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FLUORIMETRIC METHODS

OF URANIUM ANALYSIS

By F. S. Grimaldi, Irving May, and M. H. Fletcher

S. GEOLOGICAL SURVEY FLUORIMETRIC METHODS OF URANIUM ANALYSIS

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PREFACE

This manual was written to serve as a guide for analysts interested in the determination of small amounts of uranium (Assayers Guide, 1949; Rodden, 1950). All the methods presented here have been developed in the U. S. Geological Survey and are based on the measurement of the fluorescence of uranium in fluoride melts. These methods have been used for the analysis of almost every material thought to contain uranium.

The manual presents a general discussion of the fluorimetric method of analysis for uranium, detailed procedures for the analysis of representative materials, and shop drawings of the fluorimeters used in the Survey.

The methods and instruments described here were completed as part of a program undertaken by the Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

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INTRODUCTION

Melts obtained by fusing uranium salts with sodium fluoride fluoresce a brilliant yellow green when exposed to ultraviolet light (Nichols and Slattery, 1926). [1] The intensity of the fluorescence is proportional, within wide limits, to the amount of uranium present, and this relationship is the basis for the quantitative fluorimetric determination of uranium.

The fluorescence test for uranium in specific when the excitation is with long wavelength (3650 A) ultraviolet light. Niobium fluoresces only weakly when exposed to short wavelength light (2536 A). In spite of this specificity, many elements may interfere by quenching the uranium fluorescence. For example, a few micrograms of Co, Cr, Ni, or Mn will reduce the fluorescence of uranium by more than 10 percent.

The uranium fluorescence may be enhanced by minute amounts of other elements which by themselves do not fluoresce in fluoride phosphors. This effect is seldom encountered in practice. Jacobs (1950) has shown that this enhancement is frequently instrumental and results from a shift in the spectrum of the emitted light to a region generating a greater response from the phototube. Depending upon the particular combination of filters and phototube used, this shift in the spectrum may appear as enhancement or quenching. In some cases the opposing effect of increased phototube sensitivity and decreased transmission by the filter will be balanced, and no change will be apparent.

Two techniques are commonly used to reduce or to eliminate interference due to quenching. One technique, called the "dilution" method (or direct method) involves no chemical separations. It originated with Price and others (1945), who found that it is possible to reduce quenching to a negligible factor by using sufficiently small samples for analysis. The degree of quenching depends only on the concentration of the quencher in the flux, and not on the ratio of concentration of quencher to concentration of uranium.

In the second technique the uranium is separated from quenching elements before the fluoride phosphor is prepared. In one type of procedure uranium may be freed from quenching elements by precipitating them with alkali carbonate solution; the uranium remains in solution as a complex carbonate. Alternately, the separation may be accomplished by extraction of uranyl nitrate by organic solvents. The latter procedure is also very useful for the concentration of uranium.

GENERAL DISCUSSION OF REAGENTS AND APPARATUS

Mixed carbonate-fluoride flux

Although sodium fluoride is still used for the preparation of the uranium phosphors, it has been replaced largely by other fluxes having more desirable properties. Ideally a flux should give high sensitivity and have desirable physical characteristics. It is difficult to work with sodium fluoride because of its high melting point and its tendency to stick to platinum and gold containers. The attack on platinum and gold containers is also more serious at elevated temperatures,

resulting in some quenching of the uranium fluorescence by the dissolved metal. We employ a mixture of 9 parts by weight NaF, 45.5 parts by weight Na_2CO_3, and 45.5 parts by weight K_2CO_3. This flux melts at about 605 C, does not stick to platinum vessels, produces mechanically strong melts which develop no cracks, and gives about the same sensitivity as pure NaF. Melts prepared from this flux deliquesce under high humidity but keep for short periods when stored in a desiccator.

For the measurement of fluorescence obtained from less than 10^{-8} g of uranium, a flux that yields reproducible blanks at a high instrumental sensitivity is necessary. This flux is prepared by fusing together in platinum the three components in 100-g batches, combining and crushing the melts to -5 mesh, and ball-milling to about -65 mesh. We call this the "fused flux" in the procedures in this report. For amounts of uranium greater than 10^{-8} g, the instruments are used at a lower sensitivity; a sufficiently uniform flux is obtained by simple mixing or grinding of the components of the flux in a ball mill (porcelain, with flint pebbles). This flux is used unless otherwise stated.

Containers

Either platinum or gold containers may be used for the preparation of the standard melts. Platinum crucibles or lids from platinum crucibles may be used if specially designed containers are not available. Figure 1 illustrates the platinum containers used by the Geological Survey.
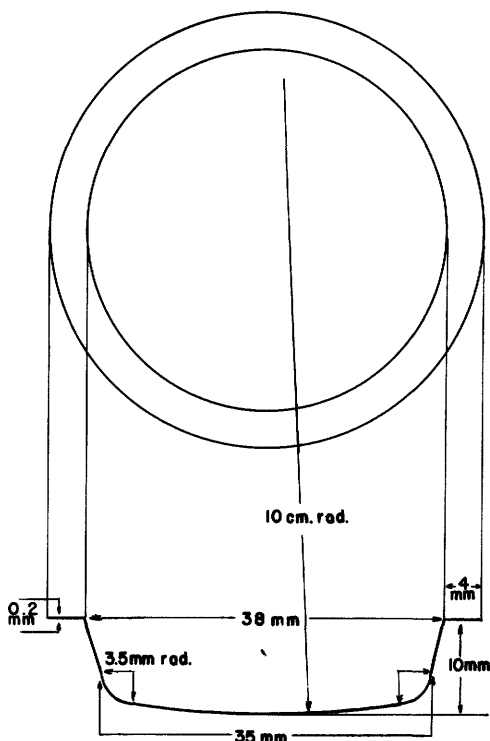

10 cm. rad.

0.2 mm

38 mm

4 mm

3.5mm rad.

10mm

35 mm

Figure 1. --Platinum dish.

[1] See literature cited.

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Fluorimeters

The main parts of a fluorimeter are:
1. An ultraviolet light source.
2. Primary and secondary filters.
3. A phototube together with an electrical system for measuring its response.

Ultraviolet light source

As the source of excitation, long wavelength ultraviolet light (3650 A) as produced by General Electric EH-4 (now the H 100-E4) and CH-4 (now the H 100-C4) high-pressure mercury-vapor lamps, is preferable to short wavelength ultraviolet light (2536 A). The shorter wavelength ultraviolet light can excite interfering fluorescence, such as that of columbium, and is also more dangerous to the eyes. The EH-4 and CH-4 lamps are operated from a constant-voltage transformer with built-in ballast, such as the Sola no. 30,852 for H-4 lamps (superseded by the Sola constant wattage transformer no. 301,883).

Filters

The primary filter absorbs visible light from the light source without seriously reducing the intensity of the ultraviolet light. Corning filters, nos. 5860, 5874, 5mm thickness, are satisfactory. The secondary filters allow the visible fluorescent light to pass through but absorb ultraviolet light. These secondary filters may be glass filters, such as either Corning no. 3484 or no. 3486 used in conjunction with no. 9780. An interference filter whose transmission is peaked at 5550 A may be substituted for the Corning secondary filters.

Detection of fluorescence and measurement of photoelectric currents

Most fluorimeters use phototubes for detecting the fluorescent light and converting it to electrical current which is then measured with or without amplification. Some instruments, such as those employing a Photovolt Model 512 (superseded by Model 514M) electronic photometer, use a simple phototube. Such instruments generally use d-c amplifying circuits to amplify the photoelectric currents before they are measured. The Photovolt photometer ordinarily contains two scales in a ratio of 1:10. The photometer can be purchased with intermediate scales; a convenient arrangement is four scales in a ratio of 1:2:5:10.

Other fluorimeters use photomultiplier tubes such as the RCA 1P21, 931A, or 5819 tubes. These tubes amplify the initial photocurrent several hundred-thousand times by means of a series of secondary-emission multiplications. The over-all amplification obtained can be varied over a wide range by changing the voltage per dynode stage. A d-c amplifier can be used with a photomultiplier tube although, for most applications in the fluorimetric method for uranium, the photoelectric current from the photomultiplier tube can be measured directly with a microammeter.

Types of fluorimeters

Fluorimeters used in the determination of uranium may be divided into two types, the schematic diagrams of which are given in figures 2 and 3.

In the so-called reflection instrument the components are generally arranged so that a part of the fluorescent light emerging from the irradiated side of the
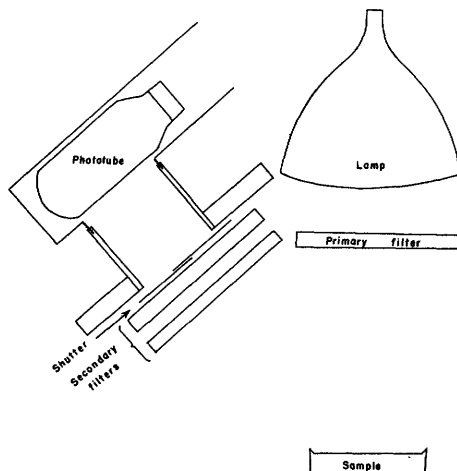
Figure 2. --Schematic diagram of "reflection "-type fluorimeter.

melt is measured. In transmission instruments, the phototube and ultraviolet lamp are placed on opposite sides of the melt so that the fluorescent light which is measured emerges from the side opposite to that exposed to ultraviolet light. Detailed descriptions of one instrument of each type are given under Details of fluorimeters.
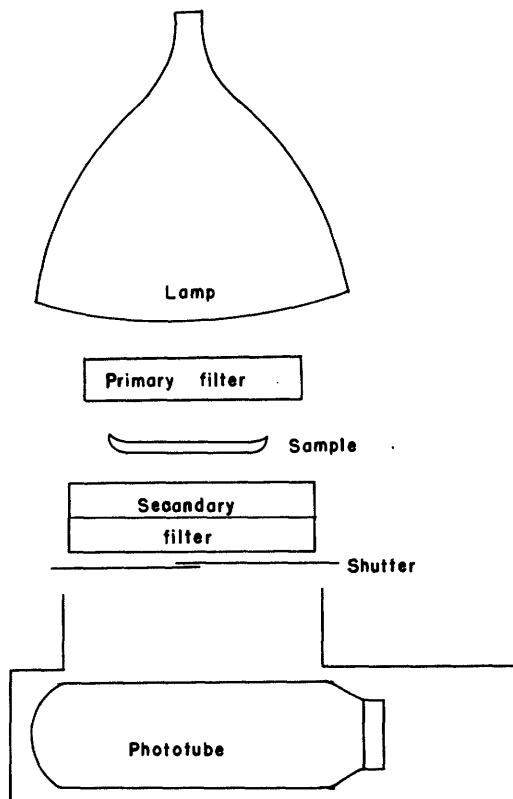
Figure 3. --Schematic diagram of a transmission-type fluorimeter.

The transmission instrument is capable of giving greater sensitivity than the reflection instrument. It is, therefore, the instrument of choice as a research tool and is necessary when uranium is to be determined in very small samples. When the direct method is used on large samples, the melts obtained are sometimes stained. In measuring the fluorescence of stained melts, we have found that the reflection instrument may give more reliable results.

GENERAL DISCUSSION OF PROCEDURES

Preparation of melts

The proper preparation of the fluorescent melts is probably the most important step in the procedure. The flux may attack the platinum container and may introduce platinum into the melt. The amount of platinum so dissolved increases with time and temperature of fusion. In low temperature fusions the amount of platinum dissolved can be tolerated, but serious quenching of the uranium fluorescence by platinum results from fusions made at high temperatures, especially for prolonged periods of heating. The time-temperature curves in figure 4 (Fletcher, 1950) were obtained with furnace heating and illustrate the serious effects of overheating. It can be seen from these curves that the fluorescence of a melt is almost independent of the time of heating when low fusion temperatures are used.

The melts may be prepared either in a furnace or over a burner. The procedure for furnace heating is to heat for a total time of 10 min at 650 C with intermittent agitation of the melt. Heating over a burner is done at the lowest temperature at which the flux is fluid and for a period of 2 to 4 min from the time when the flux melts completely. It is easy to maintain the proper temperature in burner heating because radiation of heat to the air from an open dish limits the maximum temperature that may be attained and because momentary overheating cannot take place at too high a temperature.

Figure 4. --Effect of time of heating and temperature of heating on the fluorescence of a fixed weight of uranium.

Direct fluorimetric or "dilution" method

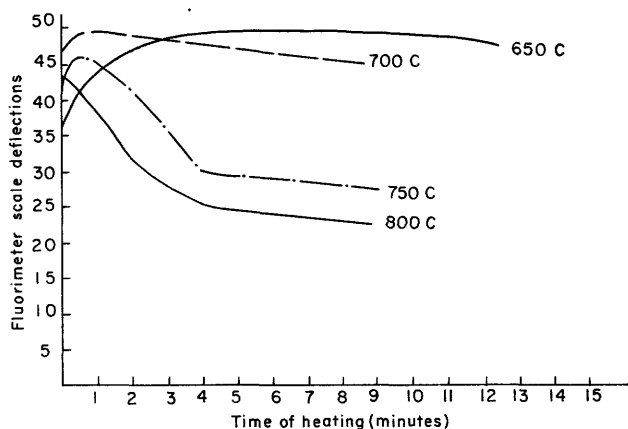The direct fluorimetric method consists of taking a small aliquot of an acid solution of the sample, evaporating it in a standard platinum or gold container, adding the fluoride flux, and preparing the phosphor by fusing at a low temperature. The fluorescence of the melt is then measured in a fluorimeter.

The size of the aliquot to take in the direct method depends on the composition of the material to be analyzed. This size may vary from a few micrograms of sample (for materials containing very strong quenchers such as chromium or manganese) to a few milligrams of sample (for materials with low concentration of quenchers and/or containing relatively mild quenchers). Table 1 summarizes the magnitude of quenching produced by various elements. In general a 0.1-mg sample results in negligible quenching for most rock samples; for some materials (phosphate rocks) several milligrams of sample usually yields little or no quenching. It is always preferable to use the maximum size sample that results in no serious quenching in order that the level of fluorescence to be measured is considerably above that introduced by background contamination. When many samples of approximately the same composition are to be analyzed, it is advantageous to determine the maximum-size sample that can be used in the direct method. The measurement of very low fluorescence intensity levels requires the use of sensitive fluorimeters.

Extraction-fluorimetric method

In the extraction-fluorimetric method the uranium is separated from quenchers before preparation of the fluoride phosphor. This separation usually involves the extraction by means of organic solvents of uranyl nitrate from nitric acid solution after the addition of a salting agent. A portion of the solvent is then transferred to the standard container and after evaporation of the solvent the phosphor is prepared. The fraction of uranyl nitrate extracted depends both on the solvent and on the salting agent used, and for this reason a particular procedure may lend itself to either batch or continuous extraction. For example, with ammonium nitrate as the salting agent and ether as the solvent, continuous extraction is recommended. The Geological Survey procedure (Grimaldi and Levine, 1950) uses batch extraction with aluminum nitrate as the salting agent and ethyl acetate as the solvent. Aluminum nitrate serves also to complex F^-, $PO_4^{\equiv}$, and SO_4 ions which otherwise seriously hinder the extraction of uranium. Aluminum nitrate is also advantageous in that any aluminum extracted does not quench the uranium fluorescence. Vanadium and quadrivalent cerium, thorium, and zirconium are partly extracted. Neither vanadium nor zirconium quenches the uranium fluorescence significantly, but cerium or thorium quenching may be serious. Interference due to cerium is eliminated when necessary by reducing the cerium to the trivalent state before extraction. With large concentrations of cerium, it is usually necessary to repeat the extraction. Because larger samples may be used with the extraction-fluorimetric procedure, less sensitive fluorimeters may be used; errors due to contamination are less serious.

Table 1.--Quenching data on elements for 2 g of flux

°																	°
Be												°	°	°	°	°	°
[Mg]												°	°	°	°	°	°
°	°	Sc	[Ti]	°	[Cr	Mn]	[Fe]	[Co	Ni]	[Cu	Zn]	Ga	Ge	°	Se	°	°
°	°	°	°	Nb*	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	[Sn]	Sb	Te	°	°
°	°	[La]	Hf	Ta	[W]	Re	Os	Ir	[Pt	Au]	Hg**	Tl	[Pb]	Bi	Po	°	°
°	Ra	Ac	[Th]	Pa													
[Ce	Pr	Nd]	°	°	Eu	°	Tb	Dy	Ho	Er	Tm	Yb	Lu				

Heavy solid lines enclose elements that are strong quenchers (1-10 ɣquench uranium fluorescence by 10 percent or more).

Heavy dotted lines enclose elements that are moderate quenchers (10-50 ɣquench fluorescence by about 10 percent).

Light solid lines enclose elements that are weak quenchers (50-1,000 ɣquench fluorescence by about 10 percent).

For elements shown but not enclosed there are no data. The transition elements are probably moderate to strong quenchers. Elements not shown do not quench the uranium fluorescence.

* Niobium fluoresces only with short-wave excitation (2536 A).

** Mercury has been reported as a strong quencher of uranium fluorescence, but it is volatilized in the preparation of the melt.

Carbonate-fluorimetric method

In the carbonate-fluorimetric method (Guttag and Grimaldi, 1951) an aliquot of a sulfuric acid solution of the sample representing 15 mg or less of the sample is treated with alkali carbonate solution in excess to precipitate quenching elements; the uranium remains in solution. After filtration, an aliquot of the filtered solution is transferred to a standard container, the solution is evaporated, and the standard melt is prepared as before. Cerium, cobalt, and copper may interfere in this procedure. A very small amount of cerium and cobalt follow uranium because the precipitates formed from sulfate solutions tend to pass through the filter. Most materials do not contain sufficient cerium to interfere. With suitable modification the procedure may be used even for the determination of uranium in monazite. Cobalt is quantitatively removed when another element in addition to cobalt is precipitated with alkali carbonate. Copper may remain completely in solution yielding an intense blue solution. If the amount of copper not precipitated is insufficient to yield a blue solution, no quenching of the uranium fluorescence results. When a blue solution is obtained, a small amount of hyroxylamine is added after the alkali carbonate to precipitate Cu_2O and thus remove the interference of this element.

The carbonate procedure has been devised to accommodate no more than 15 mg of various metal oxides and should not be extended without testing to determine that no occlusion of uranium occurs in the carbonate precipitate for greater quantities of metal oxides.

Accuracy of the fluorescence method

With careful work uranium may be determined by the fluorescence method with no greater error than ±4 percent of the uranium content. Under routine conditions, where speed may be important, the error generally is greater and may amount to ±8 to 15 percent of the uranium content. When errors occur the results are generally low.

DETAILED PROCEDURES

Direct fluorimetric method or "dilution" method

Range: 0.001 percent U and more

Application

The direct method is generally applicable except where the ratio of concentration of quenching elements

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to concentration of uranium in the sample is exceptionally high. A limiting ratio is of course determined by the sensitivity of the fluorimeter, by the element that is producing the quenching and its concentration, and by the concentration of uranium in the sample. These factors determine the maximum possible dilution. Some authors have set the limiting ratio of concentration of quenching elements to concentration of uranium at 1,000 to 1. This ratio applies to the strong quenchers. (See table 1.)

Preparation of the solution
for analysis

Phosphate rocks. --Simple attack by nitric acid which dissolves the uranium.

Silicate and carbonate rocks. --(a) Attack by $HF-HNO_3$ mixture, or (b) fusion with alkali carbonate and then solution of the melt in hydrochloric acid plus a few drops of alcohol.

Refractory materials. --(a) Fusion in platinum with carbonate-borate flux (3 parts Na_2CO_3 to 1 part $Na_2B_4O_7$) followed by solution of the melt in HCl, or (b) fusion in platinum with sodium fluoride followed by solution of the melt in HCl.

Fluorimeters

Depending on the concentration of uranium in the melt, either the reflection or transmission fluorimeter may be used to measure the fluorescence. When very low levels of fluorescence are to be measured, the melts must be prepared with fused fluoride flux described previously in the text.

Example: Determination of uranium in
Florida phosphates by the direct method
using "large" samples (Grimaldi and Guttag, 1950)

Range. --0.001 percent U and more.

Procedure. --1. Weigh a 0.150-g sample of phosphate rock (-80 mesh) into a dry 125-ml Erlenmeyer flask.
2. Add 50-ml of (18 + 82) HNO_3 from an automatic buret. Cover the flask with a small watch glass.
3. Bring the solution to a boil on a hot plate and gently boil the solution for an additional 2 min. Cool.
4. Transfer a 0.40-ml aliquot of the supernatant solution to the standard platinum container and evaporate the solution to dryness on the steam bath. Gently ignite to remove free nitric acid or organic matter if present.
5. Add 2.0 g of the fluoride flux (9 parts NaF, 45.5 parts Na_2CO_3 and 45.5 parts K_2CO_3 by weight).
6. Heat over a burner at a low temperature (less than 700 C) until the flux melts. Then heat for an additional 2 to 4 min, at the lowest temperature at which the flux stays fluid, swirling and agitating the flux to insure a uniform melt. Set the dish on an asbestos pad to cool and then place in a desiccator for about 30 min.
7. Read the relative fluorescence of the melt with the reflection fluorimeter.

8. Determine the percentage of uranium by reference to a standard curve relating the relative fluorescence (scale deflections) of uranium to the amount of uranium in a series of standard melts.

Caution: In preparing the melts it is most important that the temperature not exceed 700 C (Fletcher, 1950). Overheating will cause low results because of the quenching effect of platinum dissolved from the container. The deleterious effect of overheating must be emphasized.

Notes: 1. Uranium results obtained on phosphates from the northwestern part of the United States by the above method are generally 10 to 15 percent too low due possibly to the quenching effect of chromium usually present in these samples. More accurate results can be obtained if smaller samples are used.
2. The direct method may also be used for the determination of uranium in ashes from plants by fusing a 5-mg portion of ash with the flux directly in the platinum container without preliminary solution of the sample.
3. Phosphoric acid byproducts and wastes from phosphoric acid plants usually may be analyzed by the direct method using 1 mg of sample.
4. For shales and most rocks a 0.1-mg sample results in no quenching of the uranium fluorescence.
5. Uranium in monazite may be determined directly on sample sizes of a few micrograms.
6. Whereas uranium is normally determined by volumetric procedures in uranium ores such as carnotite and pitchblende, a rapid although less accurate uranium determination may be made fluorimetrically. Low-grade carnotite ores (about O.X percent U) are easily handled by the direct method even with less sensitive fluorimeters.

Extraction-fluorimetric method

Range: 0.001 percent U and more

Application

The method is generally applicable except for samples unusually high in thorium and cerium such as high-grade ores of these elements. However, with suitable modifications the procedure may be used for the determination of uranium in monazite.

Preparation of the solution
for analysis

Phosphate rock. --Simple attack by nitric acid.

Silicate and carbonate rocks. --(a) Attack by $HF-HNO_3$ mixture. (b) Alkali carbonate fusion followed by solution of the melt in nitric acid.

Refractory materials. --Fusion with either $NaOH-NaNO_3$ mixture or with Na_2O_2 in a porcelain crucible followed by solution of the melt in nitric acid. Whatever method of solution is used, the aliquot taken for extraction should contain approximately 15 percent by volume HNO_3.

Silica or other hydrolytic precipitates such as TiO_2 are not filtered off because they have been found not to occlude uranium.

Fluorimeters

Either the reflection or transmission fluorimeter may be used to determine the fluorescence.

Example 1: Determination of uranium in shales after extraction of uranyl nitrate (Grimaldi and Levine, 1950)

1. Weigh a 0.150-g sample (-80 mesh) into a platinum dish. Gently burn off organic matter if present.
2. Moisten the sample with a small amount of water and add 5-10 ml HF and 10 ml of (1 + 1) HNO_3. Digest the sample on the steam bath and evaporate the solution to dryness.
3. Add 10 ml (1 + 1) HNO_3 and evaporate the solution to dryness. Repeat if insoluble fluorides remain.
4. Add 15 ml (1 + 1) HNO_3 and digest the sample. Transfer the solution to a 50-ml glass-stoppered graduated cylinder. Carefully scrub and rinse the dish with water adding the washings to the graduate.
5. Make to 50 ml with water and mix.
6. Transfer a 5-ml aliquot of the solution to a dry 30-ml glass-stoppered test tube containing 9-1/2 g of $Al(NO_3)_3 \cdot 9H_2O$. The $Al(NO_3)_3 \cdot 9H_2O$ should be free from uranium. (See note 5.) Aluminum nitrate available from several of the manufacturers of laboratory chemicals has been found to be sufficiently pure as purchased.
7. Place the tube in a beaker of hot water until the aluminum nitrate dissolves and then mix. Cool the solution to room temperature by removing the tube from the hot water and placing it in a beaker of cold water.
8. Add 10 ml of ethyl acetate by pipet or buret. Stopper the tube and shake the mixture for 30 sec. Allow the two layers to separate.
9. After several minutes filter about 5 ml of the ethyl acetate through a dry paper into a dry test tube. The filter paper is conveniently held in place by the test tube.
10. Transfer an 0.80-ml aliquot of the filtered ethyl acetate to the standard platinum container. Place the container on four layers of water-soaked absorbent paper in an enameled pan containing about 1/16 in. of water. Ignite the ethyl acetate by means of a lighted splinter and allow the ethyl acetate to burn completely.
11. Gently ignite the residue over a burner, add 2 g of flux and fuse as previously indicated.
12. Read the relative fluorescence of the melt in the reflection or transmission fluorimeter.

Notes: 1. Alternately, the solution of shales may be prepared by Na_2CO_3 fusion followed by solution of the melt in sufficient nitric acid to give a nitric acid concentration of approximately 15 percent by volume. Silica or other hydrolytic precipitates need not be filtered off as they do not occlude uranium.
2. For phosphate rocks prepare the solution by simple boiling with 50 ml of (18 + 82) HNO_3 as described under the "direct" method. Use a 5-ml aliquot of the solution for extraction.
3. The same general procedure is used for determining uranium in silicate rocks, lignites, carnotites, pitchblendes, and many other naturally occurring materials.

4. Phosphoric acid may be extracted directly after the addition of aluminum nitrate.
5. For the preparation of "pure" aluminum nitrate, the aluminum nitrate is dissolved in (15 + 85) HNO_3 in the proportion of 9-1/2 g $Al(NO_3)_3 \cdot 9H_2O$ to 5 ml of HNO_3 and extracted with ether instead of ethyl acetate. After the separation of the two layers the aqueous solution is evaporated until about one-third of its volume is removed and then is cooled to allow the aluminum nitrate to crystallize. The crystals are filtered off on a Buchner funnel and dried in air and stored.

Example 2: Determination of 0.00001 percent uranium in feldspar

Application. --This procedure (Robert Meyrowitz, personal communication) is designed for use when the amount of sample available is small and the uranium content low.

Precautions. --For the determination of such small amounts of uranium scrupulous cleanliness must be observed. All reagents should be sufficiently free from uranium so that no significant blank is obtained. The nitric acid and hydrofluoric acid should be purified by distillation if necessary. The hydrofluoric acid can be distilled with a platinum still but it is better to test the HF from various suppliers and select one with a low uranium content. The aluminum nitrate used as the salting agent invariably requires purification which should be repeated if necessary until a reasonably low blank for uranium is obtained. A blank should be run on all the reagents as used in the procedure and it should be deducted from the results obtained on samples.

Procedure. --1. Weigh 0.0250 g of finely ground feldspar and transfer it to a small platinum dish. Burn off organic matter if present. Cool.
2. Add 2 to 4 drops of water, 2 ml HF, and 0.5 ml of HNO_3. Digest the sample on the steam bath and evaporate the solution to dryness. Cool.
3. Add 2 ml of (1 + 1) HNO_3 and evaporate the solution to dryness. Repeat. Cool.
4. Add 3 ml of $Al(NO_3)_3$-HNO_3 solution by pipet. (See note 1, p. 7.) Warm gently to effect complete solution. Mix by swirling. The heating should be conducted in a manner that avoids any loss of solution through evaporation. Cool.
5. Pipet 2 ml of the solution to a 20-ml glass-stoppered test tube.
6. Add 5 ml of ethyl acetate and shake for about 30 sec. Allow the layers to separate for about 5 min.
7. Filter most of the ethyl acetate layer through a dry no. 42 Whatman 5.5-cm paper into a dry test tube (which holds the filter paper).
8. Transfer 3 ml of the filtered ethyl acetate to a standard platinum container. Place the dish on several layers of water-soaked absorbent paper which rests in a pan containing about 1/16 in. of water.
9. Immediately ignite the ethyl acetate by means of a lighted splinter and allow the ethyl acetate to burn completely.
10. Ignite gently to destroy organic matter.
11. Add 2 g of the specially prepared fused flux and prepare the phosphor as previously described.
12. Measure the relative fluorescence with the transmission instrument at highest sensitivity.

Notes: 1. Preparation of $Al(NO_3)_3$-HNO_3 reagent

   a) Dissolve 190 g $Al(NO_3)_3 \cdot 9H_2O$ in 100 ml of (15 + 85) HNO_3 (use redistilled nitric acid). Cool.
   b) Add an equal volume (about 200 ml) of ether and extract in a separatory funnel for about one minute. Allow the layers to separate.
   c) Filter the aqueous layer through a fast filter paper into a pyrex bottle.

If, after this preparation, the $Al(NO_3)_3$ still has a significant blank, it should be crystallized from this solution and the extraction-purification procedure repeated.

Example 3: Determination of 10^{-7} percent uranium in fresh, saline, and sea water

   Principles. --Preliminary concentration of the uranium is made by precipitating uranyl phosphate using aluminum phosphate as the carrier (Pietsch and Grimaldi).

   Procedure. --1. Transfer a 500-ml aliquot of water to an 800-ml beaker.
   2. Add 3 ml of HNO_3, 20 mg Al_2O_3 (using a solution of aluminum nitrate), and 5 ml of $(NH_4)_2HPO_4$ solution (1 cc = 12 mg $(NH_4)_2HPO_4$). Heat to boiling to remove CO_2.
   3. Add ammonium hydroxide until methyl red indicator is just yellow.
   4. Digest the precipitate on the steam bath for about 10 min. Stir in paper pulp.
   5. Filter the solution on a fast paper and wash the precipitate with 1 percent NH_4NO_3 solution.
   6. Transfer the precipitate and paper to a 25-ml clean porcelain crucible and ignite at a low temperature until the paper is completely ashed .
   7. Add 5 ml of (15 + 85) HNO_3 and warm gently to dissolve the salts (avoid any evaporation of solution).
   8. Add 9-1/2 g $Al(NO_3)_3 \cdot 9H_2O$ and warm to dissolve the salt.
   9. Pour the solution into a 30-ml glass-stoppered graduated test tube draining as completely as possible. Do not wash the crucible.
   10. Add 10 ml of ethyl acetate by pipet and shake the mixture for about 30 sec. Allow the layers to separate for a few minutes.
   11. Filter about 8 ml of the ethyl acetate through a dry paper into a dry test tube.
   12. Transfer a 2-ml aliquot of the filtered ethyl acetate into a standard platinum container and burn it off as previously described under the extraction-fluorimetric method.
   13. Add 2 g of flux and prepare the fluorescent melt as before.
   14. Measure the relative fluorescence of the melt with either the reflection or transmission instrument.

   Notes: 1. In sampling waters in the field, it is good practice to add acid (about 8 ml HNO_3 per gallon of water) immediately after collection. Should the water sample contain sediment, it is necessary to filter the water when collected before the addition of the acid. Unacidified water samples tend to decrease in uranium concentration during storage; some of the

uranium is precipitated and some adsorbed on the glass (Koczy, 1950).
   2. Alternately, fresh water and waters containing relatively small amounts of dissolved salts can be evaporated and the extraction procedure applied without preliminary concentration of the uranium with aluminum phosphate.

Carbonate-fluorimetric method

   Range: 0.001 percent U and more

Application

   The method is generally applicable except for samples unusually high in thorium and cerium such as high-grade ores of these elements. With suitable modifications, however, the procedure may be used even for the determination of uranium in monazite, as given in a later section.

Preparation of the solution for analysis

   Silicate, carbonate, and phosphate rocks. --Attack by HF-H_2SO_4 mixture. Nitric acid is avoided because the sodium nitrate formed by the alkali carbonate attacks platinum during the preparation of the phosphor. This leads to low results due to platinum quenching.

   Refractory materials. --Fusion with a mixture of $K_2S_2O_7$-NaF or NaF alone followed by removal of fluoride with H_2SO_4.

Fluorimeters

   The fluorescence may be measured by either the reflection or transmission fluorimeter.

Example 1: The fluorimetric determination of uranium in lignites after alkali carbonate separation (Guttag and Grimaldi, 1951)

   1. Weigh a 0.150-g sample (-80 mesh) into a 70-ml platinum dish.
   2. Ignite the sample gently to remove organic matter. Cool and moisten the sample with water.
   3. Add 0.5 ml H_2SO_4 (by pipet) and cautiously add 5-10 ml of HF. Digest the sample on the steam bath and then evaporate the solution to remove water.
   4. Bring the sample to fumes of sulfuric acid and fume for several minutes. Cool.
   5. Add 25 ml of water cautiously, digest the sample on the steam bath, and stir to dissolve the salts. Cool to room temperature.
   6. Transfer the contents of the dish to a 50-ml glass-stoppered graduated cylinder. Dilute to 50 ml with water. Mix.
   7. If suspended insoluble sulfates are present, mix the solution thoroughly. Immediately draw off a 5-ml aliquot and transfer the solution to a 25-ml glass-stoppered test tube.
   8. Add 5 ml of mixed carbonate solution (10 g Na_2CO_3 + 10 g K_2CO_3 per 100 ml of water) and mix.
   9. Place the stoppered tube in a beaker of hot water and let stand for 10 min at about 90 C. If a blue solution persists (indicating copper), cool slightly and add 0.05 ml of hydroxylamine hydrochloride (made by dissolving 20 g of $NH_2OH \cdot HCl$ in

100-ml H_2O). Continue the heating at about 90 C for an additional 20 min for all samples whether or not hydroxylamine has been added.

10. Remove the tube from the bath and allow the solution to cool for 1 hr at room temperature.

11. Filter part of the solution through a dry filter paper (Whatman no. 42) into a dry test tube. The filter paper is conveniently held in place by the test tube.

12. Transfer an 0.80-ml aliquot of the solution to a standard platinum container and evaporate the solution on the steam bath. Ignite gently.

13. Add 2 g of flux and prepare the phosphor as described in the Direct method.

14. The relative fluorescence of the melt is then read in the reflection or transmission fluorimeter.

Notes: 1. The amount of sulfuric acid added in preparing the solution must be controlled. If more than the prescribed amount is used, the additional alkali sulfates formed in the carbonate step may alter the composition of the flux sufficiently to change its sensitivity. Nitric acid solutions are to be avoided, but hydrochloric acid solutions are permissible.

2. The same general procedure is used for determining uranium in shales and other silicate rocks, carnotite and other naturally occurring materials.

Example 2: Determination of uranium in monazite after alkali carbonate separation

Range. --0.01 percent and more.

Application. --The method is especially useful for refractory materials. For samples containing much smaller amounts of cerium and thorium than occur in monazite, the range may be extended downward by use of larger samples.

Principles. --The procedure for monazite differs only on the method of preparing the solution and in the final size of sample taken. Almost all of the cerium is removed by alkali carbonate. What remains after the separation would normally quench the uranium fluorescence in a 1.2-mg sample of monazite. The uranium content of monazite is usually greater than 0.1 percent. This fact enables us to use the dilution method after the carbonate separation, and for a 0.12-mg aliquot quenching by cerium is eliminated.

Procedure. --1. Weigh 0.0800 g of finely ground monazite into a platinum crucible.

2. Add 0.6 g of flux (2 parts by weight NaF and 3 parts by weight $K_2S_2O_7$).

3. Fuse the sample over a low burner until a clear melt is obtained (about 30 sec). Cool.

4. Add 0.4 ml of concentrated H_2SO_4. Heat gently until all the fluoride is removed and a clear pyrosulfate melt is obtained. This fusion proceeds through several stages. In the first stage some frothing is apparent until the melt disintegrates. The melt is usually colored and muddy at this point. In the second stage the melt thickens and becomes lighter in color. In the final stage a clear pyrosulfate melt is obtained. The total time for the complete process is about 3-1/2 min. Cool.

5. Add 10 to 15 ml of water and 2 ml H_2SO_4 by pipet. Digest the melt on the steam bath. Stir occasionally until the melt is completely disintegrated.

6. Transfer the sample to a 100-ml glass-stoppered graduated cylinder and make up to 100 ml

with water. Mix. Generally a complete solution is obtained within 5 min. Sometimes a cloud (presumably anhydrous rare-earth sulfates) persists after 5 min. This is not important as long as the sample has been completely decomposed.

7. Disperse the mixture by shaking. Immediately draw off a 5-ml aliquot and transfer to a glass-stoppered test tube.

8. Proceed according to steps 8 through 11 of the procedure for lignites.

9. Take a 0.30-ml aliquot at step 12 and proceed as directed for lignites steps 12 through 14.

Notes: 1. For refractory materials not broken up by $\overline{K_2S_2O_7}$-NaF flux, use pure NaF as the flux.

2. The range for monazite may be extended downward to 0.001 percent uranium by using the fused flux and the transmission instrument set for high sensitivity.

DETAILS OF FLUORIMETERS

Reflection fluorimeter (Fletcher and May, 1950)

The reflection fluorimeter described in this report is a modification of the Oak Ridge Model R fluorimeter (Coleman, 1949). The new instrument was designed to better meet the needs of the Survey Laboratory with respect to sensitivity and stability. The model described in this report is an early one and can be built with relatively limited shop facilities. Organizations with a good shop can readily make appropriate modifications in the design to enable the construction of a more compact and rigid instrument.

The instrument is built on the base of the Model R fluorimeter and retains the sample slide, the Photovolt measuring unit, and the secondary filters of the Model R instrument. The substitution of the more intense General Electric E-H4 or C-H4 lamp in the new instrument increases the sensitivity, yet allows the continued use of the Photovolt electronic photometer (Model 512). The lamp is supported on a stand and is ventilated by a ventilating fan (obtainable at photographic stores). After an initial warmup the operating temperature remains constant, and the lamp can be left on all day if desired. As the lamp is not mounted directly on the instrument, the distance between the lamp and the sample may be readily changed, thus providing for greater or less sensitivity.

The housing for the filters and shutter is made from 26-gauge sheet brass painted a flat black (figs. 5, 6, 7). A no. 6 Packard shutter, obtainable from photographic shops, with a 1-1/2-in diameter opening is attached directly above the secondary filters. The top plate of the shutter is replaced with a bakelite cover having a 1-1/4-in diameter hole in the center. One end of a brass collar is held in this hole by a friction fit, and the other end is threaded to screw directly into the search unit. All joints are secure and light tight. The secondary filters are the yellow and green filters (Corning nos. 3486 and 9780, moulded thickness). The Corning filter no. 5874, 3-1/4-in square, serves as the primary filter. A sheet-metal shield provided with air vents is placed around the instrument, and the enclosure is ventilated with the ventilating fan. The sample slide has two 2-inch-square depressions cut in line with each other

PRIMARY FILTER FRAME

HOUSING

HOUSING

SECONDARY FILTER FRAME

SHUTTER BASE FRAME

SHUTTER COVER PLATE

SEARCH UNIT CONNECTOR

1¼" x 1¼" dia. tubing - one end threaded to fit search unit

drill 4 holes (one each corner) to suit Packard shutter

slot for extended arm to Packard shutter

drill 2 holes for placement of shutter trigger mechanism

provide 1¼" dia. hole - counter bore to provide friction fit for search unit connector

drill 4 holes (one each corner) to suit Packard shutter

offset material thickness

45°

135°

EXPANDED DETAILS
OF THE
MODIFIED FLUORIMETER
(rear view)

Figure 5. --Expanded details of the modified fluorimeter.

A - Lamp
B - Primary filter
C - Primary filter frame
D - Housing
E - Housing
F - Secondary filter frame
G - Secondary filter
H - Shutter base frame
I - St'd. $1\frac{1}{2}$" Packard shutter
J - Shutter cover plate
K - Shutter trigger
L - Search unit connector
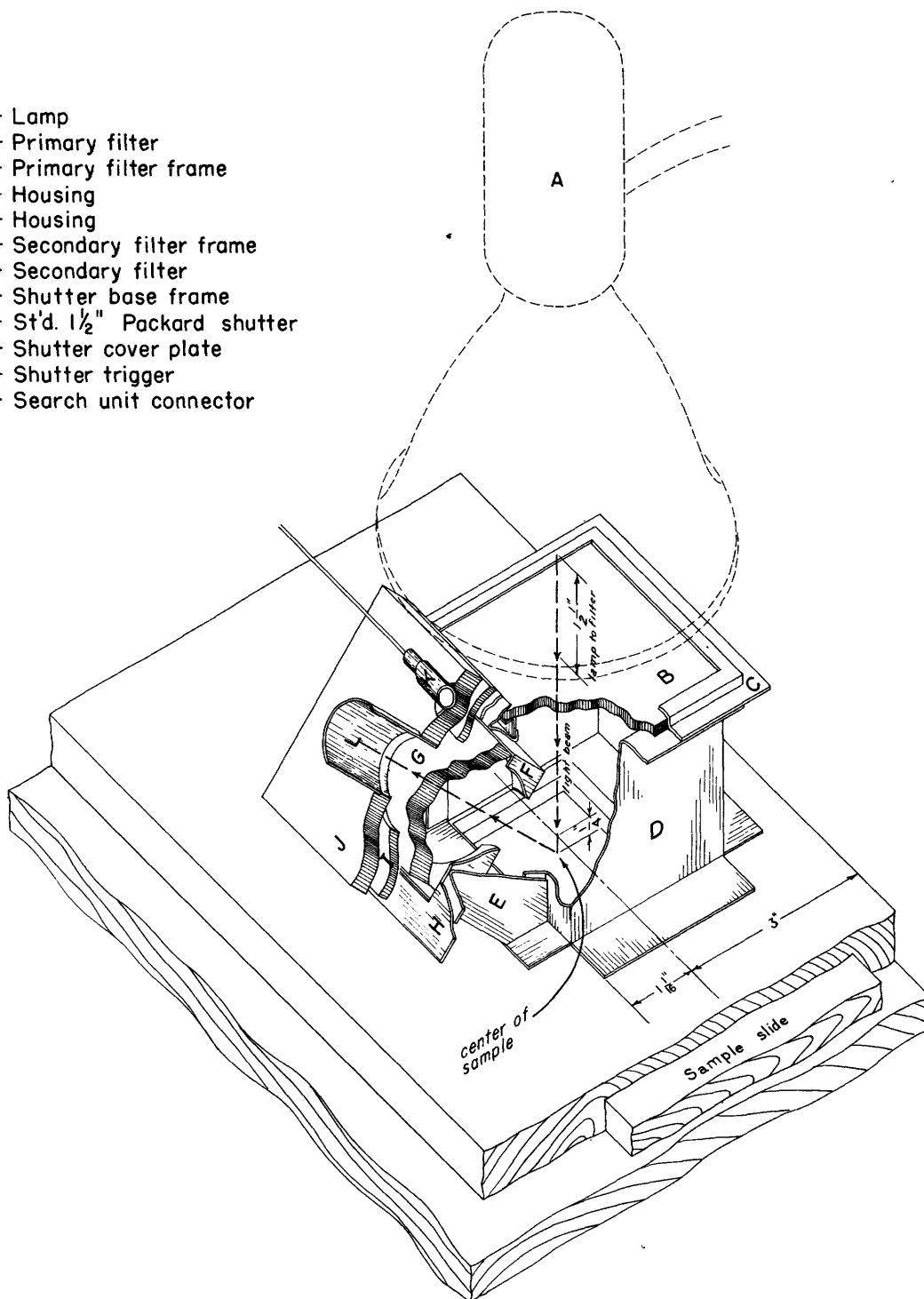
REAR VIEW ASSEMBLY
OF THE
MODIFIED FLUORIMETER

Figure 6. --Rear view assembly of the modified fluorimeter.

Figure 7. --Complete assembly of the modified fluorimeter.
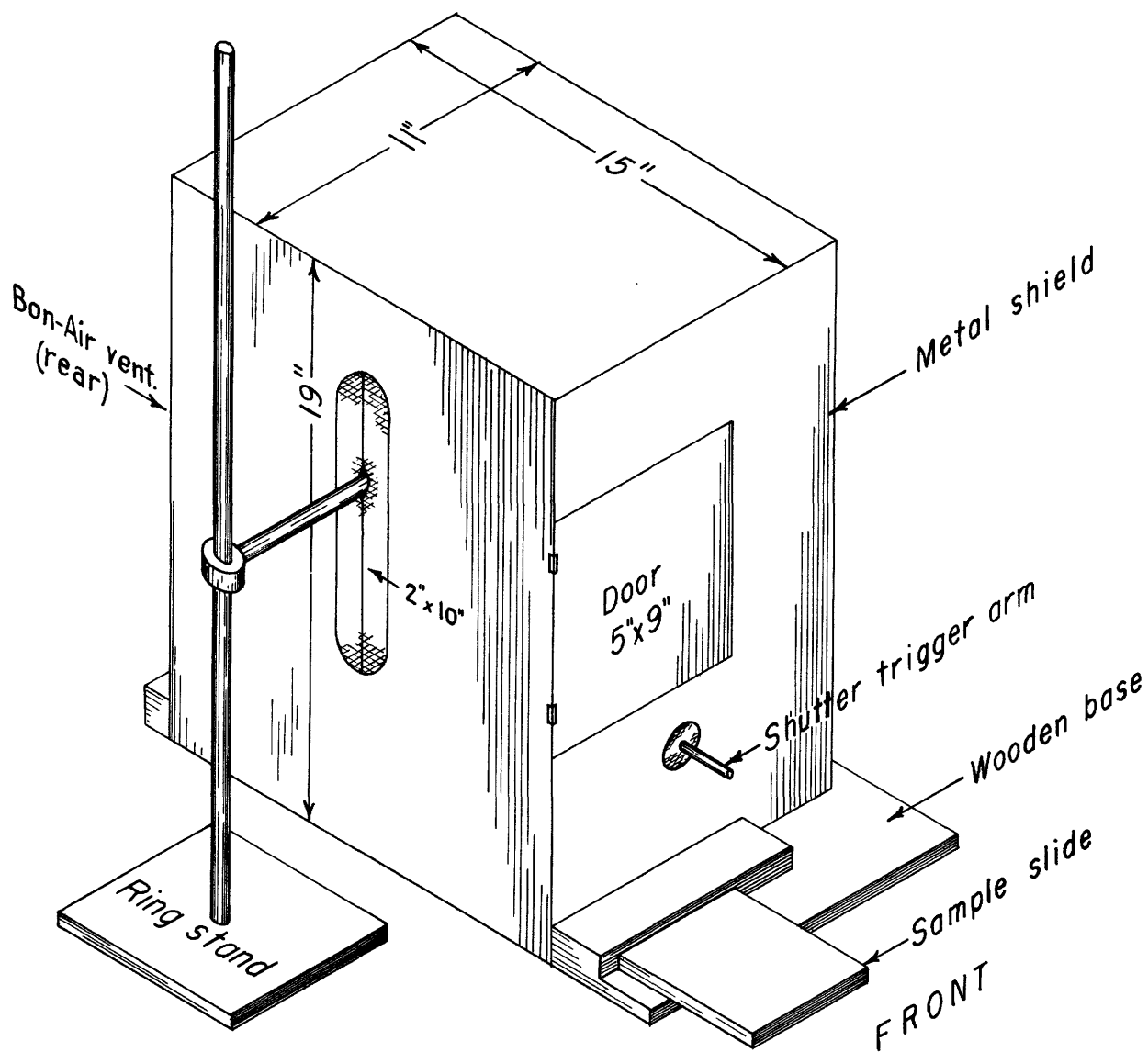
COMPLETE ASSEMBLY
OF THE
MODIFIED FLUORIMETER
(front view)

so that either one may be placed in the path of the ultraviolet light beam. A standard fluorescent glass is mounted in one of the depressions; an adapter to accommodate the sample discs is mounted in the other depression. The standard glass provides a convenient reference point in terms of which both the relative fluorescence of standards and of samples are measured. The reading due to the fluorescence of the standard glass is adjusted to a fixed value near the upper part of the scale -- large adjustments are made by varying the height of the lamp, smaller adjustments are made with the sensitivity control of the photometer. The standard fluorescing glass which we use is the Corning filter no. 3384, standard polished thickness, melt 600. We have found that there is a pronounced difference in the fluorescence of one or the other side of these filters and there is an even greater difference in the intensity of fluorescence of filters from other melts. Figure 8 illustrates a typical curve relating the intensity of fluorescence of uranium ("Lo" scale reading on Photovolt electronic photometer Model 512, standard glass set for a deflection of 80) with the amount of uranium in a 2-g melt. Using the "Lo" scale of the photovolt photometer, the sensitivity of this instrument allows 10^{-8} g of uranium to be determined as a **lower limit for a 2-g melt.**
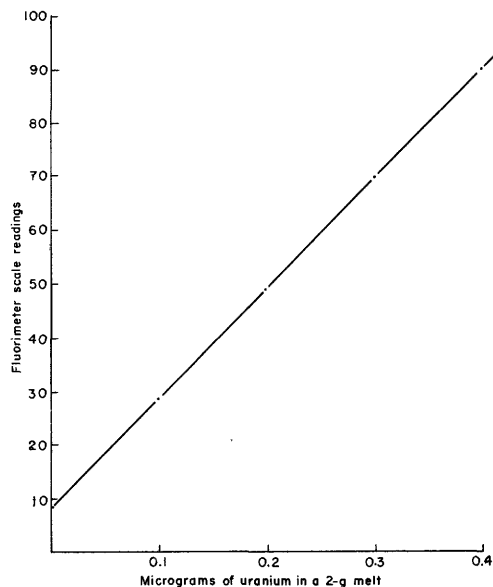

Figure 8, --A working curve for a "reflection" fluorimeter.

Transmission fluorimeter

The word "fluorimeter", in quotation marks, as used in this section refers to that part of the complete fluorimeter which houses the filters, sample slide, and shutter.

The model V transmission fluorimeter (Fletcher and others, 1950) is machined from solid brass. The fluorimeter head includes the sample slide, shutter, and a holder for the

primary filters. The sample slide is provided with adapters so that several sizes of fluoride melts may be accommodated. The secondary filters are in the bottom plate which screws into the fluorimeter head. The bottom plates are of two types - A and B. Type A is used with an RCA-1P21 photomultiplier tube or with the Photovolt photometer. It is threaded to fit the Photovolt search unit. Housings for the 1P21 photomultiplier tubes were built to have the same thread as the Photovolt search unit so that either phototube can be used with the type-A plate. The type-A plate is constructed so that phototube housings can be removed or installed while the fluorimeter is in position on the supporting stand. The type-B bottom plate is used with the RCA 5819 photomultiplier tube. The cinch no. 3M14 socket with mounting ring 3R14 is used with this tube.

The filter holders are made for 2-inch-square filters. An adapter ring for each filter holder permits the use of filters of different thicknesses.

The instrument is shown in detail in figures 9-15. In figure 9, one-half of drawing A is a section showing the fluorimeter assembly with type-A bottom plate and Photovolt search unit in place; figure 9, drawing B shows the arrangement with type-B bottom plate and RCA-5819 photomultiplier tube. The stand, lamp support, and shield are the same for both arrangements. Figure 10 is a cut-away drawing showing additional details of the fluorimeter. The remaining figures are detailed shop drawings for the construction of parts shown in figures 9 and 10. All parts of the fluorimeter shown in figures 11 and 12 must be machined to a class-4 fit or better; those shown in figure 13 need be only a class-3 fit.

A thin glass disc (not shown in figures) is required in the sample slide under the adapter ring. The purpose of this disc is to prevent flakes of the melt from falling into the fluorimeter. This glass must be nonfluorescent. Discs cut from photographic plates used in spectrum analysis are satisfactory.

The lamp shown in figure 9 is a General Electric EH-4 or Ch-4 lamp. This lamp requires a porcelain socket with an admedium base and is cooled by ventilation with a "Bon-Air" darkroom ventilator. The lamp is operated with a Sola no. 30,852 constant-voltage transformer designed especially for H-4 lamps.

The primary filters are 2-inch-square Corning no. 5874 ultraviolet filters, standard polished thickness. Two of these filters are generally used. The secondary filter may be either a combination of Corning filters nos. 3486 and 9780, standard moulded or polished thickness, or an interference filter peaked for maximum transmission at 5550 A.

Various combinations of phototubes and current amplifying and measuring devices which

A Shield supports
B Adjustable lamp support assembly
C Support rods 3/4 inch stainless steel 29 inchs high
D "Fluorimeter" support
E Filters 2" x 2" x 3/10 to 1/2"
F Adapter ring
G Glass sample plate
H Sample slide
I Shutter
J Filters 2" x 2" x 3/10" to 1/2"
K Filter ring
L Amphenol connector
M Support for tube socket

Aluminum light shield 7 1/8 dia.

Door felt lined

Ultraviolet lamp No. CH 4 or EH 4

Slot felt lined

Air Vent

Door felt lined

"Fluorimeter"

Phototube housing

Wood base 16" square

A

"Fluorimeter"

RCA phototube 5819 2 1/2" dia

9" ±

1/2"

3/16"

B

Figure 9. --Fluorimeter assembly (transmission).

13

No.	PART	SIZE	QTY	MATERIAL	SHEET
	SLIDE ADAPTER RING		4	BRASS	
	FLAT HEAD SCREW	No.6-32x5/16	4	"	4
	FLAT HEAD SCREW	No.8-32x5/8	4	"	4
	BOLT	2-56x1/8	1	"	4
	HDLS. SET SCREW	No.4-40x3/8	1	"	4
	BUTTON HD SCREW	No.4-40x1/4	12	"	3
	BUTTON HD SCREW	No.8-32x1/4	2	"	3
15	TOP PLATE		1	"	FIG. 4
14	BLACK OUT PLATE		1	"	" 4
13	FILTER RING		2	"	" 4
12	FILTER PLATE		1	"	" 3
11	FILTER CLIP		4	"	" 3
10	FILTER CLIP		4	"	" 3
9	SPANNER NUT		1	"	" 4
8	PLATE FLANGE		1	"	" 4
7	BOTTOM FILTER PLATE		1	"	" 4
6	SHUTTER		1	"	" 3
5	SHUTTER SLIDE		1	"	" 3
4	SLIDE GUIDE L.H.		1	"	" 3
3	SLIDE GUIDE R.H.		1	"	" 3
2	SAMPLE SLIDE		1	"	" 3
1	FLUORIMETER HOUSING		1	BRASS	FIG. 3

ALL FITTINGS TO BE LIGHT TIGHT

FILTER

15

10

9

FELT PAD
TO BE GLUED

1

14

2

3

4

5

6

7

8

"FLUORIMETER" ASSEMBLY WITH BOTTOM FILTER PLATE TYPE "A"
CUT AWAY SECTION EXPOSING CONSTRUCTION, SHUTTER OPEN

FLUORIMETER HEAD

TUBE HOUSING

11

12

13
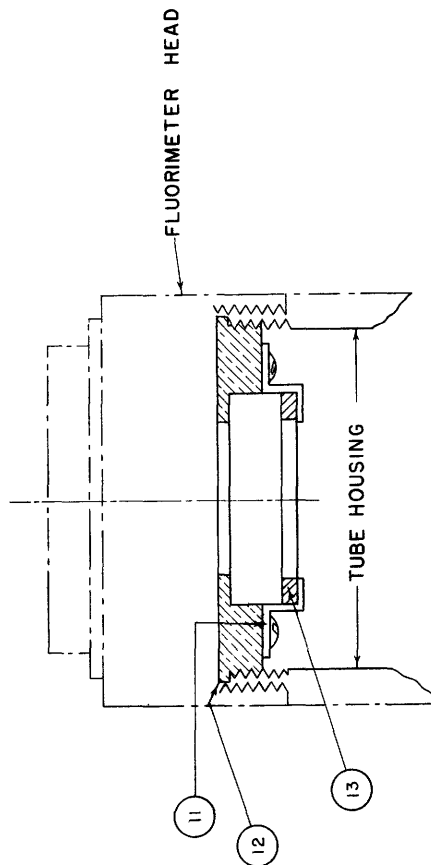
CROSS - SECTION OF BOTTOM FILTER PLATE "B"
AT ASSEMBLY IN TUBE

Figure 10. --Fluorimeter -- cut-away and cross-section.

14

Figure 11. --Details of parts shown in figure 10.

15

Figure 12. --Details of parts shown in figure 10.

16

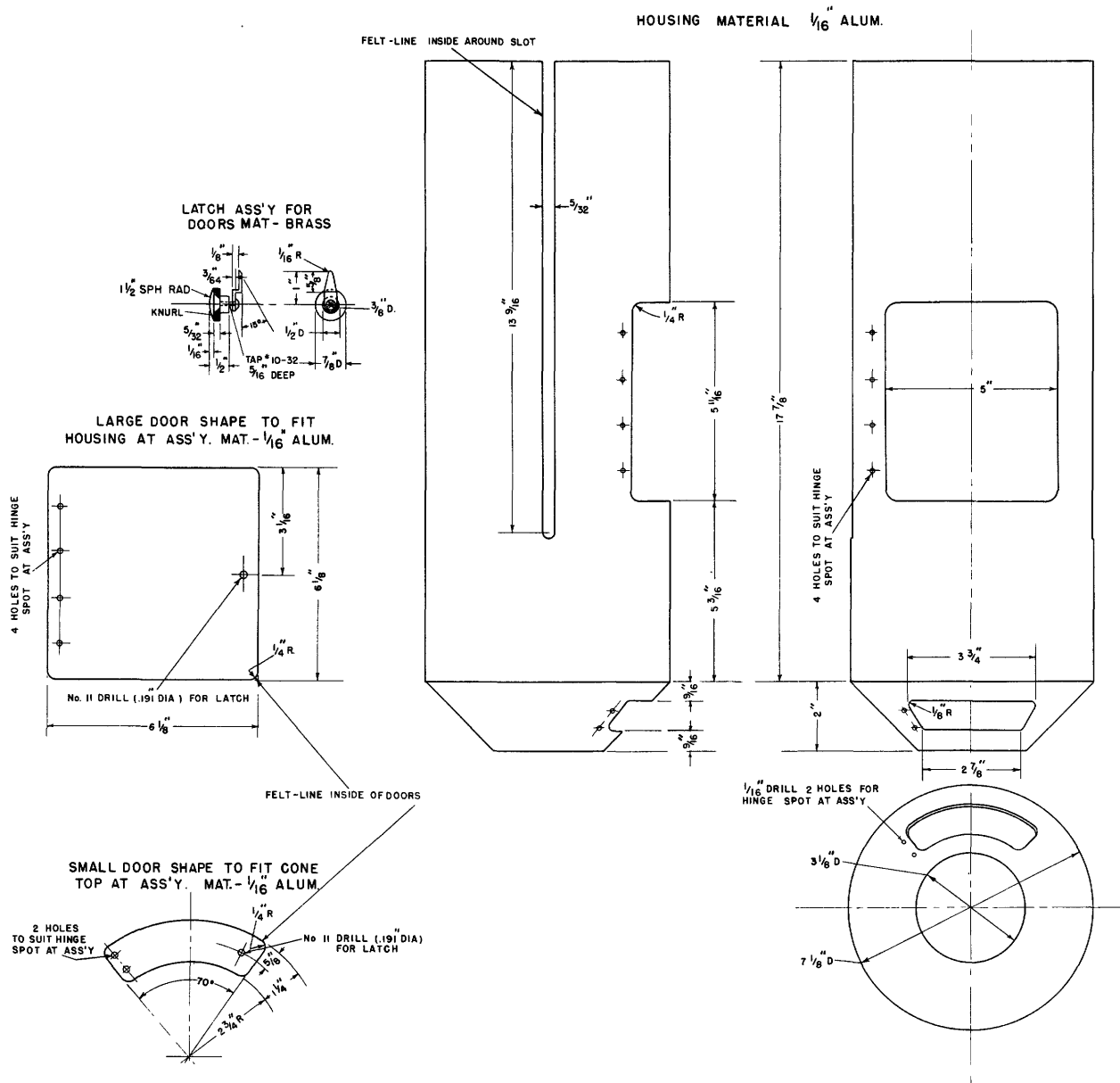Figure 13. --Details of parts shown in figure 9.

17
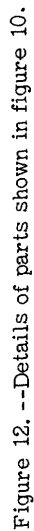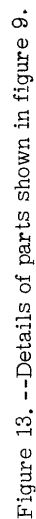
Figure 14. --Details of construction of shield.

have been used with this fluorimeter have been described elsewhere (Fletcher, May, and Slavin, 1949; May and Fletcher, 1950).

Figure 16 illustrates a typical working curve relating the uranium content of a 2-g disc to its· relative fluorescence. . Fluorescence measurements were made with the Photovolt photometer Model 512 using the "C" search unit and most sensitive scale. It is apparent that as little as 3×10^{-10} g of uranium may be measured.
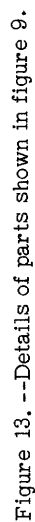
Unlike the reflection instrument where all fluorescence measurements are referred to a standard fluorescing glass, the transmission fluorimeter measurements are referred to a

18

CORRECTION SHEET

U. S. Geological Survey Circular 199

Please substitute attached sheet for pages
17 and 18 of this circular.

Figure 13. --Details of parts shown in figure 9.

17

HOUSING MATERIAL 1/16" ALUM.

FELT-LINE INSIDE AROUND SLOT

LATCH ASS'Y FOR
DOORS MAT- BRASS

LARGE DOOR SHAPE TO FIT
HOUSING AT ASS'Y. MAT.- 1/16" ALUM.

No. 11 DRILL (.191 DIA.) FOR LATCH

FELT-LINE INSIDE OF DOORS

SMALL DOOR SHAPE TO FIT CONE
TOP AT ASS'Y. MAT.- 1/16" ALUM.

4 HOLES TO SUIT HINGE
SPOT AT ASS'Y

1/16" DRILL 2 HOLES FOR
HINGE SPOT AT ASS'Y
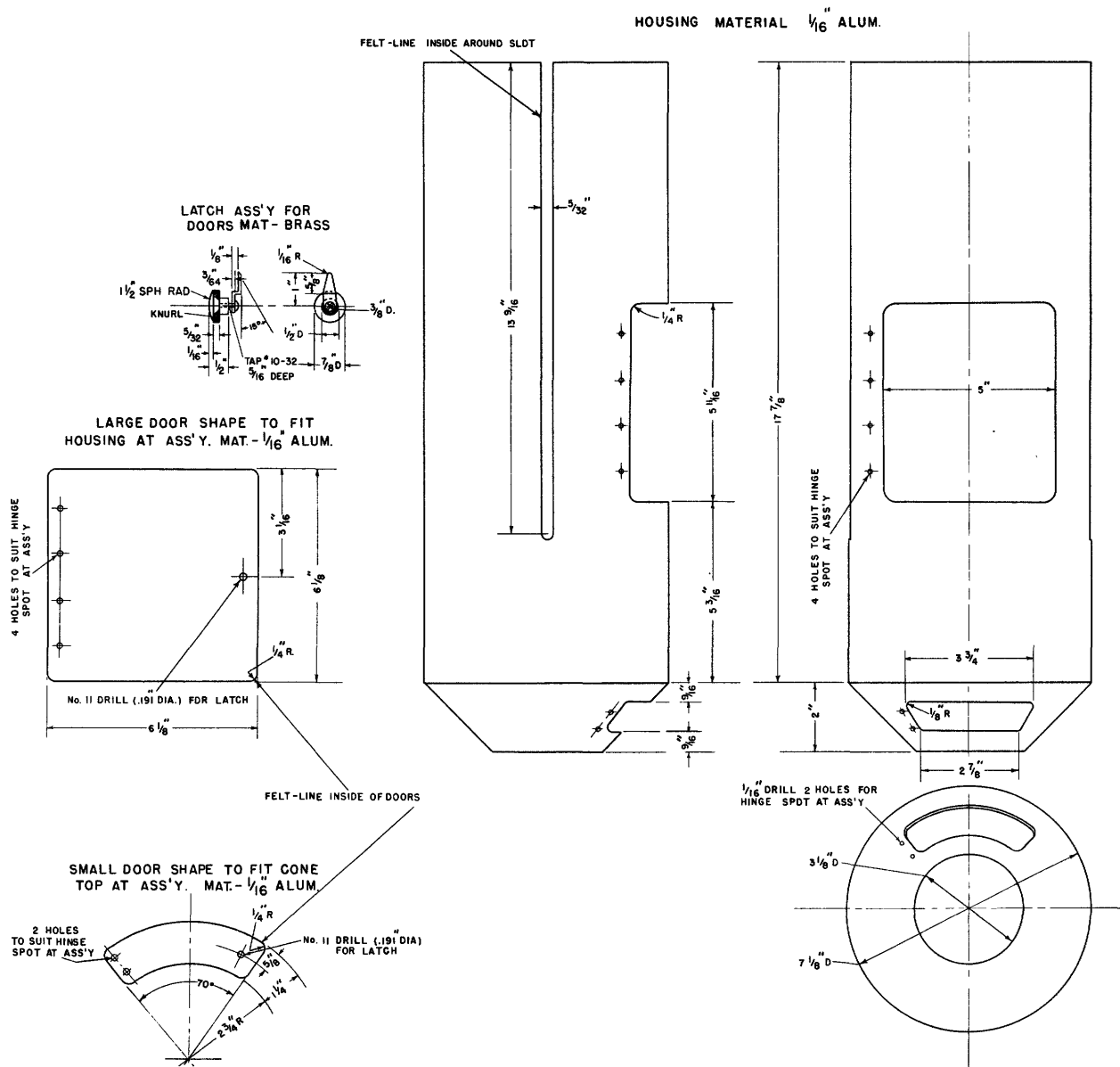
Figure 14. —Details for construction of shield.

18

Figure.15. --Details of construction of phototube housing type B.

HOUSING CAP I REQ'D ③

½" UNDERCUT
½"
7/16
5/16
KNURL

4" D-24 THD
FIT TO HOUSING

4¼" D

TUBE PLUG FLANGE I REQ'D FOR CINCH SOCKET 3 M4 WITH MOUNTING RING 3 R-14 ②

3½" D
2 1/16" D
2 7/32" D
3 9/16" D
3/8"
3/8"
½"

TAP *5-40 THD
5/16 DEEP 4 HOLES

2 ¾" D

Material Aluminum
Fittings to be light tight

SECTON A-A

COUNTER BORE FOR
AMPHENOL CONNECTOR
NO. AN-3102A-14S-5S

3/32

PHOTOTUBE HOUSING I REQ'D ①

4" D

3½" D

9/32

3 ¾ - 24 THD
3 9/16 24 THD

9½"

TAP *10-32 THD.
4 HOLES

6"

2¼"
1 1/16"
3/8"

45°
5/8" R
A
A

*8-32 FLAT HD SCR
DRILL & CO SINK FOR
4 HOLES

1 11/16" D

1 1/16"

4"D-24 THD
7/8 DRILL
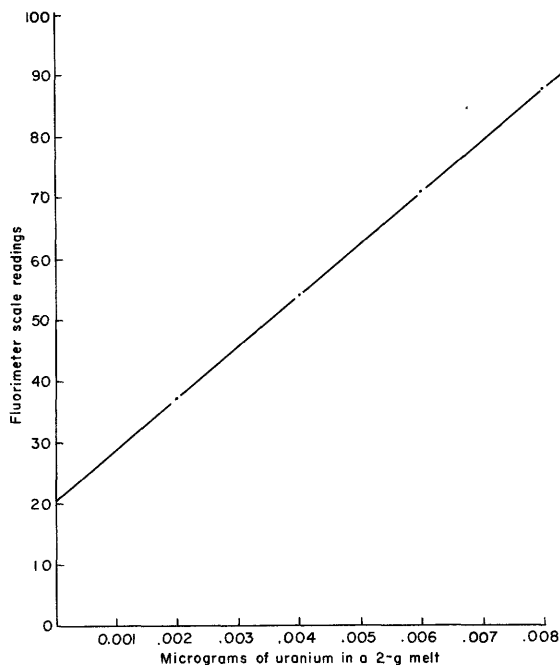
Figure

Figure 16.--A working curve for a transmission
fluorimeter.

"standard deflection" which is a reading obtained
with no sample in position. The standard deflection
results from filter leakage and fluorescence and has
been found to be reproducible. This reading may be
adjusted to a convenient figure by changing the posi-
tion of the lamp or the sensitivity controls on the
photometer.

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