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A THERMAL-EMISSION MASS SPECTROMETER FOR
RAPID AND ACCURATE DETERMINATION
OF URANIUM ISOTOPES

W. T. McBryde
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August 1978

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OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

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ABSTRACT

A 60-degree ($\pi/3$ -radian) magnetic-sector, 6-inch (152.4-mm) mass spectrometer has been designed and built for uranium isotopic analyses. The instrument uses a Nier-type geometry and has several improvements, both optically and electrically, which make it rapid and precise. Instrument control is good and the analytical results for uranium isotopes are excellent.

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SUMMARY

The main features of this thermal-emission instrument that are not found in many commercial designs are: an improved magnet, a power-input-controlled filament for thermal emission, and a different approach to ion-beam intensity measurements. The principle of function is essentially that of the commonly used 60-degree magnetic-sector spectrometer in that a small quantity (100 to 500 micrograms) of sample is dried on the filament and the uranium isotopes are mass resolved in the magnetic field after the beams are generated and conditioned in a more or less standard-lens-plate system. The usual defining slits are used in both the source and the receiver. An electron multiplier detects the individual isotope beams as they are rapidly positioned in the receiver resolving slit. Beam signals are integrated and reduced to isotope concentrations by machine computation.

INTRODUCTION

The most appropriate manner in which the isotopic analysis of uranium can be approached is mass spectrometry. Through the years, a number of developments have improved both the instruments and the methodology of isotopic analysis.

The principal objectives in seeking technological advance in isotopic mass spectrometry remain the same—rapid and precise analyses. Rapid isotope analyses have been emphasized with the application of nuclear safeguards requirements. The nature of the productive effort in the Oak Ridge Y-12 Plant^(a) demands that these objectives be pursued almost constantly.

In designing and building this spectrometer, it is believed that significant advances have been made in analyzing for isotopes in uranium while the precision has not been degraded; viz, for ^{235}U . It is implied that the application is directed toward the element uranium. However, as the technique is practiced and instruments of this type are built, additional elements may be added to the capability. A view of the mass spectrometer is presented in Figure 1.

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Figure 1. A THERMAL-EMISSION MASS SPECTROMETER FOR RAPID AND ACCURATE DETERMINATION OF URANIUM ISOTOPES.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the Department of Energy.

This work is, in part, an extension and improvement of an earlier effort which resulted in an ion-counting mass spectrometer for the rapid analysis of uranium concentrations in environmental waters.¹

DESIGN AND APPLICATION OF A THERMAL-EMISSION MASS SPECTROMETER

EXPERIMENTAL WORK

Preliminary Considerations

A review of the instruments now in use in the Y-12 Plant Laboratory led to the decision that the upgrade needed is in the ion-beam-intensity measurement and data-processing systems. The effort can be confined to certain specific improvements in only parts of these systems since much of the equipment, such as the amplifiers and voltage supplies, are currently of good quality. Specifically, real help would result from good emission control, a more homogeneous deflection field, and ion-beam measurements which are very close to being simultaneous. A previously constructed instrument using similar principles has been built in the Y-12 Plant Laboratory and is described in an earlier Y-12 document.¹ Normally, the mass resolution of these afocal-sector instruments is about 400 to 500 $M/\Delta M$, with the final resolving limit imposed by the width of the receiver slit. This resolution is quite adequate for measurements of the UO_2^+ species. Beam-intensity measurements currently made with a scanning system could be much improved by a system which ideally senses and measures all individual isotopic beams at the same time.

Instrument Design

Ion Source and Beam Conditioner - The vacuum lock² permits the insertion of a loaded filament and its extraction without pressurizing the rest of the ion optical system. The filament power supply is controlled by a newly designed power controller, which is an improvement over previous voltage or current-control devices.³ Power control involves both parameters (current and voltage) and compensates filament differences to give a more reproducible ion-beam intensity. The beam-conditioning system is precisely the same as that used for a number of years in this laboratory, which is the five-plate system designed by Nier^{4,5} for gas ionization and modified by Sladky⁶ for thermal ionization.

Flight-Tube Analyzer System - The flight tube and analyzer differ from most arrangements in that the hardware is actually machined to form the correct Y-axis curvature rather than by bending. Residual stresses are thus avoided, and warping can be eliminated along with various other irregularities. The inside surfaces of both the tube and analyzer are polished to a depth of some ten micrometers instead of using a very thin gold film which can be troublesome as the instrument becomes older. The tube and analyzer are fitted with resistive heater bands to provide bakeout periods when required. To make the analyzer adaptable to other applications, a 1/8-inch cajon fitting is provided at the top of the source section of the tube.

Receiver (detector) - The detector is a Dumont fourteen-stage multiplier. The ion beams pass through an adjustable (unilateral) slit which is open to a width equal to 1.1 times the beam width. The slit is thus said to be 110% open. Suppressor plates are not used since the detector is an electron multiplier. Although they are not used, suppressor plates are inserted to increase versatility in the instrument.

Magnetic Sector - The magnet⁷ of this instrument is essentially a 60-degree sector, the top of which is a "dished-in" hemisphere 6 inches (152.4 mm) in radius, while the bottom is a "dished-out" surface similar to the top. The shoes and end brace are one solid piece of iron. When the analyzer is placed in the pole gap, the top and bottom radii are concentric with the magnet poles in all three planes. (X, Y, and Z). Measurements with a Hall-effect probe show a very uniform field which contributes to the overall improved function of the instrument.

Beam-Intensity Measurements - The data-taking system incorporated into the new thermal instruments is a four-channel multiplexing system. The timing signals used to synchronously and rapidly switch from one isotope to another are derived from a data multiplexer housed in a double-wide NIM-bin module. This module supplies synchronized signals to a programmable high-voltage power supply and to a four-channel amplifier/integrator called the "quadrachannel analyzer". A block diagram of the electronics is presented in Figure 2. The data multiplexer is interfaced to a calculator for program control of the "start", "stop",

Figure 2. PRINCIPAL COMPONENTS OF THE MS-300 ELECTRONICS.

and "reset" signals. The ion-accelerating potential is altered by switching the reference signal at the rate of approximately 31 times per second, which means that each individual isotope is sampled 7.8 times per second, or 468 times per minute. At the time (see Figure 3) the

high voltage is switched, all amplifiers and integrators are gated off to allow a stabilizing time for the electrometer. The actual delay is 13 msec. At the end of this delay, the appropriate amplifier is gated "on" and allowed a 2-msec stabilizing period. At the end of this period, the associated integrator is gated "on" for a duration of 15 msec. The amplifier remains on for 2 msec following the conclusion of the integrators "on" period, then is gated "off". At the same instant, the high voltage is switched to the next voltage point, starting the cycle over with the next amplifier in the sequence. The accelerating voltage and amplifiers are switched in a triangular manner to smooth out variations in the ion-beam intensity.

The digital signals from the data multiplexer to the high-voltage power supply are optically coupled into an HV switch module. This module, through the use of solid-state switches,

Figure 3. FOUR-PEAK DATA-MULTIPLEXER TIMING DIAGRAM FOR THE MS-300.

converts the digital signals to a variable analog reference signal. This reference signal is adjustable from 0 to 10 V and is coupled to a fast programmable power supply whose positive output is connected to the floating negative side of a super-regulated HV power supply, the positive side of which is the ion-accelerating potential. The programmable power supply has a gain of five for the reference signals which gives a range of adjustment from 0 to 50 volts in its ion-accelerating potential.

Under program control, the calculator can "talk" to the high-voltage power supply. In small increments (mV steps), the calculator steps the high voltage up or down, depending upon the location within the program, by means of a 10-bit digital word being impressed upon the digital-to-analog converter located in the high-voltage switch. Each time the calculator steps the high voltage, it reads into the register the magnitude of the major isotope. Using various registers within the calculator to keep track of such things as the number of steps taken to reach 50% of the starting magnitude, direction of travel, and intensity readings, the calculator can determine precisely the location of the median of the major isotope. Once this location has been established, the high voltage is latched at the determined potential and a "start" signal is issued to the data multiplexer, starting the integration of the four isotopic beams. Approximately every 50 msec, the calculator samples the amplitude of the integrator channel of the major isotope. Upon reaching a predetermined amplitude (software controlled), a "stop" signal is issued to the multiplexer. Each integrator channel is read and stored. A "reset" signal is sent to the integrator as well as a signal to the source control to turn the beam off. The multiplexer is restarted and allowed to run for a time duration, that is identical to the one required to obtain the data. The purpose of this sampling period is to establish a zero-offset correction. Once the calculator has this information, a printed copy of the corrected weight percent isotopic abundance for each isotope is calculated and issued. Prior to its issuance, the calculator samples an arc circuit to determine if there has been a high-voltage arc, within the source, which would cause an erroneous answer. If there was such an arc, the calculator does not print the results; but, instead, displays the fact that an arc occurred, signifying the need to rerun the sample. The calculator also monitors a vacuum sensor to determine if the sample was taken at a pressure which exceeds a predetermined level. If it finds the pressure to be above the set point, it prints a message, along with the answer, to signify the condition.

RESULTS

Uranium isotopic analyses of control batches and routine samples by the mass spectrometer show that this instrument is satisfactory for the routine analysis of samples.

The average of three controls run at the beginning, middle, and end of the day was used to compute a daily standardization factor to apply to controls and routine samples done during the day. Additional control samples were done to estimate the bias.

Results are summarized in Table 1—oralloy (uranium enriched in ^{235}U content) metal results, Table 2—Savannah River Operation (SRO) nitrate solution and metal data, and Table 3—depleted material results. The control-batch data show no significant biases. The

Table 1
COMPARISON OF THE ISOTOPIC ANALYSIS OF ENRICHED URANIUM BETWEEN
THE MS-300 AND OTHER MASS SPECTROMETERS
(All Results are in Weight Percent Except Precision)

Control Batch Results by the MS-300 and MS-5 ⁽¹⁾						
Uranium Isotope	Standard Value	Number of Results	Mean $\pm$ LE of Mean	Bias $\pm$ LE of Bias	Relative Percent LE of a Single Result	
					MS-300 Precision	MS-5 Precision
234	1.00	23	0.999 $\pm$ 0.001	-0.001 $\pm$ 0.001	$\pm$ 0.53 ⁽²⁾	$\pm$ 1.4
235	93.16	23	93.159 $\pm$ 0.007	-0.001 $\pm$ 0.007	$\pm$ 0.036	$\pm$ 0.035
236	0.40	23	0.400 $\pm$ 0.000	0.000 $\pm$ 0.001	$\pm$ 1.1 ⁽²⁾	$\pm$ 5.0
Comparison of Routine Sample Results by the MS-300 and MS-5						
Uranium Isotopes	Number of Samples	Mean $\pm$ LE of Mean		Mean Difference of Paired Results $\pm$ LE of Mean Difference		
		MS-300	MS-5			
234	49	0.998 $\pm$ 0.003	0.999 $\pm$ 0.001	-0.001 $\pm$ 0.002		
235	49	93.169 $\pm$ 0.006	93.170 $\pm$ 0.005	-0.001 $\pm$ 0.007		
236	49	0.445 $\pm$ 0.013	0.447 $\pm$ 0.013	-0.002 $\pm$ 0.004		

(1) The MS-5 is a 1950-vintage uranium hexafluoride-gas-source mass spectrometer.

(2) The MS-300 precision is significantly better than the MS-5 precision.

Table 2
ISOTOPIC ANALYSIS OF URANYL NITRATE SOLUTION AND METAL CONTAINING 40 - 57% ²³⁵U
(All Results are in Weight Percent Except Precision)

Internal Control Batch Results on the MS-300 Instrument						
Uranium Isotope	Standard Value	Number of Results	Mean $\pm$ LE of Mean	Bias $\pm$ LE of Bias	Relative Percent LE of a Single Result	
					MS-300 Precision	MS-AVCO ⁽¹⁾ Precision Program 8 Batch 812
234	1.69	16	1.690 $\pm$ 0.002	0.000 $\pm$ 0.002	$\pm$ 0.47 ⁽²⁾	$\pm$ 1.9
235	44.82	16	44.821 $\pm$ 0.015	0.001 $\pm$ 0.015	$\pm$ 0.13	$\pm$ 0.11
236	38.16	16	38.340 $\pm$ 0.008	0.000 $\pm$ 0.008	$\pm$ 0.078	$\pm$ 0.15
Comparison of Routine Sample Results by the MS-300 and MS-AVCO Instruments						
Uranium Isotope	Number of Samples	Mean $\pm$ LE of Mean		Mean Difference of Paired Results $\pm$ LE of Mean Difference		
		MS-300	MS-AVCO			
234	44	1.485 $\pm$ 0.018	1.463 $\pm$ 0.018	0.022 $\pm$ 0.004 ⁽³⁾		
235	44	43.103 $\pm$ 2.340	43.085 $\pm$ 1.520	0.018 $\pm$ 0.015 ⁽³⁾		
236	44	37.065 $\pm$ 1.230	37.014 $\pm$ 1.210	0.051 $\pm$ 0.015 ⁽³⁾		

(1) The MS-AVCO is a 13-inch-radius, commercially purchased, triple-filament-ion-source mass spectrometer.

(2) The MS-300 precision is significantly better than the MS-AVCO.

(3) Statistically significant, but operationally nonsignificant.

MS-300 (a thermal-emission mass spectrometer for the rapid and accurate determination of uranium isotopes) precision is significantly better than the current laboratory precision for ^{234}U and ^{236}U in oralloy metal (Table 1) and for ^{234}U in SRO materials (Table 2). In the comparisons of current data of routine samples with the mass-spectrometer results of the

Table 3
COMPARISON OF THE ISOTOPIC ANALYSES OF DEPLETED URANIUM (0.16 - 0.24% ^{235}U)
BETWEEN THE MS-300 AND ANOTHER Y-12 MASS SPECTROMETER
(All Results are in Weight Percent Except Precision)

U ₃ O ₈ Control-Batch Results on the MS-300 Instrument						
Uranium Isotope	Standard Value	Number of Results	Mean $\pm$ LE of Mean	Bias $\pm$ LE of Bias	Relative Percent LE of a Single Result	
					MS-300 Precision	MS-7(1) Precision
235	0.2215	18	0.22135 $\pm$ 0.00038	-0.00015 $\pm$ 0.00038	$\pm$ 0.72	$\pm$ 0.89
Comparison of Routine Uranium Sample Results by MS-300 and MS-7 Instruments						
Uranium Isotope	Number of Samples	Mean $\pm$ LE of Mean			Mean Difference of Paired Results $\pm$ LE of Mean Difference	
		MS-300	MS-7			
235	41	0.1975 $\pm$ 0.0032	0.1984 $\pm$ 0.0030		-0.0009 $\pm$ 0.0006 (2)	

(1) The MS-7 is a 1950-vintage uranium hexafluoride-gas-source mass spectrometer.

(2) Statistically significant, but operationally nonsignificant.

samples, statistically significant differences were noted for ^{234}U , ^{235}U , and ^{236}U in the SRO material and for ^{235}U in tuballoy (depleted uranium material). The differences were small and are operationally nonsignificant.

Each day of the three-day test, a daily standardization factor was computed by comparing the standard value of the control batch with the average of three control batch results obtained at the beginning, middle, and end of each day's run. Results of the test indicate that three control samples run during each day are sufficient for standardization.

A reported result is the average of duplicate analyses of the sample. In case better precision is desired, replication can be done and the precision can be estimated by multiplying the LE of a single result by the square root of 2/square root of the number of replicas.

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