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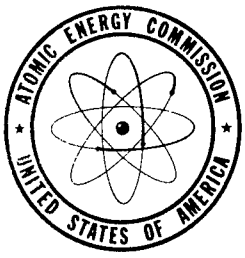

K-835

Subject Category: CHEMISTRY

UNITED STATES ATOMIC ENERGY COMMISSION

THE SPECTROCHEMICAL ASSAY OF URANIUM 235 USING PHOTOMULTIPLIER TUBES

By
T. Lee
Lewis H. Rogers

October 31, 1951

K-25 Plant
Carbide and Carbon Chemicals Company
Oak Ridge, Tennessee

Technical Information Service, Oak Ridge, Tennessee

UNCLASSIFIED

Date Declassified: January 5, 1956.

Printed in USA, Price 25 cents. Available from the Office of Technical Services, Department of Commerce, Washington 25, D. C.

Date of Issue: October 31, 1951 Report Number: K-835

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T. Lee and Lewis H. Rogers

Laboratory Division
Frank W. Hurd, Superintendent

Work performed under Contract No. W-7405-Eng-26

CARBIDE AND CARBON CHEMICALS COMPANY
K-25 Plant
Oak Ridge, Tennessee

ABSTRACT

A Jarrell-Ash 21 foot grating spectrograph was adapted to direct reading by replacing the photographic plateholder with exit slits and photomultiplier tubes. Using a hollow cathode discharge tube for excitation of the sample and the isotopic shift effect, uranium 235 was determined in several samples by comparison with a single standard. The uranium 235 content of the samples and standards was known from mass spectrometer measurements to within 0.5% of the amount present at the 95% confidence level. For a determination consisting of 10 measurements, the precision obtained was from plus or minus 1.2 to 1.8% of the amount present over a concentration range of from 8% to 11.9% uranium 235.

THE SPECTROCHEMICAL ASSAY OF URANIUM 235 USING PHOTOMULTIPLIER TUBES

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THE SPECTROCHEMICAL ASSAY OF URANIUM 235 USING PHOTOMULTIPLIER TUBES

The spectrochemical assay of uranium 235 utilizing the isotope shift effect differs very little from other spectrochemical analyses. The complexity and the heavy optical background of the uranium spectrum, however, present certain difficulties. The wavelength difference between the two isotopic lines used here is 0.244 A., although isotopic shifts of greater and lesser magnitude have been observed at other wavelengths (11). Due to these factors, high resolution and dispersion are required.

Earlier work using the direct current arc as the excitation source and photographic recording has been described in a previous report (7). The present report deals with the use of the hollow cathode discharge tube for the excitation source and photomultiplier tubes for recording using a Jarrell-Ash 21 ft. spectrograph. Studies of a similar nature have been carried out by Brody (1).

EXPERIMENTAL

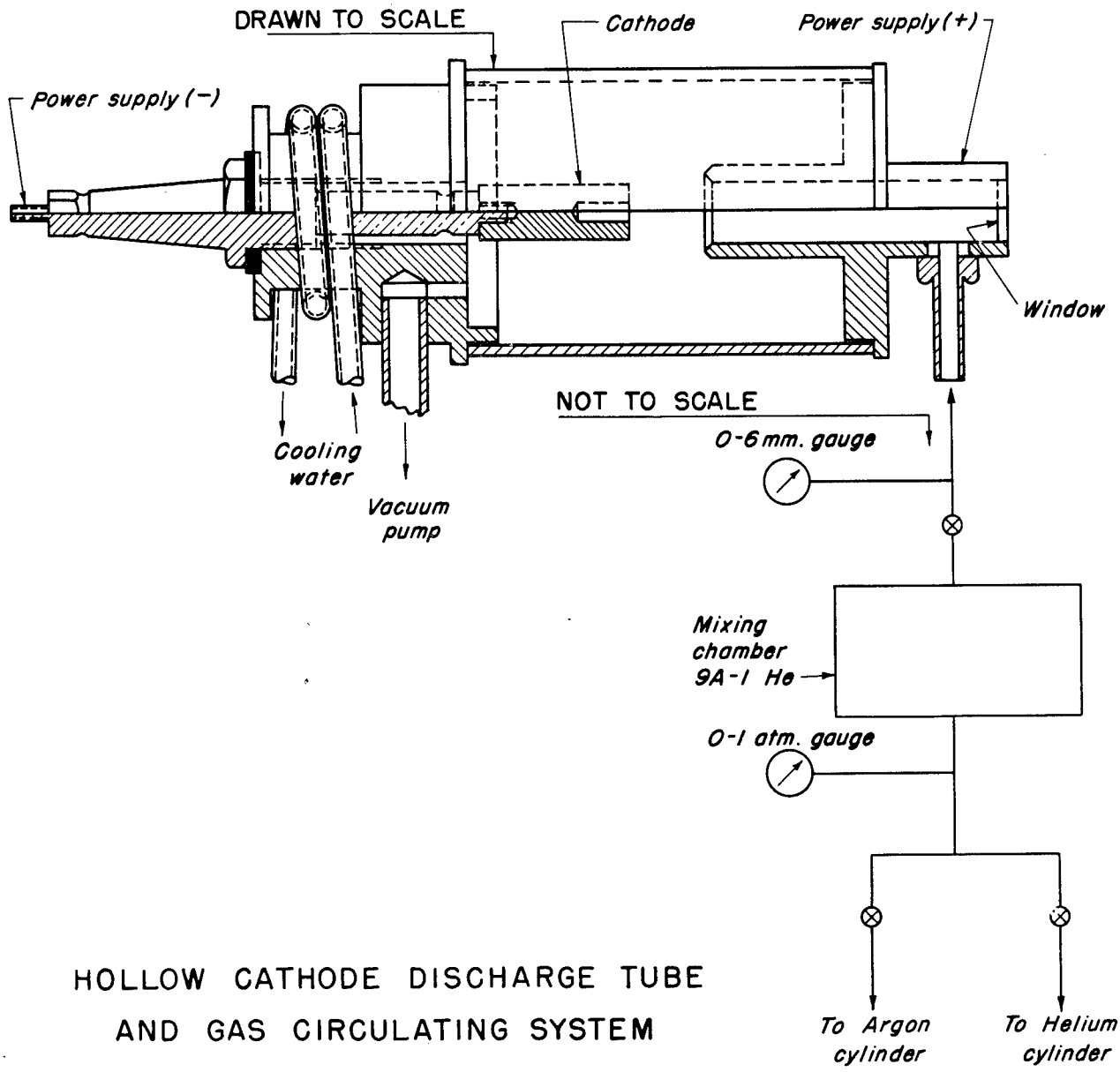
Hollow Cathode Discharge Tube

A hollow cathode discharge tube was used as an excitation source because of its stability, production of narrow spectral lines, economy of sample, and continuity of operation over long periods of time. This tube was designed by McNally; a prototype was described by McNally, Harrison, and Rowe (8). A sketch of the tube and the open system for gas circulation is shown in figure 1. A direct current power supply capable of delivering 500 milliamperes at 1500 volts was connected to the tube through a 2000 ohm ballast resistor. Photographs of these units are shown in figures 2 and 3.

Sputtering gas mixtures of 1:2, 1:1, 2:1, 4:1, 9:1, and 19:1 parts of argon to helium as well as the pure argon and pure helium were investigated. It was found that a maximum intensity of the uranium spectrum was obtained using a mixture of 9 parts of argon to 1 part of helium. Different gas pressures were also examined, and it was found that the greatest intensity was obtained at a pressure of 3 mm. of mercury absolute. These results are in agreement with those obtained by Brody (1).

It was found that the intensity of the uranium spectrum was greatly enhanced and the ratio of the intensity of the spectral line to the intensity of optical background was improved by increasing the excitation current of the discharge tube to 300 ma. Still higher currents may prove useful. The improvement in the ratio of the intensities of the spectral line to optical background may prove to be useful for measuring low concentrations of uranium 235. All of the present work, however, was done with 100 milliamperes.

The operating conditions which were used are summarized in table I.



HOLLOW CATHODE DISCHARGE TUBE AND GAS CIRCULATING SYSTEM

FIGURE 1

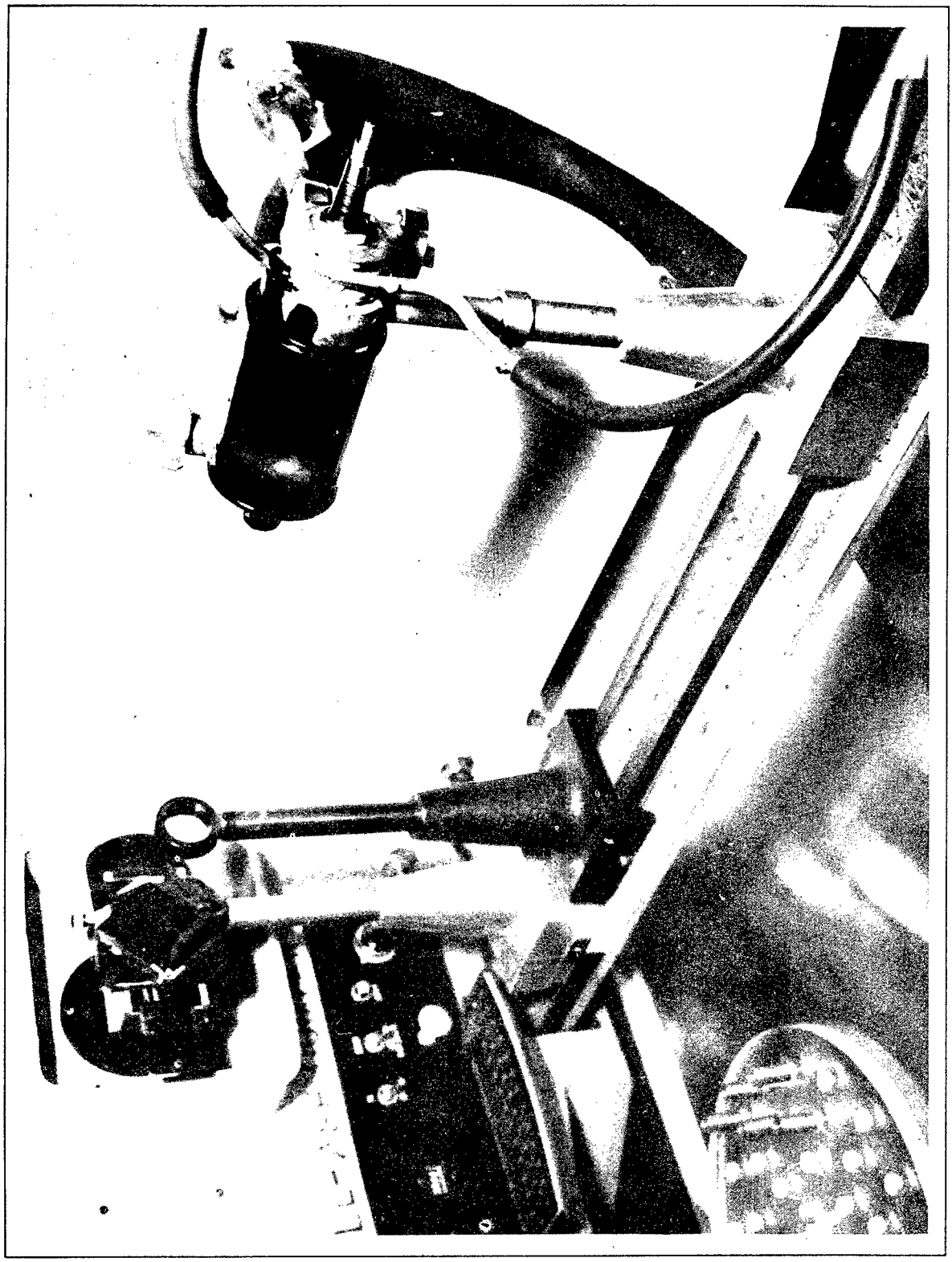


Figure 2. Hollow Cathode Discharge Tube

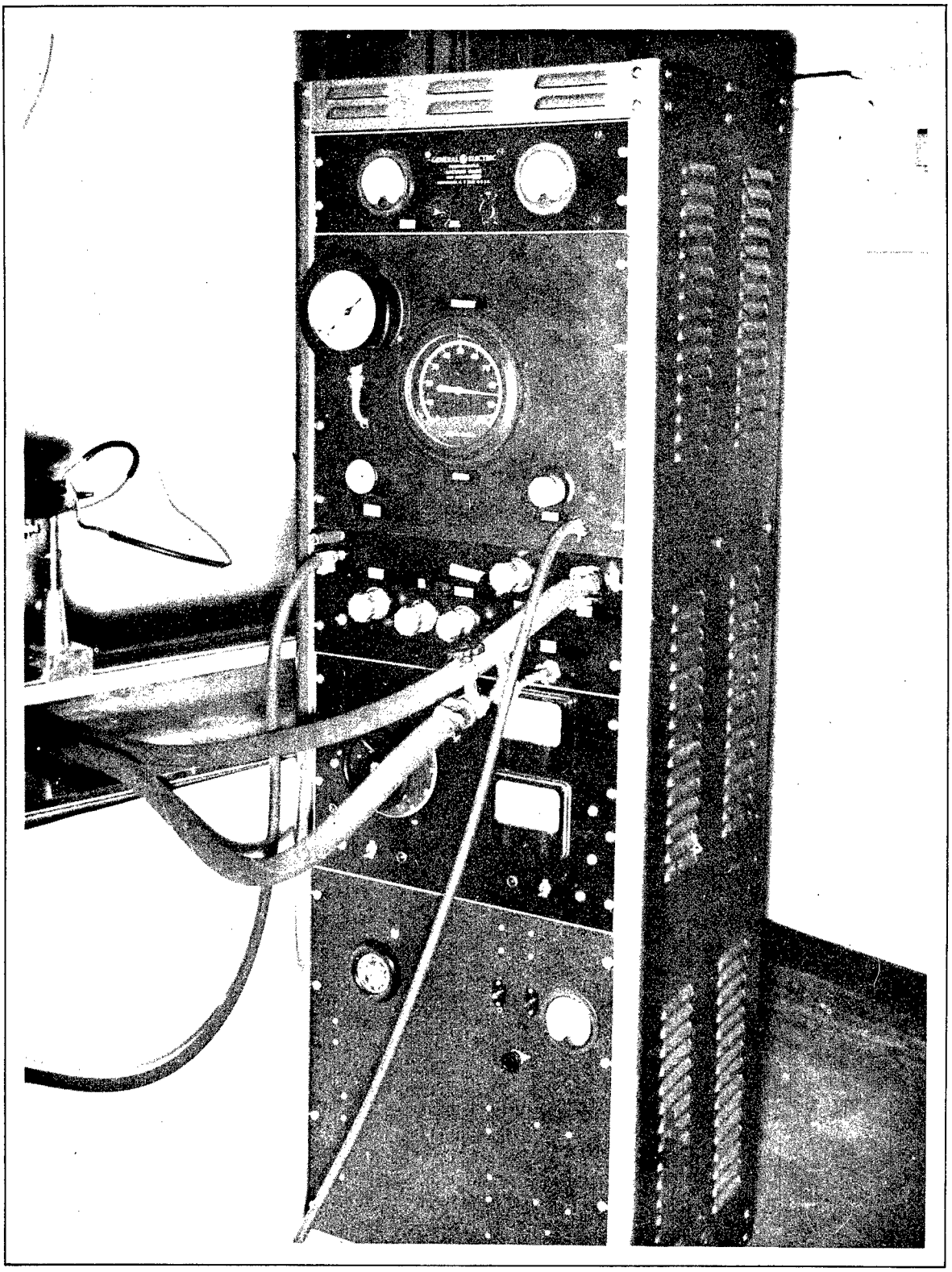


Figure 3. Power and Control Unit for Hollow Cathode Discharge Tube

TABLE I

OPERATING CONDITIONS FOR HOLLOW CATHODE DISCHARGE TUBE

Composition of Sputtering Gas:	9 parts of argon to 1 part of helium.
Pressure Gas:	3 mm. of mercury absolute
Current:	100 milliamperes
Sample:	6 mg. of uranous uranic oxide; or 4 mg. of uranyl nitrate, the solution of which is evaporated in the hollow of the cathode.

A graphical trace of the light intensity of the uranium 235 spectral line as a function of time to show the build up and decay of the intensity from the discharge tube was made, as shown in figure 4. This trace indicates that there is a rapid build up of the intensity of the uranium spectrum during the first fifteen minutes, after which the intensity levels off and then decreases slowly. Intensity measurements on samples were, therefore, made after the fifteen-minute build-up period.

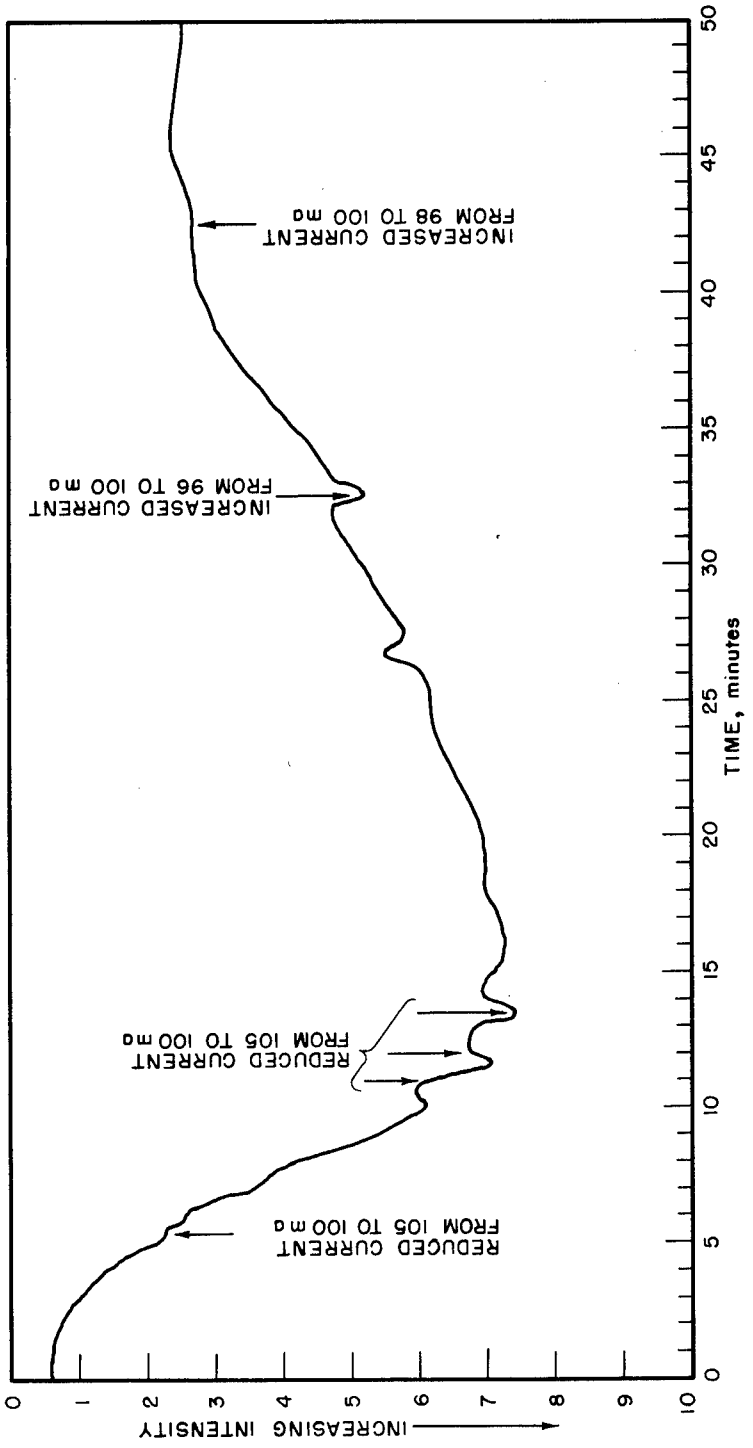
Uranium spectra were obtained using either solid uranous uranic oxide or uranyl nitrate solution. In the latter case, a few drop of a solution of the nitrate were transferred to the hollow of the cathode and evaporated to dryness.

The Spectrograph

A Jarrell-Ash spectrograph with a six inch grating having 15,000 lines per inch and a focal length of 21 feet 10 inches was used in the second order. The entrance slit was 10 microns wide and 15 mm. high. The light from the source was made parallel with a 10 cm. spherical lens, which also served as the window for the discharge tube. Crossed cylindrical lenses as used by G. Hansen and described by Harrison (4) were used: a 10 cm. cylindrical lens (axis vertical) was used to focus the parallel light on the slit in the horizontal plane, and a 60 cm. cylindrical lens (axis horizontal) was used to focus the parallel light on the collimating mirror. A sketch of the optical system, not drawn to scale, is shown in figure 5. With this arrangement, a narrow beam of light was produced along the length of the entrance slit, and most of the light that passed through the entrance slit fell on the collimating mirror. The filter was used to remove interference from other orders.

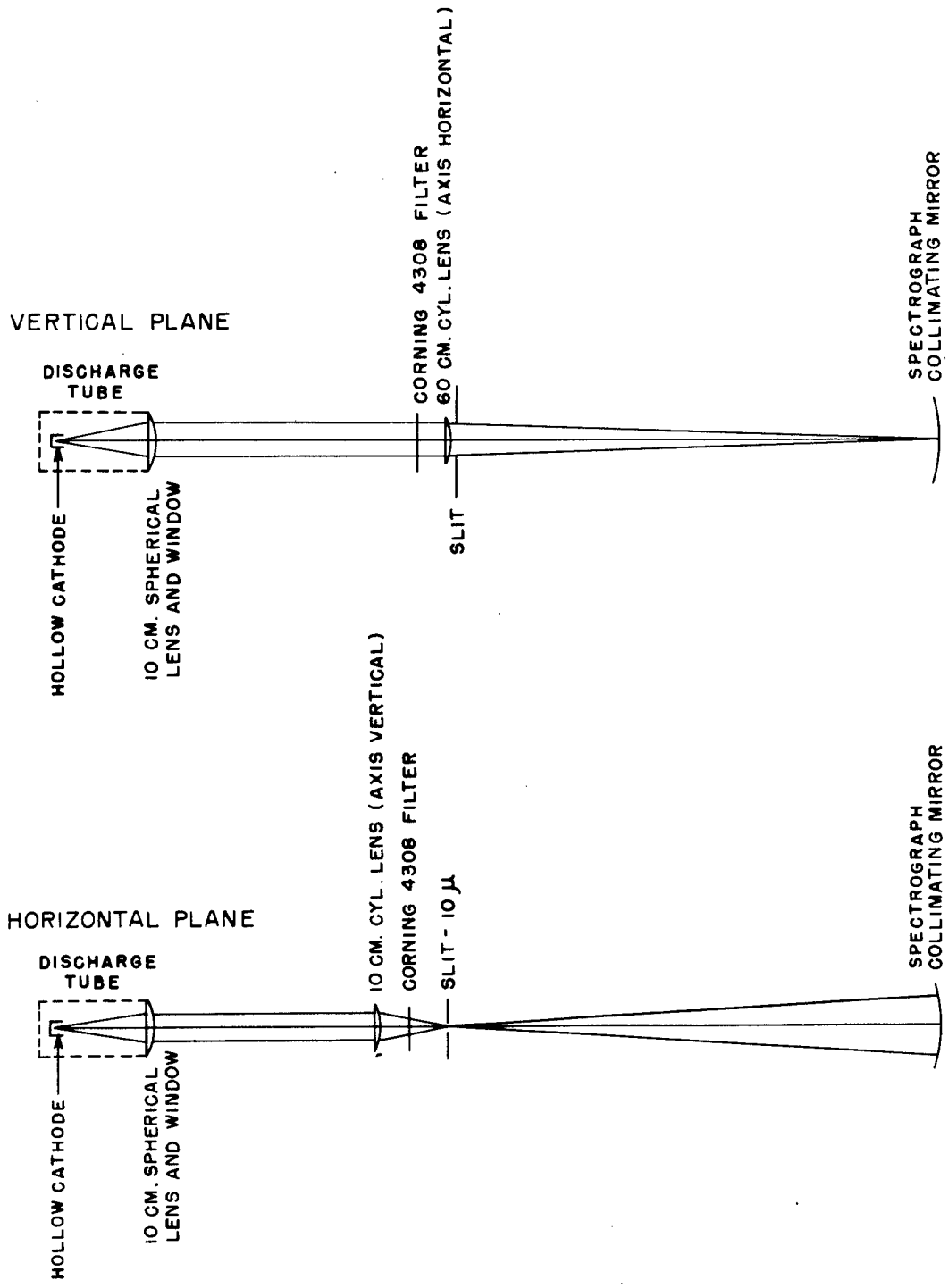
Recording Using Photomultiplier Tubes

Two procedures, designated as scanning and integrating, for measuring the intensities of the two spectral lines and the optical background have been investigated. A description of each method together with the results obtained follows.



INTENSITY OF U-235 (4244.127 Å) AS A FUNCTION OF TIME

FIGURE 4



OPTICAL SYSTEM USED WITH THE JARRELL-ASH SPECTROGRAPH

FIGURE 5

Scanning. A single slit and a single photomultiplier tube, similar to that used by Crosswhite (2) and Dieke (3), were mounted inside a light-tight metal box which was mounted on the back of the Jarrell-Ash spectrograph in place of the photographic plate holder. In this instrument wavelength is changed by moving laterally a steel beam which is pivoted at one end. The grating is mounted at the pivoted end and the photomultiplier and exit slit case at the other end. The scanning drive consisted of a 1/4 h.p., 1800 r.p.m. electric motor coupled to a two stage reduction gear with a ratio of 600 to 1 per stage, or a total reduction of 360,000 to 1. A bearing was attached to the gear box shaft by means of a bushing with the shaft hole 11/32" off center. A sketch of the bearing and bushing is shown in figure 6. The case of the bearing was attached to the steel beam of the spectrograph through a 1/4" connecting rod. Rotation of the shaft in the off-centered bushing caused the steel beam to move laterally, which in effect moved the exit slit with respect to the spectrum. The motor speed, ratio of the gear reduction boxes, and the eccentricity of the bearing were such that the scanning speed of the spectrum with respect to the exit slit was 0.2 mm. per minute. Using the 4244 A. isotopic line pair, 30 seconds were required at this rate to scan from the peak of the uranium 238 line to the peak of the uranium 235 line, and an additional 15 seconds to scan from the peak of the uranium 235 line to the region selected for measurement of background.

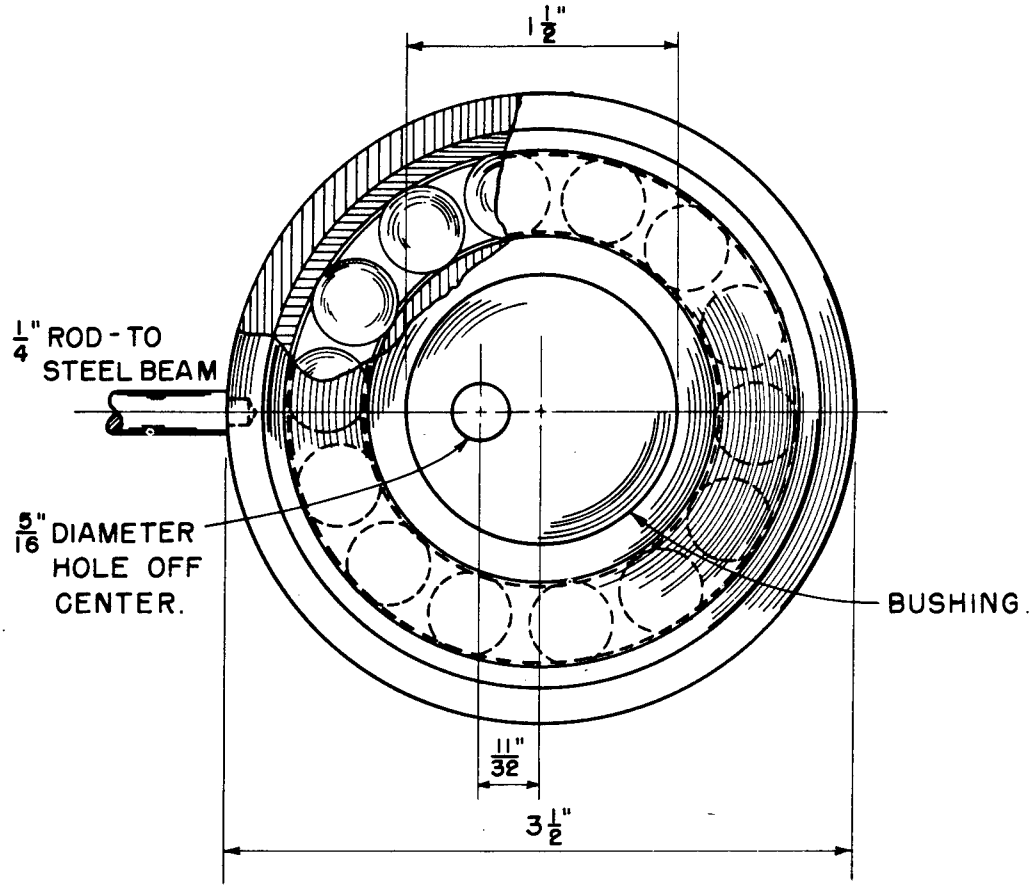
The output from the photomultiplier tube was connected to a recorder through a 4 stage 100% negative feed back amplifier (9). A simplified schematic diagram of the circuit for scanning is shown in figure 7.

A trace of the region from 4244 A. to 4246 A. is shown in figure 8. The uranium 235 line (4244.127 A.), the uranium 238 line (4244.371 A.), and the region (4244.0 A.) where background was measured are indicated on the trace.

Figure 9 is a trace of a measurement of the intensity ratio of uranium 235 to uranium 238 at the 10.366% uranium 235 level. The intensities of the uranium 235 line and the uranium 238 line were measured above the photomultiplier tube dark current and the optical background, as indicated in the figure. The amplifier was adjusted for sufficient sensitivity to record the intensity of the relatively weak uranium 235 line. To measure the intensity of the strong uranium 238 line, a bucking voltage was introduced which caused the recorder pen to move down-scale a known amount. The "shoulders" on the trace on either side of the uranium 238 line were caused by the introduction of the bucking voltage in ten division steps just as the exit slit jaw cleared the uranium 238 line and then the removal of this bucking voltage as the jaw moved over the uranium 238 line.

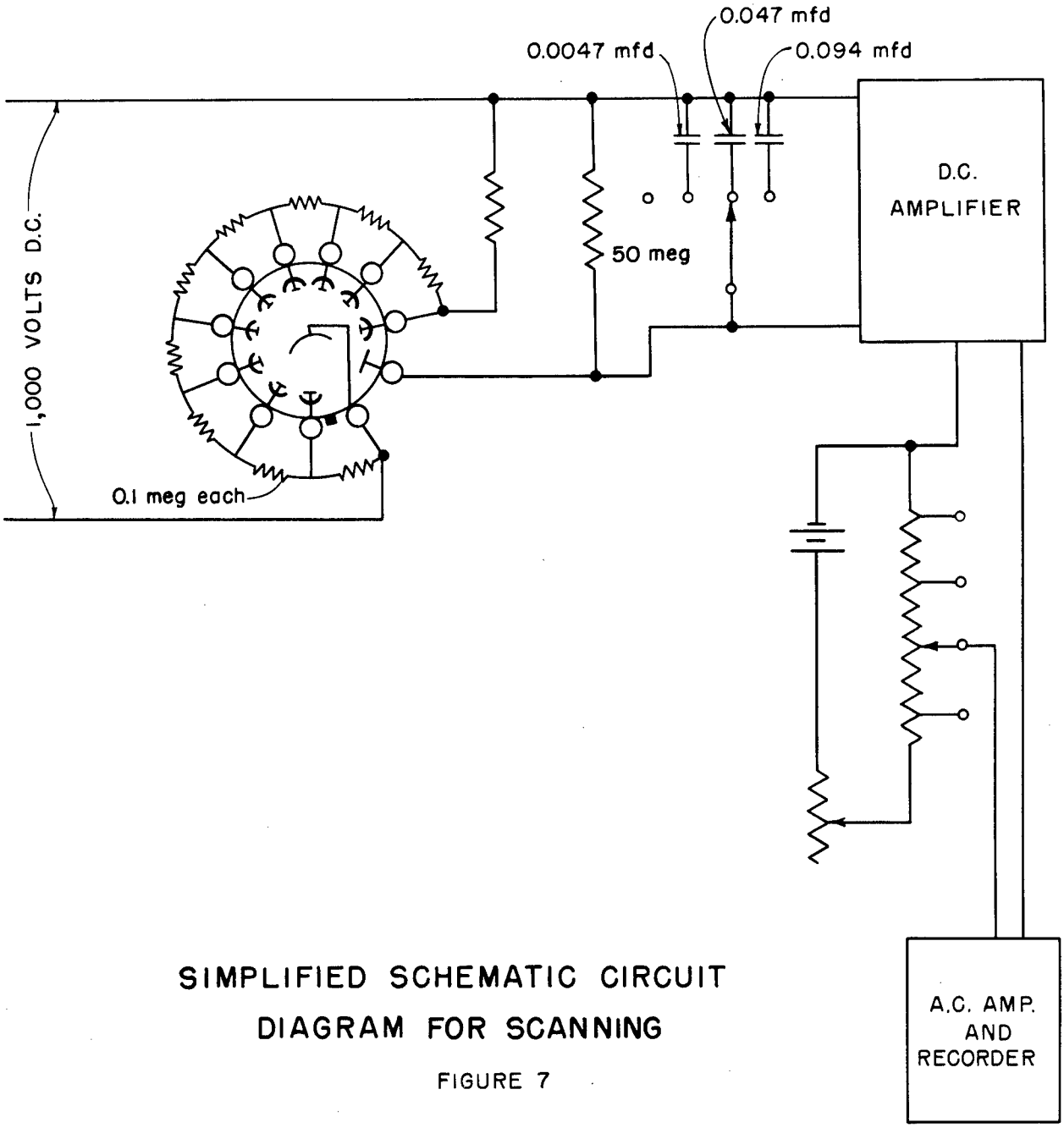
A damping condenser was included to filter out the shorter period fluctuations in the output of the photomultiplier tubes. This technique increased the period of the circuit so that the recorder did not respond to the shorter period variations.

An exit slit having a width of 50 microns was used. This width was equal to one half the distance between the centers of gravity of the two isotopic lines, and was chosen so that the slit opening would be over each spectral line the same period of time that it was over the background region between these lines.



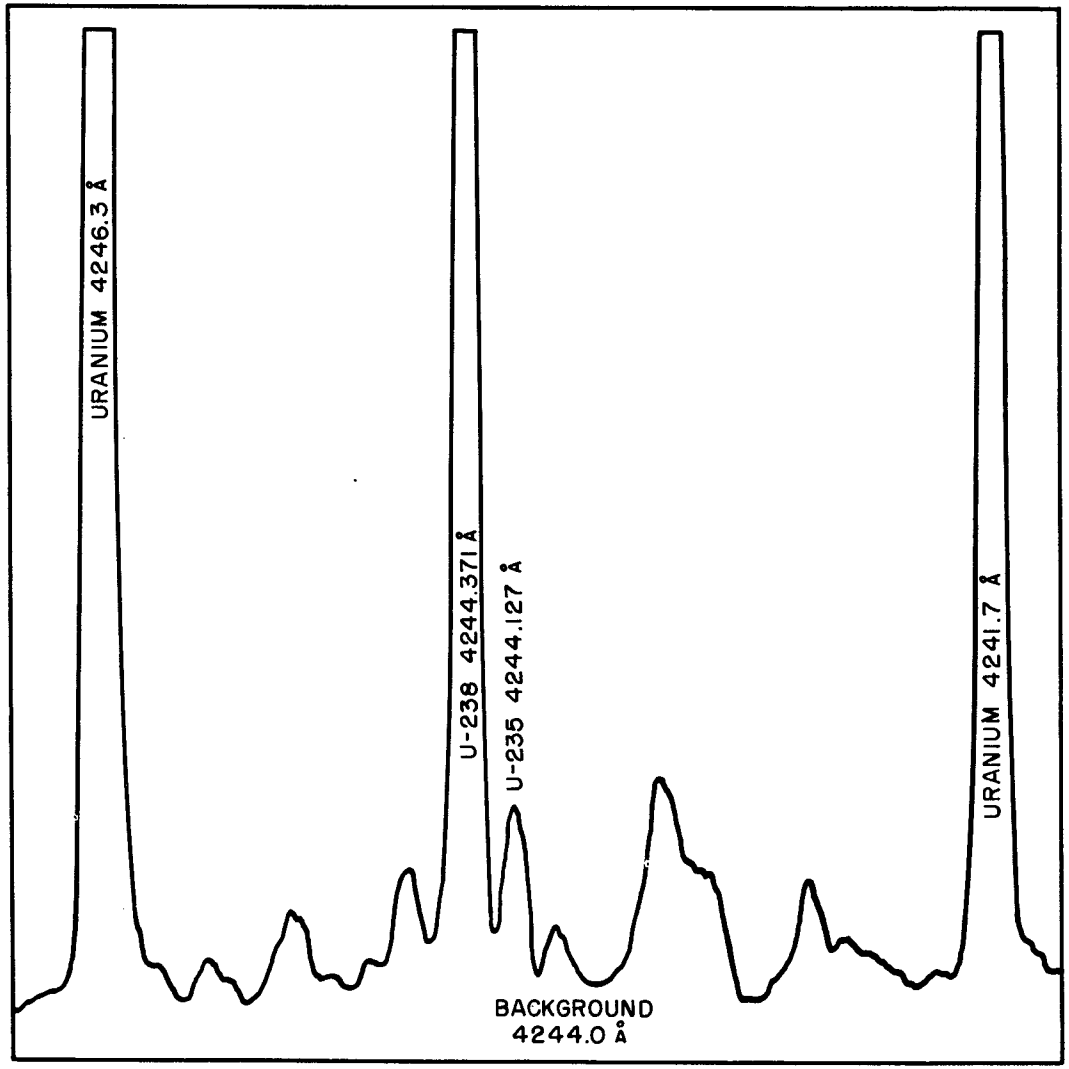
DETAILS OF BEARING AND BUSHING

FIGURE 6



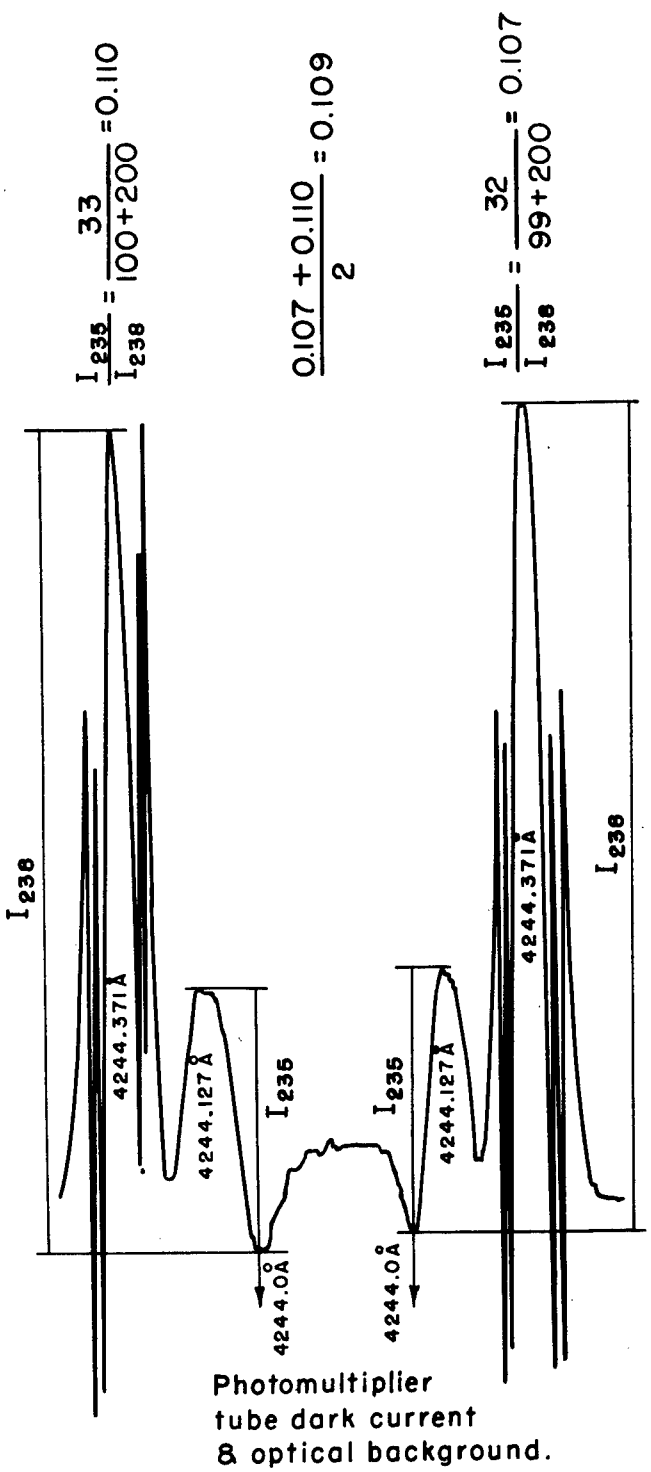
SIMPLIFIED SCHEMATIC CIRCUIT DIAGRAM FOR SCANNING

FIGURE 7



TRACE OF THE SPECTRAL REGION FROM 4241 Å TO 4251 Å

FIGURE 8



INTENSITIES OF URANIUM-235 AND URANIUM-238

FIGURE 9

The intensity ratios of the uranium 235 spectral line to the uranium 238 spectral line were measured on a series of standards, for each of which the percent uranium 235 was known from mass spectrometer measurements. Each standard was then treated in turn as an unknown, and the percent uranium 235 present was determined from a single standard and the intensity ratios of the unknown and of the standard as measured on the optical spectrograph. The results obtained, together with a statistical evaluation at the 95% confidence interval, are given in table 2. In appendix I appear the individual ratios from which the average value reported in table 2 were obtained. The method used to calculate the percent uranium 235 in the unknown from the intensity ratios and a single standard is similar to that used on the mass spectrometer at K-25 and is shown in appendix II (6,12).

TABLE II

MEASUREMENTS OF URANIUM 235 USING SCANNING

Percent Uranium 235 (Optical Spectrometer)	Percent Uranium 235 (Mass Spectrometer)
10.52 ± 0.17 (1.63%)	10.366 ± 0.046 (0.44%)
11.89 ± 0.19 (1.59%)	11.903 ± 0.051 (0.43%)
9.72 ± 0.12 (1.21%)	9.860 ± 0.044 (0.45%)
8.00 ± 0.14 (1.79%)	7.962 ± 0.035 (0.44%)

All limits shown are at the 95% confidence level.

Each optical value is an average of ten individual measurements.

Integration. In this method, which is based on those used by Hassler (5) and Saunderson (10), a separate fixed exit slit and a photomultiplier tube are placed behind each spectral line the intensity of which is to be measured. One exit slit and a photomultiplier tube were mounted behind the uranium 235 line at 4244.127 A., a second exit slit and photomultiplier tube were mounted behind the total uranium line at 4567.687 A., while a third exit slit and photomultiplier tube were placed at 4429.0 A. to measure the background.

A switch connected each photomultiplier tube to a condenser, and the outputs of the three photomultiplier tubes simultaneously charged the three condensers. After an exposure period of one minute, the condensers were disconnected from the photomultiplier tubes by the switch, and the background condenser was connected with opposed polarity in series with the uranium 235 condenser. The voltage across this combination, which was proportional to the intensity of the uranium 235 line corrected for optical background, was measured with the amplifier used in the scanning procedure. The background condenser was then disconnected from the uranium 235

condenser and connected in series with the non-isotopic or total uranium-line condenser, again with polarity opposed. The voltage of this combination, which was proportional to the intensity of the total uranium line corrected for optical background, was then measured. After the measurements were made, the condensers were discharged and the instrument was ready for the next measurement. A simplified schematic circuit diagram is shown in figure 10. A photograph of the amplifier, switching unit, and the photomultiplier tube housing is shown in figure 11. A photograph showing the arrangement of the exit slits and the photomultiplier tubes is shown in figure 12. The amplifier was of the null type and used the potentiometer principle for the integration measurements, so that the ratio of the two net voltages, which was equal to the ratio of the intensities of the uranium 235 line to the total uranium line, was read directly from four dial decades mounted on the amplifier panel.

The dark current of the photomultiplier tubes was compensated for by permitting a small current equal to but opposite in polarity to the dark current of the photomultiplier tube to flow into the condenser during the charging period.

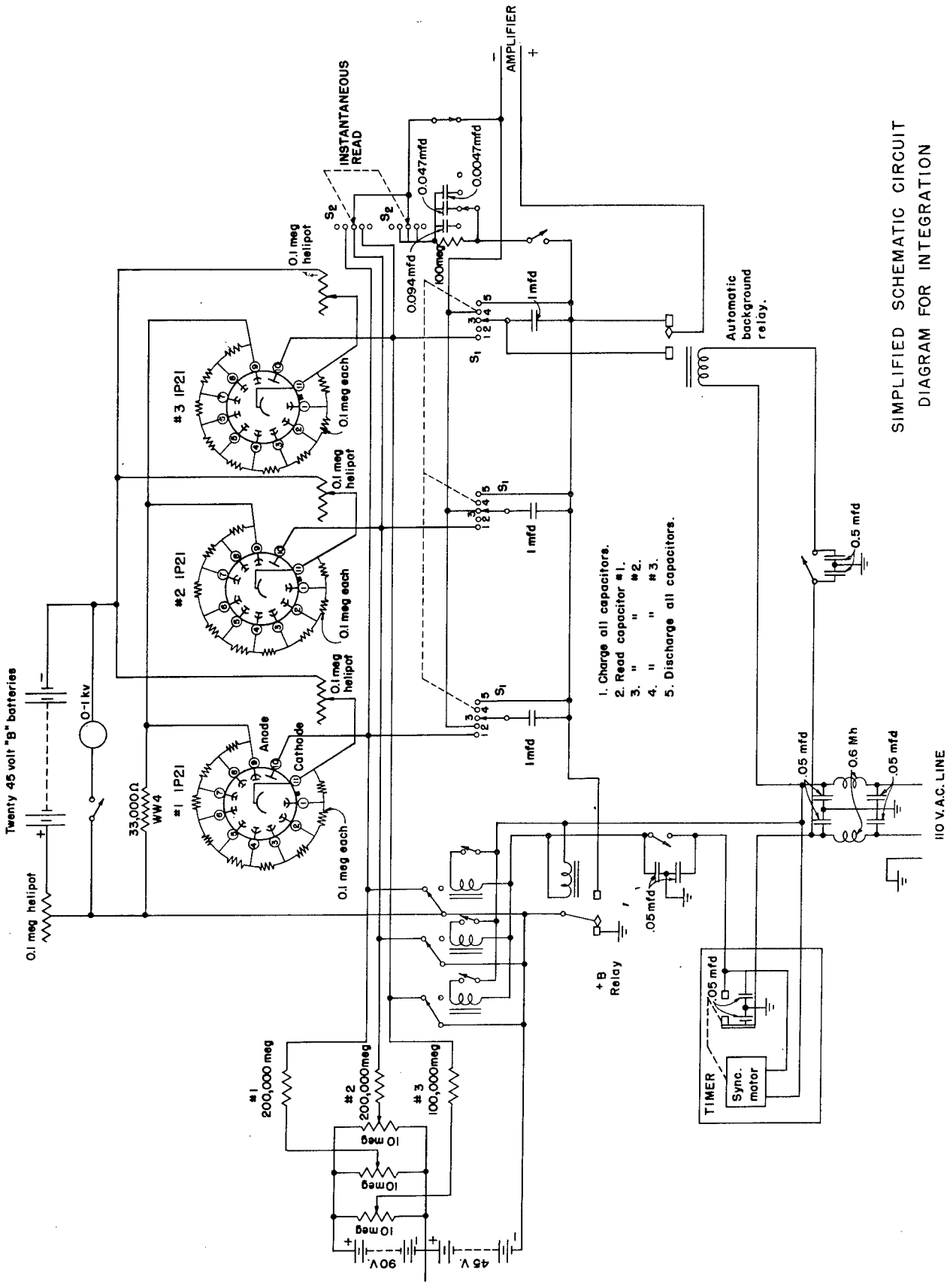
To make proper corrections for the optical background, it was necessary that the sensitivities of the three tubes be adjusted so that the background readings at the uranium 235 and at the total uranium line be equal to the background reading of the photomultiplier tube measuring the background. This adjustment was made by moving the uranium 235 exit slit to one side of the uranium 235 line, and the total uranium slit to one side of the total uranium line, at which points the optical backgrounds were assumed to be equal to the optical backgrounds under the uranium 235 line and under the total uranium line respectively. The voltages applied to the three photomultiplier tubes were then adjusted until the output of each tube was the same. The slits were then returned to their proper positions over the spectral lines.

A series of 10 ratios of the intensity of the total uranium line to the intensity of the uranium 235 line were measured for material at a concentration of 50% uranium 235. The mean ratio and the precision at the 95% confidence level were 0.3506 ± 0.00064 (0.18%). The individual ratios are given in appendix III.

DISCUSSION

Scanning. Random fluctuations in the output of the photomultiplier tube limit the precision of the measurement of small light intensities. These fluctuations are believed to arise from leakage current across the insulation and from thermionic emission, and can be minimized by taking proper precautions with the insulation and by cooling the photomultiplier tube in liquid nitrogen. The effects of these fluctuations can be reduced by increasing the period of the circuit so that the recorder does not respond to the shorter period fluctuations.

Additional factors must be considered when using a damping condenser to increase the period of the circuit. The scanning must be slow enough for the voltage across the damping condenser to build up to the output voltage



SIMPLIFIED SCHEMATIC CIRCUIT DIAGRAM FOR INTEGRATION

FIGURE 10

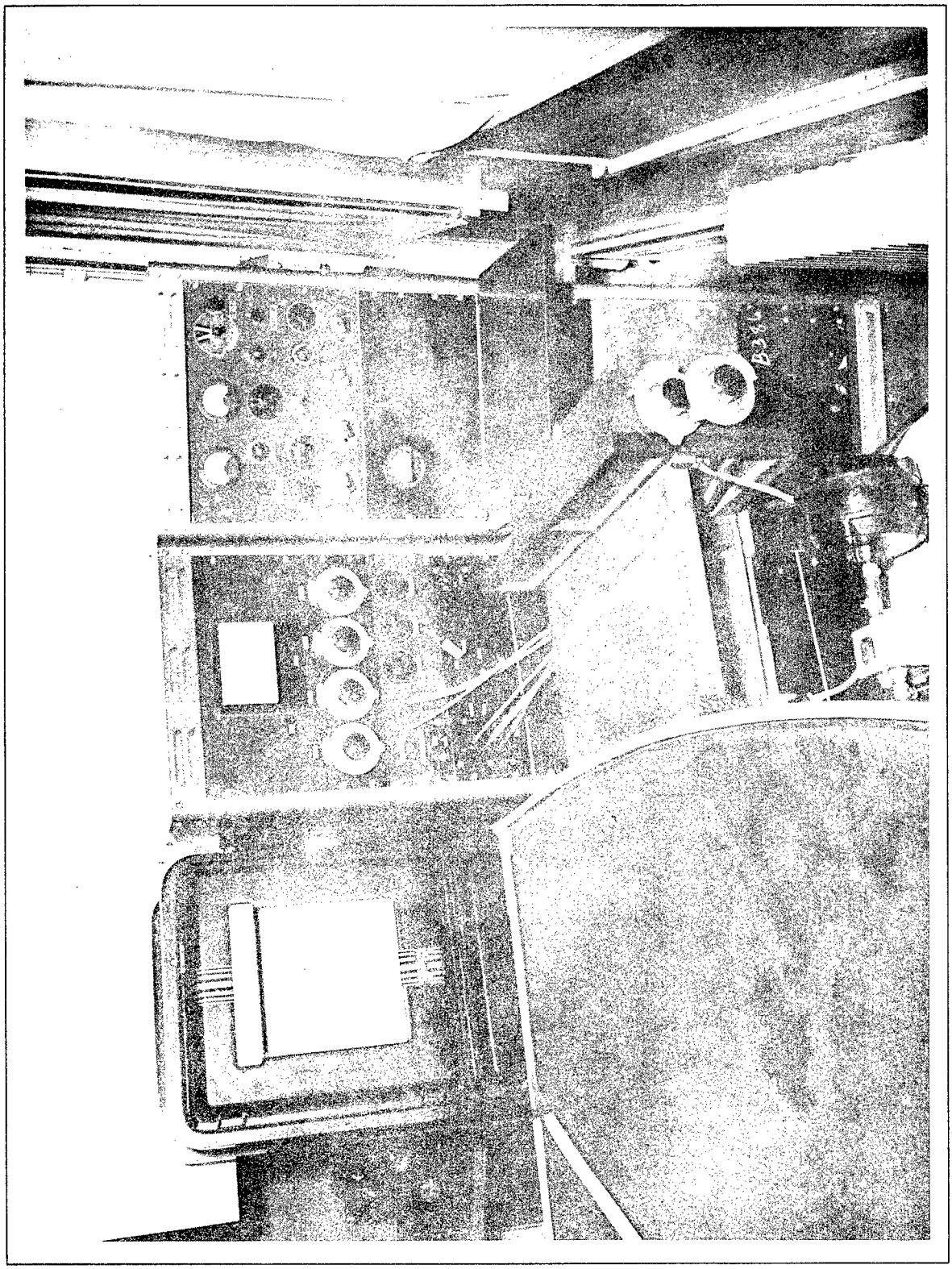


Figure 11. Amplifier, Switching Unit, and Photomultiplier Tube Housing

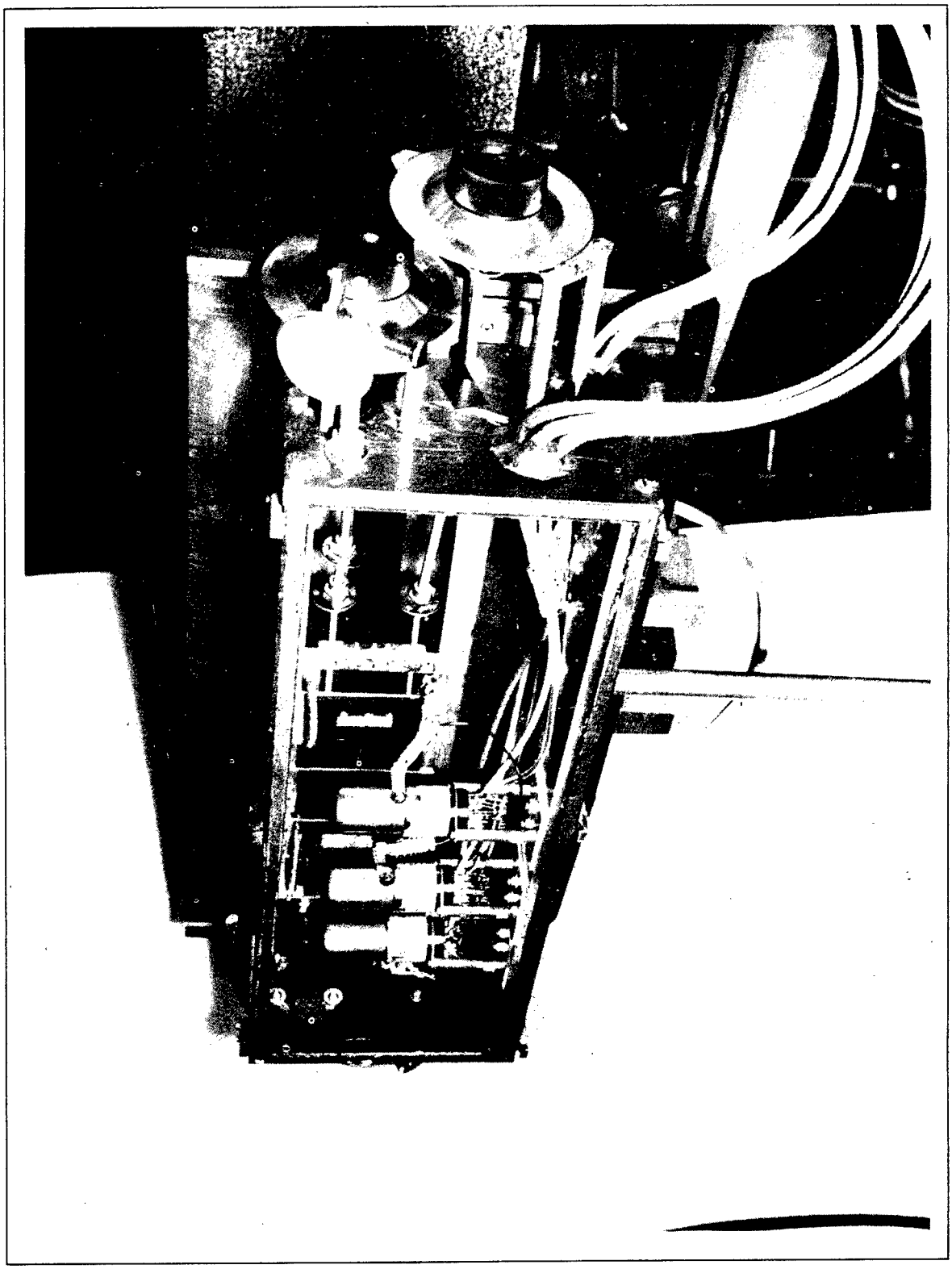


Figure 12. Arrangement of Exit Slits and Photomultiplier Tubes

of the photomultiplier tube while the exit slit is over a spectral line and to decay to the output voltage of the photomultiplier tube while the exit slit is over the background region or over a weaker spectral line. In other words, since the speed of response of the recorder has been reduced so that it does not respond to the short period random fluctuations, it is necessary that scanning be slow enough so that the recorder can respond quantitatively to the changes in the output of the photomultiplier tube as the exit slit moves across the spectral lines and background regions.

If the scanning period is to be used most economically, it is necessary that the exit slit remain over each of the isotopic spectral lines for the same period of time as it does over the background region between the lines. The damping condenser will then have equal periods to reach equilibrium with the output voltage of the photomultiplier tubes during the build up and decay. This condition was fulfilled when the exit slit width was made equal to one half of the distance between the center of gravities of the isotopic spectral lines.

Since the scanning speed was such that it took 45 seconds to scan uranium 238, uranium 235, and the background region (see figures 8 and 9), it was essential that the absolute intensity of the excitation source remain constant during this period. Examination of figure 4, which shows a trace of the absolute intensity of uranium 235 as a function of time, indicates that the requirement that the absolute intensity remain constant during the 45 second scanning interval was met approximately after the initial 15 minute build-up period.

To reduce the effect of the variance in the absolute intensity of the excitation source, a reversing switch was installed on the scanning motor. This reversal permitted scanning first in one direction in which the order of recording was uranium 238, uranium 235, and background, and then in the reverse direction in which the order was background, uranium 235, and uranium 238. The measurements in both directions were averaged and treated as a single measurement. A more direct and probably more precise method to compensate for variations in the absolute intensity would be to use a second photomultiplier tube as a reference tube and record the ratio of the outputs of the scanning tube to the reference tube (2,3).

Integration. The integration method of recording is in the process of development, and additional work, particularly regarding the reproducibility of the intensity ratio with time and with variations in the absolute intensity of the excitation source, is required.

SUMMARY

A Jarrell-Ash 21 foot spectrograph using a 6 inch, 15,000 line per inch grating was adapted for direct reading of the spectral lines by attaching a specially constructed housing containing exit slits and photomultiplier tubes. Using this instrument in the second order and a hollow cathode discharge tube for excitation of the sample, a series of measurements was made to determine the 95% confidence interval for several concentrations of uranium 235. Two methods of direct reading, designated as scanning and as integration, were used.

A precision ranging from 1.2 to 1.8% of the amount present on samples assaying between 8 and 12% uranium 235 was obtained using the scanning technique. Ten measurements were made on each unknown and the percent uranium 235 was evaluated from a single standard, which was known from mass spectrometer data to 0.5% of the amount present.

Using the integration method, a series of ten intensity ratio measurements was made on material containing 50% uranium 235. The mean ratio and the precision were 0.3506 ± 0.00064 (0.18%). Additional work is required for the integration method.

ACKNOWLEDGEMENT

The authors wish to express their thanks and appreciation to Mr. John Farquharson for the electronic equipment and to Mr. E. F. Babelay for the machine shop work. This study would not have been possible without their cooperation.

The authors also wish to express their thanks to Mrs. Olive Warram for the statistical treatment of the data, to Dr. J. R. McNally, Jr. for the use of a hollow cathode discharge tube, and to Dr. R. H. Lafferty, Jr. for his many helpful suggestions.

BIBLIOGRAPHY

1. Brody, J. K., private communication; also "The Isotopic Assay of U^{238}-U^{235} Mixtures," part 4.1.3 of Summary Report for Period October through December, 1950, Chemistry Section, C-II, Argonne National Laboratory, ANL-4564, p. 111-113.

2. Crosswhite, H. M., "Photoelectric Intensity Measurements in the Iron Arc," Spectrochimica Acta, 4, 122-151 (1950).

3. Dieke, C. H., "Photoelectric Intensity Measurements in Spectra," The Transactions of Instruments and Measurements Conference Stockholm, 17-37 (1947).

4. Harrison, G. R., Lord, R. C., and Loofbourow, J. R., Practical Spectroscopy, New York, Prentice-Hall (1948), p. 129.

5. Hasler, M. F., Lindhurst, R. W., and Kemp, J. W., "The Quantometer, A Direct Reading Instrument for Spectrochemical Analysis," J. Opt. Soc. Am., 38, 789-799, (1948).

6. Klacsmann, J. A., Tabor, C., and Smith, L. A., Spectrometer Symbols and Methods of Calculating Units of Isotpic Results, Carbide and Carbon Chemicals Corporation, K-25 Plant, June 25, 1946 (C-25).

7. Lee, T., Hallowell, A. L., and Rogers, L. H., Precision of the Photographic Spectrochemical Assay of Uranium 235 at Low Concentrations, Carbide and Carbon Chemicals Corporation, K-25 Plant, March 20, 1950, (K-721).

8. McNally Jr., J. R., Harrison, C. R., and Rowe, E., "A Hollow Cathode Source Applicable to Spectrographic Analysis for the Halogens and Gases," J. Opt. Soc. Am., 37, 93-98 (1947).

9. Nier, A. O., "A Mass Spectrometer for Isotope and Gas Analysis", Rev. Sci. Instruments, 18, 398-411 (1947).

10. Saunderson, J. L., Caldecourt, V. J., and Peterson, E. W., "A Photoelectric Instrument for Direct Spectrochemical Analysis," J. Opt. Soc. Am., 35, 681-697 (1945).

11. Smith, D. D. and Burkhart, L. E., Mass Analysis of Uranium Isotopes by Emission Spectroscopy, Carbide and Carbon Chemicals Company, Y-12 Plant, March 4, 1948, (Y-226).

12. Tabor, C., Methods of Mass Spectrometer Measurements Using Gradient Standards, Carbide and Carbon Chemicals Corporation, K-25 Plant, June 19, 1947 (A-4198).

NOTEBOOK REFERENCE

Lee, T., K-25 Notebook Number 1647.

Experimental work was completed July 31, 1951.

APPENDIX I

INDIVIDUAL INTENSITY RATIOS OF U-235 TO U-238 USING SCANNING ON THE OPTICAL SPECTROMETER

Percent Uranium 235:	7.962	9.860	10.366	11.903
	0.080	0.100	0.106	0.125
	0.078	0.102	0.108	0.125
	0.079	0.099	0.105	0.127
	0.078	0.100	0.110	0.125
	0.078	0.101	0.106	0.124
	0.082	0.100	0.109	0.123
	0.081	0.100	0.105	0.123
	0.080	0.099	0.104	0.125
	0.076	0.098	0.110	0.127
	0.081	0.098	0.109	0.127
Average	0.079±0.001	0.100±0.001	0.107±0.002	0.125±0.001

The precisions of the average intensity ratios are at the 95% confidence level.

APPENDIX II

Calculations. The method used to calculate the percentage uranium 235 in the unknown from a single standard is similar to that used by the Mass Spectrometer Section. The equation used is given below. The symbols used are as follows:

subscript U ≡ unknown
subscript S ≡ standard
R ≡ intensity ratio
$\frac{N_{235}}{N_{238}}$ ≡ mole ratio
I ≡ light intensity

$$\%U\text{-}235_U = \frac{100 \quad \frac{R_U(\%U\text{-}235_S)}{R_S(100-\%U\text{-}235_S)}}{1 + \frac{\text{Numerator}}{100}}$$

The basis for this relationship is as follows:

$$\frac{N_{U\text{-}235}}{N_{U\text{-}238}} = \frac{\left(\frac{\%U\text{-}235}{235}\right)}{\left(\frac{\%U\text{-}238}{238}\right)} = \frac{I_{U\text{-}235}}{I_{U\text{-}238}} = R$$

assumed, and no correction being made for U-234

$$\frac{\left(\frac{\%U\text{-}235_U}{100-\%U\text{-}235_U}\right) \quad \left(\frac{238}{235}\right)}{\left(\frac{\%U\text{-}235_S}{100-\%U\text{-}235_S}\right) \quad \left(\frac{238}{235}\right)} = \frac{R_U}{R_S}$$

$$\%U\text{-}235_U = \frac{R_U}{R_S}\left(\frac{\%U\text{-}235_S}{100-\%U\text{-}235_S}\right)(100-\%U\text{-}235_U)$$

$$\%U\text{-}235_U + \frac{R_U}{R_S}\left(\frac{\%U\text{-}235_S}{100-\%U\text{-}235_S}\right)(\%U\text{-}235_U) = 100\,\frac{R_U}{R_S}\left(\frac{\%U\text{-}235_S}{100-\%U\text{-}235_S}\right)$$

$$\%U\text{-}235_U\left[1 + \frac{R_U}{R_S}\left(\frac{\%U\text{-}235_S}{100-\%U\text{-}235_S}\right)\right] = 100\,\frac{R_U}{R_S}\left(\frac{\%U\text{-}235_S}{100-\%U\text{-}235_S}\right)$$

$$\%U\text{-}235_U = \frac{100 \quad \frac{R_U(\%U\text{-}235_S)}{R_S(100-\%U\text{-}235_S)}}{1 + \frac{R_U(\%U\text{-}235_S)}{R_S(100-\%U\text{-}235_S)}}$$

APPENDIX III

INDIVIDUAL INTENSITY RATIOS USING INTEGRATION

0.3512
0.3509
0.3499
0.3520
0.3510
0.3517
0.3505
0.3491
0.3500
0.3500

$X = 0.3506 \pm 0.00064$ (0.18%) at the 95% confidence level.

GPO 970884