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CHEMISTRY

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THE PREPARATION OF FLUORIDE MELTS FOR USE IN THE FLUORIMETRIC METHOD OF URANIUM ANALYSIS

BY

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JULY 11, 1955

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Chemical Research Sub-Section

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THE PREPARATION OF FLUORIDE MELTS FOR USE IN THE FLUORIMETRIC METHOD OF URANIUM ANALYSIS

INTRODUCTION

The determination of uranium by the fluorimetric method depends upon the fact that certain uranium compounds, presumably with the uranyl structure, will fluoresce if illuminated with ultraviolet light. This phenomenon was first observed by Stokes(1) and Becquerel.(2) The intensification of this fluorescence by fusion with sodium fluoride was discovered by Nichols and Slattery.(3) Investigations by Price(4) and others indicate that ultraviolet in the region of 350 mμ is the most efficient in exciting the visible fluorescence which is peaked at about 560 mμ.

During the past 25 years, particularly with the advent of the atomic energy programs, a great deal of effort has been placed upon the development of instrumentation and techniques to improve the precision and accuracy of this method. The procedure consists of a fusion of the uranium sample in a flux, the determination of the resulting fluorescence intensity, and the conversion of this fluorescence intensity to uranium concentration. A brief consideration of these steps from the historical standpoint will be made. A more detailed survey of the literature is presented by Price(5) and Rodden.(6)

Fusion of the flux and uranium mixture has been accomplished by several means. Beads of fluoride flux on platinum wire fused in a Meker flame produced reasonably good results at higher concentrations of uranium, but the use of sodium fluoride flux contained in platinum dishes, and fused with burners or gas fired stoves as used in the procedure of Price(4) and others has probably been the most satisfactory method. Grimaldi(8) and co-workers as well as Adams(9) and Maeck, using a somewhat lower melting flux, were able to make the fusions with gold dishes in a low temperature muffle. Induction heaters and multiple gas burners are used widely at the present time.

Probably the greatest expenditure of effort has been placed upon development of fluorimeters for the determination of the fluorescence. The classical methods of detection, the eye or photographic plates, have been largely supplanted by electrical methods. Procedures employing these classical detectors were capable of good results at relatively high uranium concentrations, provided good standards for comparison were used.

As more stable power supplies and amplifiers became available, the use of phototubes, both multiplier and nonmultiplier types, permitted construction of more sensitive instruments. In most cases the instrument is so designed that the melt is illuminated on the same side as the fluorescence is read, although Grimaldi(8) and co-workers obtained good results with a transmission instrument wherein the ultraviolet illumination was made from one side, and the visible read from the other. In general, most instruments employ an optical system to increase the ratio of fluorescent to stray light at the photocathode. In addition, a filter system to remove the visible from the ultraviolet, and the wave lengths above 700 mμ from the visible, improves the sensitivity. The more recent commercial instruments have been simplified by removal of some of the optics, and by use of cold mercury lights to remove the necessity of cooling the multiplier tube.

Two general methods are used to convert the fluorescent reading to uranium concentration. One, as used by Price,(4) depends upon a calibration curve of a fluorimeter reading vs. uranium content. Where large quantities of foreign ions which reduce the fluorescence are present, a known amount of uranium (spike) is added and the calculation made on the basis of the spike recovery. The other method requires the addition of a spike to every sample to make the conversion from fluorescence to uranium concentration. This is done by reading the sample fluorescence, then adding the spike, re-fusing, and rereading the fluorescence. The uranium content is obtained by assuming that the fluorescence is a linear function of the uranium content.

A reduction in fluorescence, such as that caused by the presence of certain foreign elements, is called "quenching". The foreign element is called the "quenching agent". Many of the quenching correction problems can be avoided by use of large dilution factors. This results from the fact that the extent of quenching is dependent only upon the ratio of quenching agent to flux and is independent of uranium concentration. However, Jacobs(10) points out that certain ions such as calcium, antimony, tellurium, and magnesium, in very low concentrations may enhance the fluorescence, thus making extreme dilutions questionable. Where there is severe quenching that cannot be corrected by one means or another, chemical treatment may be used. Organic or chromatographic separations are usually employed to separate the uranium from the quenching elements.

The precision with which the uranium concentration can be calculated depends upon a number of factors. According to Price, (4) at low levels of uranium, the precision is limited by the extent of contamination from dishes, atmosphere, hands, etc. At high uranium concentration, the reproducibility of the optical properties is probably the limiting factor. Precisions have been reported as low as 2.8 per cent, (9) but, in general, most investigators report that the best results vary between 5 and 10 per cent, depending upon the amount of uranium present. Price(4) reports that near the detection limits, a standard error of 20 per cent requires considerable care. In general, the reports of the previous investigators do not agree on many points, nor has any study been sufficiently complete to clarify the many factors involved in the fluorescence method for uranium.

OBJECTIVE

The objectives of this study were:

1. The determination of the factors limiting the precision at various levels of uranium concentration.

2. To improve the precision and accuracy of the method, particularly at the lower levels.

3. To extend the practical detection limit, if possible.

4. To arrive at a better understanding of the phenomenon of quenching.

SUMMARY AND CONCLUSIONS

The fluorimetric method of uranium analysis was examined to determine the effect of such factors as fusion method, flux distribution, uranium distribution, dish characteristics and quenching agents on the precision obtained. Three methods of fusion, namely muffle, tube furnace, and burner, were examined in some detail and found capable of producing acceptable results. Adequate fusion control can be accomplished with the use of a muffle only if some means of annealing the melt is employed. Probably the simplest solution of the fusion problem is with the use of burners, through which the melts are continuously moved for fusion and annealing.

Fluorescent melts were prepared under various conditions, and the resulting discontinuities in flux, uranium, and quencher distributions demonstrated. The even distribution of flux, and uranium within the flux, are important factors to be controlled for maximum precision. Local high concentrations of uranium at various points in the flux result in loss of fluorescence from self-absorption, or in variable fluorescence if the field of view of the phototube is limited. Good mechanical shape and level mounting of the dish during fusion and cooling provide adequate control of the flux distribution.

The precision of the method is influenced very little by small variations in the quantity of flux in the melt, provided the quenching is nominal. The quality of the flux, in terms of magnitude of blank, exerts little influence on precision, even at low levels. This is true provided the blank, as determined for each dish, is used in the calculation of net fluorescence, rather than assuming a blank value from two or three "characteristic" dishes.

The use of modern, highly sensitive, fluorimeters permits the detection of uranium down to the 10^{-11} gram level. If the usual precautions are exercised in handling platinum with tongs, reducing atmospheric contamination, proper fusing control, and adequate cleaning of dishes, a precision of 20 per cent is easily attained at the 10^{-10} gram level. The optimum range was found to be from 1×10^{-9} to about 1×10^{-7} grams of uranium per dish. The precision was still acceptable near this lower limit and did not improve above the 10^{-7} level. In general, the melts of lower uranium concentration gave less trouble in dish clean-up. Furthermore, consistent working at the 10^{-9} gram level permitted greater dilutions to be made, thus avoiding quenching problems. In this optimum range, the precision was limited by reproducibility of the optical character of the melt. Good results in the 10^{-11} range are extremely difficult to achieve. In the opinion of the author, results are not limited by the flux blank, as commonly believed, but by factors as yet unknown. It was demonstrated that fusions could be repeated with a constancy equivalent to about 2×10^{-11} grams of uranium as computed from the average of 5 dishes.

The dilution technique appears to be the best method of treating the quenching problem. Since dilution may result in samples of extremely low uranium content, the lower range of the fluorimeter is important. Spike techniques, whether applied to separate dishes or a single dish from which the unknown fluorescence is determined, are subject to errors due to fusion variation or changes in optical properties with fusion time. The use of the ratio of black to bright dish readings, as a measure of optical property and hence quenching arising therefrom, is a somewhat more rapid technique but again requires an adequate fusion control. Further work with other quenching agents is required to determine the applicability of this correction method to all systems. Chromium was the only element, of the eleven studied, which did not follow the theoretical curve of black to bright ratio versus quenching factor. If the absence of chromium in the sample can be assured, this technique may prove to be completely valid.

EXPERIMENTAL

A. General Procedure

Certain choices of materials and possible procedures presented themselves in the use of the fluorimetric method of uranium analysis. The method consists of the following steps:

1. The addition of the uranium sample to a flux contained in a clean dish.
2. Fusion of the flux.
3. Quantitative determination of the resulting fluorescence.
4. Conversion of the fluorescent reading to uranium concentration.

Since many thousands of determinations are made by this method, it is desirable to employ a flux that is readily available, and usable as a reagent grade chemical requiring no further blending or treatment. The choice of pure sodium fluoride as the flux, over mixtures such as 10 per cent sodium carbonate - 90 per cent sodium fluoride, is certainly indicated from the standpoint of convenience and the elimination of uncertainties incidental to the blending of such mixtures. The low melting point of the mixed fluxes is an advantage only if high temperature fusion equipment is not available.

The choice of sodium fluoride as the flux limits the dish material to platinum, since gold dishes are usable only with the lower melting mixtures. Figure 1 indicates the general size and shape of two dishes in common use. The wide, shallow dish, fabricated from 20 mil platinum sheet, was used exclusively in this study. This dish was easier to clean, and produced melts of slightly higher sensitivity than the smaller dish.

The cleaning of dishes between samples is an important step because cross contamination, even in small amounts, seriously limits the sensitivity and precision obtainable. Several methods of cleaning the dishes were tried. In general, the most satisfactory method proved to be a fusion cleaning similar to the one suggested by Price.(4) Acid baths such as sulfuric, phosphoric, nitric, citric, oxalic, hydrochloric and various combinations of these are used extensively by various laboratories. The blanks obtained with dishes cleaned in acid were generally somewhat higher and more erratic than those obtained with dishes cleaned in a 30-minute sodium fluoride fusion. What is more important, the blanks obtained from fusion-cleaned dishes showed less change upon refusion than acid-cleaned dishes. This is an important characteristic since any increase in fluorescence between fusions must be assumed to be a result of sample addition. If instead, uranium diffuses from fissure, cracks, or other imperfections in the platinum, an error will result.

For extremely low level work the best results were obtained by fusing the entire dish for 30 minutes in a 10 per cent sodium carbonate--90 per cent sodium fluoride bath. After fusion, the flux was dissolved with 2 M sulfuric acid, followed by a final 10-minute clean-up in boiling 2:1 hydrochloric-hydrofluoric acid. A pure sodium carbonate bath produced equally clean dishes and required a lower temperature muffle; however, the platinum showed some signs of attack. Tables I and II are tabulations of characteristic blank values obtained by these two methods of cleaning. The values were obtained by fusing a sodium fluoride pellet twice in the dish, taking a fluorescence reading after each fusion.

TABLE I

STABILITY OF BLANKS - ACID CLEANED DISHES

	Deflection (Cm)		
Sample No.	First Fusion	Second Fusion	Diff.
1a	5.2	6.5	1.3
2a	7.6	8.0	0.4
3a	5.2	7.8	2.6
4a	7.2	8.2	1.0
5a	12	13	1.0
		Av.	1.2

TABLE II

STABILITY OF BLANKS - FUSION CLEANED DISHES

	Deflection (Cm)		
Sample No.	First Fusion	Second Fusion	Diff.
1f	6.7	7.0	.3
2f	6.6	6.6	0
3f	7.5	6.7	.8
4f	6.7	6.8	.1
5f	8.0	9.2	1.2
		Av.	.48

The average rise between fusions in Table I amounts to the equivalent of approximately 5 x 10^{-11} grams of uranium while that for Table II is equivalent to approximately 2 x 10^{-11} grams. The absolute value of the reading (deflection) is of only secondary importance.

In the preparation of the fluoride pellet for the sample fusion, a petri-dish was used as a shallow container for the sodium fluoride which was to be used in the melts. The pelleter, a 5 ml syringe cut off at the end, was filled by pressing it into the sodium fluoride powder until the plunger was raised to a given mark. With care in the use of the pelleter, pellets of 0.3 to 0.6 grams, ± 10 per cent, could be delivered to the platinum dishes. The effect of this flux weight variation on fluorescence will be included in a later discussion of the quenching phenomena.

The choice of two general methods of sample addition and fusion presented themselves. The first, as used by Price(4) and others, requires the preparation of duplicate dishes each of flux only (blank), of sample, and of standard. From the dishes containing the known uranium, a calibration curve is constructed which is used in the determination of the unknown sample. If quenching is suspected, duplicates are also prepared containing the unknown plus a known "spike". A single fusion is thus performed on each dish.

The alternative procedure involves three fusions of each dish. A blank fluorescence is obtained from the first fusion. The unknown is then added to this fused pellet, the pellet refused, and the fluorescence determined. Following this, a known uranium spike is added and a third fusion performed. The final fluorescence obtained consists of the blank plus the unknown plus the spike. The uranium calculation is then made according to the following relation:

$$U\ (\text{sample}) = \frac{F_2 - F_1}{F_3 - F_2}\ U\ (\text{spike})$$

where

U (sample) = grams of uranium in unknown sample aliquot
F_1 = fluorescence after 1st fusion
F_2 = fluorescence after 2nd fusion
F_3 = fluorescence after 3rd fusion
U (spike) = grams of uranium added in spike

The latter method was chosen for use in this study because it provided more certainty in the blank, largely eliminating errors due to variations between dishes and pellets, thus appearing to offer greater accuracy at the lower limit of detection. Furthermore, this method is somewhat more convenient in routine laboratory practice.

The first method requires fusion control to the extent that all melts from a given fusion are identical. In addition, all the dishes must have the same reflectivity. The second method requires the same measure of control on three separate fusions. Further, the second method assumes the optical density of the melt to be constant when actually the optical density increases slightly with fusion time.

B. Instrumention

The fluorimeter used was of the conventional reflection type employing an H-4 mercury arc light source, collimating lens in both the ultraviolet and visible paths, 1P21 photomultiplier, and galvanometer with Aryton shunt. The instrument employed filtering in the ultraviolet path to remove the visible spectra and a filter combination in the visible path to isolate a region peaked at 560 mμ.

Initially two important shortcomings of this instrument existed. First, the 1P21 phototube has a cathode surface which is narrower than the projected image of the dish, which results in the instrument seeing only a band across the dish. Thus, if major irregularities in the distribution of the melt or uranium exist, different readings will be obtained depending upon the rotational position of the dish. Second, the galvanometer and shunt load are of such low impedance that the phototube fatigues at high levels of illumination. This fatigue requires constant, careful resetting of the voltage to obtain reproducible readings.

In order to overcome these difficulties, a Beckman Model V amplifier and an RCA 5819 phototube were substituted. This amplifier effectively overcame the objection of a low impedance load and the 5819 permitted viewing the entire dish because of the larger cathode surface of that tube. Some improvement was realized as indicated by the values shown in Table III. This improvement was ascribed to the better viewing of the dish, since great care was taken to keep the proper voltage setting on the 1P21 when it was used.

TABLE III

EFFECT OF VIEWING AREA ON PRECISION

		Standard Deviation (%)	
U (g)	N	1P21	5819
2×10^{-9}	18	14	11
4×10^{-7}	24	6.2	4.3

In general, dish rotation produced less change in fluorescence with the 5819 than with the 1P21. Very little fatigue, even at the highest levels (5×10^{-6} g), was evident when the high impedance Beckman was used.

A number of determinations were made using the Jarrell Ash Model JA-2600 fluorimeter. The precisions obtained were not significantly better than obtained with the same dishes read on the galvanometer-type instrument. The Model JA-2600, which was designed with twin illumination sources and high impedance load for the 935 phototube, does have better fatigue characteristics and is less sensitive to dish rotation. However, the lower detection limit is somewhat limited by a rather high stray light level.

No attempt was made to make design changes in the existing equipment other than those mentioned above, because there was ample evidence that the limiting factor in the precision of the method was to be found in the melt preparation.

C. Fusion

Four methods of fusion were examined in some detail with respect to their effect upon melt properties. Muffle, tube furnace, and burner methods are compared to the induction heater since the latter is commonly used, particularly on highly radioactive samples.

1. Muffle Fusion

A muffle fusion would appear to offer advantages in atmosphere and temperature control which might be expected to improve the precision of the fluorimetric method. Accordingly, a Hevi-Duty Model GO-5-PT high temperature muffle was selected, since provisions are made for atmosphere control in this model. Further, the globar heating elements provide sufficiently high temperatures without working near their design limit, a disadvantage of nichrome would muffles.

The platinum dishes containing the flux were supported on platinum trays and covered with platinum crucibles. The covers prevented any possibility of cross-contamination between dishes, or contamination from the muffle liner. Trays were withdrawn from the muffle 1 to 3 minutes after the flux had completely fused. After a 5-minute cooling period, the fluorescence of the melt was read.

The melts prepared in this way were very similar in appearance to those obtained using the induction heater. The fluoride completely wet the platinum, the surface was irregular, being fractured into a large assortment of crystal fragments. The melt could not be removed from the dish without prolonged soaking or boiling in acid, and even then the last traces were difficult to remove. A very slight brownish cast was visible but, in general, the melts were whiter than obtained with the induction heater. Figure 2 illustrates a characteristic melt produced by this method. In spite of the nearly identical treatment received by all dishes, considerable variation in color, surface and fluorescence was apparent. Variable stains, as shown in Figure 3, were found on the platinum. The average fluorescence was the same as obtained from the induction heater melts.

Since the surface and crystal properties depend upon the cooling cycle, a measure of control was applied to this cycle. In place of the platinum trays, a fire brick one inch thick was substituted. Holes were drilled into the brick so that the dishes would set flush with the surface. The platinum covers were again used, and allowed to remain in place six minutes after the brick was withdrawn from the muffle. The heat capacity of the brick, in addition to the platinum cover which reduced the radiation loss, permitted a slower cooling of the melt. Figure 4 illustrates the characteristic appearance of the melt obtained. Much less fracturing of the surface was evident, the dish bottom was plainly visible because the melts were more transparent, and no melt discoloration was apparent. The fluorescence was approximately 25 per cent higher than that obtained from the induction fusions, and the precision was improved. However, the flux adhered strongly to the platinum, again requiring prolonged soaking or boiling for removal.

To further check the variation in level of fluorescence with cooling rate, three groups of dishes were run as follows:

a. The dishes were fused and cooled slowly on the brick described above.

b. The same dishes were fused a second time on the platinum tray and cooled rapidly.

c. The dishes were fused a third time and again cooled slowly.

The mean value of the fluorescence obtained after each fusion is tablulated in Table IV.

TABLE IV

EFFECT OF COOLING RATE ON FLUORESCENCE

Group	Number	Average Deflection (cm)			Decrease from 1st to 2nd (%)	Recovery from 1st to 3rd (%)
		1st	2nd	3rd		
G-1	6	767	566	696	26	91
G-2	5	630	472	560	33	89
G-3	5	552	332	534	40	96

The fact that the final fluorescence was not as high as the initial was not surprising in view of the additional fusion time the melt had sustained. However, even with the quenching, which may have resulted from the prolonged fusion, this final fluorescence is consistently greater than was obtained with rapid cooling. It was further observed that the brownish cast of the melt, apparent after the second fusion, was absent after the third. Therefore, the addition of an annealing or slow cooling step appeared to offer the advantage of higher sensitivity and better reproducibility of physical properties.

A number of qualitative experiments were made with various atmospheres in the muffle. The physical appearance of the melts prepared with helium, carbon dioxide, water, water plus carbon dioxide, and water plus helium did not show a significant difference from those prepared in an ordinary air atmosphere. Carbon dioxide was of particular interest since Price(5) observed that such an atmosphere would completely quench the fluorescence. Melts were prepared with filter paper discs added to the dishes, and the fusion carried out with carbon dioxide continuously fed to the muffle. The dishes were kept covered for 10 minutes after withdrawing them from the muffle. That the atmosphere was free of oxygen was indicated by the presence of free carbon in the melt after cooling; however, the fluorescence was normal.

2. Tube Furnace Fusion

In order to obtain a more uniform rate of heating and cooling, a tube furnace as illustrated in Figure 5 was constructed. The 2" x 8" alundum core was uniformly wound with platinum wire, resulting in a rather steep temperature gradient toward the center of the tube. A platinum, platinum-iridium thermocouple placed at the maximum temperature position was used as a control element to maintain the desired temperature. A Celectray proportional controller maintained this temperature at 1100° C ± 20°. Two ceramic rods, 1/4" x 36", were supported at the ends to provide a track along which the platinum tray could be pulled. Dishes containing the flux were placed on the tray and moved through the fusion and cooling zones at a rate dependent upon the motor and gears selected. The rate of travel was adjusted to various values to provide one to three minutes in the fused state.

The melts obtained with this apparatus were nearly identical to those obtained with the muffle. No significant improvement could be obtained by variation in the fusion time. It is possible than an even slower rate of cooling would have been helpful, since the surfaces were somewhat poorer than those obtained in the slow-cooled muffle melts.

Qualitative experiments with the same atmospheres as tried with the muffle produced similar negative results. However, the use of a burner mounted at one end of the tube produced marked changes. The burner was mounted in such a way that the flame was directed down the axis of the tube. The air was reduced to the point where the gases at the far end of the tube were slightly smoky. The platinum heater continued to function as the controlled source of heat for fusion. Melts obtained from this arrangement were white, of smooth surface, fine crystal structure and readily fell from the platinum dish. The average fluorescence was nearly double that obtained from induction heater fusions. Variation in fusion time did not significantly affect the precision, provided the fusion was complete in every case.

While the equipment served to provide good control of fusion temperature, fusion time, and cooling rate, it was difficult to maintain. The nichrome wire used to pull the platinum tray was subject to considerable breakage and the ceramic rods were badly attacked by the fluoride. In addition, local overheating of the winding caused considerable vaporization of platinum.

3. Burner Fusion

The use of either the muffle or tube furnace as described above is somewhat objectionable from the standpoint of heating element maintenance. Further, it has been shown that control of the cooling rate and the use of a gas burner atmosphere are desirable features, both of which are difficult with this equipment. Since fusion of the melts with a burner offers a measure of control of atmosphere and maximum temperature, this technique was examined.

The equipment, shown in Figure 6, provided a means of supporting and moving the dishes through fusion and annealing flames at a constant rate. The carriage mounted on an angle iron track was moved at a rate depending upon the motor and gear combination chosen. The four-inch pulley, to which the pull cord was attached, was rotated at such a rate as to provide a fusion time of one to three minutes. The platinum dish supporting rods were spaced on 3/4" centers, and were readily removable for cleaning.

The first burner, the fusion burner, was a gas-air type. The air was adjusted to fuse a pellet in one minute with the dish centered over the flame. The second burner, the annealing flame, was adjusted with just sufficient air to prevent smoking. Both burners were so placed that the dishes passed over the center of the flame. During the fusion process, small gas bubbles formed on the dish bottom. Unless the fused melt left the gas atmosphere in passing from the fusion to the annealing flame, these bubbles would not disengage from the melt. By carefully spacing the burners, the melts could be moved from flame to flame in the fused state, thus allowing these bubbles to escape.

The melts produced with this apparatus were very similar to those obtained with the tube furnace-burner combination described above. Somewhat less uniform distribution of the flux was apparent, but the general appearance was the same. Fluorescence, release properties, and crystal structure appeared identical.

Table V summarizes the precision obtained at various levels using the four methods of fusion.

TABLE V

PER CENT STANDARD DEVIATION OBTAINED WITH VARIOUS FUSION METHODS

U (g)	Fusing Method							
	Burner		Tube Furnace		Muffle		Induction Heater	
	N	σ	N	σ	N	σ	N	σ
5×10^{-11}	6	43						
5×10^{-10}	6	11	12	37				
2×10^{-9}			24	13	54	12	12	21
5×10^{-9}	6	6						
5×10^{-8}	6	6						
1×10^{-7}	6	3						
5×10^{-7}	12	4.0			24	4	12	12
2×10^{-6}	6	3.5						

D. Factors Affecting the Fluorescence

It is possible to prepare a series of known standard melts and, by plotting the fluorescence of each melt against its uranium content, arrive at a calibration curve for the particular procedure. This plot has been shown(4) to be linear over a several thousandfold range. As long as the unknowns are of the same composition as the standards and the procedure unvarying, good results can be obtained with the use of this calibration curve. However, in actual practice large errors in calculated uranium concentrations may result from the use of this curve. Among the possible causes of this error are:

1. The sample may contain ions which tend to discolor the melt.
2. The sample may contain salts which change the crystal structure of the melt.
3. The dish may vary in reflectivity due to stains, etching or mechanical warping.

4. The crystal structure and surface properties of the melt may be changed by variations in cooling rate or fusion techniques.
5. The melts may vary in amounts of sodium fluoride present.
6. The flux or uranium may not be uniformly distributed.

The net result of the factors listed above is usually to reduce the fluorescence to some level below that expected from the standard melt, hence the concept of "quenching".

Quenching is usually expressed in terms of the ratio of the fluorescence actually obtained, to that which would have been obtained from the same quantity of uranium fused in a standard or reference melt.

$$\phi = \frac{\text{Fluorescence obtained}}{\text{Standard fluorescence}}$$

For the sake of convenience, all the factors listed above will be considered from their quenching aspects. It is quite apparent that ϕ will be unity if the fluorescence of the melt in question is identical to the standard; less than unity if the fluorescence is reduced by light absorption, for example, as in item 1; or possibly greater than unity if the melt is particularly fluorescent for one reason or another, as in item 3.

In general, the fluorescence will be decreased if relatively large quantities of iron, platinum, thorium, chromium, or many other salts are present in the melt. It has already been shown, Table IV, that the fluorescence could also be changed by variations in the cooling rate of the fused melt. A reduction was also accomplished with the use of badly stained or etched dishes, and the staining varied according to the ions present and the fusion method. Table VI indicates the magnitude of variation obtained between dishes due to this variation in reflectivity. The results shown were obtained by transferring each of a group of six melts from the fusion dish to a second clean, bright dish and then to a dish coated with Aquadag to reduce reflectivity. Fluorescence readings were taken in each dish.

TABLE VI

EFFECT OF REFLECTIVITY OF DISH ON FLUORESCENT READING

	Deflection (cm)		
Dish No.	Fusion Dish	Bright Pt.	Aquadag Coated Dish
1	1800	2300	1400
2	2700	3500	2200
3	2200	2900	1800
4	1600	2000	1300
5	1900	2600	1600
6	2000	2600	1600

Considering the two platinum dishes only, it is obvious that the value of ϕ would vary, depending upon which value was used as the "fluorescence obtained" in the expression for ϕ. This variation in dish reflectivity is a serious problem, particularly in control laboratories where several hundred dishes are in regular use. The variation of flux weight was expected to cause some variation in fluorescence, the extent of this variation depending upon the transparency of the melt. It was found that for standard melts, the effect of flux weight variation was negligible. Doubling the size of the pellet in the case of muffle fusion reduced the fluorescence 17 per cent, while in the case of burner fusion, the reduction in fluorescence was less than the 95 per cent confidence level error. Undoubtedly, this effect would be greater with highly quenched melts, and for this reason some attempt to control the flux weight should be made.

The quality of flux, in terms of presence of quenching ions, was about the same for six different lots examined. In no case did the spectrographic analysis show the presence of a quenching element in concentration to produce significant quenching ratios.

Enhancement of fluorescence in high carbonate flux due to the presence of small amounts of such ions as antimony, calcium and magnesium has been reported by Jacobs;(10) however, this has not been demonstrated in pure sodium fluoride flux. Probably the most likely causes of enhancement are changes in optical properties due to fusion variables or increased reflection from a particularly bright dish as described above.

The conversion of fluorescent reading to uranium concentration may also be affected by the distribution of the uranium within the melt. It is this lack of even distribution which causes some melts to produce particularly erratic readings as the dish is rotated in the fluorimeter. The net effect will be to cause ϕ to be greater or less than unity depending upon whether the uranium is near the center or near the edges of the dish. These variations in uranium distribution were observed visually by using the apparatus illustrated in Figure 16 to examine and photograph the fluorescence of the melts. The filter under the ultraviolet source serves to reduce the visible portion of the spectrum, while the filter between the eyepiece and dish cuts off wave lengths above 700 $m\mu$.

Figure 7 is a photograph showing the flux evenly distributed over the dishes, whereas it is evident in the photograph of the fluorescence of these same samples, Figure 8, that the uranium is not evenly distributed throughout the flux. These melts were prepared by deliberately placing the 5 microgram uranium sample near the outside of the dish containing the flux. The best distribution of uranium within the flux was achieved by delivering small (5λ) aliquots to the center of the fused pellet, and allowing the melt to remain at least 3 minutes in the fused state. Very short fusions resulted in poor distribution of the uranium.

A group of six dishes in very poor mechanical shape is shown in Figure 9. (The rough edges are a result of intense local overheating in the induction heater.) It can be seen from Figure 10 that the uneven distribution of flux evident in Figure 9 has resulted in variable fluorescence across the face of the dish. In particular, the high centers of the dishes have caused almost no flux to remain there, with consequent loss of fluorescence at these points. Figures 11 and 12 illustrate a somewhat more ideal distribution of flux and resulting fluorescence.

The fluorescence across the dish can also be caused to vary by uneven distribution of quenching agents. Figure 13 is a top and bottom view of melts containing 2000 micrograms of iron fused over a burner. Uneven distribution of quenching agent is evident.

The lack of even distribution of uranium, and resulting fluorescence, can arise from bubble formation in the melt as previously mentioned. Figure 14 is a top and bottom view of melts showing this characteristic bubble formation as a result of improperly adjusted burners. Figure 15 is a top and bottom view of melts properly fused.

The fluorescent reading obtained from a melt, and consequently the value of ϕ, could be varied markedly by excessive temperature variation. Fortunately, nominal changes in room temperature do not change the fluorescence. However, increasing the temperature to approximately 200° C completely quenched the fluorescence. Visual observation of this phenomena indicated that the first signs of weak fluorescence as a melt was cooled were reddish-brown, then yellow and finally the characteristic yellow-green. In view of this phenomena, a cooling period after fusion is certainly necessary.

"Blank rise" with standing, as noted by Price(4) and others, is, of course, a factor at low uranium level, but can be avoided by prompt reading of the melts.

E. An Alternative Method for Converting Fluorescent Reading to Uranium Content

Two common methods were previously mentioned as possibilities for the conversion of fluorescent reading to uranium concentration: first, the use of separate dishes for blank, unknown, and known; or second, the use of a single dish fused three times with blank, unknown, and known in that order. It has been shown in the previous section that: 1) considerable variation exists between reflectivity of dishes; 2) the distribution of melt, uranium quenchers, and optical discontinuities is not always uniform; 3) the fluorescence will vary with fusion control. It is therefore apparent that the assumptions required of the correction methods are only approximately met.

In general, the variation of fluorescence from the standard value results purely from differences in the optical properties of the melts or dishes. It would appear then, that an alternative approach to this problem would be to determine the optical character of each melt and compare this quality to the standard state.

The measurement of melt transmission at any given wave length did not appear adequate, since absorption in either the ultra-violet or visible would result in decreased fluorescence. It was felt that the measurement of the fluorescence obtained from a melt read in a "bright" dish compared to that obtained in a "black" dish would adequately define the optical properties of the system. A ratio, ρ was defined as:

$$\rho = \frac{\text{Black dish reading}}{\text{Bright dish reading}}$$

This ratio should have a limiting value near 0.5 for a transparent melt since all the light traveling away from the phototube would be reflected back at the bright surface. A limiting value will also be reached as the melt becomes progressively more opaque. Since no light reaches the bottom at this limit, the reflectivity of this surface is of no consequence and the ratio approaches unity.

Burner fusion had to be used to prepare the melts for this type of reading, since they were the only melts which could be readily removed intact from the fusion dish. A well-formed clean platinum dish was chosen as the standard "bright" dish, and another, coated with Aquadag, for the "black" dish. The melts were slid from the fusion dish to the bright dish for the first reading, and then to the black for a second reading. The melts transferred readily if the burners were properly adjusted, and if the melts were not removed from the flame while in the fused state. The use of this technique overcame two major difficulties. First, variations due to the dishes' reflectivity were obviated since all melts were removed and read in the same bright and black dishes. Second, the uncertainties involved in the fusion with the spike were avoided, particularly the increase of opacity with fusion time.

Two possible means of using this ratio were examined. The first employed a plot of ρ vs. ϕ where ρ was determined by means of actually spiking the calibration standards with various amounts of quencher. The second employed a ρ vs. ϕ curve constructed on the two limiting points. In the latter case the value of ρ was established for a nonquenching melt, and the assumption made that this ratio would increase to unity for complete quenching, thus establishing the second point. In order to correct for quenching in a particular sample, ρ is determined and from the plot the proper value of ϕ obtained. The standard fluorescence can then be obtained from the relation

$$\text{Standard Fluorescence} = \frac{\text{Fluorescence obtained}}{\phi}$$

The uranium content of the unknown melt can then be obtained from the linear relation between fluorescence and uranium content of the standard unquenched melt. Table VII is a tabulation of results obtained for one fusion condition. Figure 17 shows the average curve (solid line), as well as the theoretical curve (dotted line).

TABLE VII

VALUES OF ρ AND ϕ FOR 0.4 γ URANIUM FUSION

			ϕ		
g x 10^6	Quencher	ρ	Experimental	Theoretical Plot	Average Plot
None		0.65	1	1	1.03
500	Potassium Dichromate	0.70	0.002	0.86	0.88
2500	HNO_3	0.76	0.67	0.69	0.69
15,000	HNO_3	0.81	0.59	0.54	0.54
2000	Thorium	0.85	0.41	0.43	0.42
2000	Manganese	0.90	0.20	0.27	0.28
2200	Iron	0.93	0.15	0.18	0.20

The point obtained with dichromate quencher is completely off the plot obtained from the other six points. The melts were reasonably transparent as indicated by the value of ρ so the decreased fluorescence must have resulted from a phenomena other than optical absorption.

A number of melts were prepared using variable quantities of cobalt, magnesium, nickel, silver, molybdenum and tungsten to produce quenching in the range of 15 to 75 per cent. Good agreement with the ρ vs. ϕ curve was obtained for each of these quenching agents.

From this limited study it seems that chromium is a rare exception as a quenching agent. In the cases of the eleven elements studied, the quenching occurs simply through the mechanism of optical absorption within the melt. Judging from the color of chromium bearing melts, they must exhibit this absorption but the major cause of loss of fluorescence is due to some other mechanism. The nature of this mechanism is not known, and no data were obtained in this study which offer an explanation.

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CEM:ms

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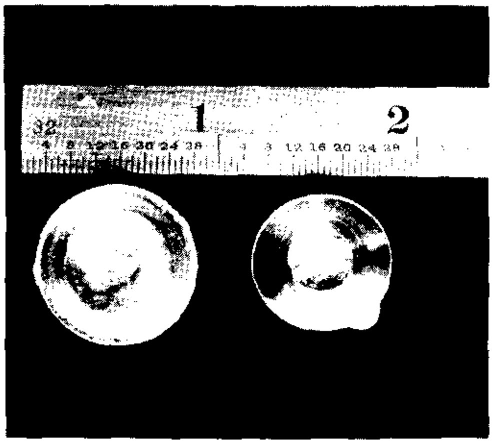

FIGURE 1
PLATINUM FUSION DISHES

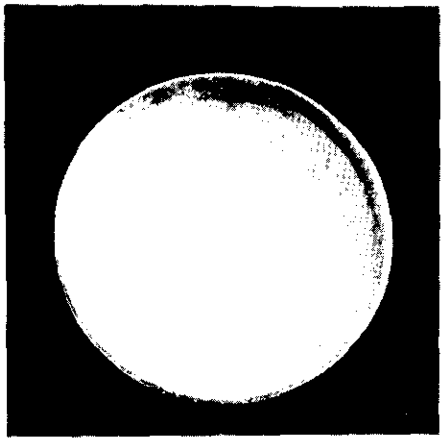

FIGURE 2
NORMALLY COOLED
MUFFLE FUSED MELT

FIGURE 3
STAINED FUSION DISH

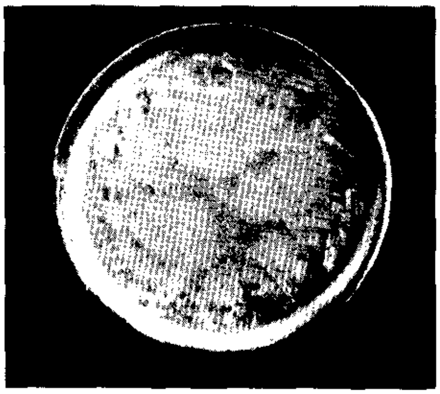

FIGURE 4
SLOWLY COOLED MUFFLE FUSED
MELT

AEC-GE RICHLAND, WASH.

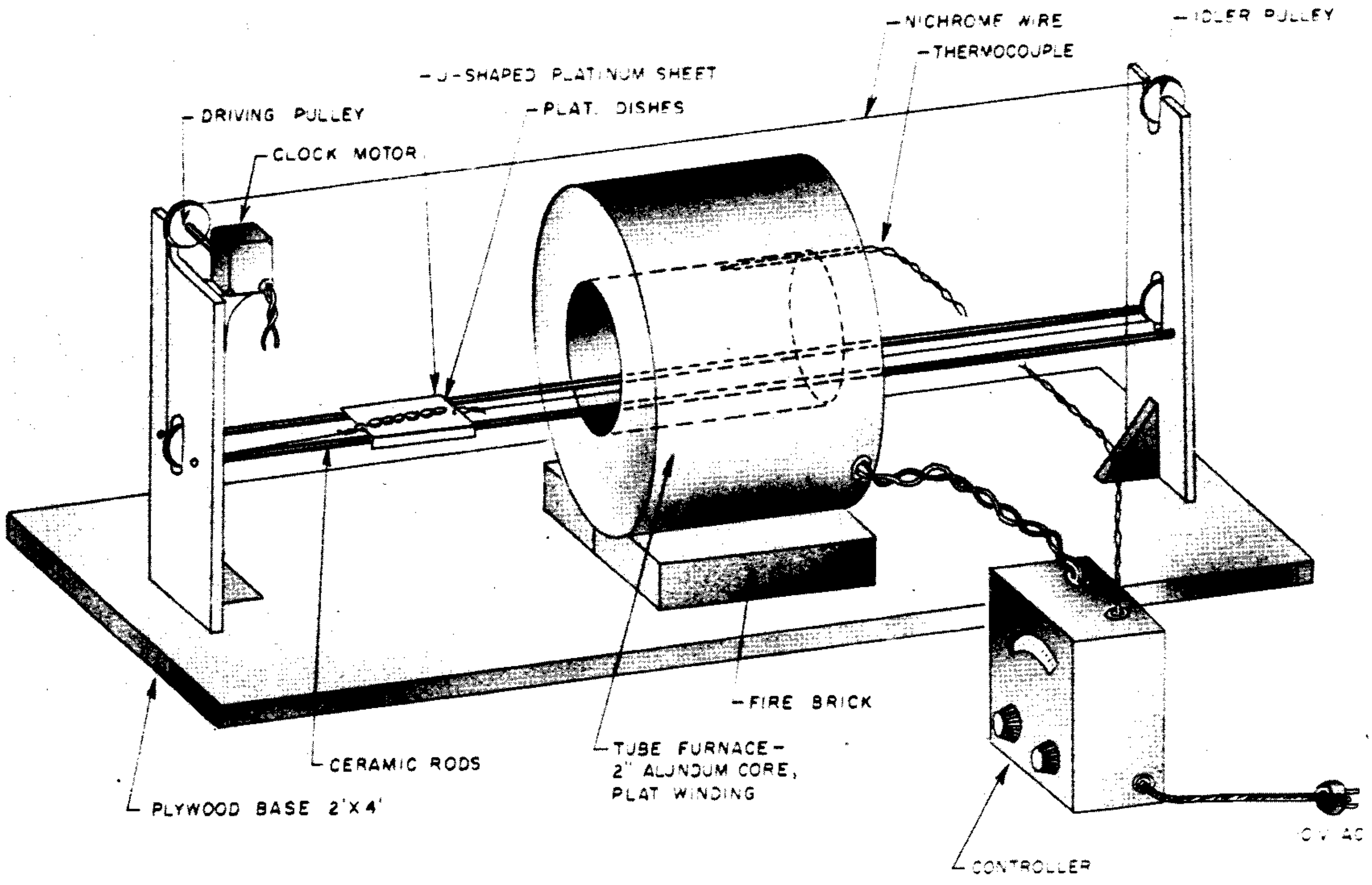

FIGURE 5

TUBE FURNACE FUSION APPARATUS

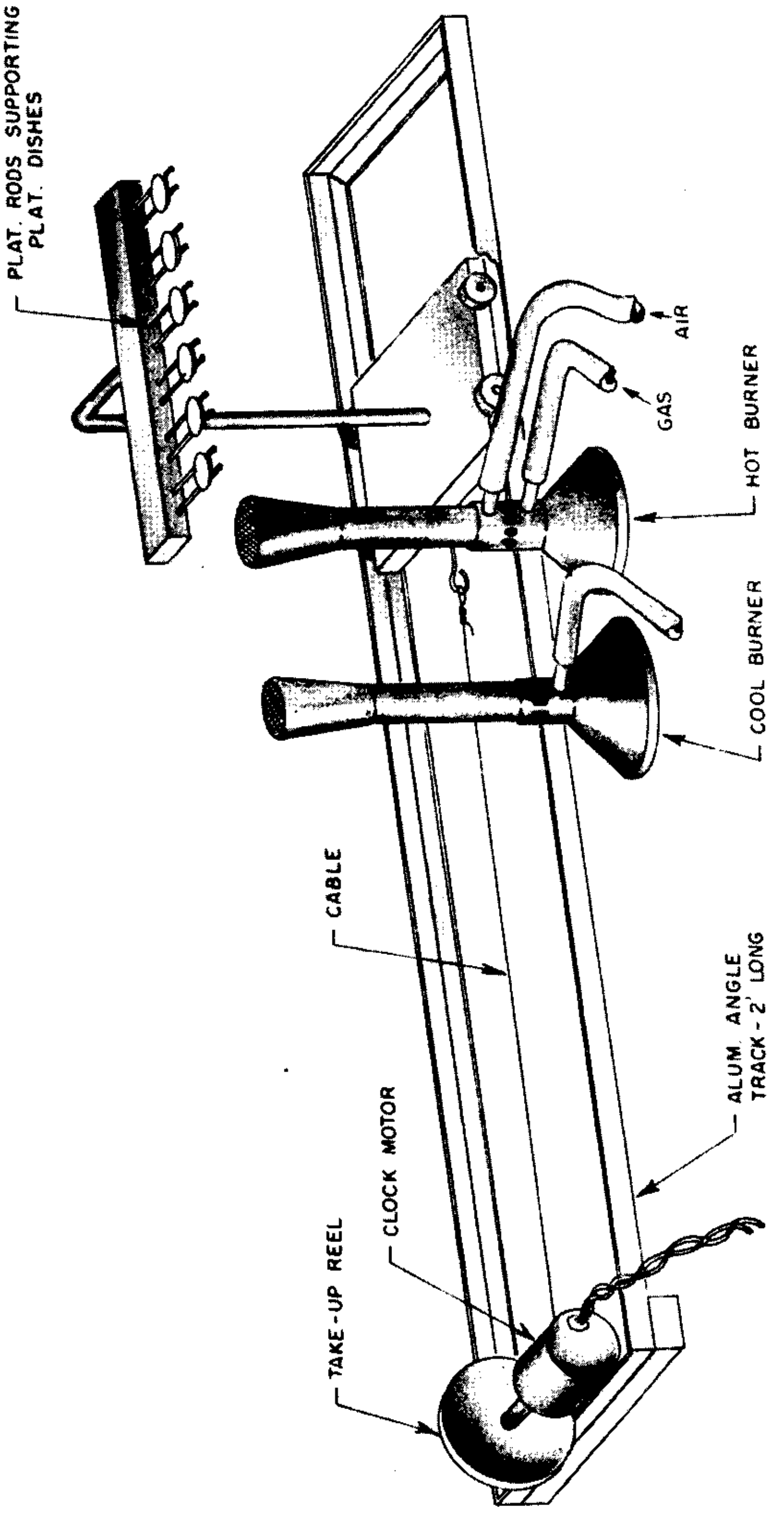

FIGURE 6

BURNER FUSION APPARATUS

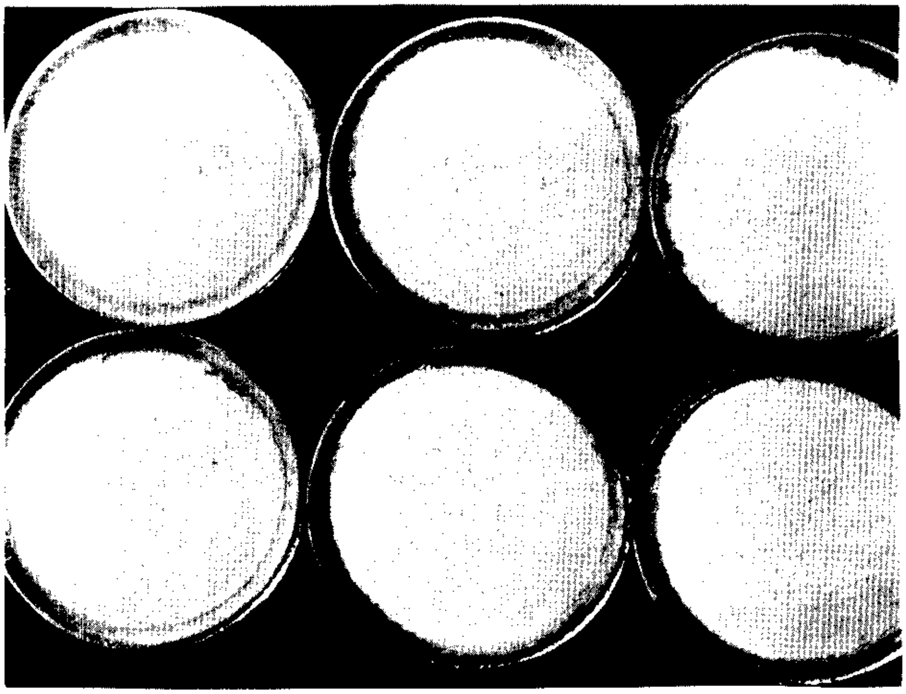

FIGURE 7

MUFFLE FUSED MELTS (Na_2CO_3) SHOWING EVEN DISTRIBUTION OF FLUX

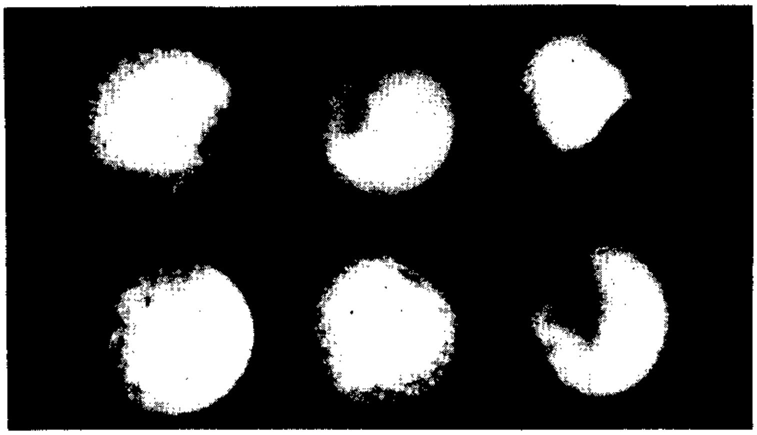

FIGURE 8

FLUORESCENCE OF MELTS (FIGURE 7) SHOWING UNEVEN URANIUM DISTRIBUTION

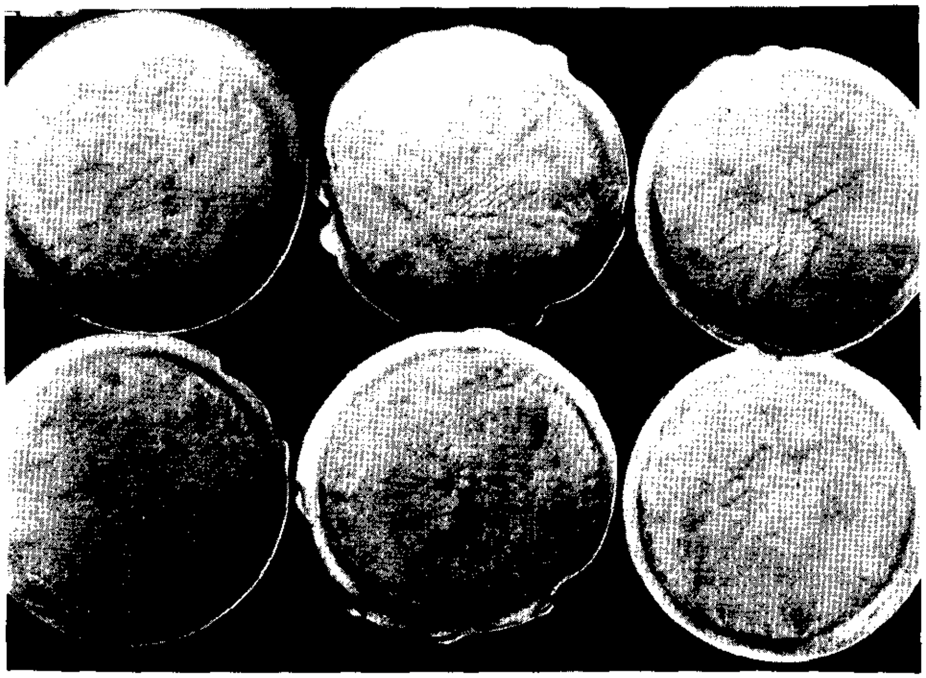

FIGURE 9
MUFFLE FUSED MELTS (NaF)

FIGURE 10
FLUORESCENCE OF MELTS SHOWN IN FIGURE 9

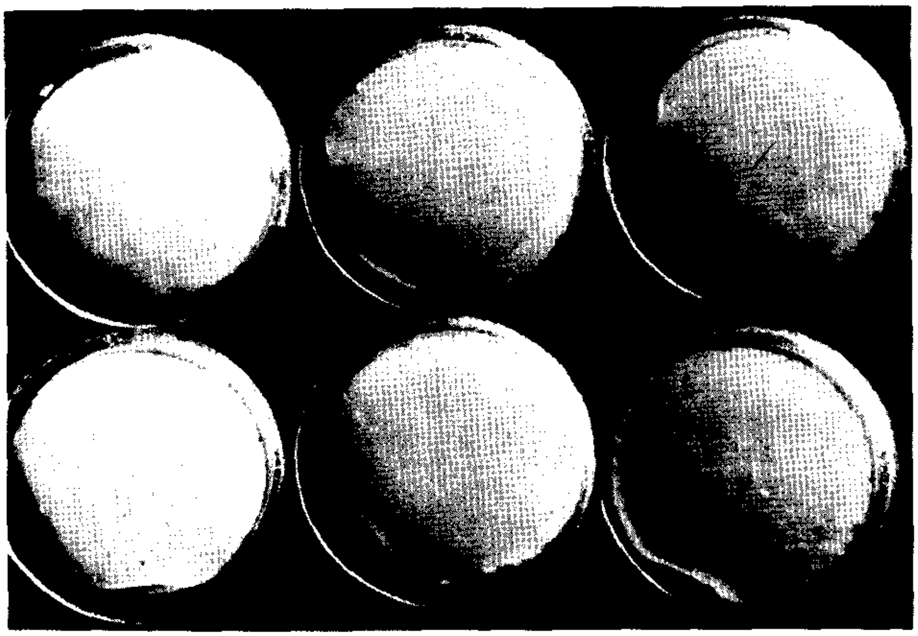

FIGURE 11
BURNER FUSED MELTS

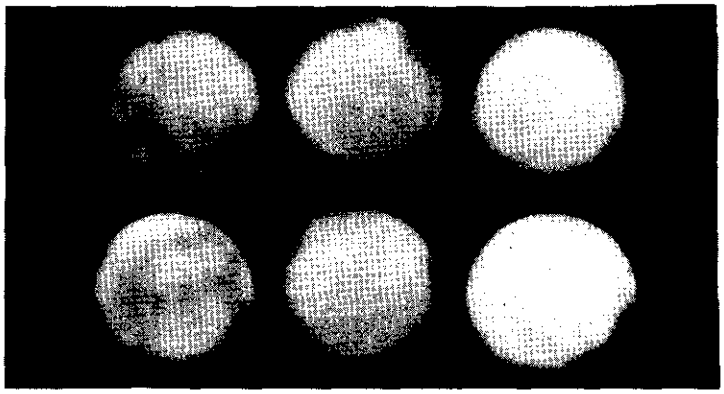

FIGURE 12
FLUORESCENCE OF MELTS SHOWN IN FIGURE 11

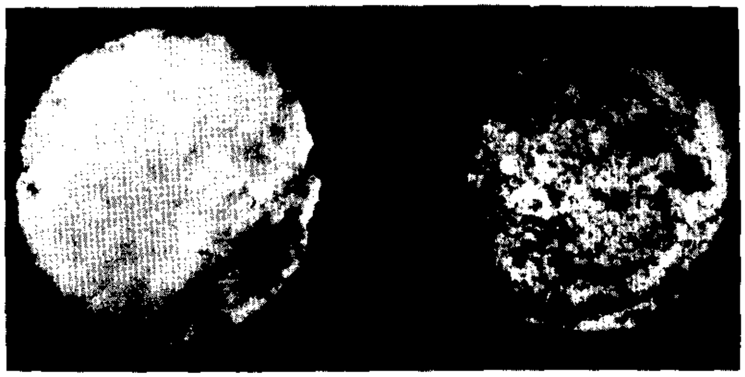

FIGURE 13

TOP AND BOTTOM OF BURNER FUSED MELTS CONTAINING IRON

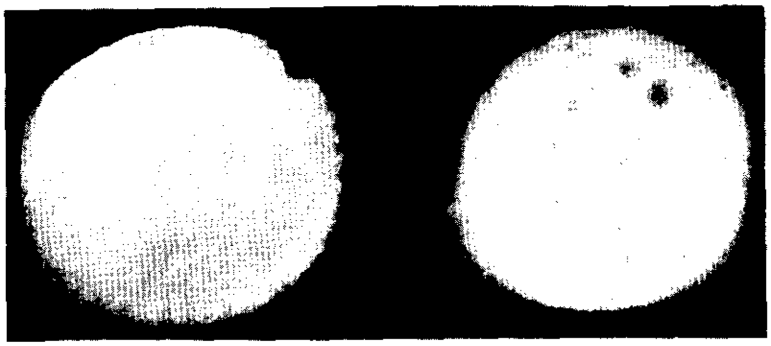

FIGURE 14

BUBBLE FORMATION IN BURNER FUSED MELTS (TOP AND BOTTOM)

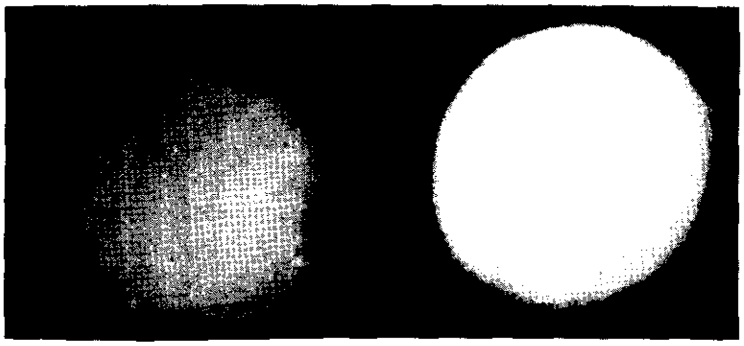

FIGURE 15

GOOD QUALITY BURNER FUSED MELTS(TOP AND BOTTOM VIEW)

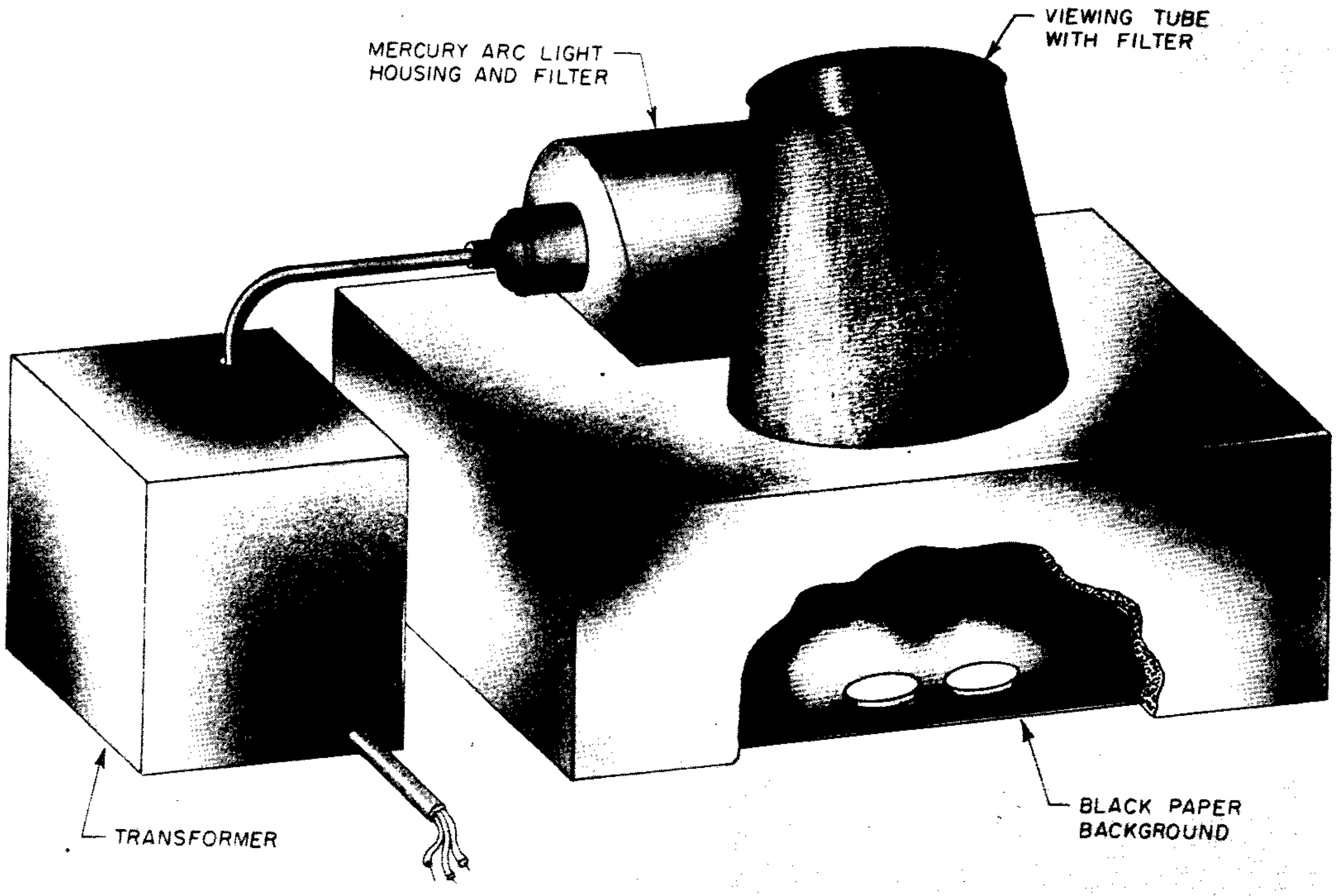

FIGURE 16

APPARATUS FOR VISUAL OBSERVATION AND PHOTOGRAPHY OF FLUORESCENT MELTS

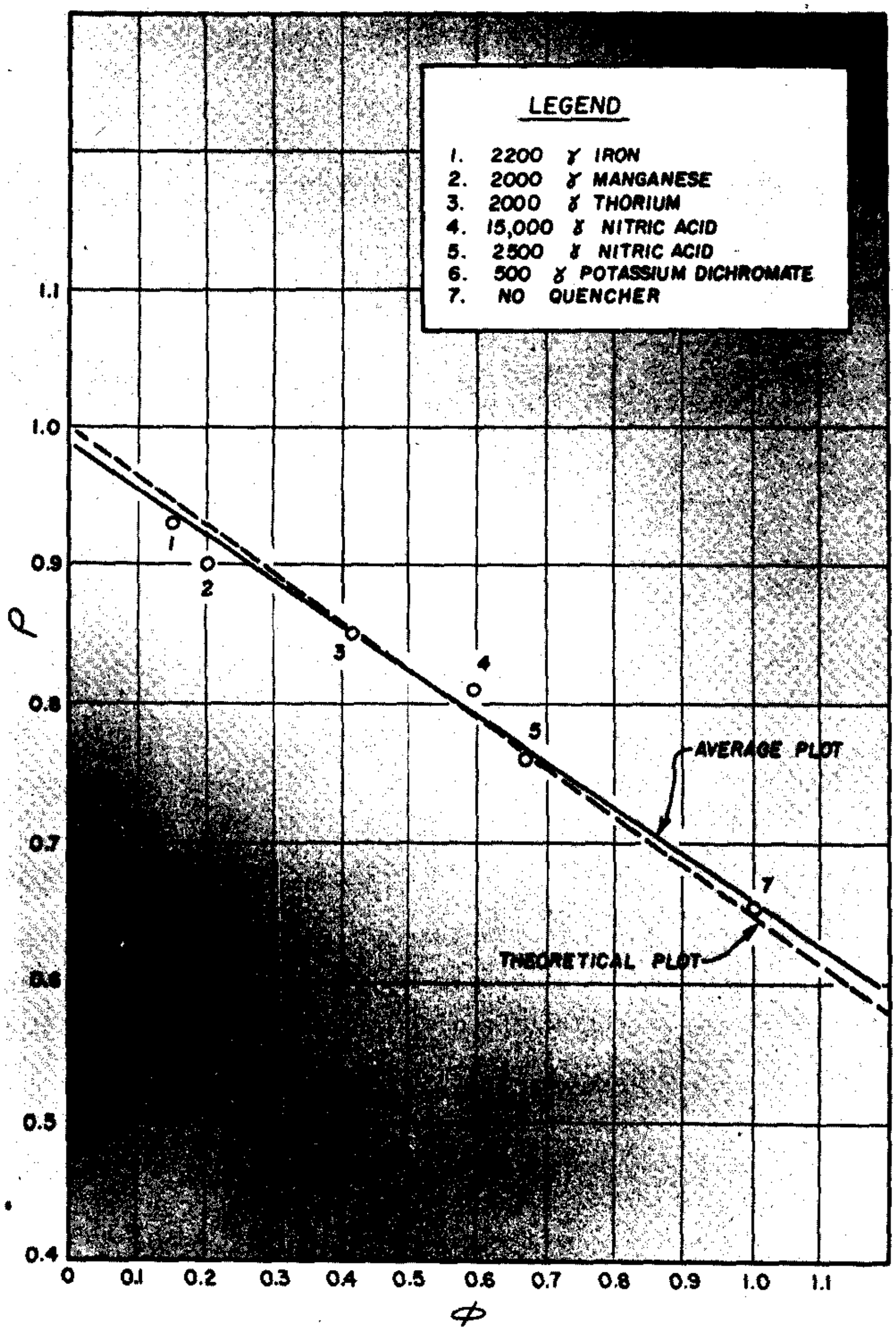

FIGURE 17

ρ VS. ϕ AT 0.4 γ URANIUM PER DISH

ABSTRACT

It was demonstrated that the precision of results obtained with the fluorimetric method of uranium analysis is generally limited by the melt preparation rather than by instrumental variables. Among the factors in this melt preparation are fusion method, dish characteristics, contamination, sample variation, and flux and uranium distribution. The extent to which they affect the precision depends upon the control that can be applied to the factors as well as the uranium level involved. In the ideal range of the method, 10^{-9} to 10^{-7} grams per dish, a precision of 5 per cent can be readily attained; however, in the range of 5×10^{-11} grams per dish a precision of 40 per cent requires great care. The classical method of avoiding the quenching problem by means of dilution appears to be the best solution to the problem; however, chemical separation or spike techniques may be required in certain cases. An alternative method of correction, based upon optical measurements, was studied. The fluorescence is read with the melt in a nonreflecting (black) dish and in a highly reflecting (bright) dish and this ratio used to determine the extent of quenching. The method shows promise of being a rapid and valid technique; however, further work is required to demonstrate its applicability with various quenchers.