

# Absolute Isotopic Abundance Ratio and Atomic Weight of Terrestrial Rubidium

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An absolute value has been obtained for the isotopic abundance ratio of terrestrial rubidium, using solid-sample thermal ionization mass spectrometry. Samples of known isotopic composition, prepared from nearly isotopically pure separated rubidium isotopes, were used to calibrate the mass spectrometers. The resulting absolute  $^{85}\text{Rb}/^{87}\text{Rb}$  ratio is  $2.59265 \pm 0.00170$  which yields atom percents of:  $^{85}\text{Rb} = 72.1654 \pm 0.0132$  and  $^{87}\text{Rb} = 27.8346 \pm 0.0132$ . The atomic weight calculated from this isotopic composition is  $85.46776 \pm 0.00026$ . 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 abundances; rubidium.

## 1. Introduction

The Analytical Mass Spectrometry 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],<sup>1</sup> chlorine [2], copper [3], bromine [4], chromium [5], magnesium [6], lead [7], and boron [8]. The present work extends the study to rubidium.

Natural rubidium consists of two isotopes,  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$ , the latter of which is radioactive with reported half-life values ranging from 47,000 to 50,000 million years [9, 10]. The amount of  $^{87}\text{Rb}$  has decreased slightly since the formation of the earth approximately 4550 million years ago but Shields et al. [11] have shown that the present-day  $^{85}\text{Rb}/^{87}\text{Rb}$  ratio is constant in nature within 95 percent confidence limits of 0.15 percent.

A number of other mass spectrometric determinations of rubidium isotopic abundances have been reported in the literature [12, 13, 14, 15, 16] but none of these could be considered absolute.

In the present study, the mass spectrometers were calibrated for bias by the use of samples of known  $^{85}\text{Rb}/^{87}\text{Rb}$  ratio, prepared from chemically pure and nearly isotopically pure  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$  solutions. The measured biases were then used to correct the raw data obtained on a standard sample of  $\text{RbCl}$ , yielding an absolute value of  $^{85}\text{Rb}/^{87}\text{Rb}$  for this sample.

Bias measurements were made on samples with  $^{85}\text{Rb}/^{87}\text{Rb}$  ratios of approximately 1.0 and 2.6, to double-check the assumption that the bias of each instrument was independent of the isotopic composition.

## 2. Experimental Procedure

### 2.1. Mass Spectrometry

Isotopic ratio measurements were made on two single-stage solid-sample mass spectrometers which are identical except for very minor differences in the vacuum systems. Each instrument has a 6-in radius of curvature  $60^\circ$  analyzer tube,  $48^\circ$  sector magnet, and a Z lens in the source assembly [17]. Triple-filament rhenium-ribbon ( $1 \times 30$  mils) sources were used. All filaments were prebaked in a vacuum, under a potential field, to eliminate the possibility of significant rubidium background signals from the filament material. Blank filaments which had been prebaked did not show any rubidium ion signals under the standard analytical procedures used in this study.

Two complete sets of samples were prepared. The two sets, prepared from the same parent solutions, had identical isotopic compositions and rubidium concentrations ( $10 \mu\text{g}/\text{cm}^3$ ) but one set was made up of neutral aqueous solutions while the other consisted of 2 percent HCl solutions. The two operators used different mass spectrometers and different, but isotopically identical, samples, as well as slightly different heating and timing procedures.

<sup>1</sup> Figures in brackets indicate the literature references at the end of this paper.

One drop of solution ( $\sim 0.2 \mu\text{g Rb}$ ) was placed on each sample filament and dried with a heat lamp and an electrical current of 0.5 A for 10 min. The mass spectrometric analyses were begun when the source pressure was  $< 6 \times 10^{-7}$  Torr. An accelerating voltage of 3.8 kV was used and no memory or background signals were ever noted. The relatively low accelerating voltage is necessary because rubidium ions are very efficient producers of secondary electrons. Higher voltages would have defeated the secondary electron suppression components of the collector.

A very small amount of isotopic fractionation, on the order of 0.03 percent, was occasionally noted to occur during the data-taking period (10 min.) of an analysis, but generally the fractionation was not measurable over this small time period. However, preliminary tests showed that fractionation could be a very significant factor between analyses performed with different time, sample-size, and/or heating parameters. In view of this, each operator always performed his analyses in an identical manner; sample-size, heating pattern, and total rubidium ion signals were always kept within strict limits, and data were always taken during the same time interval.

Each analysis consisted of a set of 10 measurements, with base-line readings taken immediately before and after the data. The peak-top data were taken by step-wise changes in the magnet current and each peak-top was monitored for 30 s.

## 2.2. Purification of the Separated Isotopes

Electromagnetically separated  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$  isotopes in the form of rubidium chloride were obtained from the Isotopes Division, Oak Ridge National Laboratory of the Union Carbide Nuclear Company. About 2.83 g each of  $^{85}\text{RbCl}$  and  $^{87}\text{RbCl}$  equivalent to about 2.0 g each of  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$  were received. The  $^{85}\text{RbCl}$  and the  $^{87}\text{RbCl}$  were designated Series 144701 and Series 144801, respectively. The certificate of analysis accompanying each sample included a semiquantitative spectrographic analysis which indicated that zinc could be present at the 0.2 percent level and that several other elements could also be present up to the 0.05 percent level. To reduce these impurities to a level low enough so that they could not cause a significant error in the determination of the rubidium ion content in solutions of these isotopes, the separated isotope samples were further purified. The purification method used had been previously found by this laboratory to be effective in removing cationic and anionic impurities from rubidium chloride with the exception of potassium and cesium which co-crystallize with the rubidium.

Each separated isotope sample was treated as follows: The rubidium chloride (about 2.8 g) was dissolved in 50 cm<sup>3</sup> of water in a 100 cm<sup>3</sup> fused silica beaker and 5 cm<sup>3</sup> of "ultra-pure" grade perchloric acid were added. The precipitated rubidium perchlorate,  $\text{RbClO}_4$ , was dissolved by heating the solution almost to boiling and then slowly crystallized by allowing the solution to cool to room temperature. The solution

was further cooled to about 5 °C, by placing it in a refrigerator overnight. The crystallized  $\text{RbClO}_4$  was recovered from the solution by filtering it through a fine porosity polyethylene filter. After the  $\text{RbClO}_4$  was washed with a cold 80 percent ethanol solution, it was returned to the fused silica beaker and the crystallization process was repeated except that only 2 cm<sup>3</sup> of perchloric acid were added. The recrystallized  $\text{RbClO}_4$  was again caught on the polyethylene filter and washed with cold 80 percent ethanol. The purified material was dried by passing clean air over the  $\text{RbClO}_4$  for several hours.

After being transferred to a covered quartz crucible, the recrystallized rubidium perchlorate was placed in an electric furnace and thermally converted to rubidium chloride. This was accomplished by slowly raising the temperature to 600 °C and, to ensure complete conversion, keeping it there for 4 hrs. The crucible was kept covered during this decomposition since a liquid phase eutectic is formed which sprays material on further decomposition. (To avoid isotopic contamination, the decompositions of the  $^{85}\text{RbClO}_4$  and  $^{87}\text{RbClO}_4$  were performed in new, separate furnaces which had not been exposed to rubidium salts.) The decomposition proceeds in the following manner [18].



until all of the  $\text{RbClO}_4$  has been converted to  $\text{RbCl}$ .

Calculations based on the starting weight of the  $\text{RbCl}$  and the weight of the recovered  $\text{RbCl}$  showed that about 95 percent of the rubidium was recovered in each case.

Samples of the purified  $^{85}\text{RbCl}$  and  $^{87}\text{RbCl}$  were analyzed for potassium and cesium by flame emission spectrometry. The results of these analyses showed that the  $^{85}\text{RbCl}$  and  $^{87}\text{RbCl}$  contained  $120 \pm 5$  ppm and  $100 \pm 5$  ppm of potassium, respectively; cesium was found to be present at less than 10 ppm in both samples. The samples were also analyzed by spark source mass spectrometry. The results of this analysis showed that no other element was definitely detected at a level greater than 10 ppm.

The effectiveness of this purification procedure was first tested by the purification of natural rubidium chloride to which 0.1 percent each of twelve common cationic impurities had been added. Table 1 shows the results of the analysis of the purified  $\text{RbCl}$ . Only aluminum was detected at the 10 ppm level. This material was also shown to contain less than 2 ppm of chlorate ion by a test based on the reaction of chlorate with chloride in acid solution to produce chlorine which was detected with *o*-tolidine.

There was no apparent attack of the fused silica crucibles during these decompositions. No change in crucible weights was observed and silicon was not detected at a level greater than 10 ppm in either sample by spark source mass spectrometry. (Platinum

crucibles could not be used since they would be attacked by the decomposition products.)

TABLE 1. Results of spectrochemical analysis of purified natural rubidium chloride

Element	Initial concentration	Concentration after purification	Established limits of detection
	<i>ppm</i>	<i>ppm</i>	<i>ppm</i>
Al	1000	10	5
Ba	1000	.....	2
Ca	1000	.....	4
Co	1000	.....	3
Cu	1000	.....	2
Fe	1000	.....	4
Li	1000	.....	2
Mg	1000	.....	2
Na	1000	.....	20
Ni	1000	.....	4
Si	1000	.....	2
Zn	1000	.....	50

Note: (.....) not detected.

### 2.3. Preparation and Rubidium Concentrations of the Separated Isotope Solutions

Accurately weighted samples of the purified  $^{85}\text{RbCl}$  and  $^{87}\text{RbCl}$  were transferred to 200 cm<sup>3</sup> volumetric flasks whose necks had been cut off so that only about 1 cm remained. The separated isotope samples were dissolved in water and diluted to about 110 cm<sup>3</sup> after the additions of 1 cm<sup>3</sup> of (1+1) hydrochloric acid. After the solutions were thoroughly mixed by swirling the flasks for several minutes, each flask was sealed with a rubber serum septum and left overnight in a balance case to insure thermal equilibrium. The flasks and contents were weighed to  $\pm 0.2$  mg and preliminary rubidium concentrations were calculated. The solution of  $^{85}\text{RbCl}$  was labeled "Rb 85" and the solution of  $^{87}\text{RbCl}$  was labeled "Rb 87".

Four weighed portions were withdrawn from each separated isotope solution in the following manner. A 4 in platinum needle was inserted through the septum. A short second needle, which just punctured the septum served as a vent. A 10 cm<sup>3</sup> polyethylene hypodermic syringe was attached to the Kel-F hub of the Pt needle and the desired amount of solution was withdrawn. The syringe was then disconnected from the hub and the tip was capped with a polyethylene cap. Any static charge that might be present on the syringe was dissipated by wiping it with a damp paper towel, and the syringe and contents were weighed on a semimicro balance to  $\pm 0.02$  mg. The solution was then delivered from the syringe to a tared 15 cm<sup>3</sup> platinum crucible 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.

About 0.4 cm<sup>3</sup> of "ultra-pure" grade perchloric acid was added to each weighed portion and the solutions were evaporated to constant volume on a hot

plate at about 85 °C. A few drops of water were added to each and the solutions were again evaporated to constant volume. The temperature was then raised to 110 °C and held there until fumes of  $\text{HClO}_4$  were observed. Then the temperature was reduced to about 85 °C; 10 cm<sup>3</sup> of hot water were added to each solution and they were heated to near boiling until the  $\text{RbClO}_4$  dissolved. The solutions were again evaporated to constant volume and heated to fumes of  $\text{HClO}_4$  at 110 °C. This process of dissolving the  $\text{RbClO}_4$  in water, evaporating, and heating to fumes of  $\text{HClO}_4$  was repeated. The temperature of the hot plate was held at about 110 °C until all of the excess  $\text{HClO}_4$  had been fumed off.

After fumes of perchloric acid were no longer noted, the samples were again dissolved, evaporated to dryness, and heated at 150 °C. This process was repeated two more times. (The first series of repeated evaporations frees the  $\text{RbClO}_4$  from chloride. The second series frees the  $\text{RbClO}_4$  from occluded perchloric acid.)

The crucibles were then covered with platinum covers and transferred to an electric furnace. The temperature of the furnace was slowly raised to 250 °C and the crucibles were kept at this temperature for 16 hr (overnight). Then the covers were removed and the crucibles were cooled and weighed. This procedure of heating, cooling, and weighing was repeated, except that the time of heating was reduced to 6 hr, until a constant weight was obtained, that is, until the weighings agreed to within 5  $\mu\text{g}$ . For simplicity of calculations, the vacuum weight of the rubidium perchlorate was converted to milliequivalents (meq) of rubidium using the 1967 atomic weights for chlorine and oxygen and a calculated atomic weight for the separated rubidium isotope based on the ORNL isotopic analysis. The results of these determinations are shown in table 2.

TABLE 2. Concentration of rubidium isotope solutions

Solution	Sample number	Wt solution	Rubidium	Concentration of solution Rb/g soln
		<i>g</i>	<i>meq</i>	<i>meq</i>
"Rb 85"	1	8.69052	1.359758	0.156465
	2	8.92782	1.397106	.156489
	3	8.33577	1.304329	.156474
	4	8.94403	1.399395	.156461
			Average Corrected for K	.156472 ".156436
"Rb 87"	1	8.46749	1.409229	.166428
	2	8.25201	1.373551	.166450
	3	8.63473	1.437179	.166442
	4	8.88910	1.479380	.166426
			Average Corrected for K	.166437 ".166405

<sup>a</sup> The standard error of the average is estimated to be 0.0000085 meq/g soln and the uncertainty of the concentration at the 95 percent confidence level is 0.0000162 meq/g soln.

This method for the determination of the concentrations of the rubidium isotope solutions was adopted after it became apparent that none of the conventional methods for rubidium analysis were capable of yielding precise enough results. It is a valid method as long as the purity of the rubidium chloride is known. As stated previously, the only element detected at the 100 ppm level by spark source mass spectrometry and flame emission spectrometry was potassium. The potassium correction amounted to 0.000036 meq/g sol for the "Rb 85" solution assay and 0.000032 meq/g sol for the "Rb 87" solution assay.

The rubidium concentrations of the two solutions as determined by this method were in good agreement with the preliminary concentrations calculated from the starting weights of rubidium chloride and solution. The "Rb 85" solution was calculated to be 0.156464 meq/g sol and was found to be 0.156432 meq/g sol by this method. The "Rb 87" solution was calculated to be 0.166399 meq/g sol and was found to be 0.166405 meq/g sol.

This method for determining the concentration of rubidium solutions was tested on solutions containing known amounts of rubidium. Seven solutions were prepared from fused high-purity natural rubidium chloride and three solutions were prepared from thermally decomposed rubidium perchlorate (made from the same rubidium chloride). Analysis of this rubidium chloride showed that it contained less than 50 ppm of detected impurities. Four samples containing from 1.2 to 2.0 meq of rubidium were withdrawn from each solution and the rubidium ion concentrations were determined as described above. Analyses of the rubidium perchlorate resulting from the above assay have shown it to contain less than 0.001 percent chloride and less than 0.0002 percent chlorate. The chloride was determined by silver chloride turbidity and the test for chlorate was based on the reaction of chlorate with chloride in acid solution to produce chlorine which was detected with *o*-tolidine. Comparison of the calculated and measured concentration of the ten solutions showed that: (a) the concentration of rubidium ion as determined by this method agreed to within 0.01 percent of the calculated rubidium concentration, (b) systematic errors were negligible, and (c) the analyses of the ten solutions were of equal precision.

From these analyses and from the analyses of the separated isotope solutions, the standard deviation of an individual measurement of the concentration of a rubidium solution was computed to be 0.0000172 meq/g sol, with 36 degrees of freedom. The standard error of the average of four determinations is therefore 0.0000086 meq/g sol and the uncertainty of the concentration is  $2.03 \times 0.0000086$  or 0.0000162 meq/g sol at the 95 percent confidence level. This corresponds to an uncertainty of 0.010 percent for solutions containing 0.16 meq Rb/g sol.

## 2.4 Isotopic Analyses of the Separated Isotope Solutions

The separated isotope solutions were analyzed four times each on each instrument. Sources were dismantled, cleaned and reassembled between the analyses of the two solutions, as a protection against the possibility of cross-contamination from the source parts. Except for the sake of complete security, the cleanings were not really necessary. Tests showed that the two separated isotope solutions could be analyzed back-to-back on the same source with no measurable "cross-talk."

The isotopic compositions of the separated isotopes are given in table 3. They have been corrected for mass spectrometric bias, with changes becoming negligible after three rounds of iteration. Instrumental uncertainties, such as recorder dead-zone and non-linearity, make it highly improbable that any ratio can be measured to better than 0.00002. In view of this, the errors attached to the numbers in table 3 are based on errors of 0.00002 in the ratio determinations, even though the calculated 95 percent confidence limits of the ratio are well below this figure.

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

Separated isotope	Isotopic composition (atom percent)
"Rb 85" <sup>85</sup> Rb	99.8398 ± 0.0020
<sup>87</sup> Rb	0.1602 ± 0.0020
"Rb 87" <sup>85</sup> Rb	0.8433 ± 0.0020
<sup>87</sup> Rb	99.1567 ± 0.0020

<sup>a</sup> The uncertainties are based on a minimum error of 0.00002 for the ratio determinations. The calculated 95 percent confidence limits are well below this value.

The isotopic compositions reported by ORNL are: "Rb 85",  $99.85 \pm 0.02$  atom percent <sup>85</sup>Rb and  $0.15 \pm 0.02$  atom percent <sup>87</sup>Rb; "Rb 87",  $0.84 \pm 0.02$  atom percent <sup>85</sup>Rb and  $99.16 \pm 0.02$  atom percent <sup>87</sup>Rb. The ORNL limits quoted express the precision of the measurements. From known sources of systematic errors, the absolute error is estimated by ORNL to be less than 1 percent.

## 2.5. Preparation of the Calibration Samples

Six calibration samples were prepared by mixing weighed portions of the "Rb 85" and "Rb 87" solutions to produce four <sup>85</sup>Rb/<sup>87</sup>Rb ratios of about 2.6, approximately the natural ratio, and two <sup>85</sup>Rb/<sup>87</sup>Rb ratios of about 1. The portions were withdrawn from the flasks and weighed in the manner previously described. To eliminate any possibility of change in concentration of the isotope solutions with time, the portions for the calibration samples were withdrawn from the flasks on the same day that the samples for determining the rubidium concentrations were withdrawn.

Table 4 shows the composition of these calibration samples. The isotopic ratio of each calibration sample

was calculated from the isotopic analyses of separated isotopes and the meq's of rubidium from each separated isotope solution.

Each calibration sample was thoroughly mixed by stirring and evaporated to dryness on a hot plate. The calibration samples were then taken up in water and diluted so that 1 cm<sup>3</sup> of solution contained 2 mg of rubidium. Portions of these solutions were further diluted so that final solutions contained 10 μg of Rb/cm<sup>3</sup>. A second portion of each of the 2 mg/cm<sup>3</sup> calibration standards were diluted with 2 percent hydrochloric acid so that the final solutions contained 10 μg Rb/cm<sup>3</sup>. The "neutral" calibration samples were used for one set of analyses and the "acid" calibration samples were used for the other set.

TABLE 4. Composition of rubidium calibration samples

Sample number	Isotope solution	Wt soln	Concentration of solution Rb/g soln	Rubidium	Isotopic ratio
	Rb	g	meq	meq	<sup>85</sup> Rb/ <sup>87</sup> Rb
1	85	9.45359	0.156436	1.478882	2.59723
	87	3.44230	.166405	0.572816	
2	85	5.17690	.156436	.809854	1.02142
	87	4.82990	.166405	.803720	
3	85	9.66166	.156436	1.511431	2.63381
	87	3.46884	.166405	0.577232	
4	85	8.54773	.156436	1.337173	2.55500
	87	3.16429	.166405	0.526554	
5	85	4.63494	.156436	.725071	1.01470
	87	4.35317	.166405	.724389	
6	85	9.44640	.156436	1.477757	2.62705
	87	3.40035	.166405	0.565835	

## 2.6. Preparation of Standard Sample

The standard material used for this work was NBS Standard Reference Material 727, Rubidium Chloride. Solutions of this material were prepared by taking a weighed portion into solution with water and diluting so that 1 cm<sup>3</sup> contained 2 mg of rubidium. One standard solution was prepared by diluting a portion of this solution so that the final concentration was 10 μg Rb/g sol. This standard was used with the "neutral" calibration samples. A second standard solution was prepared by diluting a portion of the 2 mg/cm<sup>3</sup> standard to 10 μg/cm<sup>3</sup> with 2 percent hydrochloric acid. This standard was used with the "acid" calibration samples.

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

Two complete sets of analyses of the calibration mixes and standard sample were made, one by operator I using instrument #4 and "acid" sample solutions and one by operator II using instrument #5 and "neutral" sample solutions. Each set consisted of 24 analyses of the standard sample made in a simple alternating pattern with four analyses each of the six calibration mixes.

## 3. Results and Discussion

The results for the six calibration mixes are summarized in table 5. There are no statistically significant differences between any of the values. The slight differences between the 1:1 and 2.6:1 samples are not significant.

TABLE 5. Determination of mass spectrometer bias

Calibration sample No.	Isotopic ratio <sup>85</sup> Rb/ <sup>87</sup> Rb			Correction factor	
	Calculated	Operator I	Operator II	Operator I	Operator II
1	2.59723	2.61022	2.61369	0.995024	0.993704
2	1.02142	1.02638	1.02702	.995172	.994545
3	2.63381	2.64762	2.65195	.994785	.993161
4	2.55500	2.56754	2.57025	.995115	.994066
5	1.01470	1.01948	1.02043	.995312	.994388
6	2.62705	2.64039	2.64445	.994948	.993421
Mean values of correction factors.....				0.995059	0.993881

The results given in table 6 include the observed and corrected experimental  $^{85}\text{Rb}/^{87}\text{Rb}$  values for the standard sample as well as the final absolute value for this ratio, with uncertainty components.

The calculation of the atomic weight of rubidium is summarized in table 7. Shields et al. [11], detected no variations in the isotopic composition of samples of rubidium from various localities and origins, so the atomic weight of rubidium should be constant within the stated experimental limits. The half-life of  $^{87}\text{Rb}$  is sufficiently large so that the decay of this isotope is of no immediate consequence with respect to changes in the absolute ratio and atomic weight of this element with time.

TABLE 6. Observed and corrected  $^{85}\text{Rb}/^{87}\text{Rb}$  values for the standard sample

Observed ratios		Correction factor	Corrected ratios
Operator I.....	2.60586	0.995059	2.59298
Operator II.....	2.60827	.993881	2.59231

Mean..... 2.59265 ± 0.00170

Uncertainty components:

95% confidence limits on ratio determinations.....	± 0.00107
Bounds due to possible systematic error in composition of separated isotopes.....	± 0.00024
Bounds due to possible systematic error in chemical analyses.....	± 0.00039

TABLE 7. Summary calculations of the atomic weight of rubidium

Value	Overall limit of error <sup>a</sup>	Uncertainty components		
		Mass spectrometric analytical error	Possible systematic error in composition of separated isotopes	Possible systematic error in chemical analysis
Atomic weight = 85.46776.....	± 0.00026	± 0.00016	± 0.00005	± 0.00005
Nuclidic masses [19]				
( <sup>12</sup> C = 12)				
<sup>85</sup> Rb = 84.911800.....	± 0.000005			
<sup>87</sup> Rb = 86.909186.....	± 0.000003			
Atomic percent				
<sup>85</sup> Rb = 72.1654.....	± 0.0132	± 0.0082	± 0.0020	± 0.0030
<sup>87</sup> Rb = 27.8346.....	± 0.0132	± 0.0082	± 0.0020	± 0.0030
Isotopic ratios <sup>b</sup>				
<sup>85</sup> Rb/ <sup>87</sup> Rb = 2.59265.....	± 0.00170	± 0.00107	± 0.00024	± 0.00039

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

<sup>b</sup> From table 3.

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