200 mesh anion exchange resin and then cleaned and prepared with 20 g of 5M HCl, 30 g of H_2O and 20 g of a solution of 0.1M in KSCN and 0.05M in HCl) and eluted with 120 g of the solution 0.1M in KSCN and 0.05M in HCl.

The gallium solution was passed through a cation exchange column (20.5×1.6 cm filled to 15.0 cm with AG50×8, 100–200 mesh cation exchange resin cleaned and prepared with 190 g of 4M HCl and 50 g H_2O), washed with 20 g H_2O, and impurities eluted with 300 g of 0.4M HCl. The gallium was then eluted with 100 g of 4M HCl. This solution was evaporated to about 10 mL and, after cooling and the addition of 30 g of 5M HCl, it was passed through an anion exchange column (20.5×1.6 cm filled to 16 cm with AG1×8, 100–200 mesh anion exchange resin and cleaned with 40 g of 5M HCl, 190 g of 0.5M HCl, 40 g of H_2O, and 20 g of 5M HCl). Impurities were eluted with 150 g of 5M HCl and 50 g of 4M HCl. The gallium was eluted with 165 g of 0.5M HCl.

2.3 Preparation and Analysis of Separated Isotope Solutions

The purified ^{69}Ga and ^{71}Ga were transferred to 500 mL fused silica flasks and diluted to about 450 g with 0.5M HCl. The neck of each flask had been tooled to fit a No. 0 polyethylene stopper.

A preliminary assay of the gallium concentration of each separated isotope solution was accomplished by isotope dilution mass spectrometry. Two weighed portions (1.5–2 g) of each separated isotope solution were spiked with known amounts of natural gallium. After mixing, evaporation, con-

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[3] Ion currents are reported for Instrument #1.

[4] A reagent dilution of (1+3) indicates 1 volume of concentrated reagent diluted with 3 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 [33].

version to the nitrate form, and dilution to 100 μg Ga/g solution with HNO_3 (1+9); the ^{69}Ga/^{71}Ga ratio was determined by thermal ionization mass spectrometry. The concentration of gallium was then calculated for each solution and used to determine the amount of each separated isotope solution required for the calibration mixes.

The solution of ^{69}Ga was designated "Ga-69" and the solution of ^{71}Ga was designated "Ga-71." Samples of the two solutions were analyzed for impurity elements by isotope dilution spark source mass spectrometry (IDSSMS) [33]. Samples equivalent to about 22 mg of Ga were spiked with 1.6×10^{-6} g of ^{109}Ag, ^{137}Ba, ^{111}Cd, ^{53}Cr, ^{65}Cu, ^{54}Fe, ^{41}K, ^{26}Mg, ^{97}Mo, ^{145}Nd, ^{206}Pb, ^{110}Pd, ^{195}Pt, ^{185}Re, ^{82}Se, ^{117}Sn, ^{86}Sr, ^{125}Te, ^{203}Tl, ^{91}Zr. The solutions were evaporated to dryness, a few drops of HNO_3 were added, and the solutions were again evaporated to dryness. The HNO_3 addition and the evaporations were repeated two more times. Table 1 shows the results of these analyses as well as the results of the analysis of a doped natural gallium sample which was purified in the same manner as the separated isotopes. This sample had been doped with 0.1 percent of Ba, Cd, Cr, Cu, Fe, K, Mo, Pb, Pt, Re, Se, Sn, Sr, Te, and Tl to determine the efficiency of the purification procedure.

The only element that was detected at a concentration level high enough to interfere with the assay of gallium was iron in both separated isotopes. This apparently came from inefficiency in the purification of the separated isotopes during the separation of gallium from iron on the ion exchange column using thiocyanate, or from a higher level of iron in the two separated isotopes than reported in the spectrographic analysis that accompanied them, since the iron in the doped gallium sample was reduced by more than an order of magnitude in the purification procedure. Iron does interfere in the assay procedure but did not affect the mass spectrometric ratio measurement on test samples. Therefore it was decided to correct for iron in the assay rather than try further purification. To determine how much iron precipitated with the gallium in the tetraphenylarsonium precipitation, the material was analyzed for iron by IDSSMS. After the assay an amount equal to about 5 mg of gallium was taken from each of the precipitates and spiked with ^{57}Fe. The spiked samples were dissolved in H_2O and a few drops of HCl, and evaporated to dryness. The residue was dissolved in 5 g of H_2O and passed through a cation exchange column (6.3×0.9 cm filled to 3 cm with AG 50×8, 100–200 mesh cation exchange resin and pre-cleaned with 45 g of 3M HCl and 25 g H_2O). After elution with 30 g of 0.75M HCl, the gallium and iron were removed with 10 g of 3M HCl. This solution was evaporated to dryness, a few drops of HNO_3 were added, and the solution was again evaporated to dryness. The HNO_3 addition and the evaporation were repeated and the sample was analyzed by spark source mass spectrometry. The correction for the iron was found to be 0.176 μg of $(C_6H_5)_4AsFeCl_4$ per mg of $(C_6H_5)_4As^{69}GaCl_4$ and 0.658 μg of $(C_6H_5)_4AsFeCl_4$ per mg of $(C_6H_5)_4As^{71}GaCl_4$. This correction was applied to the weights of the precipitates in the assay of "Ga-69" and "Ga-71."

Table 1. Analysis of impurities in gallium separated isotopes.

Element	*Spike* Isotope	Ga Doped and Purified	^{69}Ga (μg/g)	^{71}Ga (μg/g)
Ag	^{109}Ag	10	6	14
Ba	^{137}Ba	10	--[a]	7
Cd	^{111}Cd	1	nd[b]	nd
Cr	^{53}Cr	4	1.7	1.2
Cu	^{65}Cu	9	8	7
Fe	^{54}Fe	94	83	434
K	^{41}K	10	9	5
Mg	^{26}Mg	2	36	5
Mo	^{97}Mo	<1	nd	<1
Nd	^{145}Nd	3	<1	<1
Pb	^{206}Pb	2	5	4
Pd	^{110}Pd	14	<2	11
Pt	^{195}Pt	<1	nd	nd
Re	^{185}Re	—	1	nd
Se	^{82}Se	<1	nd	<1
Sn	^{117}Sn	<1	6	6
Sr	^{86}Sr	1	2	18
Te	^{125}Te	<1	<1	<1
Tl	^{203}Tl	1	1	1
Zr	^{91}Zr	<1	<1	1

[a] Interference
[b] Not detected

2.4 Assay of Separated Isotope Solutions

Four weighed portions containing approximately 0.75 mmol of gallium were withdrawn from each separated isotope solution in the following manner. A No. 0 polyethylene stopper with a 20 cm Teflon needle inserted through it was used to replace the stopper in the flask. A 20 mL all-polypropylene/polyethylene syringe was attached to the 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 plastic cap. Any static charge that might be present on the plastic syringe was dissipated by wiping it with a damp lintless towel and placing it on the balance pan which was surrounded by several polonium anti-static sources. The syringe and contents were weighed on a semimicro balance to ±0.02 mg. The solution was then delivered from the syringe into a 100 mL Teflon-FEP 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 the delivery of the sample. Two assay samples were withdrawn from each solution before the calibration samples were withdrawn, and two assay samples were withdrawn after the calibration samples to ensure that no change in concentration occurred during the time interval (about 4 hours) required for the aliquoting.

Each weighed sample was assayed as follows: The sample was evaporated to constant volume at low heat (~50 °C) and after cooling to room temperature, 20 g of 6M HCl and 10 g of sub-boiling distilled acetone were added. A weighed portion of tetraphenylarsonium chloride [$(C_6H_5)_4AsCl{\cdot}2H_2O$] reagent solution (prepared by dissolving tetraphenylarsonium chloride hydrochloride in water, filtering, and diluting with water to 50 mg tetraphenylarsonium chloride hydrochloride per gram of solution) equal to 105 percent of the amount required to form $(C_6H_5)_4AsGaCl_4$ was combined with 20 g of sub-boiling distilled acetone and added to each assay sample. The solution was mixed using a Teflon rod and covered for 2 hours to allow bubbles to form and break. The cover was rinsed with water and the acetone and some water were allowed to evaporate from the uncovered beaker in a Class-100 clean air hood until approximately 23 g of solution remained in the beaker (about 48 hours). (The $(C_6H_5)_4AsGaCl_4$ that is formed is soluble in the initial acetone-water-hydrochloric acid mixture and slowly crystallizes from the solution as the acetone evaporates, producing relatively large crystals when compared to the usual method of precipitation.)

The crystallized $(C_6H_5)_4AsGaCl_4$ was transferred with 5M HCl to a tared 15 mL Munroe crucible. Since it was not possible to transfer the salt completely, the material remaining in the beaker was dissolved with acetone and 5M HCl, and the acetone evaporated at 50 °C. As much of the salt as possible was washed into the filtering crucible using 5M HCl. The dissolution, evaporation, and transfer procedure was repeated to minimize the amount of material remaining in the beaker. The material in the crucible was washed three times with 5M HCl (a total of 30–35 g of 5M HCl was used for transfer and washing). The crucible and contents were dried at 10 °C for 16 hours. (The filtrate was transferred back to the original beaker and reserved for the determination of dissolved and untransferred gallium.)

The filtering crucible and contents were cooled in a desiccator, transferred to the case of a microbalance, and allowed to stand for at least 3 hours. The crucible and contents were weighed to ±0.002 mg. A combination blank and buoyancy correction was made by averaging three crucibles that had been used to filter blank samples that had been carried through the procedure. The drying, cooling, and weighing were repeated until constant weight was reached. The air weight of the $(C_6H_5)_4AsGaCl_4$ was then determined and converted to vacuum weight using a measured value of 1.53 as the density of the salt. The micromols of gallium present in the salt were determined using a calculated atomic weight for gallium and 1983 IUPAC standard atomic weight values for the other elements. The formula weights used were 594.0886 for $(C_6H_5)_4As^{69}GaCl_4$ and 596.0770 for $(C_6H_5)_4As^{71}GaCl_4$.

The filtrate from the precipitation of the $(C_6H_5)_4AsGaCl_4$ was diluted to approximately 120 g with H_2O and warmed to approximately 40 °C to ensure that any untransferred salt was dissolved. After stirring, cooling and thorough mixing, a weighed portion (approximately 15 g) of the filtrate solution was transferred to a 50 mL Teflon-FEP beaker. The "Ga-69" solutions were spiked with about 0.2 μmol of ^{71}Ga and the "Ga-71" solutions were spiked with about 0.2 μmol of ^{69}Ga for determining soluble and untransferred gallium by isotope dilution mass spectrometry.

The spiked solution was mixed, evaporated to dryness, and dissolved in 5 g of H_2O. This solution was passed through a cation exchange column (6.3×0.9 cm filled to 3 cm with AG 50×8, 100–200 mesh cation exchange resin and cleaned with 45 g of 3M HCl and 20 g H_2O), washed with a few mL of H_2O and then 25 g of 0.75M HCl. The gallium was eluted with 10 g of 3M HCl and the eluate was evaporated to dryness on a hot plate at low heat. The residue was dissolved in a few drops of HNO_3 and the $^{69}Ga/^{71}Ga$ ratio was determined by thermal ionization mass spectrometry. The gallium found as soluble Ga was added to the amount of gallium determined by gravimetry to yield the total gallium in the sample. Table 2 shows the results of these analyses.

This method of determining the concentration of gallium solutions was previously tested on solutions containing known amounts of gallium. Solutions were prepared from high purity gallium, SRM 994. The gallium concentration in eight sets of four samples, each containing 690 to 835 μmol

Table 2. Concentration of gallium separated isotope solutions.

Solution	Sample No.	Weight GaTPA (g)	Ga From GaTPA (mmol)	Ga From Filtrate (mmol)	Total Ga (mmol)	Weight Sample (g)	Concentration (mmol Ga/g)
"Ga 69"	1	0.439984	0.740607	0.001491	0.742098	28.97604	0.0256107
	2	0.439859	0.740397	0.001350	0.741747	28.96352	0.0256097
	3	0.440873	0.742104	0.001549	0.743653	29.02848	0.0256180
	4	0.435266	0.732666	0.001275	0.733941	28.65412	0.0256138
						Average	0.0256131
"Ga 71"	1	0.488208	0.751930	0.001206	0.753136	37.17272	0.0202604
	2	0.456157	0.765265	0.001233	0.766498	37.83944	0.0202566
	3	0.465770	0.781392	0.001009	0.782401	38.61812	0.0202599
	4	0.462792	0.776396	0.001576	0.777972	38.40359	0.0202578
						Average	0.0202587

of gallium were determined as described above. Comparison of the calculated and measured concentrations detected a positive bias of about 0.06 percent, but this would have a negligible effect on the ratio of the two assays since the assay for the separated isotopes would be biased by the same 0.06 percent.

2.5 Isotopic Analysis of the Separated Isotope Solutions

Each of the separated isotope solutions were analyzed eight times on each of the instruments. The ion sources were cleaned between the analyses of the two solutions as a precaution against the possibility of cross-contamination from the source parts, however, preliminary measurements showed that the two separated isotopes could be analyzed back-to-back on the same source with no detectable cross-contamination. The precision of the $^{69}Ga/^{71}Ga$ isotopic measurements on the separated isotopes is approximately 0.25 percent, however an uncertainty of 2 percent has been assigned to the measurements to cover possible sources of systematic error [34].

As the gallium mass spectrometric procedure was being developed, small mass peaks on the high mass sides of masses 69 and 71 were occasionally observed. These small isobaric interferences are attributed to organic species and could be resolved from the ^{69}Ga and ^{71}Ga masses by careful focussing of the ion source. The maximum intensity of these interfering isobars was approximately 1×10^{-15}A. Even if not resolved from the gallium masses, the contribution to systematic errors in the measurement of the natural $^{69}Ga/^{71}Ga$ ratio would be less than 1 part in 10^5. However, in the case of the separated isotopes, these interferences, if undetected, could produce a systematic error in the measurement of the $^{69}Ga/^{71}Ga$ ratio of the separated isotopes of up to one percent. Thus the 2 percent uncertainty assigned to the separated isotope ratio measurements reflects random errors and the maximum (worst-case) systematic errors expected from possible isobaric interferences and the measurement system non-linearities associated with large isotopic ratios. The corrected isotopic compositions of the separated isotopes are given in table 3.

Table 3. Isotopic composition of the gallium separated isotopes.

Separated Isotopes		Isotopic Composition (atom percent) Operator 1	Operator 2	Mean
"Ga 69"	^{69}Ga	99.82120	99.82094	$99.8211+0.0036$
	^{71}Ga	0.17880	0.17906	$0.1789+0.0036$
"Ga 71"	^{69}Ga	0.20449	0.20417	$0.2043+0.0041$
	^{71}Ga	99.79551	99.79583	$99.7957+0.0041$

[a] The uncertainty of the ratio determination is taken to be 2 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.

2.6 Preparation of Calibration Samples

Seven calibration samples were prepared by mixing weighed portions of the "Ga-69" and "Ga-71" solutions to produce $^{69}Ga/^{71}Ga$ ratios ranging from 0.3 to 7.5. Five of the calibration mixes were within 2 percent of the natural ratio of 1.507. The portions were withdrawn from the flasks and weighed in the manner previously described for the assay of the solutions. The portions weighed from 3.2 to 24.0 g and each was weighed to ±0.05 mg. It is therefore estimated that the weighing error for each mix should not exceed two parts 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 4 hours.

Each calibration mix was thoroughly mixed, the sides of the beaker were washed with H_2O and 0.2M HCl, and evaporated to dryness at low heat (~50 °C) on a hot plate. The residue was dissolved in 2 mL of 8M HNO_3 and the mix was evaporated to dryness. The addition of 8M HNO_3 and evaporation to dryness was repeated two additional times. The residue was then dissolved and diluted with HNO_3 (1+9) to 1 mg Ga per gram of solution. After thorough mixing, a portion of this solution was diluted with HNO_3 (1+9) to 100 μg Ga per g of solution and transferred to small polyethylene bottles. The isotopic compositions of the calibration mixes are given in table 4.

2.7 Isotopic Analyses of the Calibration Mixes and the Reference 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. Each operator performed four analyses of each calibration mix and 28 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 seven calibration mixes are shown in table 5. The correction factors for each analyst varied over a range of 0.030 percent for Operator 1 and 0.017 percent for Operator 2. The major spread in the calibration mixes results from the non-point calibration mixes 1 and 7. The deviation from the five point calibration mixes is especially evident for Operator 1. Two hypotheses have been proposed to explain these results. First, if there is an error in the measured isotopic composition of the ^{69}Ga separated isotope (still within the stated uncertainty), this could bring mixes 1 and 7 into agreement with mixes 2 through 6 and would also result in improving the agreement between Operator 1 and Operator 2 on the corrected ^{69}Ga/^{71}Ga ratio of the reference sample. The second hypothesis involves the voltage coefficient of the 10^{11} ohm input resistor of the electrometers used in this experiment. In order to maintain a constant fractionation correction for the reference sample and the point calibration mixes, it is necessary to maintain a constant total signal intensity. Any non-linearities in the input resistor would be corrected by comparing the reference sample and the point calibration mixes since the signal intensity would be the same for both isotopes for each of these solutions. This systematic bias would thus be constant and self-correcting for the reference sample and the point calibration mixes, being included as part of the correction factor. For mixes 1 and 7,

Table 4. Isotopic composition of calibration mixes.

Solution No.	Isotope Solution	Weight Solution (g)	^{69}Ga[a] From Solution (mmol)	^{71}Ga[a] From Solution (mmol)	Total 69Ga (mmol)	Total 71Ga (mmol)	Ratio 69/71
1	"Ga 69"	24.02523	0.614260	0.001101	0.614426	0.082318	7.46403
	"Ga 71"	4.01722	0.000166	0.081217			
2	"Ga 69"	7.49458	0.191616	0.000343	0.191881	0.129783	1.47848
	"Ga 71"	6.40240	0.000265	0.129439			
3	"Ga 69"	7.65190	0.195638	0.000351	0.195905	0.130609	1.49994
	"Ga 71"	6.44291	0.000267	0.130258			
4	"Ga 69"	7.67884	0.196327	0.000352	0.196597	0.132142	1.48777
	"Ga 71"	6.51866	0.000270	0.131790			
5	"Ga 69"	7.98143	0.204064	0.000366	0.204337	0.133765	1.52758
	"Ga 71"	6.59828	0.000273	0.133399			
6	"Ga 69"	7.94366	0.203098	0.000364	0.203368	0.132582	1.53391
	"Ga 71"	6.53982	0.000271	0.132218			
7	"Ga 69"	3.24697	0.083016	0.000149	0.083590	0.280551	0.297950
	"Ga 71"	13.86943	0.000574	.280403			

[a] Calculated using mean value from table 3.

Table 5. Determination of correction factors.

Calibration Sample No.	Isotopic Ratio, $^{69}Ga/^{71}Ga$ Calculated	Operator 1	Operator 2	Correction Factors Operator 1	Operator 2
1	7.46403	7.568871	7.572529	0.986148	0.985672
2	1.47848	1.499598	1.499846	0.985917	0.985754
3	1.49994	1.521338	1.521528	0.985932	0.985809
4	1.48777	1.509024	1.509266	0.985917	0.985759
5	1.52758	1.549398	1.549678	0.985916	0.985738
6	1.53391	1.555855	1.555955	0.985897	0.985834
7	0.297950	0.3022232	0.3022426	0.985860	0.985796
	Mean Values of Calibration Factors			0.985941	0.985766

it was necessary to increase the signal intensity of the major isotope relative to the minor isotope thus introducing possible systematic bias due to non-linear response of the input resistor. An error for instrument #1 of approximately 70 parts per million per volt would correct the discrepancy between mixes 1 and 7 and the point calibrations. Preliminary measurements in this laboratory on resistors of the type used in the electrometers, indicate that non-linearities of this magnitude are not unreasonable. This effect would produce a systematic error in the measurement of the separated isotopes of approximately 0.03 percent, well within the conservative uncertainty of 2 percent placed on the measurement of the isotopes.

Table 6 summarizes the observed and corrected $^{69}Ga/^{71}Ga$ values for the reference sample for Operators 1 and 2, respectively, as well as the absolute isotopic abundance ratio for gallium and its uncertainty.

Table 6. Determination of corrected isotopic ratios of the reference material.

	Observed $^{69}Ga/^{71}Ga$	Correction Factor	Corrected $^{69}Ga/^{71}Ga$
Operator 1	1.528283	0.985941	1.506797
Operator 2	1.528488	0.985766	1.506732
		Mean	1.50676
		±	0.00039

Table 7 gives summary calculations for the reference sample. The atomic weight is calculated from the absolute isotopic abundance by summing the product of the nuclidic masses [16] and the corresponding atom fractions.

The reference sample is issued by the NBS Office of Standard Reference Materials as SRM 994, Gallium Metal Isotopic Standard, and is certified for isotopic composition.

Table 7. Summary calculations of the atomic weight of gallium.

		Uncertainty Components		
(1) Values	(2) Overall Limit of Error[a]	(3) Mass Spectrometric Analytical Error (2SD of the Mean)	(4) Limits to Error in Chemical Analysis (2SD of the Mean)	(5) Error in Composition of Separated Isotopes
Atomic Weight = 69.72307	±0.000127[b]	±0.000023	±0.000065	±0.000055
Nuclidic Masses ($^{12}C=12$)				
$^{69}Ga=68.9255809$	±0.0000033			
$^{71}Ga=70.9247005$	±0.0000025			
Atom Percent				
$^{69}Ga=60.1079$	±0.0062	±0.0011	±0.0032	±0.0028
$^{71}Ga=39.8921$	±0.0062	±0.0011	±0.0032	±0.0028
Isotopic Ratio				
$^{69}Ga/^{71}Ga=1.50676$	±0.00039	±0.000070	±0.000204	±0.000174

[a] The overall limit of error (2) is the sum of 2 standard deviation limits for random error plus the term covering possible systematic error in the separated isotopes. The error components are combined as follows:

$$(2)=[(3)^2+(4)^2]^{1/2}+(5)$$

Where the numbers in parentheses refer to numbers in column headers.

[b] Includes a contribution of 0.000003 for uncertainty in nuclidic masses.

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References

[1] Shields, W. R.; E. L. Garner and V. H. Dibeler, Absolute isotopic abundance of terrestrial silver. J. Res. Natl. Bur. Stand. (U.S.) **66A-1**: 1–3; 1962.

[2] Powell, L. J.; T. J. Murphy and J. W. Gramlich, The absolute isotopic abundance and atomic weight of a reference sample of silver. J. Res. Natl. Bur. Stand. (U.S.) **87-1** 9–19; 1982.

[3] Shields, W. R.; T. J. Murphy, E. L. Garner, and V. H. Dibeler, Absolute isotopic abundance ratio and the atomic weight of chlorine. J. Amer. Chem. Soc., **84**: 1519–1522; 1962 May 5.

[4] Shields, W. R.; T. J. Murphy and E. L. Garner, Absolute isotopic abundance ratio and atomic weight of copper. J. Res. Natl. Bur. Stand. (U.S.) **68A-6**: 589–592; 1964.

[5] Catanzaro, E. J.; T. J. Murphy, E. L. Garner, and W. R. Shields, Absolute isotopic abundance ratio and the atomic weight of bromine. J. Res. Natl. Bur. Stand. (U.S.) **68A-6**: 593–599; 1964.

[6] Shields, W. R.; T. J. Murphy, E. J. Catanzaro, and E. L. Garner, Absolute isotopic abundance ratio and the atomic weight of a reference sample of chromium. J. Res. Natl. Bur. Stand. (U.S.) **70A-2**: 193–197; 1966.

[7] Catanzaro, E. J.; T. J. Murphy, E. L. Garner, and W. R. Shields, Absolute isotopic abundance ratio and atomic weight of magnesium. J. Res. Natl. Bur. Stand. (U.S.) **70A-6**: 453–458; 1966.

[8] Catanzaro, E. J.; T. J. Murphy, W. R. Shields, and E. L. Garner, Absolute isotopic abundance ratios of common, equal-atom, and radiogenic lead isotope standards. J. Res. Natl. Bur. Stand. (U.S.) **72A-3**: 261-267; 1968.

[9] Catanzaro, E. J.; C. E. Champion, E. L. Garner, G. Marinenko, K. M. Sappenfield, and W. R. Shields, Standard Reference Materials: Boric acid; isotopic and assay Standard Reference Materials. Natl. Bur. Stand. (U.S.) Spec. Publ. 260–17; 1970 February, 60 pp.

[10] Catanzaro, E. J.; T. J. Murphy, E. L. Garner, and W. R. Shields, Absolute isotopic abundance ratio and atomic weight of terrestrial rubidium. J. Res. Natl. Bur. Stand. (U.S.) **73A-5**: 511-516; 1969.

[11] Gramlich, J. W.; T. J. Murphy, E. L. Garner, and W. R. Shields, Absolute isotopic abundance ratio and atomic weight of a reference sample of rhenium. J. Res. Natl. Bur. Stand. (U.S.) **77A-6**: 691–698; 1973.

[12] Barnes, I. L.; L. J. Moore, L. A. Machlan, T. J. Murphy, and W. R. Shields, Absolute isotopic abundance ratios and the atomic weight of a referene sample of silicon. J. Res. Natl. Bur. Stand. (U.S.) **79A-6**: 727–735; 1975.

[13] Garner, E. L.; T. J. Murphy, J. W. Gramlich, P. J. Paulsen, and I. L. Barnes, Absolute isotopic abundance ratios and atomic weight of a reference sample of potassium. J. Res. Natl. Bur. Stand. (U.S.) **79A-6**: 713–725; 1975.

[14] Dunstan, L. P.; J. W. Gramlich, I. L. Barnes, and W. C. Purdy, Absolute isotopic abundance and the atomic weight of a reference sample of thallium. J. Res. Natl. Bur. Stand. (U.S.) **85-1**: 1–10; 1980.

[15] Moore, L. J.; T. J. Murphy and I. L. Barnes, Absolute isotopic abundance and atomic weight of a reference sample of strontium. J. Res. Natl. Bur. Stand. (U.S.) **87-1**: 1–8, 1982.

[16] Wapstra, A. H. and G. Audi, Atomic Data and Nuclear Data Tables. Nuclear Physics **A432-1**: 1–55; 1985.

[17] Richards, T. W., and W. M. Craig, The atomic weight of gallium. J. Am. Chem. Soc. **45**: 1155–1167; 1923.

[18] Lundell, G. E. F., and J. I. Hoffman, Atomic weight of gallium. J. Res. Natl. Bur. Stand. (U.S.) **15**: 409–420; 1923.

[19] Inghram, M. G.; D. C. Hess, H. S. Brown, and E. Goldberg, On the isotopic composition of meteoritic and terrestrial gallium. Phys. Rev. **74**: 343–344; 1948.

[20] Marinenko, G., On the atomic weight of gallium. J. Res. Natl. Bur. Stand. (U.S.) **81A-1**: 1–4; 1977.

[21] DeLaeter, J. R., and K. J. R. Rosman, The atomic weight of gallium. Int. J. Mass Spectrom. Ion Phys. **21**: 403–409; 1976.

[22] Holden, N. E., and R. L. Martin, The atomic weights of the elements 1983. Pure & Appl. Chem. **56** (6): 653–674; 1984.

[23] Nief, G., and E. Roth, Sur un phenomene de separation d'isotopes provoque par passage de courant electrique dans un metal fondu. Comp. Ren. Acad. Sci. Paris **239**: 162; 1954.

[24] Goldman, M.; G. Nief and E. Roth, Influence de la temperature sur la separation isotopique sous l'effet du courant dans le gallium fondu. Hebd. Seances Acad. Sci. **243**: 1414–1416; 1956.

[25] Machlan, L. A., and J. W. Gramlich, Isotopic fractionation of gallium on an ion exchange column (in preparation).

[26] Gramlich, J. W., and L. A. Machlan, Isotopic variations in commercial high-purity gallium, Anal. Chem. **57** (8): 1788–1790; 1985.

[27] DeLaeter, J. R., The isotopic composition and elemental abundance of gallium in meteorites and in terrestrial samples. Geochim. Cosmochim. Acta **36**: 735–743; 1972.

[28] Shields, W. R., ed. Analytical Mass Spectometry Section: Instrumentation and procedures for isotopic analysis. Natl. Bur. Stand. (U.S.) Tech. Note 277; 1966 July. 99 p.

[29] Garner, E. L.; L. A. Machlan and W. R. Shields, Standard Reference Materials: Uranium isotopic standard reference materials. Natl. Bur. Stand. (U.S.) Spec. Publ. 260-27; 1971 April. 150 p.

[30] Gramlich, J. W., and R. W. Shideler, A programmable sample dryer for thermal ionization mass spectrometry. Natl. Bur. Stand. (U.S.) Tech. Note 1154; 1982 January. 19 p.

[31] Roy, R.; V. G. Hill and E. F. Osborn, Polymorphism of Ga_2O_3 and the system Ga_2O_3-H_2O. J. Am. Chem. Soc. **74**: 719–722; 1952.

[32] Williard, H. H., and G. M. Smith. Tetraphenylarsonium chloride as an analytical reagent. Ind. Eng. Chem. (Anal. Ed.) **11**: 269–274, 305–306; 1939.

[33] Kuehner, E. C.; R. A. Alvarez, P. J. Paulsen, and T. J. Murphy, Production and analysis of high purity acids purified by sub-boiling distillation. Anal. Chem. **44** (12): 2050–2056; 1972 October.

[34] Eberhardt, K. R., Statistical evaluation of uncertainties for the absolute isotopic abundance and atomic weight of a reference sample of gallium. (To be published.)