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MASS SPECTROMETER MEMORY REFINEMENTS REQUIRED FOR ULTRA-PRECISE UF_6 RATIO MEASUREMENTS

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R. F. Smith
J. M. Jackson

Union Carbide Corporation, Nuclear Division
Paducah Gaseous Diffusion Plant
Paducah, Kentucky 42001

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ABSTRACT

Empirical data demonstrate that a refined memory equation is applicable for precise isotopic ratio measurements of uranium hexafluoride by mass spectrometer. Ultra-high precision mass spectrometer ratio measurements of UF_6 are not appreciably limited by the ion source memory level provided appropriate slope and ratio corrections are applied to the memory factors.

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INTRODUCTION

Uranium hexafluoride molecules, entering the mass spectrometer, exchange with the molecules remaining there from the previous sample introduction, thereby resulting in the phenomenon known as mass spectrometer memory effect. Thus, memory is the inability of the spectrometer to completely forget the isotopic composition of the sample previously analyzed. Any sample introduction is biased in the direction of the isotopic concentration of the previous sample. Therefore, an observed spectrometer ratio of isotopic mol ratios is always lower than the true mol ratio.

There are other possible measurement biases such as that resulting from the inability of the spectrometer to completely resolve the ion peaks. It is practical to determine the memory factor in such a way that it includes UF_6 exchange in the spectrometer, resolution errors, and any other unidentified biases, thereby consolidating all errors in one correction factor. This memory factor is determined by measuring the ratio of isotopic mol ratios for two standards, and calculating memory from the following equation:

$$M = \frac{R - 1}{R_0 - 1} \qquad (1)$$

where:

M = Memory factor = 1 + % Memory

R = True ratio of mol ratios for standards

R_0 = Measured ratio of mol ratios for standards.

It has been known since the early days of uranium-235 enrichment that the memory factor increases as the isotopic concentration decreases. In 1969, G. L. Ragan issued a draft of derivations showing that memory varied directly with R_0, and those derivations were subsequently published as Appendix D of an internal report.[1] That same year, C. Sulfridge wrote Limitations On Mass Spectrometer Memory Corrections[2] in which he defined guidelines for performing isotopic measurements without appreciable memory error. To our knowledge, refinements to the conventional memory factor were not utilized until recently when Paducah Gaseous Diffusion Plant (PGDP) personnel performed ultra-precise ratio measurements on spectrometers with up to 10% memory.

DISCUSSION

Mass spectrometers used for ultra-precise UF_6 ratio measurements will be described briefly followed by a cursory description of the analytical procedure. Next, the conventional memory factor measurement procedure will be explored followed by a more detailed treatment of procedures for refining the memory factor. Finally, statistics will be presented to demonstrate quality of measurements.

APPARATUS

The two mass spectrometers used for ultra-precise isotope ratio measurements at the Isotopic Measurements Laboratory were designed and built by C. Sulfridge and A. Langdon of the ORGDP Analytical Services Laboratory under the direction of L. A. Smith. The analyzer is of the first-order angular focusing type with a 90° sector magnetic field and a 40-cm radius of curvature. An adaptation of the molecular beam ion source is utilized to minimize memory effect without limiting productivity. Each spectrometer is computer controlled with a Hewlett-Packard 9820A calculator for automatic operation.

MEASUREMENT PROCEDURE

To evaluate barrier performance, ultra-precise isotope ratio measurements are required. Such measurements are made by ionizing UF_6 and comparing the ratio of mol ratios, $(^{235}UF_5{}^+)/(^{234}UF_5{}^+ + {}^{236}UF_5{}^+ + {}^{238}UF_5{}^+)$, of a top test sample to that of a corresponding bottom test sample. Top and bottom sample designations merely signify relative isotopic levels. The top sample is taken from a higher point in the enrichment cascade than the bottom sample. A single determination consists of the following top sample readings (T) and bottom sample readings (B): 100B, 100T, 100B, 100T, 100B, and 100T. The first 100B is automatically excluded from the calculation, leaving 3 top sample and 2 bottom sample introductions to compute the ratio. A spectrometer measurement consists of 9 determinations, the first of which is automatically excluded from calculating the average ratio. A similar measurement on the second mass spectrometer normally completes a sample pair analysis except for memory corrections. Instrument time is less than 2 hr per spectrometer, and operator time is about 10 min.

CONVENTIONAL MEMORY FACTOR

As discussed in the introduction to this report, memory is the inability of the mass spectrometer ion source to completely forget the isotopic composition of the sample previously analyzed. In addition to UF_6 exchange in the ion source, there are other possible measurement biases such as that resulting from the inability of the spectrometer to completely resolve the ion peaks. The memory factor is determined empirically such that it includes UF_6 exchange, resolution error, and any other unidentified biases, thereby consolidating all errors. The bias or memory factor is determined by measuring the ratio of mol ratios, $(235UF_5^+)/({}^{234}UF_5^+ + {}^{236}UF_5^+ + {}^{238}UF_5^+)$, of an isotopic standard to that of a lower isotopic standard, and the memory factor is calculated from the following equation:

$$M = \frac{R - 1}{R_0 - 1} \qquad (2)$$

where:

M = Memory factor = 1 + % ion source memory

R = True ratio of mol ratios for standards

R_0 = Observed ratio of mol ratios for standards.

Spectrometer memory changes with time so it must be measured frequently to attain maximum accuracy and precision. At the PGDP Isotopic Measurements Laboratory, sample pairs are analyzed on the day and evening shifts, and memory standard pairs are analyzed unattended on the midnight shift. The last eight memory determinations before the beginning of the day shift are averaged with the first eight after the end of the evening shift to obtain a bracketed memory factor for application to sample pairs analyzed that day. The same factor may be applied to as many as eight sample pairs since less than 2 hr of instrument time is required for each.

Typically, the memory of a 40-cm spectrometer with a freshly cleaned ion source is less than 1% at the natural isotopic concentration level. If the spectrometer is operated continuously for five days per week and permitted to rest 2 days, the memory increases each week. Recently, a PGDP Isotopic Measurements Laboratory ion source was removed after 15 months and 6 days operation (21,730 determinations). During the life of the source, memory at the natural isotopic concentration level increased from about 0.5% to 5%. It should be pointed out that memory drops during the 2 days of rest each week, and it takes a few days of the following week to attain the plateau of the previous week.

Appendix A shows how the memory factor increases as the isotopic concentration decreases. It will be observed that memory increased from 3.6% to 10.5% while traversing the uranium-235 isotopic range from 1.82 to 0.23 wt % on a specific ion source with 15 months analytical service. Correcting for memory slope is complicated by the fact that it does not increase linearly as uranium-235 decreases, but increases faster at the lower uranium-235 assay levels. Although isotopic standard values are certified to 0.02% of themselves by preparation and calibration techniques, this uncertainty is enough to appreciably bias a memory measurement as the ratio approaches unity. Isotopic standard uncertainty contributes less error to the memory factor measurement as the standard ratio increases. A ratio of 1.10 to 1.15 is practical for high precision memory measurements. Thus, to evaluate the conventional memory factor for a sample pair, two isotopic standards are selected with a ratio of about 1.10 and an average isotopic value approximately that of the sample pair.

Since 1969, it has been known that memory varies directly with the ratio being measured. As the ratio of isotopic mol ratios increases, so does percent memory. Sample pair ratio measurements are generally in the range of 1.02 to 1.04 compared to a ratio range of 1.10 to 1.15 for memory standards. Thus, for ultra-high precision measurements, memory measured on the higher ratio must be corrected before it is applied to the lower ratios.

The conventional memory factor is perfectly adequate for routine measurements where the ultimate in precision is not required. It is also adequate for ultra-high precision measurements if certain parameters are controlled, one of which involves maintaining memory below about two percent. A spectrometer with a memory less than 2% at the natural isotopic concentration level may have memory as high as 5% at 0.2 wt % uranium-235, and many PGDP measurements are on sample pairs with assays between 0.2 and 0.3 wt % uranium-235. Thus, holding memory below 2% at the PGDP Isotopic Measurements Laboratory presents troubleshooting and operational difficulties which limit productivity. For example, the recent ion source that operated over 15 months would have been removed for high memory after a small fraction of its life.

Even at low memories, small biases exist in reported isotope ratio measurements if ratio and slope corrections are not applied. It is more practical at the PGDP Isotopic Measurements Laboratory to apply corrections at all levels of memory, thereby permitting operation at higher memory levels and providing accuracy throughout the range. For these reasons, refinements to the memory factor were initiated in December, 1978, and those will be discussed in the next section of this report.

MEMORY FACTOR REFINEMENTS

As described earlier, the conventional memory factor is measured using two known isotopic standards. Two corrections to that factor are required to make it applicable to a sample pair. A slope correction is required to correct the factor to the average uranium-235 assay of the sample pair. A ratio correction is required to correct the factor to the sample ratio.

Slope Correction

Isotopic standards are prepared at about 5% intervals throughout the cascade isotopic concentration range. Thus, the ratio of adjacent standards is in the order of 1.05. Two standards selected for a memory factor measurement usually have a ratio of 1.10 to 1.15.

The slope correction is a linear interpolation to the average sample assay from two pairs of memory standards with average uranium-235 assays bracketing that of the sample pair. If the selected memory standards have an average uranium-235 assay less than the sample average, slope memory standards are selected with higher assay and vice versa. As described previously, the regular memory standards are analyzed unattended on the midnight shift. The ratio of slope memory standards is only measured once per spectrometer for each series of related samples. That measurement is always performed adjacent to the regular memory standard ratio measurement.

It can be shown that the following equation defines linear interpolation to the average sample assay:

$$\Delta m = \frac{(X - X_m)}{(X_s - X_m)} (m_s - m) \qquad (3)$$

where:

Δm = slope correction in % memory

X = median ^{235}U assay of sample pair

X_m = median ^{235}U assay of memory standard pair

X_s = median ^{235}U assay of slope standard pair

m_s = % memory measured on slope standards

m = % memory measured on regular memory standards

The long term average Δm for a high memory source is about 0.06% with a range of 0 to 0.2%. For a source with memory less than 2%, the long term average Δm is about 0.02% with a range of 0 to 0.1%.

Ratio Correction

Memory factor measurements are performed on standard pairs with ratios ranging from about 1.10 to 1.15 while sample pair measurements are usually in the range of 1.02 to 1.04. G. L. Ragan[1] has shown theoretically that the memory factor is directly proportional to the sample ratio. Appendix B summarizes his original derivations and adaptations which have been effected by C. Sulfridge[2] and Paducah Gaseous Diffusion Plant personnel.

At the PGDP laboratory, the ratio correction for memory is calculated from the following equation:

$$m' \simeq m \frac{(R' + 1)}{(R + 1)} \qquad (4)$$

where:

m' = % memory for sample pair

m = % memory for standard pair

R' = Ratio of mol ratios for sample pair

R = Ratio of mol ratios for standard pair

If standard and sample ratios were 1.10 and 1.03 respectively, the correction factor $(R' + 1)/(R + 1)$, would be 0.967. Standard memory would be multiplied by this factor to get sample memory. For standard memories of 1% and 10%, sample memories would be 0.97% and 9.67%, respectively.

Empirical data have been accumulated over a period of months to check the accuracy of the ratio correction. In each empirical test, two pairs of standards were selected; one pair with a much higher ratio of isotopic mol ratios than the other. Standards were selected such that the average uranium-235 assay of the two test pairs were about the same to preclude appreciable slope errors. Memory measured on the high ratio standard pair was corrected by the ratio correction equation and compared to the corresponding low ratio memory measurement. Data are summarized in Appendix C and there is no apparent bias in the ratio correction equation. Based on 23 comparisons, there is no significant difference between the memory measured on the low ratio standard pair and that calculated from the measurement on the high ratio standard pair ($\bar{d} \pm LE_{\bar{d}} = +0.002 \pm 0.04$). Thus, when ratio corrections are applied to high memory spectrometer ion sources, unbiased isotope ratio measurements result. The 95% symmetrical confidence interval of a memory difference calculated in this manner is about 0.2% ($LE_d = \pm 0.19\%$ memory). Thus, memory uncertainty does not prevent ultra-high precision isotope ratio measurements.

It will be noted in Appendix C that a uranium-235 assay range from about 0.13 to 1.75 wt % was covered in comparing low and high ratio standards. The equation developed for memory ratio correction is apparently good at low uranium-235 concentrations as well as at higher levels.

Composite Memory Correction

Slope and ratio corrections are combined to get the composite correction for application to isotope ratio measurements. The following equation suffices:

$$m' \approx m \frac{(R' + 1)}{(R + 1)} + \Delta m \qquad (5)$$

$$\text{and } M' = 1 + m'$$

where:

m' = % memory for sample pair

M' = memory factor for sample pair

m = % memory for standard pair

R' = Ratio of isotopic mol ratios for sample pair

R = Ratio of isotopic mol ratios for standard pair

Δm = slope correction in % memory

DEMONSTRATED PRECISIONS

Analytical data on barrier performance measurements completed from February through June 1979 have been evaluated to determine agreement between two mass spectrometers. During that time, ion sources in Spectrometer #7 exhibited memories ranging from 0.53% to 4.31%. Memory range on the source in Spectrometer #8 was 3.28% to 10.61%. Based on 176 ultra high precision measurement comparisons, there is no significant difference between Spectrometer #7 and Spectrometer #8 ($\bar{d} \pm LE_{\bar{d}} = +0.000004 \pm 0.000008$). From these comparisons, the 95% symmetrical confidence interval of a single difference is ±0.00011, which indicates a precision of about ±0.00006 on the average of measurements from both spectrometers. Typical data are summarized in Appendix D. Ratio measurements on high memory spectrometer ion sources are shown to be in good agreement with those on low memory ion sources.

CONCLUSIONS

An equation has been devised which corrects spectrometer memory for slope and ratio biases. Empirical data indicate the equation is applicable for uranium hexafluoride over the isotopic assay range 0.13 to 1.74 wt % uranium-235. Since the equation is applicable through the depleted isotopic concentration range where memory is higher, its applicability up through power reactor feed enrichments is highly probable.

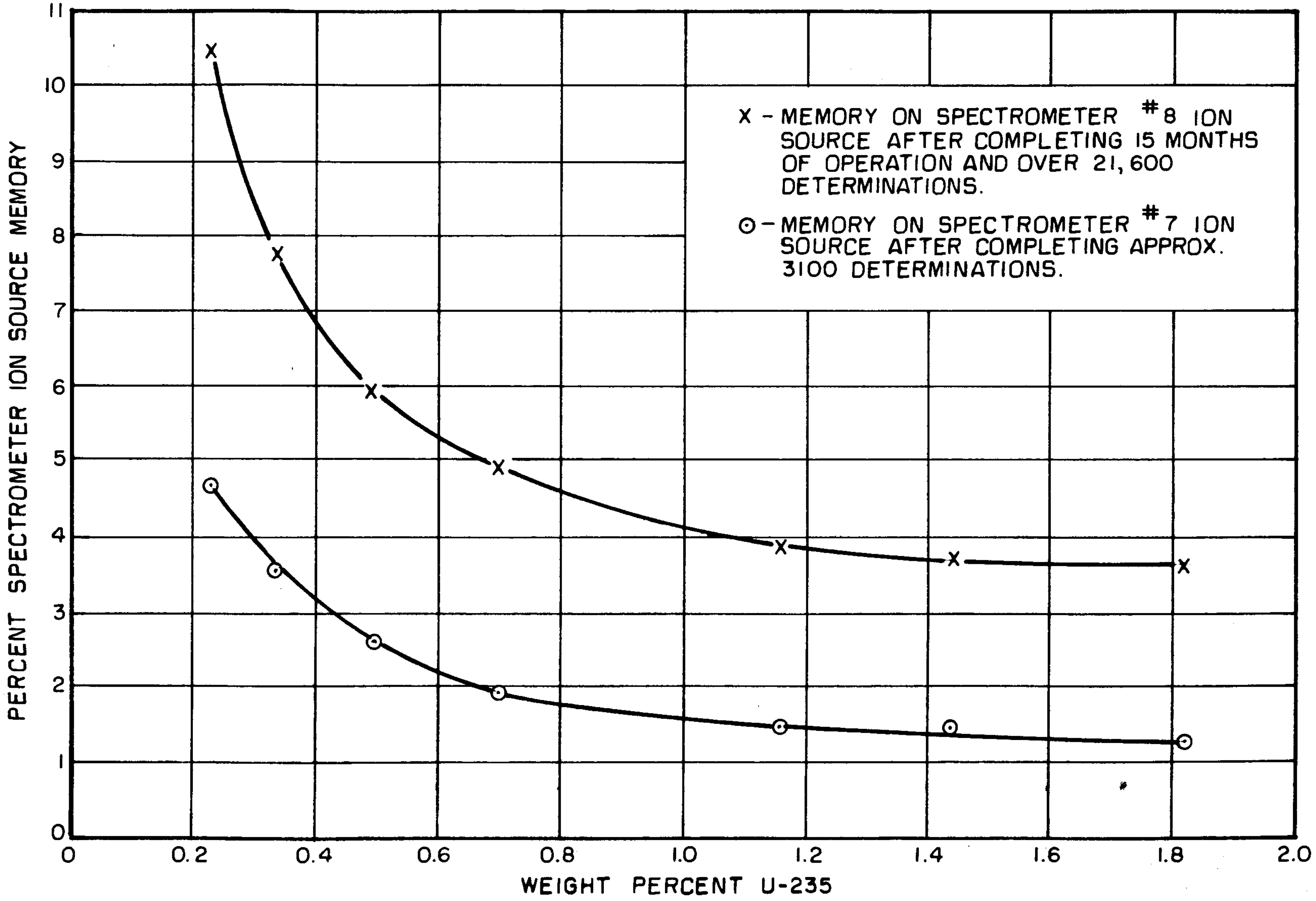
When slope and ratio corrections were applied to mass spectrometer memory factors, ultra-precise ratio measurements were obtained on spectrometers with up to 10% memory. Based on 176 ratio measurement comparisons, there was no significant difference between two spectrometers even though their memories differed by as much as 6% ($\bar{d} \pm LE_{\bar{d}} = 0.000004 \pm 0.000008$). Considering agreement of that data, the 95% symmetrical confidence interval of a single ratio difference was ± 0.00011. Thus, a confidence interval of about ± 0.00006 was indicated for the average of two ratio measurements, one from each of two spectrometers.

REFERENCES

1. Ragan, G. L., Measurement of α (^{233}U) in MSRE, Union Carbide Corporation, Nuclear Division, ORNL, Oak Ridge, Tennessee, March 1969 (MSR-69-20, Appendix D).

2. Sulfridge, C., Unpublished Calculations and Notes Covering Limitations on Mass Spectrometer Memory Corrections, Union Carbide Corporation, Nuclear Division, Oak Ridge Gaseous Diffusion Plant, 1969.

EMPIRICAL DATA SHOWING SPECTROMETER ION SOURCE MEMORY VARIABILITY RELATIVE TO U-235 ISOTOPIC CONCENTRATION



APPENDIX B

RATIO CORRECTION EQUATION

Assume that a fraction, v, of the gas pressure in the ionization region is contributed by remnants of the previously run sample and that v is constant throughout a series of determinations. Further, assume that relatively low concentrations of minor isotopes (^{234}U and ^{236}U) can be neglected in derivations without appreciable error in memory factor equations.

Let: N_5' = mol fraction ^{235}U in top memory standard
N_8' = mol fraction ^{238}U in top memory standard
N_5 = mol fraction ^{235}U in bottom memory standard
N_8 = mol fraction ^{238}U in bottom memory standard

Then: $R = (N_5'/N_8')/(N_5/N_8) = N_5'N_8/N_5N_8'$ = true ratio

$$R_0 = \frac{N_5'(1 - v) + N_5v}{N_5(1 - v) + N_5'v} \cdot \frac{N_8(1 - v) + N_8'v}{N_8'(1 - v) + N_8v} = \text{observed ratio}$$

Divide numerator and denominator by (1 - v) and
set $n = v/(1 - v)$

$$R_0 = \frac{N_5' + nN_5}{N_5 + nN_5'} \cdot \frac{N_8 + nN_8'}{N_8' + nN_8}$$

Manipulation of these equations yields the expression

$$M = \frac{R - 1}{R_0 - 1} = \frac{1 + n\left(\frac{N_8'}{N_8}\right)\left(R + \frac{N_8}{N_8'}\right) + n^2R}{1 - n^2}$$

N_8'/N_8 and N_8/N_8' can be approximated by unity without significant error in the memory term. Equation can then be simplified to:

$$M \approx \frac{1 + nR}{1 - n}$$

"M" as defined here is the memory factor which is 1 + % memory. Let m = % memory

$$m \approx \frac{1 + nR}{1 - n} - 1 \quad \approx \quad \left(\frac{n}{1 - n}\right) (R + 1)$$

Since "m" is defined as % memory of standard pair and R the ratio of those standards, let m' and R' equal memory and ratio of sample pair. Then divide m' by m

$$\frac{m'}{m} \approx \frac{R' + 1}{R + 1}$$

or $$m' \approx m \frac{(R' + 1)}{(R + 1)}$$

Thus, the ratio correction factor for memory becomes $\frac{(R' + 1)}{(R + 1)}$.

If standard and sample ratios were 1.10 and 1.03 respectively, the correction factor would be 0.967. Standard memory would be multiplied by this factor to get sample memory. The following table shows how the ratio correction effects memory at various levels.

Measured memory standard ratio = 1.10	Corrected memory applied to sample ratio of 1.03
1%	0.97%
2%	1.93%
3%	2.90%
5%	4.84%
8%	7.74%
10%	9.67%

APPENDIX C

EMPIRICAL DATA CERTIFYING RATIO CORRECTION FOR MEMORY

Standard Ratios	Measured % Memory Small Ratio	% Memory, Large Ratio		% Difference Measured-Calculated
		Observed, m	Calculated, m'	
H-.58178/H.35050 = 1.65986	1.50	1.86	1.46	+0.04
H-.48931/H-.44702 = 1.09460	7.41	9.34	7.35	+0.06
H-1.7488/H-1.1920 = 1.46711	0.84	0.97	0.83	+0.01
H-1.5313/H-1.3902 = 1.10150	3.20	3.68	3.14	+0.06
H-.58178/H-.42749 = 1.36092	3.81	4.46	3.89	-0.08
H-.51948/H-.48939 = 1.06148	7.00	8.21	7.17	-0.17
H-.64128/H-.38621 = 1.66044	1.40	1.81	1.43	-0.03
H-.54074/H-.48931 = 1.10511	5.84	7.59	6.00	-0.16
H-.64128/H-.35050 = 1.82961	1.44	1.90	1.42	+0.02
H-.51941/H-.46867 = 1.10826	6.96	9.24	6.88	+0.08
H-.58178/H-.33393 = 1.74222	1.40	2.02	1.51	-0.11
H-.46869/H-.44704 = 1.04843	6.96	9.44	7.05	-0.09
H-.87701/H-.64128 = 1.36759	1.56	1.81	1.62	-0.06
H-.80204/H-.71638 = 1.11957	2.25	2.48	2.22	+0.03
H-.44704/H-.25000 = 1.78816	2.45	3.31	2.43	+0.02
H-.35050/H-.33393 = 1.04962	3.36	4.50	3.31	+0.05
H-.87701/H-.58178 = 1.50746	1.51	1.91	1.55	-0.04
H-.74053/H-.71638 = 1.03371	2.10	2.47	2.00	+0.10
H-1.4427/H-.99304 = 1.45281	1.14	1.37	1.14	0.00
H-1.2368/H-1.1920 = 1.03758				
H-.38621/H-.20724 = 1.86359	3.56	4.78	3.42	+0.14
H-.30049/H-.28608 = 1.05037	8.61	12.05	8.63	-0.02
H-.21900/H-.13051 = 1.67803	5.03	6.30	4.82	+0.21
H-.18035/H-.17177 = 1.04995	10.96	14.35	10.98	-0.02

APPENDIX D

TYPICAL ISOTOPE RATIO MEASUREMENTS SHOWING SPECTROMETER AGREEMENT WITH CONVENTIONAL AND REFINED MEMORY CORRECTIONS

Spectrometer No.	% Memory	R_o	R	
			Conventional Memory Correction	Refined Memory Correction
7	3.24	1.02404	1.02486	1.02482
8	10.61	1.02247	1.02497	1.02485
7	3.24	1.02402	1.02484	1.02480
8	10.61	1.02247	1.02497	1.02485
7	3.24	1.02403	1.02485	1.02481
8	10.61	1.02247	1.02497	1.02485
7	3.24	1.02409	1.02491	1.02487
8	10.61	1.02247	1.02497	1.02485
	Spect. #7 Avg.	1.02404	1.02486	1.02482
	Spect. #8 Avg.	1.02247	1.02497	1.02485
7	0.88	1.02478	1.02501	1.02500
8	8.33	1.02305	1.02505	1.02497
7	0.88	1.02471	1.02494	1.02493
8	8.45	1.02296	1.02498	1.02490
7	0.88	1.02472	1.02495	1.02494
8	8.33	1.02301	1.02500	1.02493
7	0.92	1.02471	1.02495	1.02494
8	8.45	1.02299	1.02501	1.02493
	Spect. #7 Avg.	1.02473	1.02496	1.02495
	Spect. #8 Avg.	1.02300	1.02501	1.02493

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