CANADA
DEPARTMENT OF MINES AND TECHNICAL SURVEYS
MINES BRANCH

THE DETERMINATION OF URANIUM IN ORES

FLUOROPHOTOMETRIC METHOD

by

J. B. ZIMMERMAN
RADIOACTIVITY DIVISION

1951

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ILLUSTRATIONS

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INTRODUCTION

The fluorescence of certain uranium compounds when exposed to ultra violet light was first reported by Stokes[8] and Becquerel[1] and, indeed, it was the study of this phenomenon that led Becquerel indirectly to the discovery of the radioactive properties of uranium. This new discovery was of such import and interest that the fluorescence question was relegated to the background until Nichols and Slattery[4] reported after much investigation that the fluorescence of uranium was greatly enhanced when fused in a bead of a substance such as borax or sodium fluoride. The bead test, in which a small amount of suspected uranium-containing substance is fused in borax on a platinum wire loop and then viewed under ultra violet light for fluorescence, has been used by prospectors and laboratories as a qualitative test for uranium. The first quantitative application of the method is attributed to Hernegger and Karlick[2]. Subsequent investigators, notably Price, Ferretti, Schwartz,[5] have developed the method to a high degree of accuracy and precision.

This report describes the procedures used at the Mines Branch, Ottawa, in the operation of a sensitive fluorimeter.

THE FLUORIMETER AND ITS ACCESSORIES

The fluorimetric method of analysis for U_3O_8 content has proved superior both in accuracy and in speed to all other known methods for the assay of low uranium concentrations.

The standard deviation for the method is approximately 5 per cent over the working range. The greatest value of the instrument is therefore at lower uranium concentrations, and assays by the fluorimetric method at the Mines Branch are restricted to samples containing less than 1 per cent U_3O_8. However, there are occasions when preliminary tests are made in which a greater than 5 per cent accuracy is not required and the fluorimetric method has given satisfactory results up to >50 per cent U_3O_8 content.

The fluorimeter in use was designed and manufactured by the Massachusetts Institute of Technology, Mineral Dressing Laboratory in Boston, Mass., and is known as M. I. T. Model #3.

The instrument utilizes the recognized principle of irradiating a sample of uranium fused in sodium fluoride with monochromatic ultra violet light of 3650A. The resulting fluorescent light emitted by the bead falls upon the light sensitive cathode of an IP21 photomultiplier tube and the amplified current produced is registered by a sensitive galvanometer.

The M. I. T. Model #3 fluorimeter is very sensitive, being capable of detecting $<10^{-9}$ gm of U_3O_8. The response is linear (galvanometer reading vs. U_3O_8 concentration) at lower light levels (Figure 5). Experimental work has indicated that the linear response extends at least from 5×10^{-9} gm to 10^{-6} gm of U_3O_8.
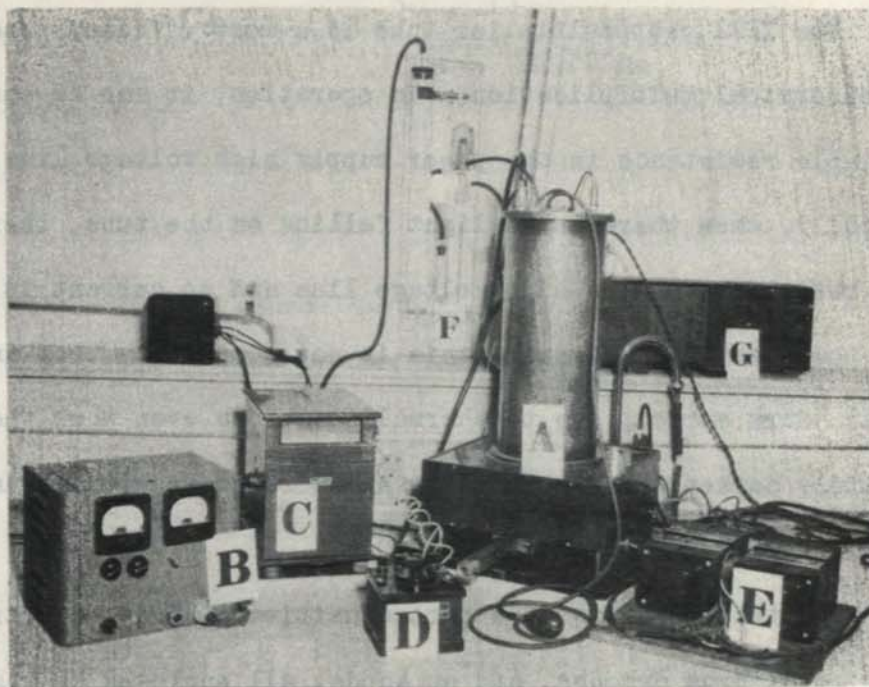
Figure 1 - Fluorimeter

A - The fluorimeter   E - Transformers
B - Power supply   F - Air dryer and manometer
C - Galvanometer   G - Constant voltage transformers
D - Ayrton shunt

Figure 2 - Fusion burner

Photomultiplier Tube

The IP21 photomultiplier tube is a most efficient means of gaining electrical multiplication. In operation, it can be considered as a variable resistance in the power supply high voltage line. Theoretically, when there is no light falling on the tube, there is infinite resistance in the high voltage line and no current is drawn from the power supply. However, this is not completely true as there is a small, dark current due to thermal electrons even when the tube is completely darkened. The tube has an S4 response with maximum response at a wave length of 4000 $\pm$ 500 $\mathring{A}$.

The tube consists of a photosensitive cathode, electrostatic shielding grid, nine dynodes, and an anode, all enclosed in a glass envelope.

The electrostatic shield allows only quanta of light to impinge on the photocathode. The light energizes the photocathode and primary electrons are emitted and accelerated towards the first dynode which is electrically positive with respect to the photo cathode. The primary electrons impinge on the first dynode and release secondary electrons from the dynode surface which is geometrically placed so as to focus the secondary electrons towards the second dynode which is at a still more positive potential. This process is repeated through the nine dynodes, the final charge being received by the anode and the output current taken off between the positive side of the power supply and the anode. The success of the photomultiplier tube depends upon the fact that an impinging secondary electron on a dynode must have an efficiency greater than 100 per cent in releasing secondary electrons.
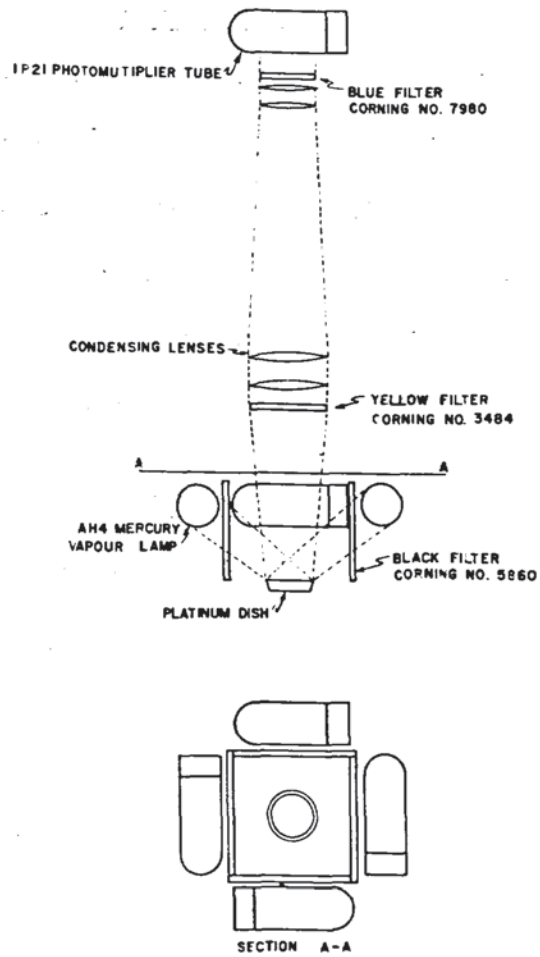
Figure 3 - Schematic diagram of fluorimeter
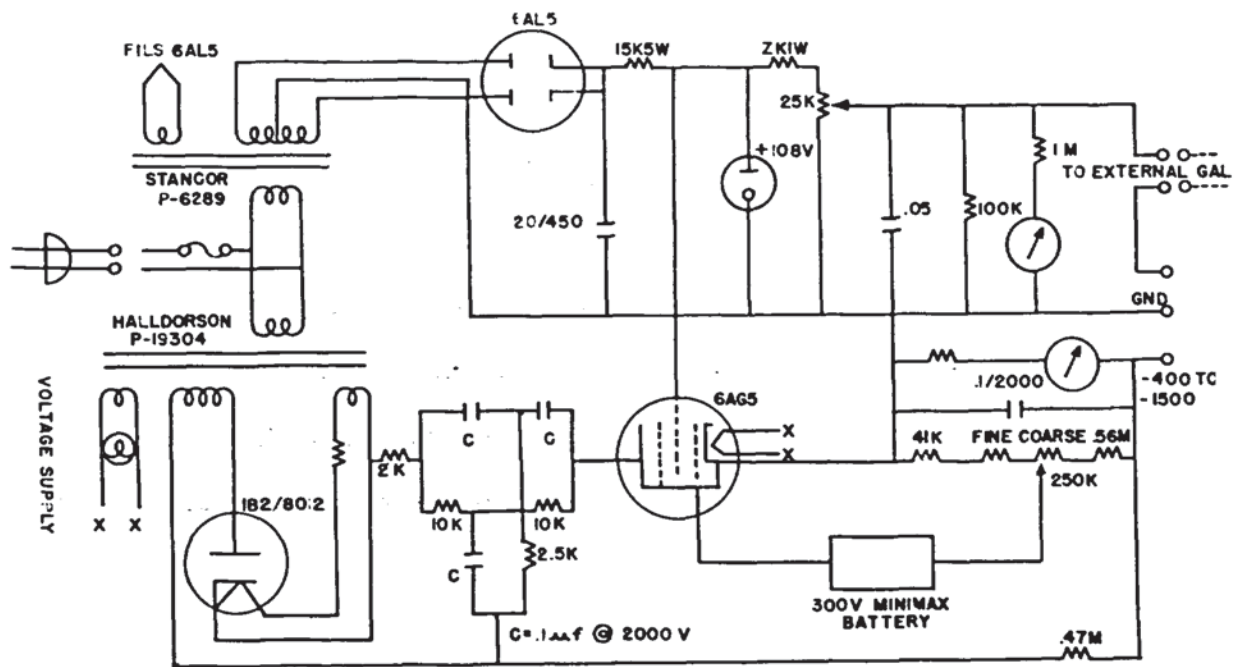
Figure 4 - High Voltage Supply

Irradiating Source

The source of irradiating ultra violet light of 365 mμ is derived from four AH4 General Electric mercury vapour lamps, each rated at 100 watts. Each lamp is supplied by its own individual transformer (General Electric Auto Transformer #89G142 for H4 mercury vapour lamps). The four transformers are fed from a Sola constant voltage transformer connected with the 60-cycle 115-volt AC main.

Voltage Supply

The voltage supply is a conventional type of regulated voltage supply designed and built by M.I.T. A circuit diagram drawn by M.I.T. is shown in Figure 4.

This type of power supply has proved most satisfactory. However, it is necessary to replace the 300-volt Mini-Max battery approximately every six months.

Filters

Three filters of different characteristics are employed in the M.I.T. Model #3 fluorimeter.

The light from the mercury vapour AH4 lamps is first filtered by a Corning #5860 black glass filter (#1), approximately 0.5 cm in thickness which has >13 per cent transmission. The resulting monochromatic light of 365 mμ then impinges on the prepared sample beads. The resulting fluorescent light from the sample beads is filtered by a Corning #3484 traffic light yellow filter (#2), the purpose of which is to block any reflected or stray ultra violet light.

The filtered fluorescent light, after passing through condensing lenses, is again filtered by a Corning #9780 blue-green filter (#3) which eliminates any fluorescent light excited in the filter (#2). This system of filters is designed to transmit the 550.5 $\overset{o}{A}$ line of uranium fluorescence.

Galvanometer

The galvanometer used with the M.I.T. Model #3 fluorimeter is a triple reflection, fiber-suspension Rubicon, (catalogue number 3414), which has a sensitivity of .0015 μa per mm, with a full scale deflection of 10 cm. The galvanometer is shunted by a Rubicon Ayrton shunt of 10,000 ohms total resistance having a manual switch which permits multiplying factors of 1, 10, 100, 1,000, and 10,000.

PROCEDURE

Sample Preparation

All samples should be -150 mesh and prepared properly so that each is representative. The large variety of samples analysed at the Mines Branch by the fluorimetric method include prospectors' grab samples containing uranium in its various mineral forms, and fractions from experimental development work.

Nitric Acid Solution of Sample

It has been found by experiment that many ores are taken readily into solution by means of a hot nitric acid leach. The following procedure is used. One to five grams of solid dependent upon the estimate of the U_3O_8 content are weighed carefully and transferred to a 250 ml

Pyrex beaker. Ten to fifteen ml of concentrated nitric acid are added and the mixture heated on an electric hot plate for approximately 10 minutes until the brown fumes have disappeared. Fifty ml of 1:1 nitric acid are then added and the whole boiled for 30 minutes. The liquid and solid are carefully washed into a volumetric flask and made up to volume. A portion is then filtered into a glass-stoppered bottle and delivered to the fluorimetric laboratory for assay.

All liquid samples are made up directly in 5 to 10 per cent nitric acid, unless a separation is necessary, due to the presence of detrimental amounts of quenchers. Quenching curves for iron and manganese are shown in Figure 6.

Use of Ratemeter for Proximate Analysis

All samples on which there is no estimate of U_3O_8 content are first assayed quickly, approximately 5 minutes per sample, by means of a beta counting ratemeter. The accuracy of the ratemeter is sufficient in most cases to establish the dilution range required to cause a sample to read in the vicinity of the standard on the fluorimeter.

Previous to the installation of the ratemeter a number of outside samples had to be re-assayed due to an incorrect dilution. The ratemeter has eliminated this uncertainty as to dilution range, and a considerable saving in time has been effected. The following table is a representative list comparing ratemeter and fluorimetric assays of solid samples.
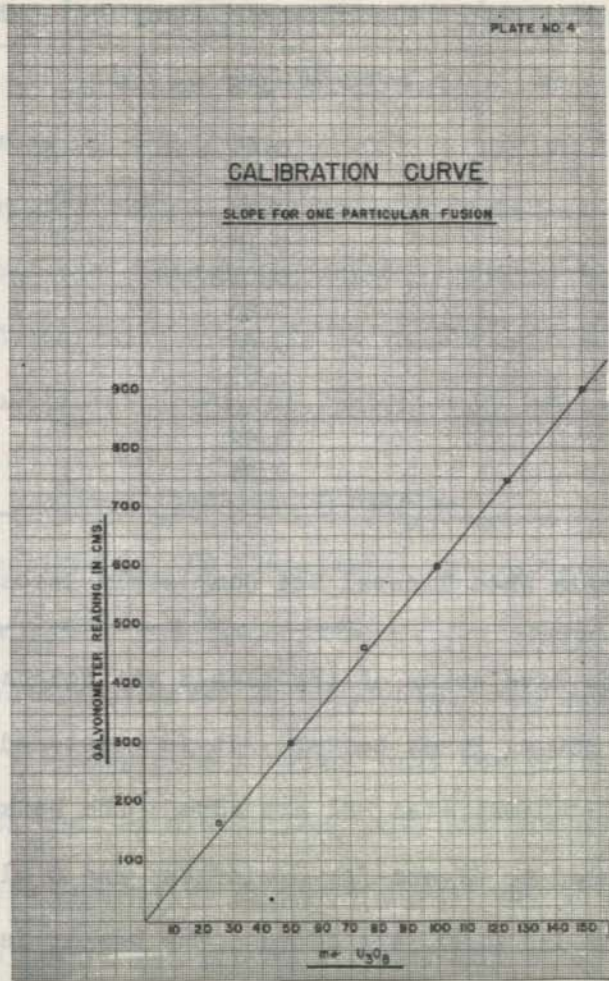
Figure 5 - Calibration curve
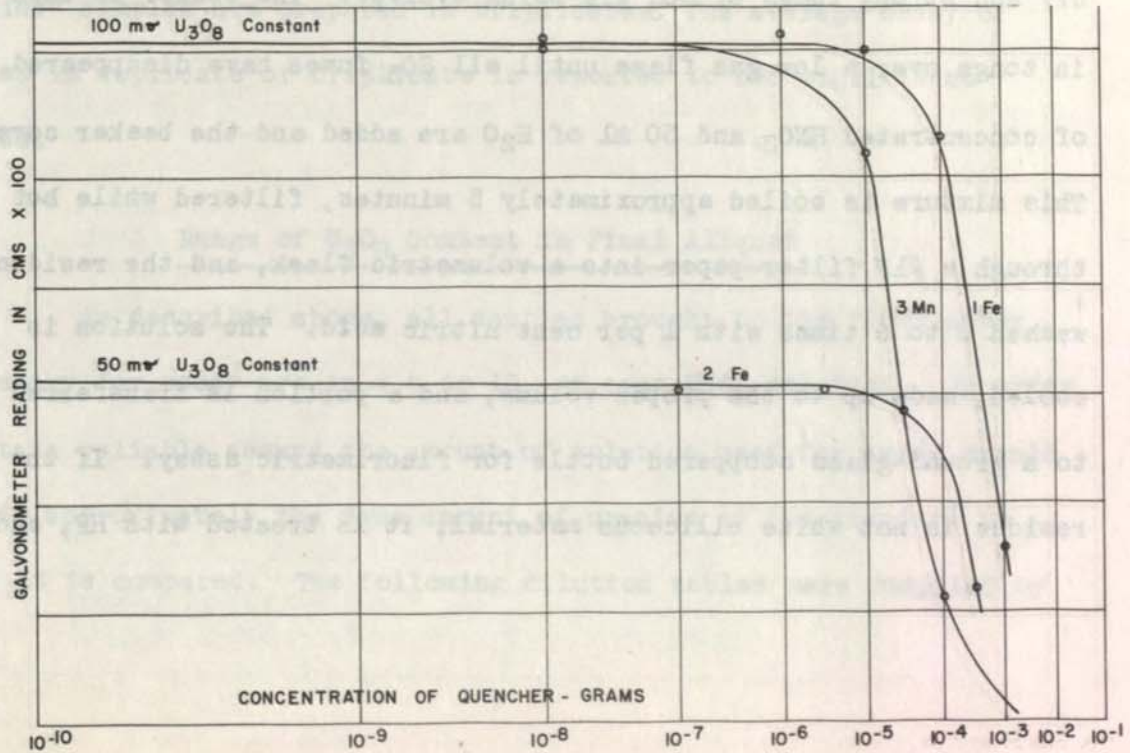
Figure 6 - Quenching effects of Fe & Mn

Sample No.	Fluorimetric Assay	Ratemeter Assay
	% U_3O_8	% U_3O_8
1	0.01	0.016
2	0.05	0.078
3	0.44	0.43
4	0.13	0.11
5	0.018	0.015
6	0.23	0.21
7	0.26	0.34
8	0.39	0.35
9	0.40	0.31
10	0.92	0.99
11	0.26	0.32

Solution of Sample When Mineral Not Completely Decomposed by Nitric Acid

One to five grams of the sample are weighed and transferred carefully to a 250 ml Pyrex beaker. It is moistened with 2 to 3 ml of water; 10 ml of concentrated HCl are added; the beaker is covered and the sample allowed to digest for 5 minutes; and 5 ml of concentrated HNO_3 and 5 ml of 1:1 H_2SO_4 are added. The beaker is then uncovered and the sample allowed to evaporate on the hot plate until it is almost dry and strong fumes of SO_3 are being evolved. The beaker is then held in tongs over a low gas flame until all SO_3 fumes have disappeared, 5ml of concentrated HNO_3 and 50 ml of H_2O are added and the beaker covered. This mixture is boiled approximately 5 minutes, filtered while hot through a #1F filter paper into a volumetric flask, and the residue washed 5 to 6 times with 1 per cent nitric acid. The solution is cooled, made up to the proper volume, and a portion is transferred to a ground-glass stoppered bottle for fluorimetric assay. If the residue is not white siliceous material, it is treated with HF, and

the silica broken up. The resulting residue is then taken to dryness, dissolved in HNO , and added to the filtered solution before the final dilution is made.

Sodium peroxide sinters have been performed on difficult soluble materials, but one disadvantage of this method is the large amount of salts produced which are left as residues in the platinum dishes when an aliquot is pipetted for fluorimetric analysis.

Classification of Samples

Samples received by the fluorimeter laboratory are classified into three groups "A", "B", and "Outside".

"A" samples are prepared in duplicate. "B" samples are prepared singly; if the sample is a solid, only one portion is weighed and put into solution and, if a solution, only one aliquot is taken. "A" or "B" samples are designated by the engineer who is conducting a specific test. This method has proved a great time saver as often intermediate results in a test are not required with maximum accuracy. "Outside" samples are prepared in triplicate. The average assay of samples in duplicate or triplicate is reported to two significant figures.

Range of U_3O_8 Content in Final Aliquot

As described above, all samples brought to the fluorimeter laboratory for assay are in a 5 to 10 per cent HNO_3 solution. In order to obtain reliable assays the amount of solution used for assay should contain approximately the same amount of uranium as the standard to which it is compared. The following dilution tables were compiled by

the M.I.T. mineral dressing laboratory so that an 0.1 ml aliquot of the final dilution of a sample falling within any of the designated ranges of U_3O_8 content will give a fluorescence reading not greater than two times or less than one half of 10^{-7} gm of U_3O_8, which is the amount of U_3O_8 in a standard bead.

Liquid Samples

Range	Dilution
g./l.	
0.001	none
0.001 - 0.005	10/50
0.005 - 0.01	5/50
0.01 - 0.02	10/100
0.02 - 0.03	10/250
0.03 - 0.065	5/250
0.065 - 0.12	5/500
0.12 - 0.3	5/1000
0.3 - 0.7	5/1000 x 10/25
0.7 - 1.5	5/1000 x 10/50
1.5 - 3.0	5/1000 x 10/100
3.0 - 6.0	5/1000 x 5/100
6.0 - 15.0	5/1000 x 10/250

Solid Samples

Range	Dilution
%	
0.001 - 0.002	5/100
0.002 - 0.005	1/50
0.005 - 0.01	1/100
0.01 - 0.03	1/250
0.03 - 0.06	1/500
0.06 - 0.1	1/1000
0.1 - 0.3	1/1000 x 10/25
0.3 - 0.6	1/1000 x 10/50
0.6 - 1.2	1/1000 x 10/100
1.2 - 2.5	1/1000 x 5/100
2.5 - 6.0	1/1000 x 10/500
6.0 - 10.0	1/1000 x 10/1000
10.0 - 25.0	0.5/1000 x 10/1000
25.0 - 70.0	0.3/1000 x 10/1000
70.0 - 100.0	0.3/1000 x 5/1000

Use of City Water for Dilution

When the microfluorimetric analysis of uranium was first
undertaken at the Mines Branch it was routine practice to use distilled
water for all dilutions. However, following a report from M.I.T. that
tap water had been successfully used in the dilution technique, experi-
ments were carried out to determine if the Ottawa city water would also
prove suitable. The following table is a comparison between assays of
identical samples diluted with distilled water and with tap water.

Sample	Dilution with Distilled Water Assay	Dilution with Tap Water Assay
	% U_3O_8	% U_3O_8
1	0.047	0.048
2	0.10	0.11
3	0.084	0.081
4	0.066	0.067
5	0.14	0.14
6	0.064	0.067
7	0.15	0.16
8	0.075	0.075
9	0.68	0.68

As the two series of assays are in good agreement, the use
of tap water for all dilutions over 500 ml and for all first dilutions
was instigated as routine procedure. There are two main advantages in
using cold tap water: the demand on the distilled water supply is
greatly reduced resulting in a considerable saving in overall costs,
and secondly, water fresh from the still is often warm, and a cooling
procedure is then necessary before a sample can be brought up to
final volume.

In cases where the tap water is of poor quality it has been found that a water demineralizer (e.g. DEEMINIZER) containing mixed cation-anion exchangers is most efficient and economical.

Assaying Technique

All samples when in the liquid form and made up to the proper dilution, are ready for assay. For reasons of simplicity, the procedure for a "B" sample is described here.

The assay of a "B" sample constitutes the reading of four beads. Two aliquots of 0.06 ml and two aliquots of 0.1 ml are pipetted into clean dry platinum dishes. The object of using two different aliquots is that, according to the dilution theory on quenching[5] the presence of quenchers effects a lower fluorescence reading in the higher aliquot which can be detected, and the proper correction procedures undertaken.

The pipetted samples are then placed under a bank of four General Electric, industrial type, 100 watt, infra red drying lamps, and dried for approximately 10 minutes or until the sample in the platinum dish is completely dry. If the sample is not completely dry there will be spattering during the fusion process.

With a pelletizer (Figure 7), 350 ± 20 mg of flux (CP Nichols NaF) are placed in each dish. The dishes are then transferred by means of platinum-tipped forceps to a chromel screen (1/4 in. mesh) suspended over a modified Fletcher burner. The gas is ignited and the gas-air mixture adjusted until the blue gas cones are approximately 1/2 in. high. Heating under these conditions is

PLUNGER THUMB PIECE   LOCK NUT

PLUNGER SPRING   RETAINING SCREW

5 1/4

PLUNGER

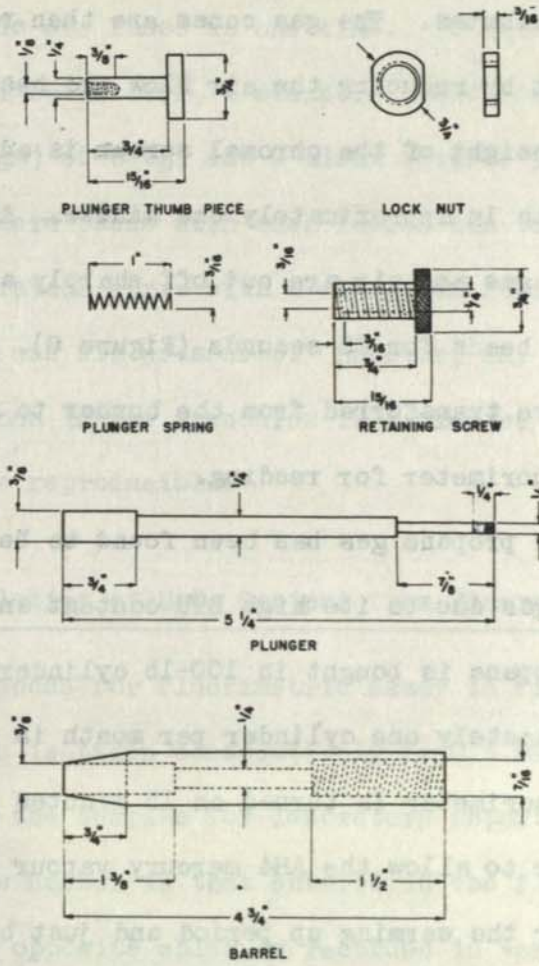1 3/8   1 1/2

4 3/4

BARREL
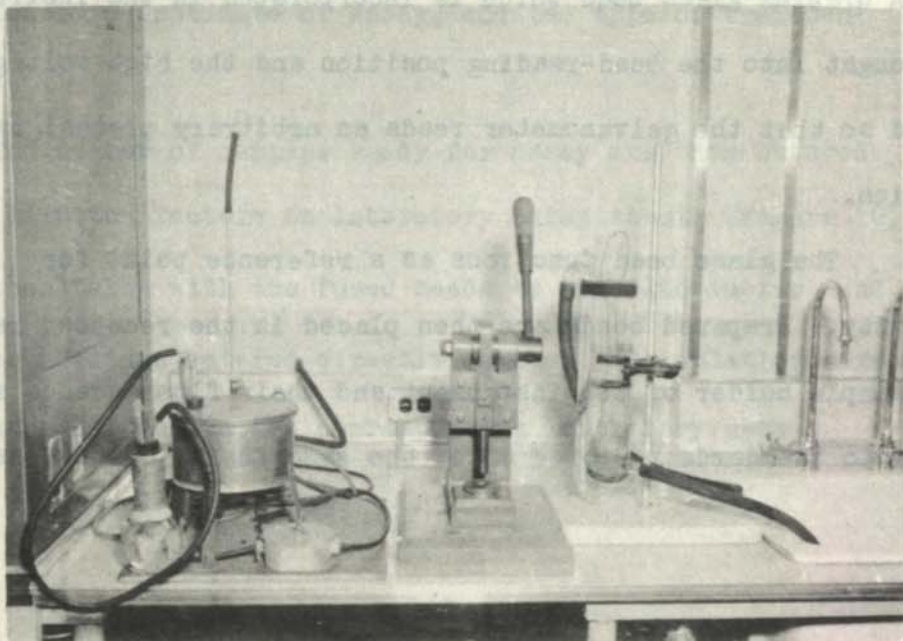
Figure 7 - Sodium fluoride pelletizer

Figure 8 - Steam generator, dish press, pipette washer

continued for $2\frac{1}{4}$ minutes. The gas cones are then raised to approximately one inch in height by reducing the air flow and heating is continued for 45 seconds. The height of the chromel screen is adjusted beforehand until the NaF melts in approximately one minute. After the 3-minute fusion period the gas and air are cut off sharply and a jet of steam is directed over the beads for 25 seconds (Figure 8). The beads in the platinum dishes are transferred from the burner to a special tray and carried to the fluorimeter for reading.

Bottled propane gas has been found to be more satisfactory than Ottawa city gas due to its high BTU content and uniform delivery pressure. The propane is bought in 100-lb cylinders. Under normal conditions approximately one cylinder per month is used.

The fluorimeter is turned on 15 minutes prior to reading the beads in order to allow the AH4 mercury vapour lamps to reach full brilliancy. After the warming up period and just before reading the beads, the shunt is set on infinity and the galvanometer adjusted to zero. A uranium glass bead which is incorporated in the instrument is then brought into the bead-reading position and the high voltage adjusted so that the galvanometer reads an arbitrary predesignated deflection.

The glass bead functions as a reference point for sensitivity. Prepared beads are then placed in the recessed receptacles in the sample holder of the instrument and their fluorescence read and compared to standards prepared under the same fusion conditions.

Fourteen beads are fused at one time. In this number are included 2 samples of 4 beads each, 4 standard beads each containing 100 milligammas (10^{-7} gm) of U_3O_8, and 2 blank beads. It was found necessary to fuse standard beads with each fusion due to a change in the slope of the calibration curve with a change in fusion conditions such as changes in gas and air pressures. However, any change shown between different fusions in the standards is reflected in the samples, and assays are reproducible.

Recording and Calculation of U_3O_8 Content from Fluorescence Data

A sample intended for fluorimetric assay is first given a laboratory number which is taken consecutively from a master record. This number designates the samples for laboratory reports and for future reference. This number is then entered in the fluorimetric laboratory record book opposite which is recorded in vertical columns, (a) sample description, (b) types of assays required, (c) number of determinations, (d) estimate of assay, and (e) type of treatment (Figure 9).

The number of samples ready for assay are then entered along with dilution factors on laboratory assay sheets (Figure 10) which are then taken with the fused beads to the fluorimeter, and fluorescence readings entered directly on them. Calculations are made and entered opposite the corresponding laboratory number.

FLUORIMETER RECORDS   PAGE NO.

LAB. NO.	SAMPLE	ASSAYS REQ'D	NO. OF DET.	RANGE	NO. OF ACIDS	DILUTIONS	FLUO. PAGE	ASSAY
1234	4-3-12 RES.	U_3O_8		.03-.01	3	2gms/500 mls	1300	

Figure 9 - Fluorimeter records

FLUORIMETER LABORATORY

PAGE: 1500

LAB. NO.	DESCRIPTION	DILUTION	ALIQ	GALV. READING		AVERAGE	BLK.	U_3O_8	ASSAY	AV. ASSAY
1234	4-3-12 RESIDUE	2gms/500 mls	.06	200	190	195	185	34.6	.0144	0.015
			.1	340	310	325	315	58.9	.0147	
STANDARD: 100 ml U_3O_8			0.1	550	540	545	535			
			0.1	530	560					
STANDARD:										

BLANKS	10	10		

FINAL ASSAY REPORTED

#1234	0.015
CALC. BY:	ENT. BY:

DIL. BY: R.J. PIPETTED BY: Joe READ BY: J.J.
DATE ENTERED: Feb. 20/51   DATE READ: Feb. 21/51
REMARKS: _____   PLATE NO.: _____

Figure 10 - Fluorimeter laboratory assay sheet

The data required for a fluorimetric assay is as follows:

1. The average value for the fluorescence of the two aliquots.

2. The average reading for four standard beads each containing 100 mγ (10^{-7} gm) of U_3O_8.

3. The average reading for two blank beads.

Example of a Calculation (Figure 10)

Average reading in cm for 0.06 aliquot   -   195

minus blank   - $\dfrac{10}{185}$

Average reading in cm for 0.10 aliquot   -   325

minus blank   - $\dfrac{10}{315}$

Slope of calibration curve from standard readings:

Reading for 100 mγ U_3O_8, in cm   .   -   545

minus blank   - $\dfrac{10}{535}$ cm/100 mγ

mγ U_3O_8 in 0.06 aliquot   = $\dfrac{185}{5.35}$ =   34.6

mγ U_3O_8 in 0.10 aliquot   = $\dfrac{315}{5.35}$ =   58.9

As the dilution factor for the sample is 2 gm of solid dissolved in 500 ml of 5% HNO_3, %age U_3O_8 based on 0.06 aliquot is:

$$\frac{34.6 \text{ m}\gamma \text{ } U_3O_8}{0.06 \text{ aliquot}} \times \frac{500 \text{ dilution factor}}{2} \times \frac{100\%}{10^9 \text{m}\gamma/\text{gm}} = 0.0144\% \text{ } U_3O_8$$

Per cent U_3O_8 based on 0.10 aliquot:

$$\frac{58.9}{0.10} \times \frac{500}{2} \times \frac{100}{10^9} \qquad\qquad = 0.0147\% \text{ } U_3O_8$$

Average assay (rounded off to two figures) = 0.015% U_3O_8

If, in the above example, the original sample had been a liquid and 2 ml had been diluted to 500 ml the same equations as above would have been applicable except that the 100 (per cent) factor would be replaced by the factor 1000 (ml/liter) and the assay reported as .15 gm/l.

Since the above example showed agreement between the 0.06 and the 0.10 aliquots, it is therefore concluded that there is no quenching present, and that the above is a true assay. If, however, there is a spread greater than 10 per cent between the 0.06 and 0.10 aliquots in which the 0.10 aliquot gives the lower assay, quenchers are considered present based on the dilution theory. Before repeating the fluorimetric analysis, chemical separations are carried out on the samples by the mercury cathode, the cellulose column (6), or other suitable separation procedures.

MINIMUM EQUIPMENT NEEDED FOR THE PREPARATION OF A BEAD FOR FLUORIMETRIC ANALYSIS

1. A precision type balance (e.g. Christian Becker Chainomatic #16).

2. Beakers and reagents for taking solids into solution.

3. Pipettes, 0.5, 1.0, 2.0, 5.0 and 10.0 ml (e.g. Kimble #27000).

4. Volumetric flasks or graduated cylinders for making up dilution (e.g. Kimble #28015).

5. 150 ml Erlenmeyer flasks or small bottles for samples.

6. Graduated pipettes of 0.2 ml capacity for pipetting samples (e.g. Kimble #37020).

7. Platinum dishes (Figure 12). The platinum dishes in use at the Mines Branch are pressed in our own laboratory by means of a hand press from platinum blanks $\frac{3}{4}$" x .015".

8. Drying lamps (e.g. G.E. industrial type 100-watt, infra-red lamps).

9. Pelletizers for dispensing NaF pellets.

10. Suitable gas burner.

11. High-purity sodium fluoride.

TYPE OF FLUX USED

The flux used at the Mines Branch is sodium fluoride powder A.C.S. manufactured by Baker and Adamson. Various types of fluxes have been tried by other investigators combining different mixtures of NaF, Na_2CO_3 and K_2CO_3. Jacobs[3] has reported the successful use of a flux containing 5 per cent NaF mixed with 47.5 per cent Na_2CO_3 and K_2CO_3. However, it has been the experience of this laboratory, that the Baker and Adamson grade of NaF when used alone has given reliable results and low blanks. The amount of NaF used as mentioned before is 350 ± 20 mg per dish. It was found that increasing the amount of flux from 300 mg to 350 mg did not noticeably decrease the sensitivity of the fluorescence of the bead. However, it gave a flatter surface to the bead since NaF wets the platinum, and the curvature of the bead was decreased due to the greater platinum area covered. The galvanometer deflection for the average blank is 10 cm $\pm$ 3 cm.

QUENCHING OF FLUORESCENCE

The term quenching is used to indicate any process which will decrease the fluorescence output of a uranium-containing phosphor.

A quencher is any substance which effects this decrease of fluorescence.

The mechanism of quenching is not entirely understood, but many empirical relations have been established and Price, Ferretti and Schwartz[5] have considered it theoretically. The fact that the amount of quenching depends upon the ratio of quencher to flux rather than upon the ratio of quencher to U_3O_8 makes the dilution technique possible. The intensity of uranium fluorescence in NaF is such that very small amounts of the element may be used and still have a measurable light intensity. This allows large dilutions of a sample to be made with the consequent lowering of the quencher to flux ratio to a point where the quencher has no effect on the fluorescence. The dilution technique is used as a routine procedure at the Mines Branch and, with few exceptions, has proved entirely satisfactory.

Two types of quenching have been encountered in the work at the Mines Branch: quenching due to elements in the sample such as iron and manganese and quenching due to an oxidizing effect on the prepared beads.

Curves have been plotted to determine the quenching effect of varying amounts of iron and manganese in a constant amount of uranium (Figure 6). These show the amount of iron or manganese which can be tolerated in a 0.10 ml aliquot of the final dilution of a sample when 350 mg of flux are used. If data are available on the content of these two elements, a calculation will show whether a preliminary separation is necessary. If iron is present in detrimental amounts, a separation is made by passing the solution through the cellulose column which retains iron[6]. If the removal

of manganese is required, $KClO_3$ is added to a few milliliters of solution in an equal volume of concentrated HNO_3. Mn is precipitated as MnO_2 on boiling the solution. The solution is filtered and proper dilution is made.

If preliminary data are not available, the quickest method is a trial assay. Beads containing large amounts of iron will have a brownish colour, and manganese beads will be tinged green. If colours are not noticeable and quenchers are present, quenching will be evident in the larger aliquot.

Brown tinged beads which show marked quenching have been produced by fusion in oxidizing atmospheres. The reason for this effect is not known, but the effect due to this brown colour was eliminated by grouping the beads in the centre of the burner so as to provide a thick layer of burned gas between the beads and the air, and by cooling the beads by spraying them with steam (Figure 8).

Success in analysing samples which are small or so low in uranium concentration that a dilution procedure is not possible has been reported by Simpson[10] of Chalk River, using a spiking technique.

The spiking theory states that, if a known amount of uranium containing no quenchers is added to an unknown uranium sample containing quenchers, the known amount of uranium will be quenched by the same percentage as the unknown sample, and thus a correction can be effected.

A useful formula for correcting a quenched sample by the spiking technique is:

Milligammas of U_3O_8 = $\dfrac{A\ M\ C}{D - A}$

where

"A" is corrected galv. reading of unknown sample

"D" " " " " " spiked sample

"M" " " " " " spiker alone

"C" " calibration constant

CARE AND CLEANING OF EQUIPMENT

Pipettes of 0.20 ml Capacity

Since a large number of 0.20 ml pipettes are used each day, a quick and easy method for cleaning them is necessary.

As each pipette is used it is dropped into a glass cylinder containing enough distilled water to cover the pipette. The bottom of the cylinder contains a cellulose sponge to prevent breakage of the pipette tips. Periodically, these pipettes are collected and placed in an automatic syphon-type pipette-washer made from glass and rubber tubing (Figure 9). The pipettes are allowed to remain in the washer for approximately 10 minutes. Cold tap water fills and empties from the washer about three times per minute. After washing, the pipettes are shaken free of excess tap water, rinsed with distilled water, and finally acetone is poured over and through them. They are then stored for use.

Platinum Dishes

As soon as the platinum dishes containing the phosphor beads have been read they are placed in a beaker, and warm tap water allowed to run over them until all the fluoride has been dissolved or washed away. The dishes are then arranged symmetrically in a porcelain casserole so as to expose the inside area of the dish to concentrated HNO_3 which is poured over them in sufficient quantity to cover all the dishes completely. The nitric acid is then boiled for approximately 10 minutes. The acid is allowed to cool and is discarded. The dishes are rinsed with distilled water and boiled a second time in concentrated nitric acid. They are given a final rinse with distilled water and stored in distilled water for future use. This procedure usually assures dishes which give low blank readings. Difficulty was encountered in cleaning dishes by this method after fusing samples with high manganese content. As a further precaution, the dishes are treated in fused potassium bisulphate approximately every two weeks.

Under repeated usage, the platinum dishes lose their bright metallic lustre and acquire a frosted, etched appearance, generally accompanied by high blank readings. When dishes reach this condition they are buffed by means of a hand motor tool to which a rubber stopper has been attached in place of a regular tool head. A small amount of abrasive (#M305 ultra fine, manufactured by the American Optical Company) is placed in each dish and the dish polished until bright and lustrous. The polished dishes are treated in fused potassium bisulphate, boiled with nitric acid, and then stored in distilled water until required.

Glassware

All other glassware is cleaned immediately after use by washing in a solution of warm water and calgonite. It is rinsed thoroughly and allowed to drain dry. Just before use, glassware used in the dilution process is rinsed with distilled water, and glassware to contain prepared samples is rinsed three to four times with the solution it is to contain.

THE FLUORIMETER LABORATORY

The section of the fluorimeter laboratory which is used for pipetting, fusing, and reading of phosphors is designed to keep contamination at a minimum.

The section is divided into two parts (Figure 11). One part is reserved for the fluorimeter and is air-conditioned by a "carrier" unit, which maintains the room between 65 and 75° F and 45 to 55 per cent relative humidity. The other section is continually supplied with warm filtered air. Because of the sensitivity of the fluorimetric method it is imperative that the room used for preparation of phosphors be adequately protected against the infiltration of dust-bearing air, especially if the fluorimetric laboratory is situated near an ore dressing mill handling uranium-bearing ores.

THE FLUORESCENCE OF ELEMENTS OTHER THAN U IN NaF

The fluorescence of uranium in a flux of NaF is not entirely specific for uranium. Jacobs[3] has reported the anomalous fluorescence of several elements such as calcium, magnesium, tellurium,
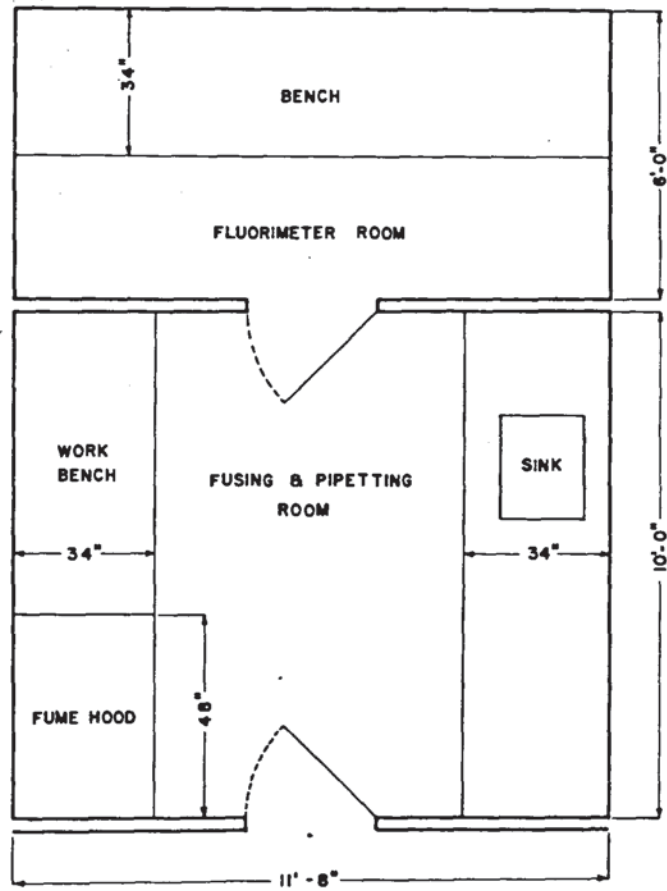
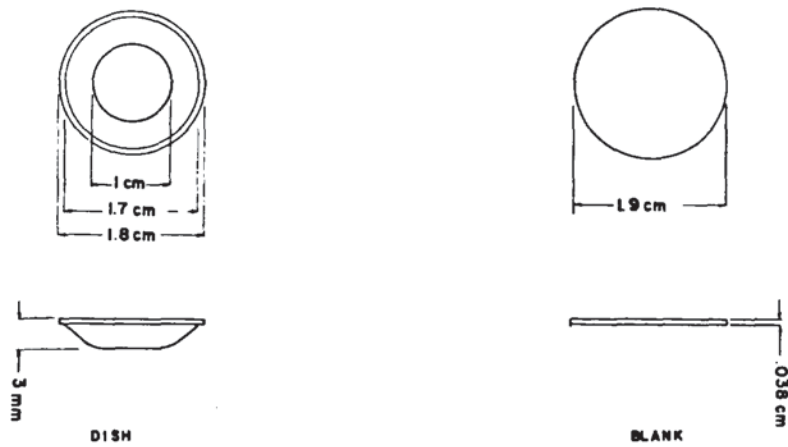Figure 11 - Fluorimeter assay laboratory

Figure 12 - Details of platinum dish for
fluoride bead

antimony, vanadium, beryllium, and molybdenum. However, under the
conditions used at the Mines Branch, and due to the relatively weak
fluorescence of the elements mentioned above compared to fluorescing
uranium in NaF, these do not seriously interfere with the assay
methods. Simpson[7] has established that the fluorescence of a
cerium salt was equivalent to 0.02 per cent of its weight of uranium
and the fluorescence of a cadmium salt was equivalent to 0.0005 per
cent of its weight of uranium.

The increase in fluorescence of prepared phosphors when
standing loosely covered has been reported by several investigators
and the phenomena has been attributed to moisture pick-up by the beads.
However, experiments at the Mines Branch indicate that beads may be
safely left for a period of up to an hour without any noticeable
increase in fluorescence. Beads left for 24 hours appear to reach a
point of maximum fluorescence. Re-fusion of these beads returns them
to their original lower fluorescence.

The same effect obtained by long standing can be obtained
in a much shorter time by placing the fused beads under the infra-red
drying lamps (Figures 13 and 14). These curves show the rise in
fluorescence of beads containing 30, 50 and 60 mγ of U_3O_8. These
beads were fused in the normal manner then left standing loosely
covered and re-read three hours later. A small increase in
fluorescence was noticed. They were heated under the infra red lamps
at a temperature of 145° C for 15 minutes and read again. A sharp
increase in fluorescence was recorded after heating. The same beads
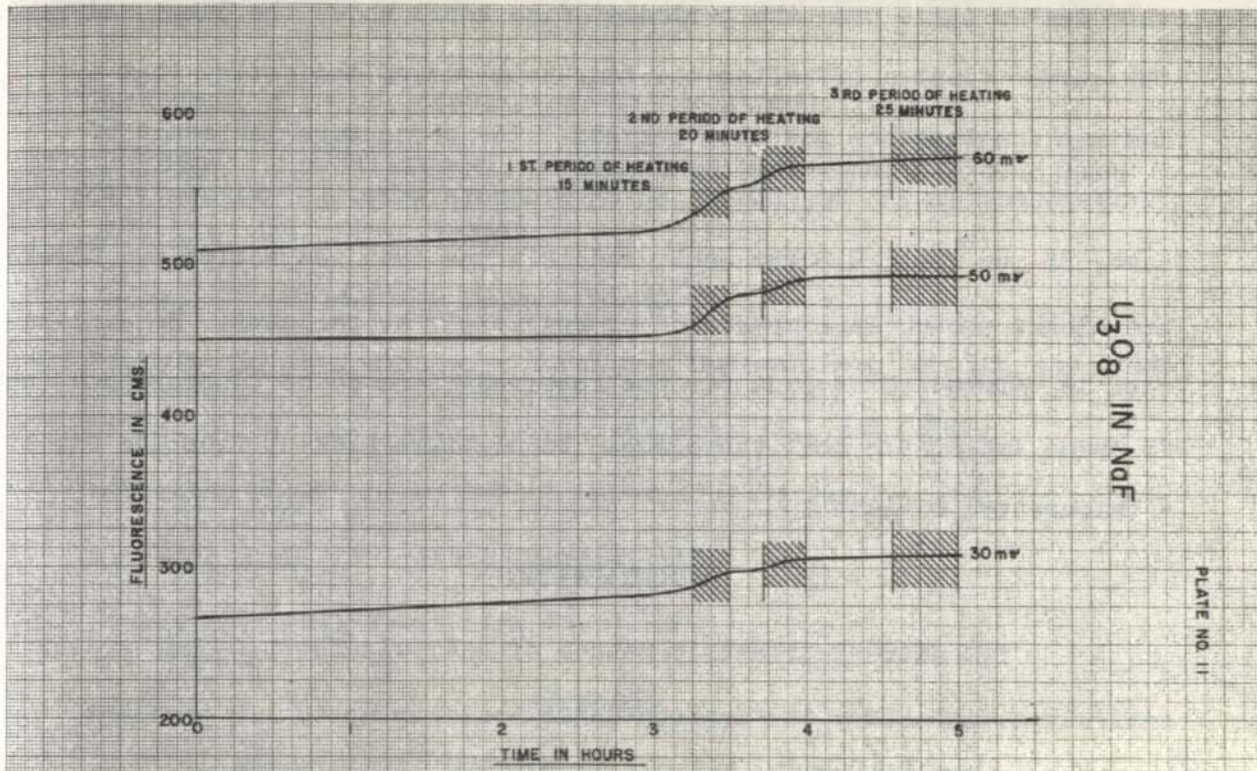
Figure 13 - Growth of fluorescence in
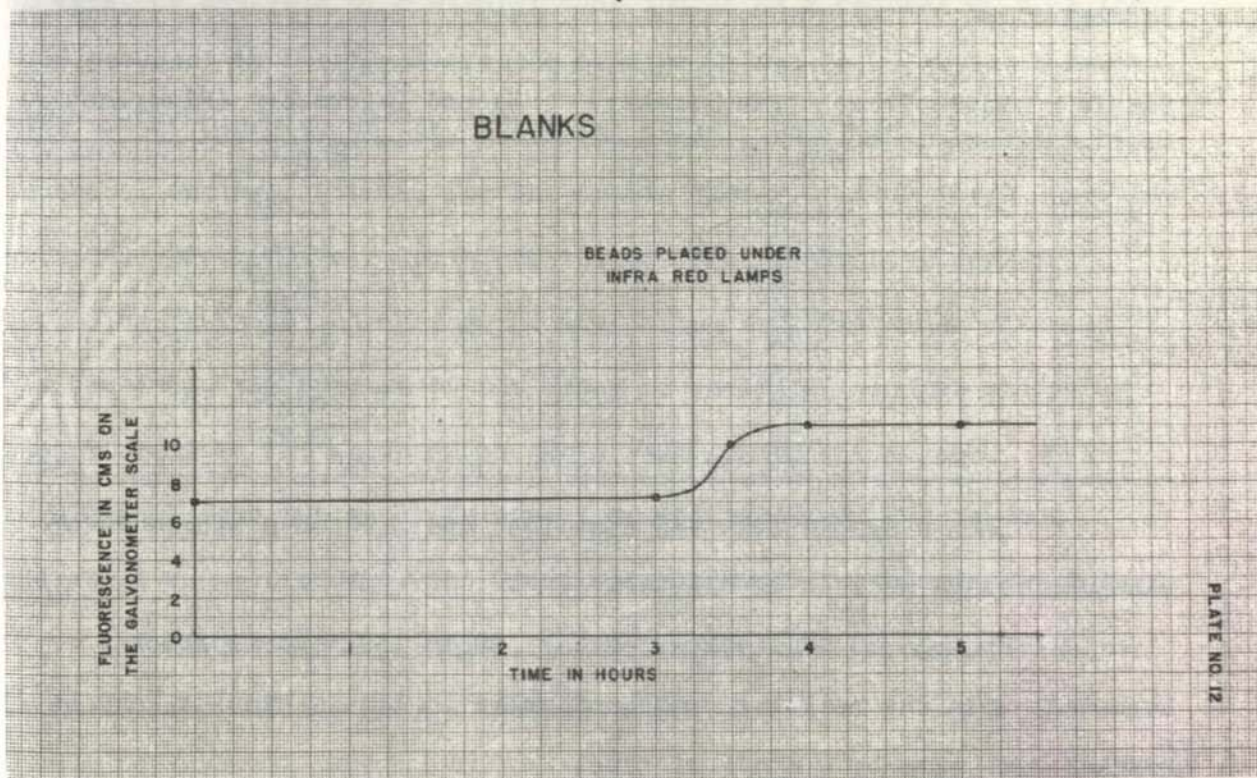phosphor beads after reheating

Figure 14 - Growth of fluorescence in
blank beads after reheating

were heated twice over the period of five hours under the lamps and read.
The curves flatten off after the four-hour period indicating that a
maximum fluorescence has been reached. The percentage increases of
fluorescence in the 30, 50 and 60 mγ aliquots were approximately the
same, 15 per cent, 9.8 per cent, and 12.2 per cent respectively. However,
the blanks showed an increase of approximately 36 per cent. No explana-
tion is offered to account for the observed increase of fluorescence, but
it seems improbable that there would be moisture pick-up from the air at
a temperature of 145° C.

CONCLUSIONS

The microfluorimetric method of analysis for U_3O_8 has proved
entirely satisfactory for uranium concentrations up to 1.0 per cent.

Check results can be obtained within close agreement. The
following table lists assays of identical samples from two independent
laboratories.

Sample	Mines Branch (Fluorimeter)	Second Laboratory (Fluorimeter)
	% U_3O_8	% U_3O_8
1	0.051	0.050
2	0.13	0.12
3	0.085	0.089
4	0.24	0.26
5	0.28	0.27
6	0.33	0.34
7	0.28	0.27
8	0.25	0.27

When a sample has been dissolved and diluted a single deter-
mination can be made in 15 minutes.

From 20 to 40 samples per day (80 to 160 determinations)
dependent upon the relative number of solid to liquid samples, may be
handled with ease by a staff of five.

The cost of the assay per sample is much lower compared to
other chemical methods.

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APPENDIX

Reporting of Uranium or Thorium Determinations

Under the Atomic Energy Regulations of Canada, the results of
an assay or analysis of a mineral that indicates a content of more than
0.05 per cent by weight of uranium or thorium are to be reported forth-
with to the Director of the Geological Survey, Department of Mines and
Technical Surveys, Ottawa, for the Atomic Energy Control Board, together
with full particulars relating to the material assayed or analysed,
including the name and address of the person from whom such material
was received, the purpose of the assay or analysis, and the origin of
the material so far as known to the person making the report. This
requirement does not apply to assays or analyses made for persons
operating under orders of the Board which provide for periodical reports.

Copies of the Regulations may be obtained on application to
the Secretary, Atomic Energy Control Board, Ottawa.