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A B S T R A C T

An automatic recording mass spectrometer has been designed; two instruments have been constructed and have operated reliably for more than seven years as process monitors.

Each is fully automatic and capable of making a uranium isotope determination every two and one-half minutes. The results are recorded directly in weight per cent U^{235} with a precision equivalent to that obtained with a manually operated instrument. Provisions have been made to transmit the results to a "slave" recorder and a valve controlling the process. The instruments are of relatively simple circuitry, and require no reference standards.

AUTOMATIC MASS SPECTROMETER FOR MONITORING URANIUM ISOTOPE CONCENTRATIONS

INTRODUCTION

The isotopic composition of the uranium hexafluoride gas in some processes must be monitored frequently for operational efficiency. To obtain adequate control, the uranium-235 content must be determined to ± 0.1 per cent, at the 95 per cent confidence level, every three minutes; the concentration usually remains within a range of less than one per cent. Although the gas pressure and chemical purity are subject to rather wide fluctuations, the process is adaptable to direct sampling into the monitoring spectrometers; since continuous day and night coverage is required, one major purpose of this development project was to reduce the cost of monitoring the process by making the spectrometers which were operated by analysts completely automatic.

SUMMARY AND CONCLUSIONS

Electronic and electro-mechanical components were added to a General Electric, Nier-type, six-inch radius isotope mass spectrometer (3) to make its operation completely automatic; it samples the process and determines the isotopic content in weight per cent uranium-235 with the required precision in two and a half minutes. A transmitting slidewire is provided in the recorder, permitting the results to be recorded remotely or applied to the operation of a process control valve.

A second instrument was also made automatic to provide continuous process monitoring coverage while the first spectrometer is being serviced, and to provide occasional accuracy checks.

Considerable effort was expended in simplifying the circuitry and servo mechanisms, and minimizing the number of component parts. For instance, the "absolute" method of operation was used mainly because it requires no standards materials and permits simpler circuitry and sampling facilities.

The spectrometers have operated satisfactorily since their installation in September of 1954.

INSTRUMENT DESIGN

Analytical Methods

The two basic isotopic analysis methods are the relative, double-collection method in which the isotopic composition of the sample is compared (or related) to a standard; and the absolute, single-collector method in which the proportional abundance of the isotopes in the sample is measured directly.

Although the relative method places less dependence upon the precision of the measuring system, is more precise than the absolute method, and does not require critical ion intensity control, the method has the disadvantage of requiring standards. Additional time and increased complexity of automatic manifolding for alternately admitting standards and samples to the instrument are needed, and isotopic analyses are affected by the presence of impurities, particularly those present in the sample but not in the standard (2). Some impurities merely raise the analyzer tube pressure and hence change the ion beam dimensions while others such as C_8F_{16} , in addition, form ions in the mass range of the isotopes being measured. Both effects can cause appreciable analytical errors.

The absolute method has the advantage of measuring ion beams from both isotopes on the same collector plate and amplifier, thereby reducing the number of variables. It is unaffected by the usual amounts of low-mass impurities. However, the simplest absolute method, in which only two major isotopes are compared, requires additional independent analyses to determine a correction for the U^{234} and U^{236} isotopes, and is subject to error from intensity drift during an analysis. The accuracy of the method is also more dependent upon the linearity of the measuring system.

Since samples are periodically withdrawn from the process and analyzed for all isotopes in the laboratory, the correction for U^{234} and U^{236} isotopes is available without additional effort. Minor isotope corrections seldom need to be revised more than once a week.

The absolute method is thus more desirable for this specific automatic process monitoring application because of the shorter analysis time required, simpler manifolding, and less dependence upon the purity of the process gas.

Instrumentation was provided to minimize the number of operations required for an absolute analysis. To obtain a single analysis, a sample is first trapped from the process and admitted to the ion source, a variable leak is adjusted to stabilize the ion intensity at a target level, and a standardizing voltage is adjusted to equal the signal from the U^{235} ion beam which is magnetically "swept" to a peak position. The magnet current is then adjusted to focus the U^{238} peak on the collector, and the voltage generated by the ions at peak position is compared to the U^{235} reference voltage and recorded as weight per cent U^{235} .

Design Requirements

Fluctuations in the process are of such frequency that an analysis is needed every three minutes, so the length of a measurement cycle was kept within this period.

It is necessary to flush out the sample supply loop and provide a fresh sample before each analysis. Experimentation with an earlier semi-automatic spectrometer showed that gas must flow through the sample loop for at least fifteen seconds before a new sample is trapped. A further

portion of the time required for an absolute analysis must be allotted to the stabilization of sample pressure in the spectrometer ion source and formation of a constant total ion current. A general plan for adapting a ratio recording system (4) to the automatic spectrometer was developed, since this type of measuring system does not impose stringent requirements on the total ion beam intensity. An intensity control period of 30 seconds proved adequate for average process conditions. This recording system could also be set to zero automatically within 15 seconds, and easily adapted to transmit the results to a remote "slave" recorder. This remote signal could then be used to direct valves controlling the process. A fully automatic, direct reading instrument requiring no operator was desirable not only to reduce operating expense but also to continue operation during periods when an operator could not be present as, for example, following a toxic gas release. (The importance of this feature has been demonstrated during radioactive gas releases which would have prevented one from operating the earlier manual instruments. But it was possible to wear a gas mask and periodically enter the room long enough to read analyses from the recorder charts of automatic spectrometers.)

A precision of ± 0.1 weight per cent U^{235} was required for one determination on the automatic mass spectrometer.

Program

The program for normal operation of the instrument is outlined in table 1.

TABLE 1
NORMAL SEQUENCE OF OPERATION

<u>Step</u>	<u>Function</u>	<u>Time, Seconds</u>
1	Sample Flowing, Intensity Control	15
2	Intensity Control, Sample Trapped	15
3	Zero Set	15
4	Standardization	60
5	Read	45
Total		150

In addition to following the normal sequence of operations, the instrument must be capable of operating during unusual process or input power conditions and recovering from most misoperations originating within itself. To handle such abnormalities without manual assistance, the first sequence was supplemented with the emergency steps shown in table 2.

TABLE 2

EXPANDED SEQUENCE, INCLUDING EMERGENCY STEPS

<u>Step</u>	<u>Function</u>	<u>Misoperation</u>	<u>Emergency Step</u>
1	Sample Flowing, Intensity Control		Magnet current reset
2	Intensity Control	Intensity not within $\pm 30\%$ of the set point for 30 seconds before step 3	Extend intensity control time
3	Zero Set	None	
4	Standardization	Fails to standardize Again fails to standardize	Sweep reverses and tries a second time. If it standardizes, step 5 is initiated. Step 1 is initiated
5	Read	Fails to sweep over peak	Step 1 is initiated

An earlier model of a semi-automatic instrument demonstrated that too much safety equipment unnecessarily complicates the spectrometer, leads to more component failures, and consumes more time in locating the trouble. Therefore, the emergency steps listed above for the new instrument handle only the most probable unusual events.

All components were designed to operate from line voltage regulated through a Sola constant voltage transformer.

Components

1. Program Control

The Program Control unit activates the various components of the automatic spectrometer in the proper sequence. It consists of a 25 position 6 pole stepping switch, two timing devices, one relay, 6 indicating lights, 3 selenium rectifiers, and the switches indicated in figure 1.

In operation, the 117 volt ac. power is directed by the stepping switch to the automatic components. It follows the normal program outlined in table 1 except when a safety device calls for an emergency step. Since there are only five steps in the program, the

25 position stepping switch repeats the program five times; that is, positions 1, 6, 11, 16, and 21 activate the same steps. This reduces the rate of wear on each contact to one-fifth that for a five-position switch. For steps requiring less than six separate switching operations the surplus contacts are paralleled with others, thereby giving additional protection against poor contacts. The operation of the stepping switch, installed as shown in figure 1, is outlined in table 3.

This is the normal sequence of operation. In the event of a failure to standardize or read properly, timer motor M1 is energized from the magnet control panel causing the program to advance one step after an interval of 15 seconds.

The functions of the manual switches in the program control panel are seen in figure 1. The power switch controls 117 volt ac. to the panel; power to the servo motor on the variable leak is supplied through the intensity control switch. The automatic leak may be disabled by placing this switch in the "Off" position, so the program will not advance from the "Intensity Control" step. To stop automatic operation the "Automatic" switch is placed in the "Off" position, after which the program may be advanced manually, a step at a time, by pressing the "Advance" button. If the automatic cycle must be stopped, the "Automatic" switch should always be turned off during the "Intensity Control" step to prevent disturbing the sequence of operation of the timers.

2. Sample Inlet Manifold

The function of the manifold is to isolate a sample of gas from the sample supply lines, and to admit it to the analyzer tube at the proper rate. As shown in figure 2, the main components are two solenoid-operated air valves (H and J), three air-operated sample line valves (D, E, and F), three manually-operated block valves (A, B, and C), and a motor-driven valve-type leak (G) (1). For operation, block valve B is closed, and valves A and C are open. During the "Sample Flow" step of the program the two solenoid valves are energized. These supply compressed air to the sample line valves, closing D and opening E and F. This permits part of the sample stream to flow in the loop connected to the leak. After 15 seconds, the solenoids are de-energized, and direct the compressed air to the other side of the diaphragm of the process valve, closing E and F and opening D. This traps a sample of gas in the loop and allows the sample stream to continue flowing through by-pass valve D. The variable leak illustrated in figure 3 is then adjusted automatically to give the proper sample flow to the analyzer.

STEPPING SWITCH FUNCTIONS

Switch Position	Program	Contacts					
		A	B	C	D	E	F
1, 6, 11, 16, 21	Sample flow and intensity control	Power to "Sample Flow" indicator light and to solenoid valves on manifold panel.		Power to 15 second timer M1.		Power to intensity control motor if intensity control switch is on, and power to "Intensity Control" indicator. (Timer M1 runs for 15 seconds, and causes mercury switch to close and then open a circuit. While the circuit is closed, ac. passes to the "Automatic" switch; if this switch is closed, the current energizes the stepping switch. When the circuit is opened the stepping switch advances to the next position.)	
2, 7, 12, 17, 22	Intensity Control (Sample trapped)	Power to "Intensity Control" indicator and to intensity control motor if intensity control switch is on. (Timer M4 on the Intensity Control panel operates whenever the intensity is within ± 30 per cent of the set point. When it has operated for 30 seconds it activates the stepping switch in the manner described for timer M1 above.)					
3, 8, 13, 18, 23	Zero	Power to "Zero" indicator, to relay R-1 which throws peaks out, a recorder solenoid which forces the drive wheel on the Zero Helipot against the split gear, and R-3 in the decade panel to ground the feedback line. (The balancing operation is described under "Measuring System.")			Power to timer M1, which advances the stepping switch to the next position in the same manner as for sample flow.		
4, 9, 14, 19, 24	Standardize	Power to R-4 which connects the feedback line to the top of the decade. Power to S-11 (which is closed to position 1 at beginning of standardize step) and then to timer M2. This timer runs about 15 seconds until cam 1 operates switch S-11 to position 2; before it stops cam 2 has moved switch S-12 to position 2, thereby furnishing power to switch S-15 in the recorder. Switch S-15, when operated to make and then break contact, energizes the stepping switch. Power to S-15 is delayed to prevent advancing the program to the next step due to recorder shaft motion before the U^{235} peak is scanned.		Power to "Standardize" indicator and to recorder solenoid which engages the "Standardize" Helipot with the recorder shaft.		Power to Magnet Control panel R-5 which activates the "separation" resistance and positions the magnet current to scan the U^{235} peak. Power to the CCW winding of scan motor M3 on the Magnet Control panel. (When the U^{235} peak is being scanned switch S-15 in the recorder is closed by the cam on the recorder shaft as the reading is being increased. When the top of the peak is reached and the recorder changes direction, this switch is opened causing the stepping switch to advance.)	
5, 10, 15, 20, 25	Read	Power through switch S-11 to timer motor M2. After timer runs about 15 seconds, switch S-12 conducts power to switch S-15 in the recorder.		Power to "Read" indicator and power to switch S-13 which closes after timer has operated 15 seconds and transmits power to lower the recorder pen and to the slave recorder.		Power to scan motor M3 on the Magnet Control panel.	

Switch S-15 in the Recorder activates the stepping switch as described in the previous step, and the program starts over.

3. The Intensity Control System

The system consists of a high-current amplifier and intensity control panel. The current amplifier measures the U^{235} ion beam collected on the slit collector plate and displays the value on an output meter.

The intensity control panel consists of a Phillips ion gauge power supply for indicating the spectrometer tube pressure, a servo-amplifier for driving the leak motor, timer M^4 for timing intensity control periods, and relay R2 for stopping timer M^4 if intensity is not within the desired range.

The high-current amplifier has 10 per cent feedback with a gain of 10. With an ion current of 5×10^{-11} amperes a 1 volt signal is developed across the input resistor and a 10 volt signal is generated at the output. This output signal is compared to a 10 volt reference to supply the difference voltage for the intensity control. Thus if the voltage across the input resistor increases to 1.3 volts, the output will be 13 volts or a voltage difference of 3 as compared to the reference. This voltage is fed to the coil of relay R2 in the intensity control panel. Should the input drop to 0.7 volts the signal across the relay R2 coil would be -3 volts; the relay closes at about 3 volts potential difference.

A portion of the difference voltage (1/10) is used as an input to the servo-amplifier which drives the leak motor as long as the program is in the intensity control period.

When the intensity is not within the desired range (0.7 to 1.3 volts) relay R2 is closed preventing timer M^4 from running until the leak adjusts the intensity to within desired limits. Therefore, the intensity control period may be longer than the 30 second interval described in table 3.

4. Magnet Control Panel

The magnet control panel sweeps the magnet current to scan the peaks. It also compensates for drift in focus and calls for emergency operation in the event the instrument fails to standardize or read properly. The main components are two Helipot driven by clock motors.

Referring to figure 1, when the program is in the "Standardize" position relay R5 is energized and shorts out the "Separation" resistance, setting the magnetic field to focus on the high-mass side of the U^{235} peak. Scan motor M^3 is driven counterclockwise and sweeps the peak. Should the instrument fail to standardize properly and the scan go to the limit of the Helipot, the lower limit switch S7 will close, energizing relay R6 and locking it by relay contact A. Contact B will power the scan motor in the reverse direction to attempt to standardize again. Contact C is

opened to prevent undesirable feedback of the ac. power when the program steps to "Read"; without this provision relay R5 would be energized by power flowing through contact B. If the instrument fails to standardize on the return scan the upper limit switch S6 will close and energize timer motor M1 on the program control panel. This will cause the program to advance one step after a 15 second interval.

With the program in "Read" position scan motor M3 is driven clockwise to scan the U^{238} peak as shown in figure 4. If it fails to scan the peak the upper limit switch S6 will operate causing the program to advance. When the program advances from "Read" in the normal manner the scan Helipot dial should be at 650. If it stops under 600 or over 700 a cam-operated switch S8 or S9 closes and completes a circuit to the motor M6 which drives the compensation Helipot. While the program is on "Sample Flowing" the motor runs (if either cam-operated switch is closed) and adjusts the Helipot an amount equivalent to 50 units on the scan Helipot in a direction toward 650. In this manner, compensation for drift of focus caused by high voltage or magnet supply drift is provided. Since this adjustment is timed at 15 seconds, stopping the program on the "Sample Flowing" position for a longer period may cause over-compensation. The range of the compensation Helipot is sufficient to permit 20 compensation steps in one direction.

5. Ratio Recorder Measuring System

The Ratio Recorder consists of a low-current amplifier with pre-amplifier, a modified Leeds and Northrup amplifier, a Leeds and Northrup Speedomax Model G recorder, and a decade panel. It compares the ratio of the U^{238} ion current of about 3×10^{-12} amperes with that of the U^{235} beam which is approximately 18 times as large. The recorder servo system also drives an additional slide-wire which transmits the reading to a slave recorder and/or a control valve.

The zero of the measuring system is adjusted automatically during step 3, "Zero". With peaks out relay R3 in the decade panel grounds the feedback line. At the same time a solenoid in the recorder is energized and pulls a drive wheel connected to a Helipot against the split gear of the recorder. These components are illustrated in figure 1. The recorder servo system then adjusts the Helipot which introduces a bucking potential into the feedback line until a null is achieved. The system is thus set for zero reference.

During the standardization cycle another solenoid in the recorder is energized and engages a gear attached to a second Helipot which adjusts a reference voltage to equal the U^{235} peak intensity. Relay R5 in the decade panel is energized to connect the feedback line to the top of the decade resistance. The servo system of the recorder seeks a null by adjusting the Helipot until the signal and

reference voltage are equal, as the U^{235} peak is scanned. When the maximum value of the peak is passed the solenoid is de-energized, the gears are disengaged, and the Helipot setting is fixed to maintain a voltage equivalent to the U^{235} peak across the decade. Next the two relays R4 and R5 are de-energized for the "Read" cycle, connecting the feedback line to the cruiser on the recorder slide-wire. The U^{238} peak is then scanned and the recorder indicates the weight per cent U^{235} if the proper decade setting is used to compensate for the U^{234} and U^{236} isotopes.

Slidewire and Decade Setting

The recorder system shown in figure 1 comes to balance at the following equality:

$$\frac{d + s}{10,000} = \frac{U^{238} \text{ ion current}}{U^{235} \text{ ion current}} = \frac{a8}{a5} \quad (1)$$

where d = ohms of decade resistance needed to balance U^{238}

s = slidewire resistance used to balance U^{238}

10,000 = total resistance across which standard U^{235} voltage is developed

a8 = a function of the number of U^{238} ions being collected

a5 = same function of U^{235} ions, etc.

In order to establish the slidewire resistance and decade settings needed to convert the readings to weight per cent U^{235} , adjusted for the presence of fixed quantities of U^{234} and U^{236} , we may let 234a4 represent the atomic mass units of the U^{234} isotope collected, 235a5 the U^{235} mass, etc., and equate the sum of all isotopes to 100 weight per cent:

$$234a4 + 235a5 + 236a6 + 238a8 = 100 \quad (2)$$

Then 234a4 = weight per cent U^{234} , or e

235a5 = weight per cent U^{235} , or z

236a6 = weight per cent U^{236} , or g

and 238a8 = weight per cent U^{238} , or q.

Using the letter symbols above, equation (2) may be rewritten

$$\frac{a8}{a5} = 0.9874 \quad \frac{100 - e - g - z}{z} \quad (3)$$

$$\text{or } \frac{a8}{a5} = 0.9874 \quad q/z$$

By combining equations (3) and (1),

$$d + s = 9874 \, q/z \quad (4)$$

The decade resistance setting, d , may be computed from equation (4) for the lowest q/z ratio to be recorded, with zero slidewire resistance, s . The total slidewire resistance needed is then found by computing $d + s$ for a z value 2.0 weight per cent lower; a typical value of s is 234 ohms.

A recorder scale whose mid-point is the average expected concentration is thus made to cover a range of 2.0 weight per cent, so each division on 100-line chart paper represents 0.02 weight per cent U^{235} . To set the decades from known isotopic concentrations where the U^{235} value may not be at mid-scale, equation (5) was obtained from equation (4):

$$d = 9874 \, q/z - s/2 \, (f.s.z - z) \quad (5)$$

where $f.s.z$ = full scale recorder reading in weight per cent of U^{235}

and q and z are obtained from complete analysis of samples typical of the U^{234} and U^{236} content.

PERFORMANCE

The spectrometers have provided continuous process analyses for more than seven years with only minor outages. One instrument is retained on standby (with sample at reduced flow into the ion source) while the other is operating, allowing necessary maintenance on one instrument while analyses are continued on the other.

The time required for servicing both instruments now averages 14 hours a week, including a routine check each day to assure operability of the standby instrument and to provide accuracy checks.

Average source life with continuous exposure to uranium hexafluoride gas has been 2-1/2 months with occasional sources lasting over six months and 60,000 determinations.

Precision and Accuracy

Instrument precision, at the 95 per cent confidence level, is about ± 0.03 weight per cent per determination when operated on trapped sample to minimize intensity fluctuations.

The accuracy is better than ± 0.09 weight per cent U^{235} , based on long-term agreement of automatic measurements with laboratory analyses of control samples withdrawn from the circulating sample supply line.

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Figure 1
AUTOMATIC ISOTOPE MASS SPECTROMETER

LEGEND:

A, B, C—Crane 1/2" S.M. Valves
 D, E, F—Special Pneumatic Valves

H, J — Skinner Electric Valves
 No. V5-4500

Figure 2
SAMPLE INLET SYSTEM

Figure 3
NEEDLE-VALVE TYPE VARIABLE LEAK

Figure 4
PEAK SCANS OF TYPICAL ANALYSES

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