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Absolute Isotopic Abundance Ratio and Atomic Weight of a Reference Sample of Rhenium

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An absolute value has been obtained for the isotopic abundance ratio of a reference sample of rhenium, using surface emission mass spectrometry. Samples of known isotopic composition, prepared from nearly isotopically pure separated rhenium isotopes, were used to calibrate the mass spectrometers. The resulting absolute $^{185}Re/^{187}Re$ ratio is 0.59738 ± 0.00039, which yields atom percents of $^{185}Re = 37.398 \pm 0.016$ and $^{187}Re = 62.602 \pm 0.016$. The atomic weight calculated from this isotopic composition is 186.20679 ± 0.00031. The indicated uncertainties are overall limits of error based on 95 percent confidence limits for the mean and allowances for the effects of known sources of possible systematic error.

Key words: Absolute ratio; atomic weight; isotopic abundance; rhenium.

1. Introduction

The Isotopic Analysis Section of the National Bureau of Standards is conducting a long term program of absolute isotopic abundance ratio and atomic weight determinations, using solid-sample thermal or surface ionization mass spectrometry. Previous elements studied include silver [1],[1] chlorine [2], copper [3], bromine [4], chromium [5], magnesium [6], lead [7], boron [8], and rubidium [9]. The present work extends the study to rhenium.

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, prepared from chemically pure and nearly isotopically pure separated isotopes, provide a bias correction (calculated isotope ratio/observed isotope ratio) which when applied to the observed isotope ratio of the reference sample being calibrated allow an absolute ratio to be calculated for this sample. The atomic weight can then be calculated from the absolute isotopic abundances and the atomic masses reported by Wapstra and Gove [10].

Natural rhenium consists of two isotopes, ^{185}Re and ^{187}Re, the latter of which is radioactive with reported half-life values ranging from 4×10^{12} to 3×10^{10} years [11, 12]. The more recent determinations trend toward the lower half-life value. Based on the lower half-life value, it would take about 18 million years to produce a 1 ppm change in the atomic weight of rhenium.

Prior to 1955, the accepted atomic weight of rhenium was 186.31 (0 = 16) based on the work of Hönigschmid and Sachtleben [13], who determined the ratio of $AgReO_4/AgBr$ to be 1.90735. This calculates to an atomic weight of 186.28 on the presently accepted scale of $^{12}C = 12$. The currently accepted value for the atomic weight is 186.2, based on the relative mass spectrometric measurements of White and Cameron [14] who reported an isotopic composition of 37.07 percent ^{185}Re and 62.93 percent ^{187}Re.

A number of other mass spectrometric determinations of the isotopic composition of rhenium have been reported in the literature [15, 16, 17], none of which may be considered absolute.

For this work seven synthetic isotope standards for rhenium were prepared with $^{185}Re/^{187}Re$ ratios ranging from approximately 10 to 0.1. The wide range in isotopic composition for the synthetic standards was used to further support the supposition that the bias of each instrument was independent of isotopic composition.

2. Experimental Procedure

2.1. Mass Spectrometry

Isotope ratio measurements were made on two solid-sample mass spectrometers. The first instrument was a two stage mass spectrometer constructed from two 90°, 12-in radius flight tubes connected to produce

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

an "S" configuration. The instrument was equipped with an air operated beam valve [18] and a thin lens "Z" focussing source [19]. Ion detection at the end of the second stage was accomplished with a 17-stage ion multiplier coupled to an amplifier, discriminator, and scaler [18]. The magnetic field of each stage was independently controlled by a controller-gaussmeter. Each mass was brought into focus at the collector by computer switching of the magnetic fields. Timing and data collection were also under computer control.

The second instrument was a single stage 60°, 6-in radius of curvature mass spectrometer equipped with a "Z"-lens source identical to that used in the two stage instrument. The collector was a deep bucket Faraday cage type equipped with a 50 percent transmission grid shadowing a series of suppression grids [19]. The measuring circuit consisted of two vibrating reed electrometers operated as a master-slave combination, a voltage to frequency converter, and a scaler-timer. As with the first instrument, data collection was by computer control.

Prior to this study, it was established that the bias of the two stage instrument was independent of the isotopic ratio through the measurement of a series of seventeen uranium isotopic standards covering a range of isotopic compositions from approximately $^{235}U/^{238}U = 0.005$ to 187. That a single bias correction is valid for the single stage instrument over the range of isotopic compositions measured has been established previously through the measurement of synthetic isotopic mixtures of boron [8], chromium [5], magnesium [6], and rubidium [9].

Samples were mounted on a single tungsten filament which had been previously degassed in a vacuum at a temperature of approximately 2000 °C and under a potential field. No rhenium background was observed from degassed filaments. About 10 μl of sample solution containing 5 mg/ml of rhenium as perrhenic acid in 5 percent sulfuric acid was placed on a tungsten filament. A high purity platinum wire anode, which was cleaned with dilute nitric acid between each plating, was placed on the top of the solution drop and rhenium was electrolytically deposited onto the tungsten at a potential of 2.25 V and a current density of 10 ma/cm^2. Approximately 1 h was required for deposition. The filament was immersed in triple-distilled water, dried under a heat lamp and placed in a bell jar purged with extra-dry hydrogen. The samples were reduced in a hydrogen atmosphere by passing a current through the filament. For samples analyzed on the two stage instrument, the current was increased slowly until white vapors were seen to emanate from the filament. After 5 s at this temperature the current was increased until the filament temperature was just below red heat. The current was turned off after 10 s at this temperature. The above plating and hydrogen reduction procedure was repeated with a second 10 μl drop of solution after which the filament was immediately placed into the mass spectrometer. Samples were analyzed on the two stage instrument at a filament temperature of 1900 °C.

Samples analyzed on the single stage machine were treated in a slightly different manner during the hydrogen reduction step. The filament was heated until fuming was observed. After fuming ceased, the current was slowly increased until the sample deposit started to bubble and change from black to gray in color. The current was maintained at this setting for 1 min and then increased until a faint red glow was observed in the filament. The current was then reduced to a point where the red glow was no longer visible and allowed to remain at this temperature for 30 s. This plating and hydrogen reduction was repeated for a total of three times after which the filament was placed into the mass spectrometer and analyzed at a temperature of 2100 °C.

Although the analysis procedure used by each operator was somewhat different, each operator performed all of his analyses in an identical manner. Filament temperature, heating pattern, signal intensity, and time of data taking were controlled within strict limits. No filament fractionation was observed during the analyses on the two stage instrument, however, at the higher filament temperature used on the single stage mass spectrometer a small amount of fractionation (less than 0.1%) was observed during the analyses.

2.2. Purification of the Separated Isotopes

Electromagnetically separated ^{185}Re and ^{187}Re isotopes, in the form of rhenium metal powder, were obtained from the Isotopes Division, Oak Ridge National Laboratory of the Union Carbide Nuclear Company. The ^{185}Re was designated Series PF Sample 184501 and the ^{187}Re was designated Series DD Sample 135001. The Certificates of Analysis which accompanied each sample included a semiquantitative spectrographic analysis which showed that the principal impurities were sodium, potassium and calcium at greater than 0.1 percent. While these elements would not interfere with the assay method for rhenium, several others which were reported at the 0.02 to 0.05 percent concentration range could interfere. Among these elements were molybdenum, vanadium, tungsten, bismuth, mercury, tin, silver, lead, and platinum all of which interfere with the assay of rhenium by tetraphenylarsonium chloride [20, 21] by forming insoluble compounds.

To reduce these impurities to a level low enough so that they could not cause a significant error in the determination of the rhenium ion in solutions of these isotopes, the separated isotope samples were further purified by a combination of chloride precipitation to remove insoluble chlorides, cation exchange to remove cationic inpurities, anion exchange to remove anionic impurities and electro-deposition to separate the purified rhenium from the organic material dissolved from the ion exchangers.

Each separated isotope was treated as follows: The rhenium metal powder (about 0.5 g) was dissolved in 50 ml of 4*N* nitric acid. The resulting solution was evaporated to constant volume at about 50 °C. (The

temperature was kept low so as to minimize the loss of rhenium through volatilization.) The residue was taken up in a little water and 1 ml of 6*N* hydrochloric acid was added to precipitate insoluble chlorides. The solution was again evaporated to constant volume at about 50 °C, and the residue taken up in about 75 ml H_2O. The solution was filtered through fine textured filter paper and passed through a cation exchange column containing about 20 ml of AG 50×8, 100–200 mesh, strongly acidic cation exchange resin to remove cationic impurities. The column was washed with 100 ml of water and the eluent was evaporated to about 35 ml.

The perrhenic acid solution was then passed through an anion exchange column containing 35 ml of AG 1×8 resin, 100–200 mesh, strongly basic anion exchange resin. The anionic impurities were eluted by successive elution with 50 ml H_2O, 100 ml of a solution 1*N* in NH_4OH and 1*N* in NH_4Cl, 75 ml H_2O, 100 ml 1*N* HNO_3, and 50 ml H_2O. Rhenium was then eluted with 350 ml of 10*N* HNO_3. This solution was then evaporated to constant volume of perrhenic acid with the last few ml being evaporated at about 50 °C to minimize the loss of rhenium. The residue was taken up in 200 ml of 5 percent (w/v) H_2SO_4, transferred to a 400 ml quartz beaker and diluted to 300 ml with 5 percent (w/v) H_2SO_4.

Rhenium metal was electrodeposited onto a platinum gauze cylindrical cathode (cylinder 5 cm × 1.2 cm) at an applied potential of 2.6V. The solution was stirred magnetically using a Teflon[2] covered stirring bar. After overnight electrolysis, the cathode was washed with water and the rhenium dissolved with 50 ml of 8*N* HNO_3. The electrodeposition was repeated until no rhenium deposited on overnight plating (five electrodepositions). After each plating, the rhenium was dissolved with the 50 ml of 8*N* HNO_3. A small amount of 30 percent H_2O_2 was added to the electrolyte between electrolysis to dissolve the rhenium which deposted on the stirrer or beaker.

The nitric acid solution containing the purified rhenium was evaporated to constant volume of perrhenic acid at low heat (50 °C). The residue was then taken up in a few ml of 6*N* HCl and again evaporated to perrhenic acid at low heat. This addition and evaporation of HCl was repeated six times to insure the removal of nitrate ion which interferes with the assay method for rhenium.

2.3. Preparation and Analysis of the Separated Isotope Solutions

The purified $H^{185}ReO_4$ and $H^{187}ReO_4$ were taken up in about 50 ml of H_2O, filtered, and transferred to special 200 ml borosilicate glass flasks. These flasks were constructed from volumetric flasks by cutting the neck of each flask about 1 cm from the body and tooling the neck for a No. 0 polyethylene stopper. The solutions were diluted to about 140 ml and 0.5 ml of 30 percent H_2O_2 was added to each. After loosly closing the flask with polyethylene stoppers, the solutions were heated overnight at low heat to insure the complete oxidation of any reduced rhenium to the perrhenate state. The excess hydrogen peroxide was then removed by adding a small piece of platinum foil to each solution and heating the loosly stoppered flask overnight.

A preliminary assay of the rhenium content of each separated isotope solution was effected by adding 2 ml of 2*N* NaCl and 2 ml of 2 percent tetraphenylarsonium chloride solution to a 15 ml, fine porosity, borosilicate glass filtering crucible. A weighed 1 ml portion of the rhenium solution was added and mixed by swirling to precipitate tetraphenylarsonium perrhenate. After standing two hours, the solution was removed from the crucible by vacuum suction and the precipitate was washed three times with small amounts of water. The approximate rhenium content of the solution was calculated from the weight of the precipitate and the weight of the solution. The volume of the solution was then adjusted so the concentration would be close to 18 μmol Re/g.

Previous tests with known rhenium solutions showed that this method is accurate to about 1 percent of the rhenium present.

The solution of $H^{185}ReO_4$ was designated "Re 185" and the solution of $H^{187}ReO_4$ was designated "Re 187".

(a) Nitrate Analysis—Since nitrate ion forms an insoluble compound with the tetraphenylarsonium ion, $(C_6H_5)_4As^+$, used to assay the rhenium, both solutions were analyzed for nitrate. The "Re 185" solution was analyzed for nitrate ion before the addition of hydrogen peroxide by the brucine sulfate test [22] and was found to contain less than 0.0001 percent NO_3^-. The "Re 187" solution was analyzed for nitrate after the addition of hydrogen peroxide. It was necessary to make the sample alkaline and evaporate to dryness to destroy the last trace of H_2O_2 before determining nitrate by brucine test. This solution was also found to contain less than 0.0001 percent NO_3^-.

(b) Impurity Analysis—Samples of the "Re 185" and "Re 187" solutions were analyzed for impurity elements by isotope-dilution spark source mass spectrometry [23] Samples equivalent to about 5 mg of Re were spiked with 10^{-7}g of ^{109}Ag, ^{137}Ba, ^{44}Ca, ^{111}Cd, ^{53}Cr, ^{65}Cu, ^{54}Fe, ^{113}In, ^{41}K, ^{26}Mg, ^{97}Mo, ^{62}Ni, ^{206}Pb, ^{195}Pt, ^{82}Se, ^{117}Sn, ^{86}Sr, ^{125}Te, ^{203}Tl, ^{183}W, and ^{67}Zn. The solutions were evaporated to small drops, evaporated onto gold wires and analyzed by spark source mass spectrometry. In addition to these elements Bi and Mn which are mononuclidic elements were estimated by comparing to other nuclides. Table 1 shows the results of these analyses as well as the results of the analysis of a doped natural rhenium sample which was purified in the same manner as the separated isotope. This sample had been doped with 0.1 percent of Ag, Bi, Cr, Mn, Mo, Pb, Sn, and V to determine the efficiency of the purification in removing elements which could interfere with the assay of the rhenium solutions.

[2] A commercial material is identified in this paper in order to adequately specify experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards.

TABLE 1. *Analysis of purified rhenium*

Element	Natural Re (ppm)	"Re 185" (ppm)	"Re 187" (ppm)
Ag	[a] 0.3	1	1
Ba	0.5	2	0.5
Bi [b]	[a] 0.2	0.2	0.2
Ca	3	5.8	5
Cd	2	5	4
Cr	[a] 1	1.5	0.4
Cu	25	5.7	12
Fe	11	10	5.1
K	6	18	16
Mg	2	1.6	1.2
Mn [c]	[a] 0.5	0.5	0.5
Mo	[a] 0.7	≤ 9	2
Ni	4	4	1
Pb	[a] 1.7	4.3	2.3
Pt		160	14
Se	< 3	< 5	< 3
Sn	[a] 0.8	2.7	1
Sr	0.2	0.5	0.2
Te	0.3	1	1
V [c]	[a] ≤ 0.5	≤ 0.5	≤ 0.5
W	≤ 5	≤ 3	2
Zn	3	17	3

[a] Concentration before purification—1000 ppm.
[b] Compared to ^{206}Pb.
[c] Compared to ^{53}Cr and ^{54}Fe.

The only element that was detected at a concentration level high enough to interfere with the assay of rhenium was platinum at 160 ppm in the "Re 185" solution. This apparently came from the platinum cathode used for the rhenium purification. To determine how much of this platinum precipitated with the tetraphenylarsonium perrhenate in the assay of the "Re 185" solution, the material was analyzed for platinum by isotope dilution—spark source mass spectrometry. After the assay, one of the precipitated samples was dissolved in acetone and an amount equivalent to 5 mg of Re was spiked with 10^{-7} g ^{195}Pt. Enough water was added to make the solution about 50 percent in H_2O and the solution was passed through a cation exchange column (6.5 cm × 1.2 cm filled to 3.5 cm with AG 50 × 8, 100–200 mesh cation exchange resin) and washed with about 20 ml of water to free the solution of tetraphenylarsonium ion. The eluate was evaporated and analyzed by spark source mass spectrometry as the previous samples. The platinum was found to be 20 ppm in the precipitate and a small correction (35 ppm) based on the Pt being present as $[(C_6H_5)_4As]_2PtCl_6$ has been applied to the weights of precipitate in the assay of the "Re 185" solution.

2.4. Assay of Separated Isotope Solutions

Four weighed portions of about 15 g were withdrawn from each separated isotope solution in the following manner. A 4-in platinum needle was inserted through a No. 0 polyethylene stopper and used to replace the stopper in the flask. A 20 ml polyethylene hypodermic syringe 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. Any static charge that might be present on the plastic syringe was dissipated by wiping it with a damp lintless towel. The syringe and contents were weighed on a semimicrobalance 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 delivery of the sample. Two samples were withdrawn from each solution before the calibration samples were withdrawn and two samples were withdrawn after the calibration samples to insure that no change in concentration occurred during this time interval (about 6 h).

Each weighed portion was then assayed as follows: A tetraphenylarsonium chloride reagent solution was prepared by diluting 150 ml of a 2 percent (w/v) solution of tetraphenylarsonium chloride hydrochloride $[(C_6H_5)_4AsCl \cdot HCl \cdot H_2O]$ to 650 ml with subboiling distilled acetone (the 2% tetraphenylarsonium chloride solution was filtered twice through close textured filter paper before use). Sixty-five ml of this reagent solution was added to the weighed portion of the separated isotope solution. The solution was mixed with a Teflon rod and the rod was removed and washed with acetone. The acetone was allowed to evaporate from the uncovered beaker in a Class-100 clean air hood and the evaporation continued until all of the acetone evaporated and about 20–25 ml of solution remained in the beaker (about 20 h). (Tetraphenylarsonium perrhenate is soluble in the initial acetone-water mixture and slowly cyrstallizes from the solution as the acetone evaporates producing relatively large crystals when compared to the usual method of precipitation.)

The crystalized tetraphenylarsonium perrhenate, $(C_6H_5)_4AsReO_4$, was transferred with 0.1 percent tetraphenylarsonium chloride solution to a tared 15 ml fine porosity borosilicate glass filtering crucible. Since it was not possible to completely transfer the salt, the material remaining in the beaker was dissolved with acetone and the acetone evaporated at 50 °C. As much of the salt as possible was washed into the filtering crucible using the dilute reagent solution. This dissolution in acetone, evaporation, and transfer procedure was repeated twice more so that the amount of material remaining in the beaker was small. The material in the crucible was washed three times with water and the crucible and contents were dried at 125 °C for 3 h. (The filtrate and original beaker were reserved for the determination of dissolved and untransferred rhenium.)

The filtering crucible and contents were cooled in a desiccator, transferred to the case of a microbalance and allowed to stand for several hours. The crucible and contents were then weighed to ±0.002 mg. A buoyancy correction for the glass crucible was made by averaging three empty tare crucibles. The air weight of the $(C_6H_5)_4AsReO_4$ was then determined and converted to vacuum weight using a measured value of 1.93 as the density of the salt at 23 °C. The micromoles

(μmol) of rhenium present in the salt was determined using a calculated atomic weight for rhenium and 1971 atomic weight values for the other elements. The formula weights used were 632.3032 for $(C_6H_5)_4As^{185}ReO_4$ and 634.2834 for $(C_6H_4)_4As^{187}ReO_4$.

The filtrate from the precipitation of the tetraphenylarsonium perrhenate was transferred to the original beaker and about 50 ml of acetone was added to insure that any untransferred salt dissolved. The "Re 185" solutions were spiked with about 1.1 μmol of ^{187}Re and the "Re 187" solutions were spiked with 1.1 μmol of ^{185}Re for determining soluble and untransferred rhenium by isotope dilution mass spectrometry.

The spiked solution was mixed, evaporated to dryness, and the residue was taken up with 10 ml of a solution that was 50 percent 2*N* HCl and 50 percent acetone by volume. This solution was passed through an anion exchange column (6.5 × 1.2 cm filled to 3.5 cm with AG 1 × 8, 100–200 mesh anion exchange resin) washed with a few ml of the acetone–2*N* HCl mixture followed by 25 ml of 1*N* HCl. The rhenium was eluted from the column with 30 ml of 8*N* HNO_3 and the eluate was evaporated to dryness on a hot plate at low heat. The residue was taken up with 15 ml of 5 percent H_2SO_4 and the rhenium was electrodeposited as rhenium metal onto a platinum wire cathode by electrolysis at 2.4V applied potential for 16 h from a stirred solution. The rhenium metal was then stripped from the platinum wire cathode with 2–3 ml of 8*N* HNO_3 and the resulting solution evaporated to dryness at low heat. This residue was taken up with about 0.05 ml of 5 percent sulfuric acid and the 185/187 ratio was determined by surface emission mass spectrometry. The rhenium found as μmol Re was added to the rhenium from the gravimetric determination to yield the total rhenium in the sample. Table 2 shows the results of these analyses.

This method of determining the concentration of rhenium solutions was previously tested on solutions containing known amounts of rhenium. Six solutions were prepared from high-purity zone-refined rhenium in the approximate concentration of the separated isotope solutions, 16.8 to 20.2 μmol Re/g. This high purity rhenium was found to contain about 15 ppm of Fe and Al by spark source–isotope dilution analysis. Several other elements were detected at less than 5 ppm so that the detected impurities totaled about 60 ppm. Four samples containing from 250 to 290 μmol of rhenium were withdrawn from each solution and the rhenium concentrations were determined as described above. Comparison of the calculated and measured concentrations detected a positive bias of about 0.03 percent but this would have a negligible effect on ratios.

Pooling the results of the separated isotope solutions as shown in table 2 with the results of the six sets described above yields a value of 0.0018 μmol/g for the standard deviation of an individual measurement (24 degrees of freedom). The standard error for the average of four determinations is therefore 0.0009 μmol/g and the uncertainty of the concentration is 0.0018 μmol/g at the 95 percent confidence level. This corresponds to an uncertainty of 0.010 percent for solutions containing 18 μmol Re/g.

2.5. Isotopic Analyses of the Separated Isotope Solutions

Each of the separated isotope solutions were analyzed four times on each of the instruments. Sources were cleaned between the analyses of the two solutions as a precaution against the possibility of cross-contamination from the source parts, however tests showed that the two separated isotopes could be analyzed back-to-back on the same source with no detectable cross-contamination. Because of the poor precision obtained from measuring large ratios on very small signals on the single stage instrument, those analyses have not been included in the average isotopic compositions reported in table 3, even though the isotopic compositions obtained on the single stage machine fall within the stated error limits. In addition, seven analyses on each separated isotope obtained on the two stage instrument prior to this study are indistinguishable from the values reported in table 3. The isotopic compositions of the separated isotopes given in table 3 have been corrected for mass

TABLE 2. *Concentration of rhenium isotope solutions*

Solution	Sample No.	Weight solution g	Rhenium From ppt μmol	Rhenium From I.D. μmol	Total rhenium μmol	Conc. solution μmol Re/g
"Re 185"	1	15.04219	269.844	0.596	270.440	17.9788
	2	15.19842	272.648	.597	273.245	17.9785
	3	15.54660	278.914	.608	279.522	17.9796
	4	15.44233	277.033	.604	277.637	17.9790
				Average		17.9790
"Re 187"	1	15.47475	277.143	0.713	277.856	17.9554
	2	15.57072	279.006	.546	279.552	17.9537
	3	15.31739	274.299	.732	275.031	17.9555
	4	15.30674	274.201	.617	274.818	17.9541
				Average		17.9547

spectrometric bias, with changes becoming negligible after three rounds of iteration.

TABLE 3. *Isotopic composition of separated rhenium isotopes used in calibration samples*

Separated isotope		Isotopic composition (atom percent)
"Re 185"	^{185}Re	[a] 99.5516 ± 0.0022
	^{187}Re	0.4484 ± 0.0022
"Re 187"	^{185}Re	0.6769 ± 0.0034
	^{187}Re	99.3231 ± 0.0034

[a]The uncertainties are based on a minimum error of 0.5 percent for the ratio determinations. The calculated 95 percent confidence limits are well below this value.

2.6. Preparation of Calibration Samples

Seven calibration samples were prepared by mixing weighed portions of the "Re 185" and "Re 187" solutions to produce ^{185}Re/^{187}Re ratios ranging to 10 : 1 to 1 : 10 with two of them bracketing the observed natural ratio of 0.60 within a few percent. The portions were withdrawn from the flasks and weighed in the manner previously described for the assay of the solutions. To eliminate any possibility of change in concentration of a isotope solution with time, the portions for the calibration samples were withdrawn from the flasks between the samples taken for assay over a period of about 6 h.

Table 4 shows the composition of these calibration samples. The isotopic ratio of each calibration sample was calculated from the isotopic analysis of the separated isotopes and the μmol of rhenium from each separated isotope solution as determined from the assay and weight of solution taken.

Each calibration sample was thoroughly mixed and evaporated to dryness at low heat (≈ 50 °C) on a hot plate. Each sample was evaporated separately to avoid any possibility of cross-contamination due to the volatility of perrhenic acid. The calibration samples were then taken up in 5 percent sulfuric acid (w/v) so that 1 ml of solution contained 5 mg of rhenium.

2.7. Isotopic Analyses of the Calibration Mixes and the Standard Sample

Two complete sets of analyses of the calibration mixes and the standard sample were made, one by Operator #1 using the two stage instrument and one by Operator #2 using the single stage instrument. Each set consisted of 22 analyses of the standard sample made in a simple alternating pattern with three analyses each of the seven calibration mixes.

3. Results and Discussion

The results for the seven calibration mixes are summarized in table 5. For each operator, there are no statistically significant differences between any of the values of the correction factor. Table 6 includes the observed and corrected experimental ^{185}Re/^{187}Re values for the standard sample as well as the final absolute value for the isotopic ratio, with its associated uncertainty components.

The calculation of the atomic weight of the reference sample of rhenium is summarized in table 7.

A limiting factor in the accuracy of an atomic weight for naturally occurring rhenium is the variability in the natural isotopic composition. Although a complete survey of the consistency of this element's isotopic composition in nature has not been undertaken, more than 10 years of measurements in this laboratory on rhenium filaments have shown no major variation in the ^{185}Re/^{187}Re ratio among various lots of rhenium from different manufacturers.

TABLE 4. *Composition of rhenium calibration samples*

Sample No.	Isotope solution	Weight solution g	^{185}Re μmol	^{187}Re μmol	Isotope ratio ^{185}Re/^{187}Re
1	"Re 185"	10.22737	183.05331	0.82458	9.362302
	"Re 187"	1.05092	0.12772	18.74123	
2	"Re 185"	1.97036	35.26624	0.15886	1.990891
	"Re 187"	0.98778	0.12005	17.61524	
3	"Re 185"	1.08449	19.41061	0.08744	0.511999
	"Re 187"	2.14960	0.26124	38.33418	
4	"Re 185"	1.14364	20.46929	0.09221	0.594056
	"Re 187"	1.94937	0.23691	34.76344	
5	"Re 185"	1.08309	19.38556	0.08732	0.628257
	"Re 187"	1.74429	0.21199	31.10621	
6	"Re 185"	1.03372	18.50191	0.08334	0.107832
	"Re 187"	10.26552	1.24759	183.06674	
7	"Re 185"	1.14517	20.49668	0.09233	1.029355
	"Re 187"	1.11881	0.13597	19.95193	

TABLE 5. *Determination of mass spectrometer bias*

Calibration sample No.	Isotopic ratio $^{185}Re/^{187}Re$			Correction factor	
	Calculated	Operator I	Operator II	Operator I	Operator II
1	9.362302	9.42064	9.40931	0.993807	0.995004
2	1.990891	2.00258	2.00046	.994163	.995217
3	0.511999	0.515458	0.514415	.993289	.995303
4	.594056	.597981	.596917	.993436	.995207
5	.628257	.632928	.631193	.992620	.995348
6	.107832	.108639	.108361	.992572	.995118
7	1.029355	1.03585	1.03403	.993730	.995480
Mean values of correction factors				0.993374	0.995240

TABLE 6. *Observed and corrected* $^{185}Re/^{187}Re$ *values for the standard sample*

	Observed ratios	Correction factor	Corrected ratios
Operator I	0.601415	0.993374	0.597430
Operator II	0.600191	0.995240	0.597334

Mean .....0.59738 ± 0.00039

Uncertainty Components:

95 percent confidence limits on ratio determinations .....±0.00016
Bounds due to possible systematic error in composition of separated isotopes .....±0.00011
Bounds due to possible systematic error in chemical analysis.....±0.00012

TABLE 7. *Summary calculations of the atomic weight of rhenium*

Value	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 = 186.20679	±0.00031	+0.00012	±0.00009	±0.00010
Nuclidic masses [10] ($^{12}C = 12$)				
$^{185}Re = 184.953007$	±0.000014			
$^{187}Re = 186.955791$	±0.000014			
Atomic percent				
$^{185}Re = 37.398$	±0.016	±0.006	±0.005	±0.005
$^{187}Re = 62.602$	±0.016	±0.006	±0.005	±0.005
Isotopic ratio $^{185}Re/^{187}Re = 0.59738$	±0.00039	±0.00016	±0.00011	±0.00012

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

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