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A TRANSMISSION FLUORIMETER FOR USE IN THE FLUORIMETRIC METHOD OF ANALYSIS FOR URANIUM

by

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ABSTRACT

A fluorimeter has been built which measures fluorescence by transmission rather than by the usual "reflection" methods. The consequence of the adoption of this new principle is a large gain in simplicity, compactness, ruggedness, sensitivity, cheapness of construction, and efficient use of light energy.

When used with an uncooled 1P21 photomultiplier tube operated at 45 volts per stage and a D.C. amplifier, the instrument has a sensitivity of one scale division equivalent to 1.7×10^{-11} grams of uranium in 1.5 grams of flux. However, in practice the lower limit is set by the blank reading. As a consequence of compactness and compartmentalization, stray light, which contributes to this blank reading, is reduced to a very small amount.

Reproducibility is such that a few thousandths of one percent of uranium can be determined on a 0.05-mg sample with an error of about 10 percent of the amount present.

If desired, the much simpler Photovolt Electronic Photometer (Model 512) with the C search unit can be substituted for the more elaborate photomultiplier tube and D. C. amplifier. Efficiency of light use is so great that still simpler measuring devices may prove adequate.

INTRODUCTION

Fluorescence of solids of the type exemplified by the alkali carbonate-fluoride melts used in the fluorimetric determination of uranium is generally measured by irradiating the surface of the melt with ultraviolet light and picking up the fluorescent light from the same surface by means of a phototube. A typical arrangement is shown schematically in figure 1. The Argonne fluorimeter (1, 2), the Oak Ridge Model R fluorimeter (3), and others are based on this principle.

In the transmission fluorimeter (4), by way of contrast, the lamp and phototube are on opposite sides of the melt. Figure 2 is a schematic drawing of this arrangement. Transmission measurements were probably overlooked by earlier workers because they considered their melts opaque or because of mechanical difficulties encountered in removal of the melts from the containers in which they had been fused, or simply because the other system worked and was satisfactory. As tests have shown that the melts are translucent, not opaque, and that proper choice of a fusion mixture gives a melt which is easily removable from its container and strong enough to be handled, transmission methods are entirely feasible.

ADVANTAGES OF A TRANSMISSION FLUORIMETER

Extreme compactness and simplicity are the first and obvious advantages of measurement by transmission. An instrument embodying this method consists of three flat members arranged in a sandwichlike array. These members are an ultraviolet filter, a

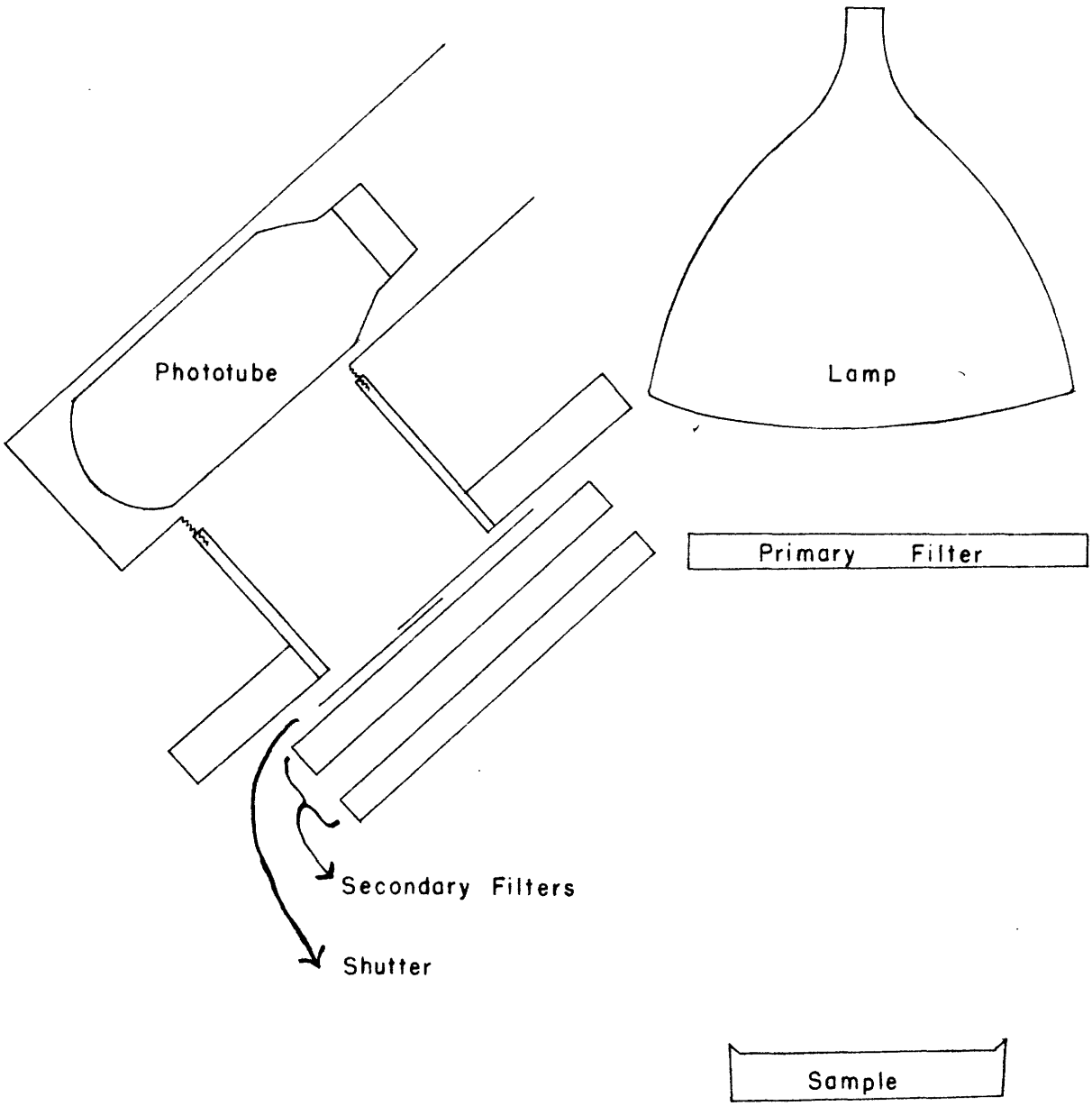

Figure 1- SCHEMATIC DIAGRAM OF A "REFLECTION"- TYPE FLUORIMETER

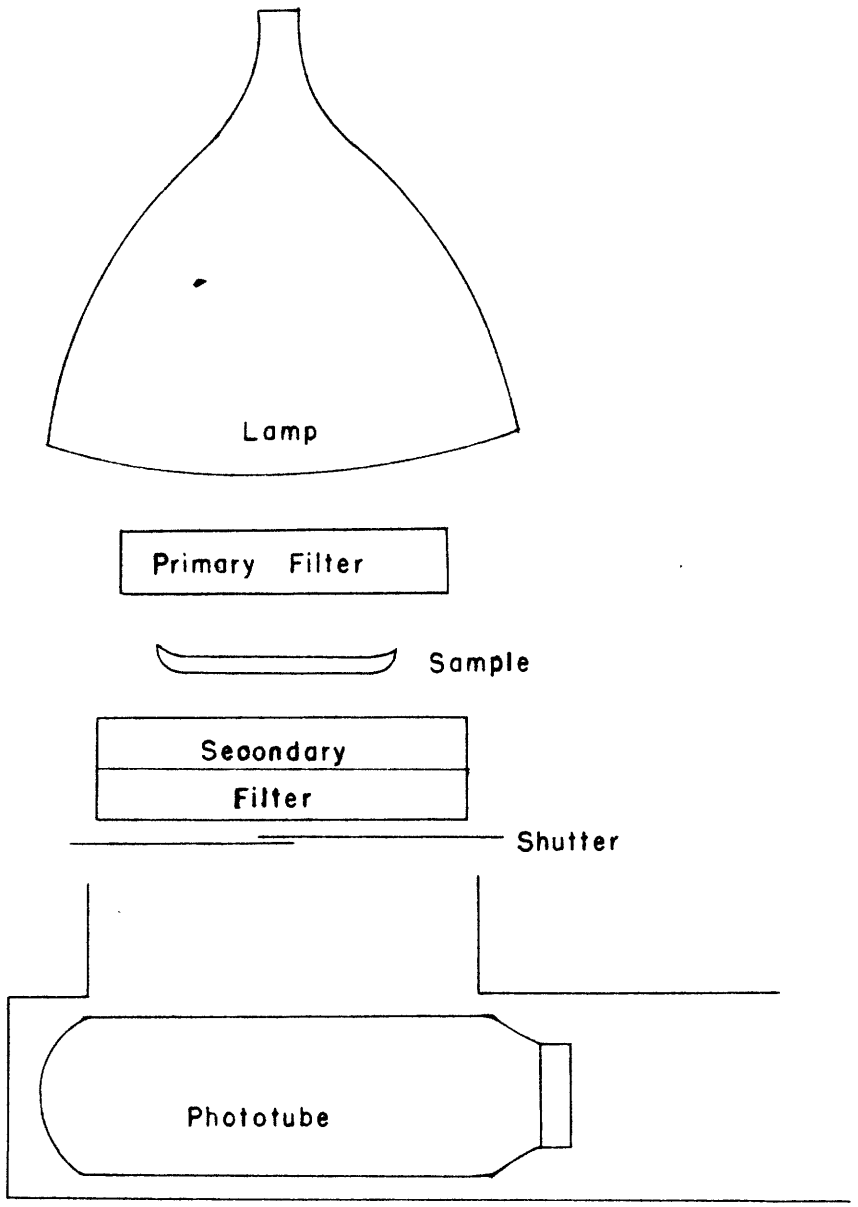

Figure 2 - SCHEMATIC DIAGRAM OF A TRANSMISSION TYPE FLUORIMETER

holder for the cake, and a yellow-green-transmitting filter. The two filters are mounted just far enough apart to permit the easy removal and replacement of the cake holder. The lamp can be brought up as close to the upper filter as desired. The phototube can be mounted in actual contact with the lower filter. Thus, the entire light path, from lamp to phototube, can be as short as two or three inches.

A consequence of the proximity of the lamp and phototube to the melt is the efficient use of light energy. Loss of light from factors involving the inverse square law is reduced to a minimum. Hence, very simple photo-measuring devices, as well as the more complicated photo-multiplier tubes, can be used.

In the sandwich arrangement the melt (or cake) divides the fluorimeter into two sections, the ultraviolet chamber and the fluorescent chamber. The melt, therefore, acts as an obstacle to the passage of ultraviolet light from upper to lower chamber. Tests show that about 95 percent of this light is reflected from the cake surface, hence, only that part of the remaining light (5 percent) which passes through the cake can get into the lower chamber. Stray fluorescence originating in the upper chamber has equal difficulty in getting through. As a result, stray light reaching the phototube is greatly reduced. This is a most important factor as apparently the complex optical system of the Argonne instrument was designed to reduce this stray light.

Simplicity of the instrument results in ruggedness and cheapness of construction. There are no lenses or mirrors and no need for delicately adjusted parts.

SENSITIVITY

The sensitivity of the Argonne and Oak Ridge fluorimeters, as well as the one described here, is such that all give a measurable blank reading. Consequently it is meaningless to express limiting sensitivity in such terms as galvanometer deflection per unit weight of uranium, for it is the blank which limits further improvement, not inefficiency of exciting light nor insensitivity of phototube. The main factcrs contributing to the blank are impure flux, fluorescent or leaky filters, and stray light in the instrument. The first is a chemical problem in purification of reagents; the second is a problem for the filter makers; only the third is amenable to reduction by good design of instrument. The transmission fluorimeter, therefore, with its sandwich arrangement of parts and consequent very low stray light, should be outstanding in sensitivity.

DESCRIPTION OF THE INSTRUMENT

The Model II transmission fluorimeter described in this paper was designed to give maximum flexibility for research purposes and is intended as an intermediate model. More specifically, all filters are readily removable and exchangeable, the exciting light is on a separate stand so that lamps may be interchanged, and the "pick-up" units of different measuring devices are in separate and identical housings which are threaded to screw into the bottom of the fluorimeter proper. Future models will not require this amount of flexibility and will undoubtedly be more compact; also, there are certain obvious changes which will be necessary. For example, the Model II as built was not as lighttight as later proved to be necessary so that masking tape had

to be used around the joints and extra light traps were added to prevent light leakage around the front and back shutter rods.

The basic design of the instrument resembles a miniature chest of drawers. The housing is made of brass and the drawers of maple and brass. The uppermost drawer carries the primary or ultraviolet filters; the middle drawer contains a disc of nonfluorescing glass over the bottom aperture and is equipped with an adaptor to hold the sample; the lower drawer holds the secondary filters.

The filter combination finally adopted for general use consists of two Corning No. 5874 2-inch polished glass squares as the primary filters, and a 2-inch square Baird interference filter peaked at 5590 A ± 50 A for the secondary. The exciting light is furnished either by a G.E. CH-4 or EH-4 lamp. Lamp voltages are regulated by a Sola Constant Voltage Transformer No. 30,852 specifically designed for use with the H-4 lamps. Temperature of the lamps is controlled by ventilation with a "Bon-Air" darkroom ventilating fan.

The measuring devices are either a Photovolt Electronic Photometer (Model 512) equipped with a C search unit, or an 1P21 photomultiplier tube in combination with a D.C. amplifier. Voltage for the 1P21 photomultiplier tube is supplied by a regulated power supply with voltage divider of conventional design. The D. C. amplifier design is slightly modified from that used by Schulman, Battey, and Jelatis (5) with their polarograph and is based on the fundamental design of Roberts (6). The modification consists in deletion of the circuit for applied voltage, reversal of polarity, and appropriate changes in the sensitivity ranges.

PREPARATION OF MELTS

The fusion mixture used for the preparation of the melts is that described by Grimaldi and Levine (7) and consists of 9% NaF in equal parts by weight of Na_2CO_3 and K_2CO_3. This mixture melts at a little below 650°C. and shrinks slightly on cooling so that the melt pulls away from its container. The melts are strong and can be handled without danger of breaking. The fusion mixture is prepared by fusing several 100-g portions which are then ground and mixed. This procedure was found necessary to obtain a uniform mixture which would give reproducible blanks. Melts were prepared by fusion of 1.5 g of this mixture in platinum lids from 30-ml crucibles. The fusions were made in a furnace at 650°C.

Although, as might have been expected, fluorescence varies inversely with thickness of the melt, these variations of thickness present no practical difficulties. Standard size lids are chosen for the fusions, hence, the weight of the flux controls the thickness. Differences in weight as large as 5 mg introduce an error in the fluorescence reading of only 0.2%. Variations in thickness with weight and the corresponding changes in the instrument response are given in table 1. It should be stressed that even relatively thick cakes are translucent. It is also seen that the greatest sensitivity occurs with the thinnest discs. This could be predicted from mathematical considerations.

It is difficult to cover the lids evenly with 0.5 or 1.0 g of flux, and for this reason 1.5 g was the most convenient weight to use. The larger amount of flux will also allow for the presence of larger amounts of quencher elements, as Price (1) has shown that the ratio weight of quencher to weight of flux is the important factor in quenching phenomena.

PERFORMANCE OF THE INSTRUMENT

A standard curve is obtained by measuring a series of melts which contain known amounts of uranium. At the same time a reading is made with no sample in place. This reading is called the "standard deflection" and represents filter leakage which is assumed to be a constant of the instrument. Once a standard curve has been drawn, the conditions under which it was made can be reproduced by adjusting the distance of the lamp to give this standard deflection. The uranium content of unknowns is obtained by interpolation in the standard curve.

The performance of the instrument with each of the "pick-up" units is shown in table 2. It will be seen from the table that the two handle about the same amounts of uranium. However, the Photovolt attachment is operated at capacity but the more elaborate system of a 1P21 photomultiplier tube and D.C. amplifier still has a large reserve of unused sensitivity. For instance, if the voltage per stage were increased from 45 to 100 the amplification would be increased 500-fold (9).

The sensitivity of the instrument with either "pick-up" unit is roughly equivalent to that of the Argonne instrument, although the available data is insufficient to make an exact comparison. However, Price operated his photomultiplier tube at 80 volts per stage (2) (compared to 45 volts in this instrument) and used dry-ice cooling.

It would perhaps be of interest to see actual figures of results obtained with the transmission fluorimeter. These results are shown in tables 3, 4, and 5. The EH-4 lamp was used at a distance of 3 inches from the primary filter, and volts per stage on the 1P21 tube were 45. The scale setting with no cake in the holder was 46.0 divisions on the 0.02 scale.

Table 1.--Effect of disc thickness on instrument response

(Measurements made with the 1P21 photomultiplier tube and D.C. amplifier)

Weight of flux (grams)	Thickness of melt (inches)	Scale divisions (0.02 scale)		Sensitivity (micrograms of uranium per scale division)
		Blank reading	0.003 micrograms of uranium	
0.5	0.017	21.8	43.5	0.000138
1.0	0.027	20.8	40.4	0.000153
1.5	0.040	20.4	38.0	0.000171
2.0	0.049	22.5	36.5	0.000214
2.5	0.058	20.6	33.6	0.000231
3.0	0.070	18.6	29.8	0.000268

It will be seen from the data in these tables that performance of the instrument is adequate for analytical purposes. The errors to be expected are of the same order of magnitude as those inherent in the chemical manipulations of sampling, weighing, pipetting, and so forth, that precede the photometry of fluorescence.

CONCLUSIONS

The fluorimeter here described, based on a new arrangement of instrumental elements, is a great improvement over existing instruments in such factors as cheapness of construction, ruggedness, compactness, and efficient use of light energy.

Compactness and light efficiency open up the possibility of developing an over-all procedure for the determination of uranium in the field by the use of portable equipment, a technique which should be of interest to geologists and public health officials.

Although the fluorimeter has been used only for solid samples up to the present time, it is probably equally adaptable to solutions.

Table 2.--Performance of the "pick-up" units

Lamp type	Lamp distance (inches)	"Pick-up" unit	Volts per stage	Blank reading (scale div.)	Sensitivity (micrograms equivalent to one div.)
CH 4	1	Photovolt unit	--	22.0 (one scale)	0.00015 (one scale)
EH 4	3	1P21, D.C. amplifier	45	20.0 (0.02 scale)	0.000171 (0.02 scale)

Table 3.--Readings of replicate blank samples

Sample No.	Scale divisions (0.02 scale)	Deviation from mean
1	21.0	0.2
2	22.0	1.2
3	21.0	0.2
4	21.5	0.7
5	20.1	0.7
6	20.2	0.6
7	20.0	0.8
8	20.2	0.6
9	21.1	0.3
10	20.9	0.1
Mean	20.8	0.54

Table 4.--Readings of replicate standard samples

(Uranium content = 0.005 micrograms)

Sample No.	Scale divisions (0.05 scale)	Deviation from mean
1	20.5	0.3
2	19.9	0.9
3	20.9	0.1
4	20.8	0.0
5	20.8	0.0
6	20.7	0.1
7	21.0	0.2
8	21.2	0.4
9	21.0	0.2
10	21.0	0.2
Mean	20.8	0.24*
Blank	8.1	

*0.24 scale divisions on 0.05 scale is equivalent to 0.6 scale divisions on 0.02 scale. In other words, the ratio of the 0.02 scale to the 0.05 scale is 1/2.5

Table 5.--Replicate analyses of standard sample GST-1
(Uranium content = 0.009%)

(100-microgram aliquots of sample)		
Replicate No.	Uranium found (micrograms) and (percent)	Deviation from mean
1	0.0085	0.0002
2	0.0085	0.0002
3	0.0088	0.0001
4	0.0088	0.0001
5	0.0088	0.0001
6	0.0088	0.0001
7	0.0091	0.0004
8	0.0086	0.0001
9	0.0081	0.0006
10	0.0086	0.0001
11	0.0088	0.0001
12	0.0088	0.0001
Mean	0.0087	0.00018

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