

CONF-770575-3



ANALYTICAL CAPABILITY
OF THE
URANIUM HEXAFLUORIDE MASS SPECTROMETER*

By

G. F. Kauffman
Mass Spectrometry Department
Technical Division

June 27, 1977

*By acceptance of this article, the publisher and/or recipient acknowledges the U.S. Government's right to retain a nonexclusive, royalty-free license in and to any copyright covering this paper."

* Presented at the Twenty-Fifth Annual Conference on Mass Spectrometry and Allied Topics, Washington, D.C., May 29 - June 3, 1977.

GOODYEAR ATOMIC CORPORATION

P. O. BOX 628

PIKETON, OHIO 45661

ACTING UNDER CONTRACT EY-76-C-05-0001
WITH THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ANALYTICAL CAPABILITY OF THE URANIUM HEXAFLUORIDE MASS SPECTROMETER*

G. F. Kauffman
 Mass Spectrometry Department
 Goodyear Atomic Corporation, Piketon, Ohio 45661

The UF_6 mass spectrometer is an indispensable instrument at the gaseous diffusion plants where vast quantities of UF_6 are processed and thousands of uranium isotopic determinations must be made every month. The electron impact ion source permits rapid exchange of samples and the dual collector provides a rapid and precise measurement of the ratio of two ion currents. The analyses are six-entry relative analyses in which the readings obtained on a sample having unknown isotopic composition are compared to readings obtained on an isotopic standard or to readings obtained on two bracketing standards. About 12 minutes are required for a determination and the analytical precision is such that the relative standard deviation of a single determination is ± 0.05 percent or better. However, the mass spectrometer readings are biased. In the literature the bias is blamed on sample interaction or "memory." In this discussion, the nonlinearity of the relationship between the mass spectrometer ratio reading and the isotopic mole ratio of the sample is shown to be responsible for the major portion of the bias, while sample interaction, amplifier zeros, secondary electron emission, and the beam width also influence the magnitude of the bias.

Ironically, the dual collector is responsible for the nonlinearity as shown in Figure 1. The mass spectrometer cannot completely separate the two ion beams, and a large fraction, d , of the ions of mass M_1 pass through the collector slit along with a small fraction, g , of the ions of mass M_2 . Thus, the ion signal at the second detector plate is $[dN_{M_1} + gN_{M_2}]$ while the signal at the first detector plate is $[(1-d)N_{M_1} + (1-g)N_{M_2}]$. If the isotopic mole ratio of the sample N_{M_1}/N_{M_2} is designated as h , the mass spectrometer ratio reading is given by $r = (dh+g)/(1-d)h+(1-g)$. The mass spectrometer reading cannot be proportional to the isotopic mole ratio of the sample unless all of the ions of mass M_1 and none of the ions of mass M_2 pass through the slit, and this condition cannot be realized. The reading not only is not linear with respect to h , it is also a function of the coefficients d and g . The coefficients, in turn, are functions of the ion beam width. The relationship between the isotopic mole ratio and the mass spectrometer reading is shown in Figure 2. Readings r_1 and r_4 are obtained on samples having mole ratios h_1 and h_4 . The straight line passing through the points (h_1, r_1) and (h_4, r_4) has an intercept, r_0 . True sample interaction will decrease the value of r_4 , increase the value of r_1 , and increase the value of r_0 . A change in the amplifier zero will increase or decrease all values of r and result in a change in r_0 . Spurious signals resulting from secondary electron emission will cause changes in the relationship and a change in r_0 . A change in beam width will also change the relationship and the value of r_0 . In any case, however, the value of

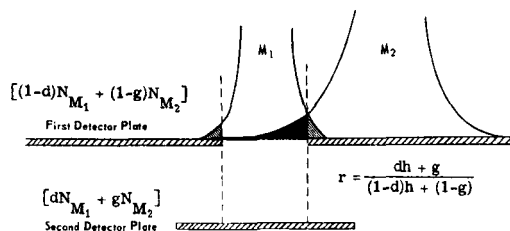


FIGURE 1 ION BEAM OVERLAP

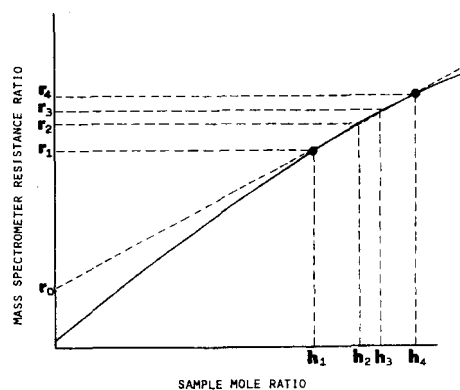


FIGURE 2 NONLINEARITY OF RESISTANCE RATIOS

NOTICE
 This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

*This work was performed under contract EY-76-C-05-0001 with the U.S. Energy Research and Development Administration.

r_0 should be determined from measurements obtained on a standard pair such as h_1 and h_2 , and this value should be subtracted from measurements obtained on sample-standard pairs such as h_3 and h_4 . The corrected ratio $(r_3 - r_0) / (r_2 - r_0)$ is equal to the ratio of sample mole ratios h_3/h_2 . In the double-standard method the intercept is automatically subtracted when the ratio of differences is calculated. Because the relationship between r and h is influenced by many operating parameters, the variability of bias is high. When direct comparisons are being made, frequent evaluations of r_0 are required. When the double-standard procedure is being used, unproductive evaluations of bias are not required.

Because the mass spectrometer ratio reading is a function of beam width, small differences in beam widths during an analysis represent an external source of random variation in the measurements. Figure 3 shows two of the family of curves resulting from changes in the coefficients d and g . The upper curve shows the relationship between r and h for a specific set of coefficients, d_1 and g_1 . For a different beam width the values of the coefficients will be different, and the lower curve represents the relationship for the set of coefficients, d_2 and g_2 . This means that, depending upon the beam width, the sample having the mole ratio h_A can have a resistance ratio of r_{A1} or r_{A2} and sample h_B can have r_{B1} or r_{B2} . In other words r_{A1} and r_{B1} are the result of one cause system, and r_{A2} and r_{B2} are the result of another cause system. During an analysis involving a comparison of the two samples, the observed ratio of resistance ratios could be either r_{B1}/r_{A2} or r_{B2}/r_{A1} , depending upon the beam widths associated with the measurements of h_B and h_A . Thus, the ratio of resistance ratios could be biased either high or low, and the bias would be completely random. Mass spectroscopists using UF_6 instruments always have recognized that the measured resistance ratio will be biased if the sample is "dirty"; i.e., if the sample contains enough impurities in the gas phase to cause a detectable increase in the ion source pressure reading. However, small differences in sample purity cannot be detected with source pressure measurements, and small changes in beam width cannot be prevented. The problem, as far as analytical precision is concerned, is that the beam widths are not necessarily the same when two samples are being compared; and one or both of the beam widths may be different when the samples are reanalyzed at a later date.

Figure 4 shows two mass scans of UF_6 samples made on an instrument having a radius of curvature of six inches. The isotopic concentrations of the two samples are identical, but the dashed line was obtained with a relatively pure sample and the solid line was obtained with a sample containing a contaminant; i.e., a "dirty" sample. When the dispersion is D_{R1} , the collector slit is located at S_1 , and the number of ions passing through the slit will be $[d_1N_5 + g_1N_8]$ for the pure sample, and $[d_2N_5 + g_2N_8]$ for the impure sample. The coefficient d_2 will be slightly less than d_1 , but g_2 will be appreciably larger than g_1 . This means that the observed resistance ratio for the impure sample will be biased high with respect to the observed ratio for the pure sample. The $^{235}UF_5^+$ ion distribution would be shifted to the right to correspond to D_{R2} if the beam widths remained the same, but the dispersion could be increased; i.e., improved resolving power. The collector slit would now be located at S_2 . At this distance, the tail of the large $^{238}UF_5^+$ ion beam of the impure sample is only slightly larger than the tail of the pure sample. This means that the difference in the values of the coefficients g_1 and g_2 would be smaller, and that the bias between the observed resistance ratios would be greatly reduced. This hypothesis was the

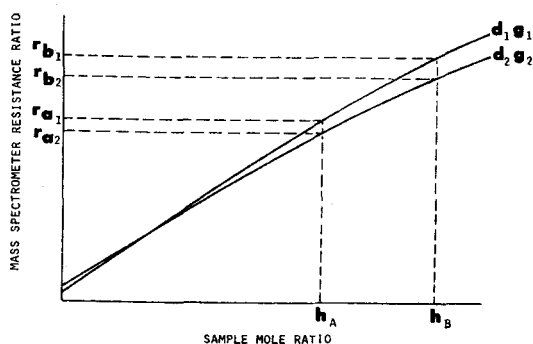


FIGURE 3 EFFECT OF BEAM WIDTH VARIATIONS ON RESISTANCE RATIOS

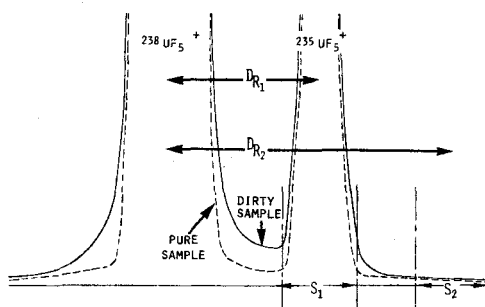


FIGURE 4 EFFECT OF SAMPLE PURITY ON BEAM WIDTH

justification for a project covering the design and fabrication of a high-resolution mass spectrometer at the Goodyear Atomic Corporation. The details of the instrument are presented in a report, GAT-655,¹ and are also available in an engineering materials package² containing reproducible drawings and photographs.

The beam width (99.9% of the ions) of the 15-inch, second-order refocusing mass spectrometer fabricated at Goodyear is 20 mils and the dispersion is 45 mils, while the beam width of the 6-inch instruments is 24 mils and the dispersion is 18 mils. The threefold increase in resolving power is sufficient to reduce the external variance to an insignificant level. It has been demonstrated that the ratio of mole ratios of a sample pair can be evaluated to 4 parts in 100,000 with only two hours of instrument time, or to 1 part in 100,000 with 39 hours of instrument time.

¹Kauffman, G. F., Lang, J., and Martin, W. E., "A Second-Order Refocusing 15-Inch Mass Spectrometer for Ultra-Precise Isotopic Ratio Measurements of Uranium Hexafluoride Samples," GAT-655, Goodyear Atomic Corporation, Piketon, Ohio, July 15, 1971.

²CAPE-2098, "High-Resolution, 15-Inch Mass Spectrometer," 1971.

GAT-655 and CAPE-2098 are both for sale from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Road, Springfield, VA 22151, USA.