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# THE MODEL VI TRANSMISSION FLUORIMETER FOR THE DETERMINATION OF URANIUM*

By

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Trace Elements Investigations Report 370

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# THE MODEL VI TRANSMISSION FLUORIMETER FOR THE DETERMINATION OF URANIUM

By Charles A. Kinser


## ABSTRACT

An improved transmission fluorimeter (Model VI) for use in the determination of uranium consists of a line-operated, low-voltage d-c supply, powering a small 3-w ultraviolet lamp as a source of long wavelength ultraviolet radiation; a Model V phototube housing and fluorimeter head containing the sample holder, shutter, and primary and secondary filters; an end-window multiplier phototube powered by a very stable, commercially available high-voltage supply; and an electronic microammeter for measuring the output current from the photomultiplier tube. The instrument has excellent electrical stability and operates over a wide range of sensitivity. Its versatility makes it useful for both routine and research work.


## INTRODUCTION

Transmission fluorimeters have been used for the measurement of uranium in alkali carbonate fluoride melts for several years. Detailed discussions of their advantages and operating principles by Fletcher and others (1949, 1950) and Grimaldi and others (1952) need not be repeated here. Other workers in the field have described experimental portable and laboratory fluorimeters operating on the transmission principle (op. cit.; May and Fletcher, 1950).

In the construction of the Model VI fluorimeter (fig. 1) an effort was made to produce a laboratory instrument that has the following features: convenience of operation, good electrical stability, compactness in arrangement of components, and wide latitude in the control of sensitivity.

The use of a commercially available high-voltage supply and ultrasensitive d-c microammeter adds materially to the ease of construction.

The entire instrument, with the exception of the microammeter, is operated from the regular 115-v a-c line, with ample regulation to absorb line voltage fluctuations. Current drain on the meter batteries is so low that they need to be replaced only about once a year.

The linearity of response of this instrument and its convenient step-wise sensitivity scales make possible the use of a set of standard curves covering three uranium concentration ranges, each a tenfold increase over the previous one.

All components are mounted on a base board 12 in. wide by 24 in. long with all controls accessible from the front.

The author is indebted to many of his colleagues in the Geological Survey for valuable suggestions and encouragement, especially to Mary H. Fletcher for assistance in various phases of the work, and to J. T. Bracken and W. R. Champion for advice on the electrical problems. This report is the result of work done on behalf of the Division of Research of the Atomic Energy Commission.

## DESCRIPTION OF THE INSTRUMENT

### The ultraviolet lamp

The ultraviolet light source is the 3-w General Electric RP-12 lamp designed to operate on 12 to 16 volts for fluorescent instrument

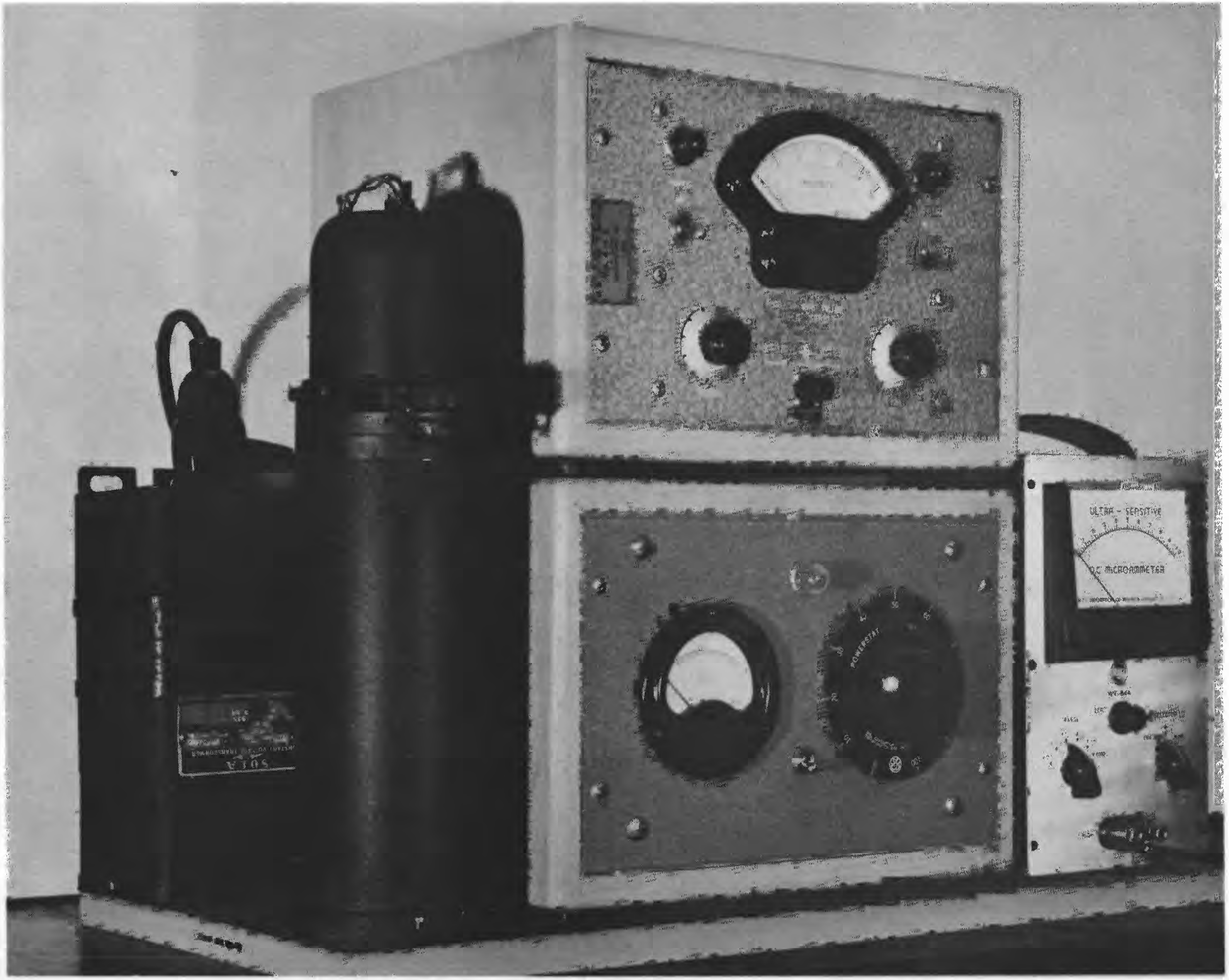



Figure 1.--Front view of fluorimeter

dial lighting on airplanes. This lamp was used successfully in a battery-powered fluorimeter designed by May and Fletcher (1950). Its inner surface is coated with a phosphor which has a radiation peak in the long wavelength with high emission at 3650 A which is considered the most desirable wavelength for the production of uranium fluorescence.

This lamp in its housing is very compact, extending only 3 1/2 in. above the fluorimeter head. Its output has been ample when used with multiplier phototubes and sufficiently sensitive measuring instruments. It replaces the usual 100-w ultraviolet lamp and obviates the necessity for bulky housings, supports, and adjustments. As the RP-12 lamp is of low wattage, it dissipates little heat and requires no blower to keep it cool.1/

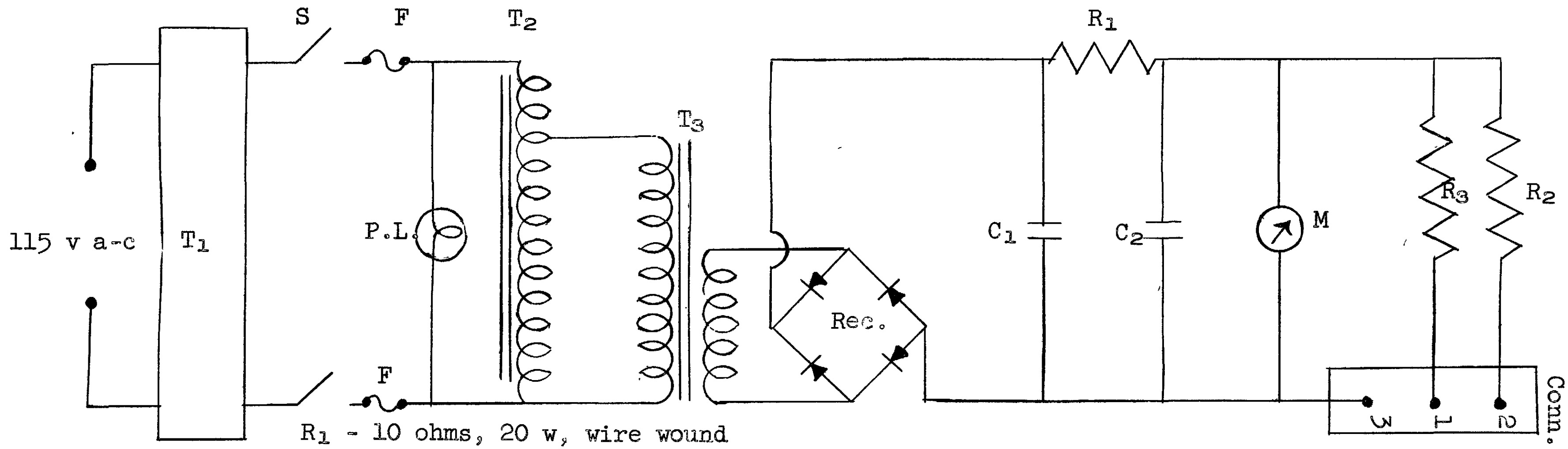
As with other ultraviolet lamps, a warm-up period of about 15 minutes is required to allow the output to stabilize before measurements are made.

The electric circuit for the lamp is shown in figure 2.

## Power supply for the ultraviolet lamp

The low-voltage d-c power supply for the ultraviolet lamp was designed to operate from the regular 115-v, 60-cycle, a-c supply. As shown diagrammatically in figure 2, the voltage for this power supply is stabilized by a voltage regulator; the output is adjustable from 0 to 17 volts by a variable autotransformer and is rectified by a full-wave bridge-type selenium rectifier and filtered to give a practically ripple-free voltage. Resistors $R_2$ and $R_3$ drop the voltage to the correct

1/ Sockets for these lamps are manufactured by the Cole-Hersee Co., Old Colony Ave., Boston, Mass., and the H. A. Douglas Manufacturing Co., Bronson, Mich.




$R_1$ - 10 ohms, 20 w, wire wound
$R_2$ - 30 ohms, 10 w, wire wound
$R_3$ - 15 ohms, 10 w, wire wound
$C_1$ and $C_2$ - 4000 $\mu$f, 25 v, (Mallory no. HC 2540)
$T_1$ - Constant voltage transformer, 120 va (Sola no. 30806)
$T_2$ - Variable autotransformer, 150 va, Powerstat type 10
$T_3$ - Step-down transformer, 115 v primary, 24 v secondary, 50 va (Chicago Transformer Co. no. NCF 2450)
Rec - Selenium rectifier, full-wave bridge (Federal no. 106B1AX1)
M - 0-25 v, d-c meter, 3 1/2 in. (Triplett no. 321)
S - Switch, DPST
F - Fuses, 2 amp
PL - Pilot lamp, 115 v
Conn - Connector, 3 contact (Cannon XL-12 plug and XL-13 receptacle)

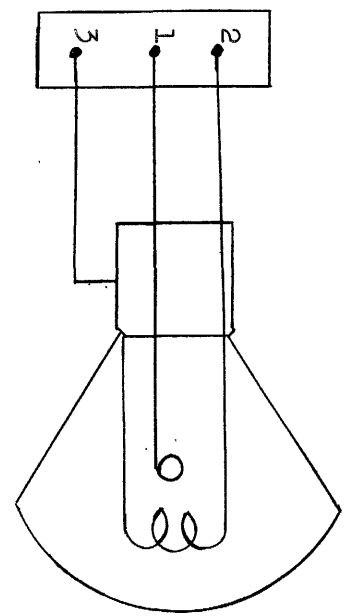



Figure 2.--Circuit for low voltage power supply

G.E. RP-12 fluorescent lamp

values for the electrodes of the lamp. A 0- to 25-v d-c meter is placed across the output of the filter section.

All components, except the voltage regulator, are mounted on a low chassis and a panel (7 x 11 in.) and enclosed in a cabinet which is the same size as that of the high-voltage power supply (12 1/4 x 8 1/4 x 10 1/4 in.). Figure 3 shows the arrangement of the components in the low-voltage power supply.

The wiring diagram and parts description is given in figure 2.

The voltage regulator is located near the instrument and both the high and low voltage supplies are operated from it.

### Fluorimeter head and phototube housing

The model V fluorimeter head and phototube housing, as perfected by Fletcher, May, and Anderson (1950), are used with the same primary and secondary filters, shutter, and sample holder. A complete description and detailed drawings are given in the above reference and need not be repeated here.

### Multiplier phototube and high voltage supply

An RCA 5819, 10-stage, end-window, multiplier phototube is used for detecting the uranium fluorescence. It is capable of multiplying the photo-electric current produced at the cathode by 600,000 times when operated at 90 v per stage.

The manufacturer recommends that for maximum stability the anode current should not exceed 100 microamperes and the anode supply voltage should not exceed 1250. We usually operate our phototube at about 725 v but occasionally use the range 500 to 1000 v for experimental purposes.

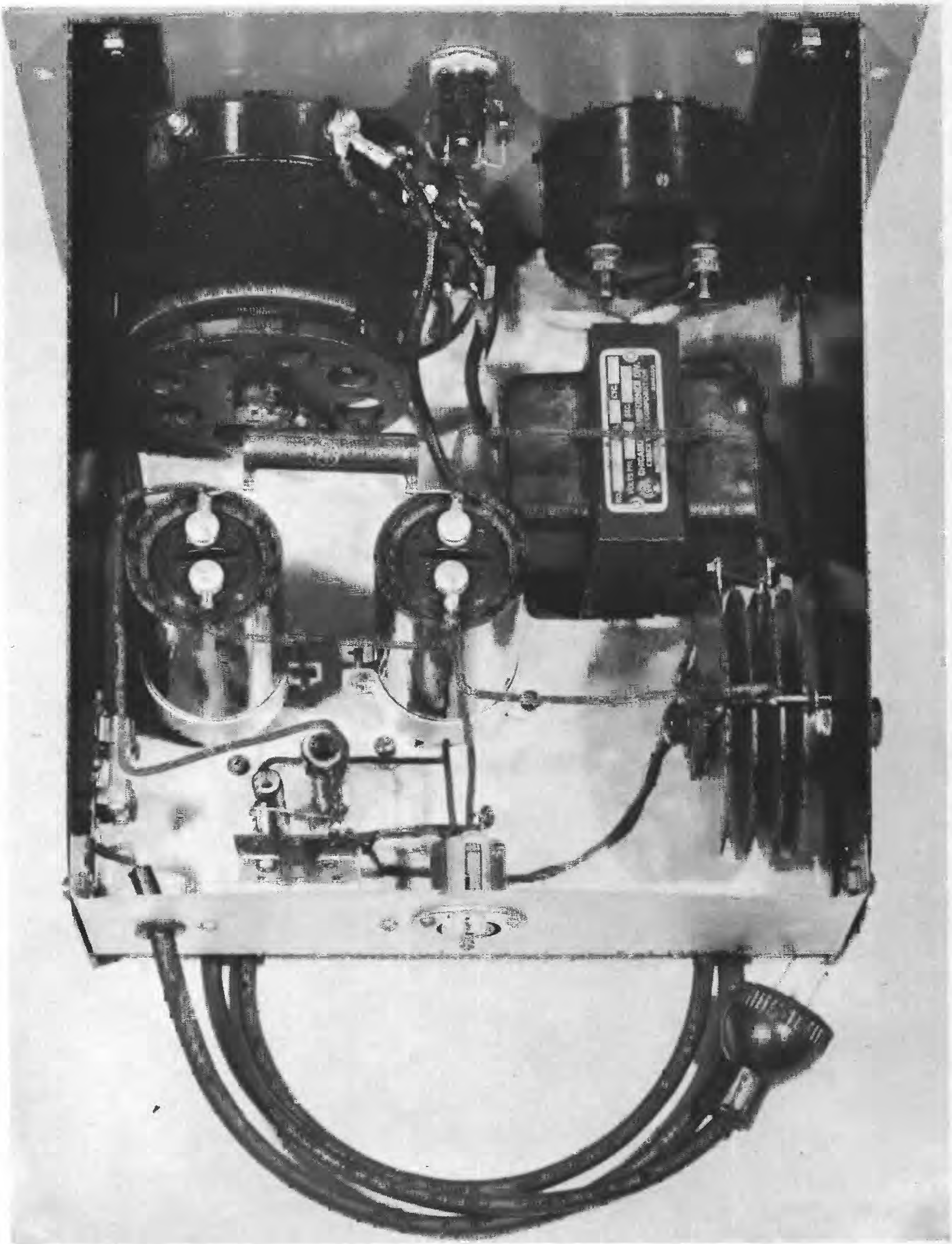


Figure 3.--Top view of low voltage power supply

The 5819 phototube has an S-9 spectral response covering the range 3000 to 6400 A with a maximum response at 4800 A. The response at 5545 A, which is the emission peak of uranium fluorescence in the fused pad, is 70 percent of the tube's maximum response.

A commercially available power supply 2/ has proved very satisfactory in powering the phototube. This unit operates from the regular 115-v 60-cycle, a-c line and has a continuous output of 500 to 3000 v which can be varied by means of a coarse and a fine adjustment, with full regulation up to 1 milliampere at 2000 v and 0.3 milliampere at 3000 v. The manufacturer's specifications state that an input voltage change from 105 to 125 v will change the output voltage less than 0.01 percent.

An output connector was mounted at the rear of the chassis and wired so that the high voltage leads to the multiplier phototube could be placed behind the cabinet. High voltage connections between power supply, phototube, and meter were made with polyethylene-insulated, RG-29/U, coaxial cable.

Figure 4 shows the circuit diagram for the 5819 multiplier phototube and the resistance values used in the voltage divider. It also indicates the connections for the high voltage supply and for the meter for measuring the phototube output current.

## Microammeter

For the measurement of the output current from the multiplier phototube a very convenient ultrasensitive d-c microammeter is used (RCA WV-84A).

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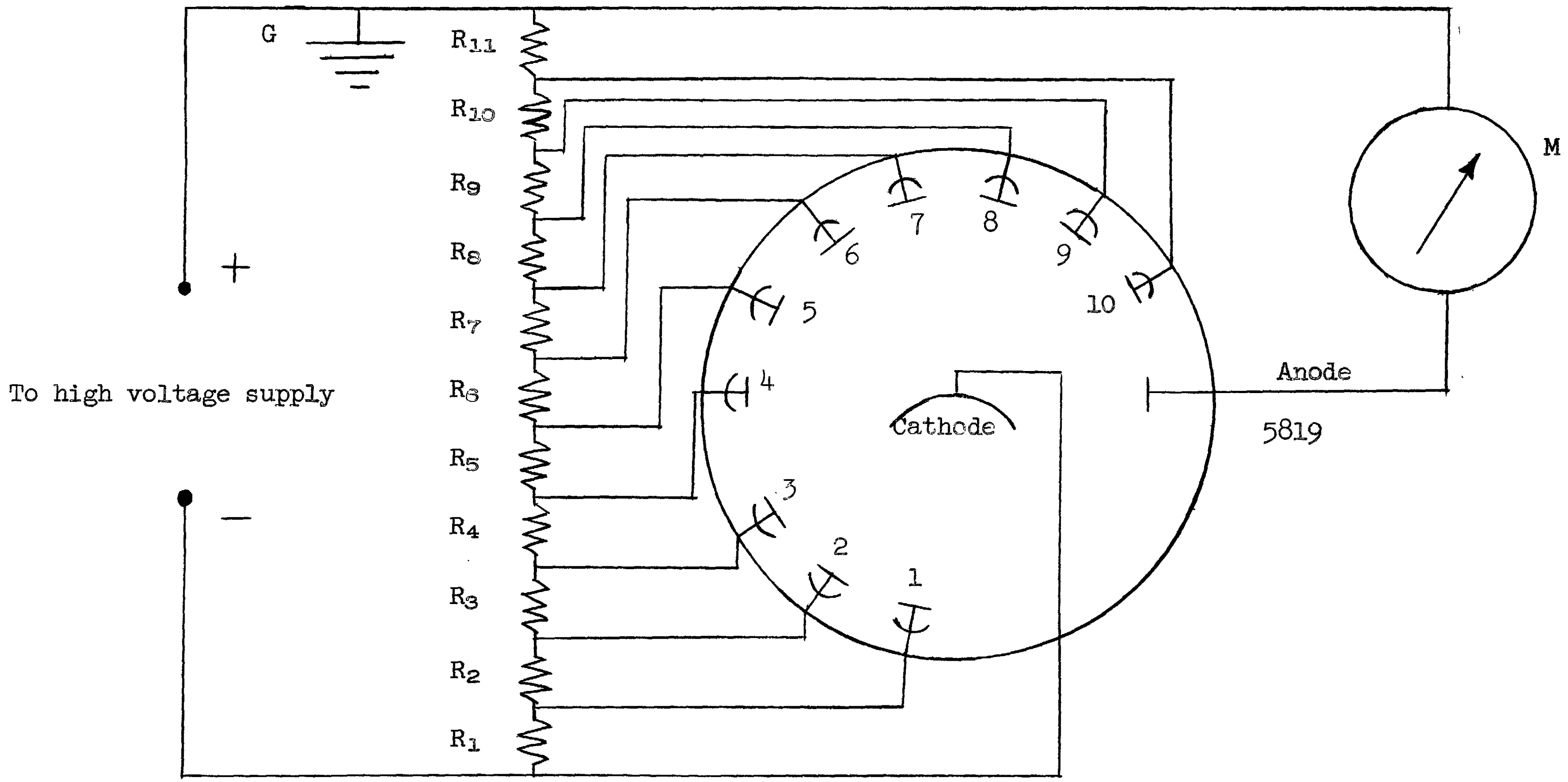
2/ Model 306 PR (positive grounded), available from: Atomic Instrument Co., 84 Massachusetts Ave., Cambridge 39, Massachusetts.




M - RCA WV-84A Ultrasensitive d-c microammeter
G - Ground. Shield of the RG-29/U cable serves as positive leads to meter and power supply
$R_1$ - Resistor, 2 megohm, 1/2 w
$R_2$ to $R_{11}$ - Resistors, 1 megohm, 1/2 w

Figure 4.--Circuit for multiplier phototube

This meter provides a wide selection of ranges and gives a full scale deflection for 0.01, 0.1, 1, 10, 100, and 1000 microamperes. Such sensitivity and choice of ranges in the meter allows the operator to measure uranium fluorescence accurately over an intensity range of several thousand fold.

This microammeter is battery-powered but inconvenience due to this feature is negligible as its miniature tubes draw so little current that battery replacement has been necessary only about once a year with the meter in use almost every day.

When measuring the fluorescence of a sample of unknown uranium content, it is desirable first to open the shutter with the meter on a low sensitivity scale to protect the instrument against the possibility of damage by too much current. Then, with the shutter open, advance the sensitivity until the meter deflection indicates that the best range for that sample has been reached.

If the meter deflection is less than 0.1 of the scale, the sensitivity can be advanced to the next higher range.

## OPERATION

It is common practice in fluorimetric analysis to adjust the sensitivity of the fluorimeter against a standard prepared from a known amount of the substance to be measured. The preparation of a uranium standard for the adjustment of the sensitivity each time the instrument is used would be both time consuming and unnecessary. Instead, a very convenient secondary standard, the fluorescence and light leakage of the filters in the instrument, is used in adjusting the instrument sensitivity.

The most convenient value for this secondary standard, which we call the "standard deflection", is determined indirectly by first adjusting the instrument to the desired sensitivity against a uranium standard, then removing the standard and noting the meter deflection with the shutter open and no sample in place. The standard deflection can thereafter be used in adjusting and checking the sensitivity before and during analyses.

Operating procedure is given in the following steps:

Selecting the standard deflection

1. Turn the ultraviolet lamp on and allow it to warm up for 15 minutes before use. The recommended operating range for this lamp is 12 to 16 v. Our lamp is always operated at 14 v for the sake of uniformity.

2. Turn on the high voltage supply and adjust the output to about 725 v.

3. Turn the meter on and move the sensitivity control to the 0.1 range and, with the shutter closed, adjust the meter deflection to zero.

4. Place a standard pad containing 0.01 microgram of uranium in the sample holder and slide it into place. The standard pad is prepared by fusion of 0.01 microgram of uranium standard with 2.0 g of fluoride carbonate flux under the controlled conditions adopted for use with samples.

5. Open the shutter and adjust the high voltage to give a meter deflection of about 0.9. This adjustment need not be exact; it is made to insure an adequate deflection with 0.01 microgram of uranium so that when standard curves are made later they will have a desirable slope (high deflection/concentration ratio).

6. Close the shutter; remove the sample and open the shutter again.

7. Record the meter deflection. This is the standard deflection for the instrument. In practice, it is more convenient to adopt as the standard deflection the nearest tenth of full scale. A value of 0.60 has been adopted as the standard deflection for the instrument used in this laboratory.

Preparation of standard curves

Prepare a series of fused pads, in duplicate or triplicate, containing known amounts of uranium in the following three ranges (micrograms): 0 to 0.01, 0 to 0.1, and 0 to 1.0.

1. Turn on the ultraviolet lamp and allow it to warm up 15 minutes before use.

2. Turn on the high voltage supply and adjust the output to about 725 v. This is merely an approximation of the voltage required to produce the standard deflection.

3. Turn the meter on, move sensitivity control to the 0.1 range, and adjust the meter deflection to zero with the shutter closed.

4. Open the shutter with no sample in place, and adjust the fine control of the high voltage supply until the standard deflection is obtained on the meter.

5. Close the shutter, place a flux blank (fused flux only, containing no uranium) in the sample holder and slide it into place.

6. Open the shutter and record the meter deflection.

7. In the same way record the fluorescence of all flux blanks and standard pads in the range of 0 to 0.01 microgram of uranium.

8. Turn the meter sensitivity control knob to the 1.0 range and record the fluorescence for all flux blanks and standards in the range

0 to 0.1 microgram of uranium.

9. Turn the meter sensitivity control knob to the 10 range and record the fluorescence for all flux blanks and standards in the range 0 to 1.0 microgram of uranium.

10. From the data obtained from the standard pads, construct the three curves relating meter deflections to micrograms of uranium as shown in figure 5.

Measurement of uranium in samples

In general the methods described in Geological Survey Circular 199 are used for the preparation and analysis of samples. We use "fused-flux" exclusively because it is more homogeneous and gives more consistent results in the lower range. Uranium separations are made by the extraction or carbonate methods when there is any likelihood of the presence of significant amounts of quenching elements. Final fusions are made over an open flame at a low temperature to minimize attack of the platinum dish and subsequent quenching of the fluorescence by platinum (Price and others, 1945, 1953).

It is recommended that the meter zero and standard deflection be checked occasionally during use so that any deviation can be corrected.

The operations to be followed in the measurement of the fluorescence are listed below:

1. Prepare fused pads from each sample to be analyzed.

2. Turn the instrument on as before.

3. Adjust the meter to zero.

4. Adjust sensitivity to give the standard deflection with the meter on the 0.1 scale.

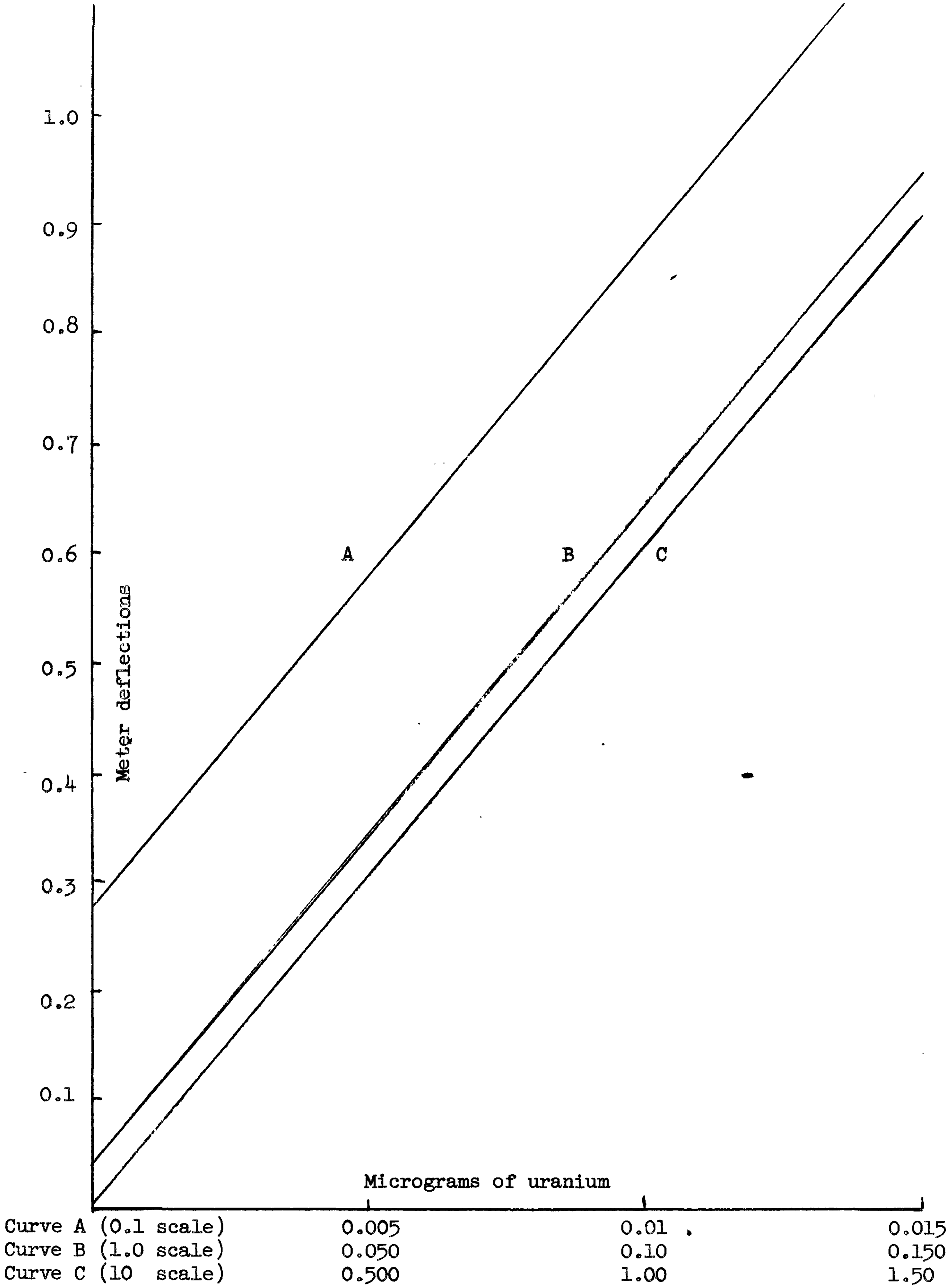



Figure 5.--Standard curves for the fluorimetric determination of uranium

5. Measure the fluorescence of each sample and record for each the deflection and the meter scale used.

6. Read the micrograms of uranium corresponding with each deflection from the appropriate curve.

PERFORMANCE

This fluorimeter has been in constant use in the Geological Survey laboratory for a year and a half, serving both as a research and a routine instrument, and has proved to be very sensitive, stable, and versatile.

Its maximum sensitivity is greater than necessary for the fluorimetric determination of uranium because the lower limit of uranium measurements is set by the fluorescence reading on reagents alone--the so-called "reagent blank". As seen in the working curves in figure 5, which were established from uranium standards, the most sensitive range (curve A) is from 0 to 0.01 microgram, giving readings from 0.028 to 0.089 microamperes. The lower reading represents a reagent blank equivalent to about 0.0046 microgram of uranium. Much greater sensitivity than this is available in the instrument if needed by increasing voltages to the ultraviolet lamp and multiplier phototube, but further increase in sensitivity would correspondingly increase the reagent blank and the curve would become useless.

Curve B is used for measurements between 0.01 and 0.1 microgram of uranium (0.03 to 0.64 microamperes). The sensitivity is 1/10 of that used in curve A and the reagent blank is lowered correspondingly.

Curve C is used for measurements between 0.1 and 1.0 microgram of uranium (0 to 6.0 microamperes). At this low sensitivity the reagent blank has become insignificant.

The maximum amount of uranium that can be measured, without changing the voltage or aperture, seems to be limited by the amount of current that can be drawn from the multiplier phototube. It has been found that when more than 50 microamperes is drawn from the tube the meter pointer drifts downward, presumably indicating tube fatigue.

When the uranium content of a sample being analyzed is too high or too low on the expected curve, it is only necessary to turn the sensitivity switch to the next range and read the uranium value from the corresponding curve.

When a new lot of reagents is put into use the reagent blank will usually change, necessitating the preparation of a new set of standard curves. It is desirable, therefore, to have a good supply of each lot of each reagent on hand so that it will not be necessary to make a new set of curves very often.

Working curves used in this laboratory over the period of a year and a half have shown excellent reproducibility; however, uranium standards and samples of known uranium content are run routinely to guard against inaccuracy that might occur in any step of the analysis.

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