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CHEMISTRY-GENERAL
ANL-4002

30852

THE FLUOROPHOTOMETRIC DETERMINATION OF URANIUM

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LASSIFICATION CANCELLED
DA February 1, 1950
FOR THE ATOMIC ENERGY COMMISSION
Charles A. Keller
CHIEF, DECLASSIFICATION BRANCH

April, 1947

HEALTH DIVISION

Report Received: July 17, 1947
Figures Received: September 12, 1947
Issued: September 25, 1947

Operated by the University of Chicago

under

Contract W-31-109-eng-38

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Acknowledgements

The work that we describe in this report has been made possible only by the generous cooperation of a very large number of people from all parts of the Laboratory. In addition to help received from the scientists, we are indebted for special favors to the Machine Shop, the Procurement Department, and to many other groups at Chicago. In particular, we wish to express our appreciation to Drs. Fred, Tompkins, and Watters of the Chemistry Division for assistance and advice in numerous analytical problems; to Mr. Sacher, Dr. Hoylande D. Young, and Professor T. F. Young for aid in the preparation of this report; and to Miss Greenberg, Miss Neylon, and Mrs. Possee for typing and other secretarial assistance.

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1. Introduction

The brilliant yellow-green fluorescence of uranyl salts provides a means for uranium determination which offers advantages possessed by few other analytical methods for any element. Not only is the fluorescence method for uranium extremely sensitive, but also, when properly carried out, it is so free from interferences that chemical purification of samples is almost never required even when other heavy metals are present in many hundredfold excess. Unfortunately, the analyst who consults the literature for advice on procedure finds that there is considerable uncertainty about what the proper or best technique is, and many recommendations directly contradict each other. The reason for this confusion is that the fluorescence method is less accurate than most quantitative methods with which the analyst is familiar, and consequently erroneous conclusions may be drawn if one does not employ a strictly statistical approach to the design and interpretation of experiments. [redacted] Because many of our conclusions disagree with those obtained by other workers, we have criticized in detail a number of experiments reported from elsewhere.

1.1 Outline of the Analytical Procedure. To orient the reader for the detailed discussions that follow, this section gives a brief description of the general analytical procedure and of the range of the method.

From an unknown solution an aliquot of 0.005 to 0.1 ml is pipetted into a shallow platinum dish about 1.5 cm in diameter, and evaporated

[redacted]

to dryness under a heat lamp. If a large residue of readily volatilizable or decomposable material remains, the sample in the dish is heated in a flame; only rarely is any other type of purification employed. To the dry residue in the dish, approximately 0.3 g of sodium fluoride or sodium fluoride-sodium carbonate mixture is added (see Fig. 9, Sec. 4.6), and the salt is fused by holding the dish in the flame of a Meker burner or by mounting it on a gas stove (see Fig. 10, Sec. 4.7). After cooling, the disc of fused salt, either still in the platinum dish or "tapped out" from the dish, is irradiated with light from the 365 mμ mercury line, and the yellow-green fluorescence is measured by a photoelectric fluorophotometer. From the reading obtained for the fluorescence of the sample, the average value for the fluorescence of blanks is subtracted, and the difference is multiplied by a previously determined calibration factor (see Fig.3, Sec. 3.1) to give the amount of uranium in the sample. If there is reason, because of the presence of color in the fused flux or from knowledge of the composition of the solution being analyzed, to suspect interference with the fluorescence, one can to a considerable degree remove this <u>quenching</u> by dilution by employing a smaller aliquot, or can correct for it by "spiking" by adding a known amount of uranium to an identical aliquot in another dish.

Instructions for building a suitable photoelectric fluorophotometer will be given elsewhere*. The "Model IV" instrument**, which was employed for the major portion of the work described in this report, is shown in Figure 1.

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*A report is scheduled for publication in the fall of 1947

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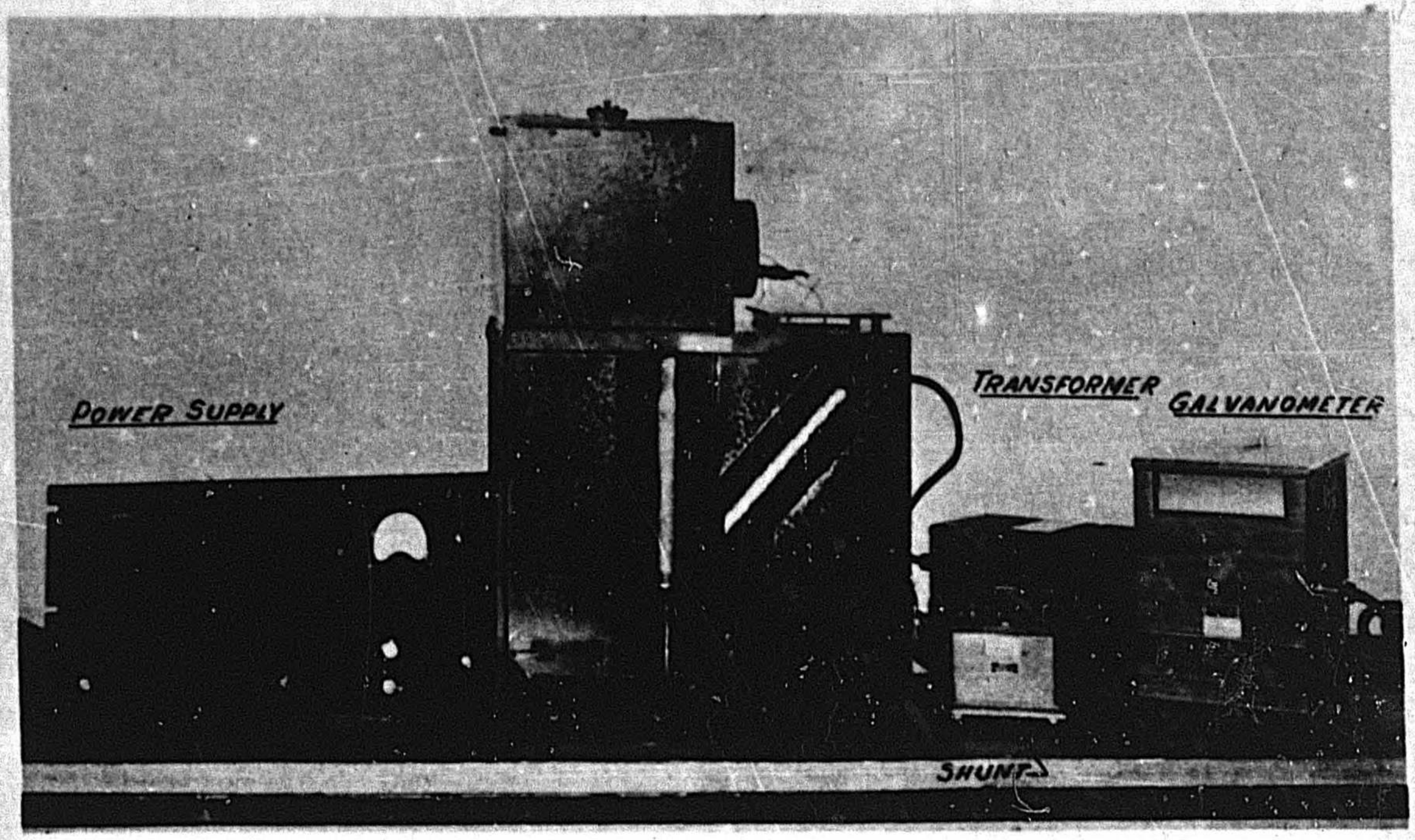

FIG. I. THE MODEL IV FLUOROPHOTOMETER.

In the base of the central unit in the photograph is a large horizontal wheel in which eight dishes and a fluorescent glass standard can be mounted simultaneously. The dishes are irradiated one at a time with 365 mμ light from a mercury arc lamp. The fluorescent light from the sample is filtered to remove reflected ultraviolet and red light from the arc, collected by large and fast lenses, and focused on an aperture. Beyond the aperture is a ground glass screen, and beyond this is an electron multiplier phototube. The tube is powered by high voltage direct current from a regulated supply, and its output goes without further amplification through an Ayrton shunt and into the galvanometer. The gain of the multiplier is adjusted by varying the output voltage of the power supply. To reduce the dark current, the phototube is cooled by a dry ice-toluene bath in the top of the unit. The minimal performance required of the fluorophotometer in connection with the recommended procedure includes linear response to fluorescent light from uranium in amounts from 10^{-10} to 10^{-6} grams; accuracy in the measurement of relative light intensity to within 2% at all levels down to 10^{-9} grams; and blank readings from stray fluorescence, filter leakage, and dark current not greater than readings from 10^{-10} grams of uranium. The performance of the Model IV Fluorophotometer greatly exceeds these requirements.

The useful range of the method is for a sample size of from about 10 to 0.0001 μg of uranium, work below 0.001 μg requiring great care in avoiding contamination. Usually analyses are run in duplicate; for routine work the standard error of the mean of the pair is generally below 10% except when the sensitivity is near its limit or when unusually large amounts of interfering substances are present, and by employing certain refinements in technique it is frequently possible to reduce the standard error to less than 5%. No element besides uranium has been shown to produce detectable fluorescence under the conditions recommended in this paper. A number of elements interfere by causing quenching of the fluorescence, but no element has yet been found to be noticeable in amounts much below 1 μg, and milligram amounts of many substances can be tolerated. This means that 1 part of uranium in 100 parts of the worst quencher known can be determined with a standard error of less than 15% by analyzing in duplicate without making a chemical separation and without "spiking"; while if "spiking" is employed, using only four dishes one can analyze with a standard error of about 20% when the ratio of strong quencher to uranium is 10,000 to 1. This means that, besides being useful for microanalysis, the fluorescence method is of value in performing macro analyses quickly and simply without chemical separation, in cases where high accuracy is not required.

The time required for analysis varies widely, depending in large part upon whether or not extreme sensitivity is desired. In favorable cases, where routine analyses are run on similar solutions with moderate uranium content and little quencher, a single experienced analyst in a properly equipped laboratory can analyze in duplicate 40 solutions per day.

1.2 Terminology and Conventions. Since there is little general agreement on terminology for fluorescence analysis, some of the terms used in this paper are defined here. The terminology employed has been designed for convenience in describing the experimental procedures; in some cases the definitions chosen may not be the most common ones.

Luminescence is employed here only in the sense of photoluminescence, the emission of light by an atom, ion, or molecule that has been excited by absorbing light itself or by interacting with some other particle that has absorbed light energy. Fluorescence is photoluminescence where emission of light immediately follows absorption; phosphorescence is photoluminescence where emission occurs (or may occur) an appreciable length of time after absorption. In cases where the duration of the decay is not important, "fluorescence" may be employed as including phosphorescence.

A phosphor is a fluorescent or phosphorescent solid solution. In describing phosphors, the following type of form can be used: "NaF-U" means sodium fluoride containing in solution a uranium compound that "activates" it. The flux is the fusion material or solvent salt with or without an activator present. The dish is the container in which the flux is fused, and frequently the contents of the container as well. The disc is the disc-shaped piece of flux obtained by fusion in a dish and then "tapped out" from the dish.

Quenching is any process occurring within a luminescent substance that interferes with its luminescence; a quencher is a chemical substance causing quenching. ϕ is a number that measures freedom from quenching. It is defined as the ratio of the luminescence found in a particular case to the luminescence given by the same amount of uranium in some arbitrarily chosen standard condition in which quenching is comparatively low. It can be called the "relative efficiency of fluorescence" or the "coefficient of absence of quenching". Q is the percent quenching. It is defined as $100(1-\phi)$.

"Spiking" is the analytical procedure of adding to an aliquot of an unknown sample, a known amount of the constituent being determined, for the purpose of measuring the recovery.

Frequently "uranium ions" are spoken of as existing in the phosphor, though it is believed that the uranium is present in the uranyl form. Another convention that has been employed concerns the description of the concentrations of known uranium solutions. Our stock uranium solutions have had concentrations that are multiples of 1.054 or 1.026 g/l, so that amounts pipetted contain 1.05 or 1.03 μg, for example. Such samples, however, are customarily treated in the analyses and spoken of as 1 μg, or 10^{-4} μg, and so on--though when reports of analyses are made, the results are multiplied by a correction factor. In this report, in all descriptions of our work except in the calibration curve (Fig. 3) and the discussions of it, these corrections have not been applied. The justification of this is that the 3 or 5% error in concentration causes no sudden qualitative change in properties, and the various experiments remain self-consistent.

A second matter requiring explanation concerns the interpretation of fluorophotometer readings. These are given as millimeter deflections on a galvanometer, multiplied by the shunt ratio of an Ayrton shunt. It has been mentioned that the gain of the multiplier phototube can be varied by changing the supplied voltage; in different experiments for various reasons the photometer has been operated at widely different sensitivity levels. As an aid to the correlation of different experiments, the relative sensitivity is stated in connection with most of the sets of data given. Since 1 μg of uranium in a dish is a standard, frequently used amount, relative sensitivity is expressed as the reading that 1 μg of uranium fused in sodium fluoride by a Meker burner would be expected to give under the sensitivity in use. Since the response of the fluorophotometer is linear, multiplication of the readings by the reciprocal of the relative sensitivity will reduce them all to the same terms.

1.3 Luminescence and Quenching. The possibility of satisfactory fluorescence analysis for uranium is dependent in part on the rarity of the type of luminescence behavior it shows. Among inorganic solids two general types of luminescence are found. In the first of these the emission spectrum consists of one or more comparatively sharp (i.e., not broader than two or three hundred wave numbers, at most) fluorescence bands, and remains very much the same in many different chemical and physical states of the particular element or radical involved. The best examples of this behavior are provided by certain of the rare earths, which as trivalent ions give characteristic narrow bands that are much the same whether the rare earths are pure solid compounds, in dilute solid solution, in aqueous solution, or as organic complexes. In this type of luminescence, the decay always obeys an exponential law and is comparatively independent of temperature, and, at all normal intensities of irradiation, the light emission is strictly proportional to the intensity of the irradiating light. Uranium fluorescence is of this type, and chromic and manganous ions in certain types of solid solutions behave very similarly. Very few other examples are known.

The other type of luminescence of inorganic solids is what might be termed "impurity luminescence," and is found in almost any impure inorganic compound that is not strongly colored.(1) Light is emitted both as fluorescence and phosphorescence, and the emission bands are frequently several thousand wave numbers broad, with little sign of fine structure. And when any structure at all is found in the spectrum, it is generally characteristic of the solvent lattice rather than of the activating impurity. Usually there is a fairly low-lying conduction band in the crystal, and photoconductivity is associated with the luminescence. The decay of the phosphorescence is usually not exponential, but depends in a complicated way on the depths of traps; and irradiation at low temperature usually can cause a storage of energy which on heating is released as luminescence.(2) Almost any type of "substance" can serve as an impurity, even lattice defects. This type of luminescence is most frequently found when the solvent has a loosely packed lattice with large lattice constant, and when the solvent lattice can itself absorb the irradiating light.

We thus see that to avoid interfering fluorescences one must first of all choose conditions that will be unfavorable to "impurity luminescence": this will mean a highly transparent solvent with tightly packed lattice. Secondly, the irradiating light should be of a wavelength absorbed by few potentially interfering substances; the more monochromatic it is and the longer its wavelength, the smaller is the likelihood of its exciting undesired fluorescences. By this means one can avoid interferences from rare earths, since they absorb only in very narrow bands. Similarly, other fluorescences can be dealt with by employing optical filters to limit the response of the fluorophotometer to a narrow spectral range. And thirdly, various chemical means are available for preventing fluorescences; as, the fluorescence of chromous and manganous ions is avoidable by means of oxidation. Since uranium fluorescence is far more independent of the nature of the solvent than is "impurity luminescence," and since it occurs under conditions of oxidation, it is at least theoretically possible to obtain conditions under which no substance but uranium will fluoresce.

The second way in which foreign materials can interfere is by quenching. The extent of quenching is rarely so great that the reduction in sensitivity causes difficulty, and thus it is not essential to prevent quenching, but is sufficient to determine the extent of quenching. The two proposed methods for treating quenching, the dilution and "spiking" methods, both depend on the assumption that ϕ is independent of the uranium concentration, that the linear relation between uranium concentration and fluorescence found in the absence of quenchers persists in the presence of quenching impurities. In general, it can be predicted that, since uranium fluorescence depends on interactions between single light quanta and single uranium ions, non-linearity will occur only when (1) the uranium ions quench each other or (2) when the uranium ions react chemically with quencher ions so that changes in uranium concentration affect the quencher concentration. In the first case, we expect linearity at low uranium concentrations and quenching at high concentrations, as is actually found. In the second case, we expect pronounced quenching at low uranium concentrations, and less quenching (proportionately -- as measured by the value of ϕ) at high concentrations, as the quencher is "used up" by the uranium. For the success of the recommended method of treating quenching, it is essential that the second type of behavior never occur, and that the first type not occur at appreciably lower uranium concentrations in the presence of a quencher than in the absence of quenchers.

That a large amount of added material, say 10 mg or so, might change the properties of the flux to such an extent as to increase the self-quenching of uranium ions, does not seem implausible, but for a minute amount to have a pronounced effect seems improbable. And since analyses where "spiking" is employed are not run at high uranium levels, it would have to be a pronounced effect in order to be objectionable. The other type of interference --for uranium concentration to affect the effective quencher concentration -- seems more probable. This would involve the formation of a non-fluorescent uranium compound or adsorption complex. In order for this process to alter appreciably the effective quencher concentration, it is necessary that the total number of quencher particles or of spaces available for adsorption be of the same order of magnitude as the number of uranium atoms; and at the same time, this very low concentration of quencher must bind the uranium more strongly than the overwhelmingly greater amount of fluoride ion. Since in aqueous solution, fluoride ions complex uranyl very strongly,(3) it need not surprise us if we find that this sort of quenching behavior does not occur.

Substances fluoresce to the extent that other paths for the loss of excitation energy are unavailable, and we may expect that uranium fused in sodium fluoride is very favorably situated in respect to fluorescence. Being in a solid, it cannot be quenched by "collisions of the second kind, the common mechanism of quenching in liquids and gases. It is unlikely to lose its energy by oxidizing a neighboring ion, as frequently happens with uranyl ions in aqueous solution, since the high temperature fusion in an oxidizing flame has probably left very few reducing agents present.

Moreover, the fusion conditions will destroy most of the anions or organic molecules that complex uranyl ions strongly in aqueous solution. Therefore, we need not be surprised if we find all types of quenching comparatively infrequent in sodium fluoride.

1.4 <u>Evaluation of Aims and Results.</u> Different analytical methods may be evaluated in terms of accuracy, range, economy, speed, and simplicity. The application of these criteria to uranium determination requires some explanation.

(a) Simplicity needs little discussion. The important simplification possible in uranium determinations is the almost complete elimination of chemical separations. This means that the most varied types of samples can be handled on a routine basis by untrained personnel, since it is the treatment of interfering substances that requires detailed chemical knowledge in most analytical methods. Some chemical problems remain, to be sure; in particular, the solution of solid samples is as difficult as in any other determination, but once the sample is in aqueous solution, the manipulations required are few and simple.

The speed of analyses is dependent principally on the difficulty of the necessary chemical separations. In addition, speed is usually increased by use of micro methods and by a wide range of permissible concentrations.

The question of economy is a complicated one, and different standards apply to different situations. The most important factor is the number of samples to be handled. In a laboratory where a large number of samples are to be analyzed every day, the major expense under any system yet proposed for uranium analysis by fluorescence will be the cost of labor, and the speediest method will be the most economical.

High sensitivity in addition to increasing the speed, is desirable in fluorescence analysis for uranium, not so much because there is great need for analyzing extremely minute samples, but because it permits great dilution, and dilution lessens quenching. Thus, the higher the sensitivity, the higher the ratio of quencher to uranium that can be tolerated. In evaluating sensitivity in these analyses, the important consideration is is not simply the amount of uranium that can be detected, but rather the amount of uranium per unit weight of flux. With a satisfactory fluorophotometer, the factor limiting the amount of uranium detectable is the fluorescence of the blanks, and not the sensitivity of the instrument. One can reduce the luminescence of the blanks by reducing the amount of flux they contain, but with a smaller dish, only a correspondingly smaller volume of solution can be pipetted in, and nothing will have been gained in sensitivity as measured in terms of concentration of uranium in the unknown solution. Consequently, in comparing sensitivities reported by different workers, values will be recalculated in terms of concentration and expressed as equivalent amounts of uranium in 0.5 g of flux.

In contrast to the qualities previously discussed, the evaluation of accuracy is a thoroughly complicated problem. The most important consideration to bear in mind is that the uranium phosphors employed by different workers (with the single exception of Lipkin and Weissman--see Sec. 2.2) are all very far from being optically homogeneous or of geometrically simple form. Instead of a clear solution in a glass cell with optically flat parallel sides, we deal with an uneven disc or bead ranging in appearance from moderate translucence to opaque whiteness. The optical properties depend markedly on the size and shape of the crystals, and these in turn are affected in a somewhat unpredictable fashion by slight variations in methods of preparation. The system, then, is one to which statistical methods should be applied, and the experimenter who neglects to do so will find that he can "prove" almost any sort of relationship he wishes.

An example will make this clear. Let us suppose that an experiment is being performed to determine whether ϕ is or is not a function of the uranium concentration. Constant amounts of quencher are pipetted into a number of dishes, and then varying amounts of uranium are added. The dishes are "hand- fused" one at a time in the flame of a Meker burner. They are prepared in order of increasing uranium concentration to lessen the danger of high level samples contaminating low level ones; and then they are read in a fluorophotometer, and ϕ is computed. We shall suppose that it is found that ϕ increases from an average of 0.54 with 0.1 µg of uranium to an average of 0.63 with 1.5 µg of uranium. It is concluded that ϕ is a function of uranium concentration, that quenching is reduced as uranium is added. Is such a conclusion justified? It is obvious here that a statistical analysis must be made before the question can be answered. But even if the statistical study shows that the results are without question significant, the conclusion still may not be justified. What is lacking is the employment of <u>randomization.</u> There has been no safeguard to insure that some crucial factor has not changed progressively as the experiment is being run. Let us assume, for example, that the amount of uncombined oxygen in the flame has an important effect on the fluorescence readings, and that the experimenter is not aware of this. As he fuses the dishes he may unintentionally shift their position slightly toward the center of the flame. If he knows the contents of the dishes he is fusing, he will unconsciously (and consciously as well) tend to hold the position much more nearly constant while he is fusing samples containing the same amount of uranium than he will when he finishes one level and starts in at a new level. Thus he may find that dishes at the same level agree with each other excellently, while they are markedly different from dishes at other levels. From exactly the same causes, one can obtain precision that is much better than the accuracy. If one prepares unknowns without mixing knowns in among them, the unknowns may give excellent checks and yet the results be inaccurate.

The necessary procedure for obtaining results that can be trusted is, therefore, not merely to submit the results to a statistical test of significance, but in addition to design the experiment to exclude not only all known sources of error but all unknown sources of error as well. When two types of preparation are being compared, the desirable procedure is to intermingle the dishes randomly and to have them fused by someone who does not know which dishes are which. To a considerable extent, although not nearly so much as would be desirable, our own work has contained such precautions; we have no knowledge to what extent, if at all, other workers have employed these methods. Such work is very time consuming, and the progress made to date has not been striking. When there are many different sources of error of roughly the same magnitude, it is difficult to determine the effect of variation in a particular factor unless one is employing a

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large number of samples. Thus the method of approach is gradually to eliminate one source of error after another. As different factors are elucidated and the precision increased, earlier experiments are repeated and possibly effects are observed that previously were hidden by the large inaccuracies in the earlier technique.

The question arises of which statistics will be most satisfactory as measures of accuracy and precision: are we more interested in absolute errors or in per cent errors?

In fluorescence determinations, as in all quantitative analytical methods, there are some errors that remain largely independent of the concentration of the constituent sought, while other errors are almost in direct proportion to the concentration. If we denote by *A* the absolute standard error introduced by the first type of interference, and by *P* the per cent standard error introduced by the second type of interference, and if *c* is concentration, then the resultant total absolute standard error, $\varepsilon_{\bar{x}}$, will obey the following equation (assuming that the error distribution is approximately normal):

$$\varepsilon_{\bar{x}} = \sqrt{A^2 + (cP/100)^2}$$

A is a measure of the variability found in the blanks, and *P* can be evaluated from studies of high level samples. If *A* is much larger than cP/100, then the standard error should, for constancy, best be measured in absolute units; if cP/100 is much larger than *A*, then it is most convenient to express standard error as a per cent. Probably, with most common analytical methods, *A* is the more important term; but with any system with extreme concentration range cP/100 is more important except at the very lowest concentrations. Accordingly, in this paper in discussions of accuracy, standard errors will usually be expressed as per cents of the mean. Similarly, the precision of fluorophotometric uranium determinations has been found by most of the more successful workers to be, over a wide concentration range, a nearly constant fraction of the concentration; and hence the coefficient of variation is a more satisfactory (more nearly constant) statistic than the standard deviation.

The errors of constant absolute magnitude should be due only to the variations of fluorescence found in blanks; this fluorescence of blanks is probably mainly the result of uranium contamination. With an unsatisfactory fluorophotometer, other nearly constant errors may be introduced by stray fluorescence inside the instrument, by light leakage, by "zero drift," or by dark current fluctuations. The errors of constant relative magnitude are principally due to variations in the optical properties of the phosphor and its container, though other errors of this type can also be introduced by an unsatisfactory fluorophotometer. In addition to the light scattering by the flux, the light reflection from the bottom of the dish is of major importance in many cases, and discolorations of the platinum surface produced by chemical action of the flux frequently leads to large errors. The factors involved in these effects are so complicated that is has not yet proved possible to do much more than reduce the variations by standardizing the techniques and eliminating human factors wherever possible.

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*For example, Hernegger and Karlik, and Neumann; see sec. 2.

2. A Survey of Work Elsewhere

[redacted]

2.1 **Historical.** The fluorescence of the uranyl ion was one of the earliest known and has been among the most intensively studied of all types of fluorescence. In his classic first paper on "The Change in the Refrangibility of Light," Stokes$^{(4)}$ described in 1852 the behavior of pure uranyl compounds and of uranium in solid solution in glass and in fused borax; and the uranyl salts were among the first compounds observed by E. Becquerel$^{(5)}$ in his phosphoroscope. [redacted] An extensive study of uranyl fluorescence [redacted] was made by Nichols and Howes,$^{(6)}$ who in 1919 published the results of eight years of work at Cornell in which emphasis was placed on the effects of cooling uranyl compounds to liquid air temperature. [redacted] a considerable amount of work was done by Dieke$^{(7)}$ and co-workers at Columbia and Johns Hopkins on absorption and emission spectra of uranyl salts at liquid hydrogen temperature, [redacted]

The present analytical method began with the discovery by Nichols and Slattery$^{(8)}$ that the intensity of uranium fluorescence is greatly increased by fusion in sodium fluoride. In a later paper Slattery$^{(9)}$ described tests on the fusion of uranium in many other salts, and reported that only lithium fluoride gave an effect comparable to that of sodium fluoride. A study of the relation between fluorescence and uranium concentration in sodium fluoride was published by Merritt,(10) who based his theory upon Nichols and Slattery's data. The earliest actual analytical use of the sodium fluoride fusion method was by Papish and Hoag(11) in 1927. They made a brief study of specificity and of impurity quenching. One year later, Kitel (12) employed the fluorescence of uranium in nitric acid and in fused borax to demonstrate the presence of uranium in the kidneys of animals that had been injected with the metal. The first quantitative analyses were by Hernegger and Karlik,(13) who in 1935 used spectrographic measurement of the fluorescence intensity of NaF-U beads to determine the uranium content of sea water. Since then, many others have employed fusion with fluorides in qualitative or quantitative analysis for uranium. The most important recent papers in the unclassified literature are by Northup,(14) who used visual study of sodium fluoride beads as a qualitative test for uranium in minerals, and whose report includes the longest list yet published of substances tested for fluorescence in fused sodium fluoride; and by Gibb and Evans,(15) who describe a portable fluorophotometer for field use, and give a long list of elements tested for quenching. A paper by Sill and Peterson(16) on a qualitative test by fluorescence in aqueous solution has also recently appeared. The most extensive series of papers on uranium determination by fluorescence is by Joseph Hoffmann,(17) who has followed the procedure of Hernegger and Karlik except that he employs visual instead of photographic measurement of light intensity; there are a number of reasons, as will be pointed out in later sections, for questioning the reliability of his work.

a large number of groups have worked on fluorescence methods for uranium analysis.

2.2 <u>General Properties of the Fluorescence of Uranium in Sodium Fluoride.</u> The common fluorescent uranium compounds are all uranyl salts. Whether or not the uranium is in the uranyl form in the NaF-U phosphor has not been definitely established. Slattery(9) investigated this question by spectrographic studies of NaF-U and LiF-U and of what she believed were uranyl fluorides, both at room temperature and at liquid air temperature, and she concluded that the uranium probably was not in the uranyl form. Other spectrographic studies of NaF-U were described by Nichols and Slattery(8) and by Hernegger and Karlik.(13) Whereas ordinary uranyl fluorescence bands are separated by intervals of around 800 to 900 wave numbers, an interval that has been identified with the symmetrical valence frequency of the uranyl ion as shown by Raman spectra, in sodium fluoride the frequency intervals are shorter and less regular. Because of this, Slattery suggested that something like uranium hexafluoride might be the fluorescent species. This, however, besides being strongly improbable on chemical grounds, is unlikely because the fluorescence spectrum of the hexafluoride is quite unlike the uranyl spectrum, since it is shifted toward shorter wavelengths and its most characteristic interval is about 220 wave numbers.(30) Although the question is not settled, it would seem that the uranyl* form is the most probable on chemical grounds, and a change in length of the interval in sodium fluoride is not a proof that uranyl ions are not involved.

2.3 General Analytical Methods. The methods of different workers have differed according to whether fluorescence was measured visually, photographically, or photoelectrically; whether dishes or beads on wire loops were employed; whether pure sodium fluoride or some fusion mixture was used; and in regard to techniques of fusion.

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*Or possibly uranate.

[redacted]

Most of the early workers and many of the more recent ones have prepared their phosphors as beads instead of fusing in dishes. While cheap, quick, and simple, the procedure is far less satisfactory for quantitative work than is the method of performing all manipulations in the dish in which the final results are obtained. Dishes are usually made of platinum, though gold,(37) silver,(38) and even nickel(26) have been recommended for use with low melting, high carbonate fusion mixtures. [redacted]

[redacted] Some workers have used as dishes the covers of large platinum crucibles, which hold 2.5 g of flux; Bloor and Neuman have used small dishes made from 5 mil platinum foil and holding 80 mg of flux. It would seem that the smaller size would be the more satisfactory, since large dishes will have the following disadvantages: (1) greater expense, (2) more time required for evaporations and fusions, (3) smaller optical efficiency in any optical system in which light is focussed, (4) lesser convenience in handling, (5) more space required for cleaning and storage, (6) greater tendency to deform, and (7) greater difficulty in "tapping out."

Neuman and most of the earlier workers have used pure sodium fluoride as flux. Other fluxes that have been employed include lithium fluoride,(39) a 1:1 mixture of sodium fluoride and potassium carbonate,(25) and mixtures of 1 to 10% of fluoride in mixed sodium and potassium carbonates. The compositions of two of the high carbonate mixtures are as follows:

2.5% by weight KF, 42.5% K_2CO_3, 55% Na_2CO_3 (38)

1.8% NaF, 48.3% K_2CO_3, 49.9% Na_2CO_3 (40)

In this paper the first mixture will be briefly referred to as the A mixture, while the second will be called the B mixture.

Fusions of low melting materials contained in dishes have usually been performed in muffle furnaces;* most workers using beads fuse in gas-air flames; no one has yet reported successfully fusing pure sodium fluoride in a muffle furnace,

Dishes fused in muffle furnaces will often have received similar treatment in fusion, though it is not impossible to have variations in conditions within a furnace. Attempts have been made to increase the precision of flame fusions by mounting the dishes on wire racks, fusing each dish once with each of two Meker burners, and regulating by a water column the pressure of gas to the burners. Such procedures, while not so nearly infallible as randomization, greatly decrease the need for randomization.

2.4 **Specificity**. Three elements in addition to uranium have been reported to give visible fluorescence when fused in sodium fluoride, and three other elements have been reported to fluoresce in high carbonate fusion mixtures. Fluorescence of columbium in NaF was described by Papish and Hoag(11) and by Northup.(14) The former found a faint green fluorescence under ultraviolet light from a carbon arc with a Corning "Violet Ultra" filter, and pale blue fluorescence with unfiltered light from an iron spark; the latter used an argon lamp with and without filter for excitation, and observed a faint greenish-yellow fluorescence. Neither used photoelectric or photographic methods of study, although Northup did attempt various methods of distinguishing between uranium and columbium and claimed that a hand spectroscope revealed differences between the fluorescence spectra when a large amount of columbium was present, though not when the fluorescence was very faint. Nichols and Howes(41) studied spectrographically the fluorescence of neodymium and of erbium in sodium fluoride irradiated by light from an iron spark; they found that neodymium gave blue fluorescence, while erbium gave green. Northup observed greenish-yellow fluorescence with neodymium under an iron spark, but no fluorescence under an argon lamp; he could not observe erbium fluorescence under either condition.

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[redacted]

Part of the work just described is open to the criticism that insufficient care was taken to prove that the observed fluorescence was not due to uranium. [redacted] Papish and Hoag did not present in their short article any good evidence that the luminescence found with columbium was not due to uranium. Northrup did attempt to distinguish between the two, but the only strong evidence he presents is his spectroscopic observation, in which he claimed to observe a difference between uranium and columbium at high concentrations of the latter. However, since he did not describe this difference, and gave no data regarding the amount of columbium employed, as far as we know, the difference may have been due to absorption of part of the uranium fluorescence.

2.5 *Sensitivity and Accuracy.* It was mentioned in Section 1.4 that sensitivities should best be compared in terms of amounts of uranium per unit weight of flux. Since the dishes in use at this laboratory hold approximately 0.3 g of flux, values reported by different workers will be recalculated as equivalent amounts of uranium in 0.3 g of flux.

The highest sensitivities reported by workers outside the Manhattan Project were obtained by Hernegger and Karlik, and Hoffmann. Hernegger and Karlik photographed, using a 135 minutes exposure, the spectrum of a 25 mg NaF bead containing 10^{-4} µg of uranium.(13) Since the beads weighed approximately 25 mg each, this would be equivalent to detecting 0.0012 µg of uranium in our dishes. This was purely a *detection* of uranium, not a *measurement*, for the authors state that for practical purposes the sensitivity limit is 0.001 µg, and that there is difficulty below 0.01 µg from reciprocity law failure. Hoffmann, apparently using visual observation, claimed to be able to detect 10^{-5} µg of uranium in 25 mg NaF beads;* this would be equivalent to 0.00012 µg in our dishes.

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* *Sprechsaal*, *73*, 153 (1940). The word "apparently" is used because it is by no means certain what Hoffmann is saying. Even men whose native tongue is German, have had difficulty understanding this article, and even the *Chemical Abstracts* (Vol. *36*, p. 5108 (1942)) reviewer made at least two errors in translation.

In evaluating these sensitivities, it should be noted that, since no information is given regarding standard error or standard deviation at the limit of sensitivity, the limits claimed depend to a considerable extent on the attitude of the analyst, on how great an error he is willing to tolerate.

When one is investigating accuracies attained by different workers, a cursory reading of the literature would give the impression that the method of Joseph Hoffmann is by far the most accurate, for in his later papers Hoffmann has reported his analytical results to three "significant" figures.(45) Careful study, however, reveals that he makes his determinations visually, and that he may, for example, decide that the fluorescence of an unknown bead appears about midway in intensity between two standard beads containing respectively 0.001 and 0.005 µg of uranium, and that therefore the uranium content of the unknown is 0.0025 µg. He will then divide the 0.0025 by a weight obtained on an analytical balance to four significant figures, and retain three figures in the quotient. It would seem very remarkable if in his method the standard error of a single determination is as good as 10%.*

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*A report that Hoffmann claims an accuracy of better than 1% is probably an error in translation; see the preceding footnote.

The work of Hernegger and Karlik is probably far more accurate than Hoffmann's, since they used a more precise method of light measurement. The precision of their determinations was such that in their sea water analyses the mean of the coefficients of variation for the seven samples was 13%. Information on the accuracy can be obtained from an experiment in which they added a known amount of uranium to a portion of sea water that they had previously analyzed; the mean recovery was in error by only 10%. As this is smaller than the coefficient of variation, one would expect that in an extended series of determinations the accuracy would not be quite so high. Even so, since in this work it was necessary to concentrate and purify large volume of sea water, the results seem very satisfactory.

3. Experimental

Our work, which began early in 1944 in the Clinical Medicine Section of the Health Division of the Metallurgical Laboratory, was originally designed for determinations in urine and other biological materials, but it soon proved possible to develop our methods into general ones for determinations in any type of chemical system. The early stages of the work are described by Ferretti, Price, and Schwartz is a "final" report on the biological applications. In

the present paper we give instructions for analyses in all types of materials that can be brought into aqueous solution; in the present section we present some of the experiments on which our recommendations are based. It will be seen, in comparing our work with that described for other laboratories, that our principle advantages have been the possession of a fluorophotometer of far greater sensitivity than others have used, and the employment of our methods of treating quenching.

3.1 General Properties of the Fluorescence of Uranium in Sodium Fluoride. Emission spectra of uranium phosphors are shown in Figure 2. In order from the bottom up, the plate shows an iron arc,

100 µg in NaF exposed for 2 minutes, 10 µg in NaF exposed 20 minutes, and 100 µg in NaF exposed 10 minutes. All discs were irradiated at the same intensity from a strong mercury arc lamp filtered to transmit almost solely the 365 mµ line. The plate was an Eastman spectrographic plate with 1-F emulsion, and the spectrograph was a high dispersion grating instrument.*

The most important information given by the plate is the close similarity of the spectra in the two fusion materials, in one of which the

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*Messrs. James Brody and Claire Patterson operated the spectrograph.

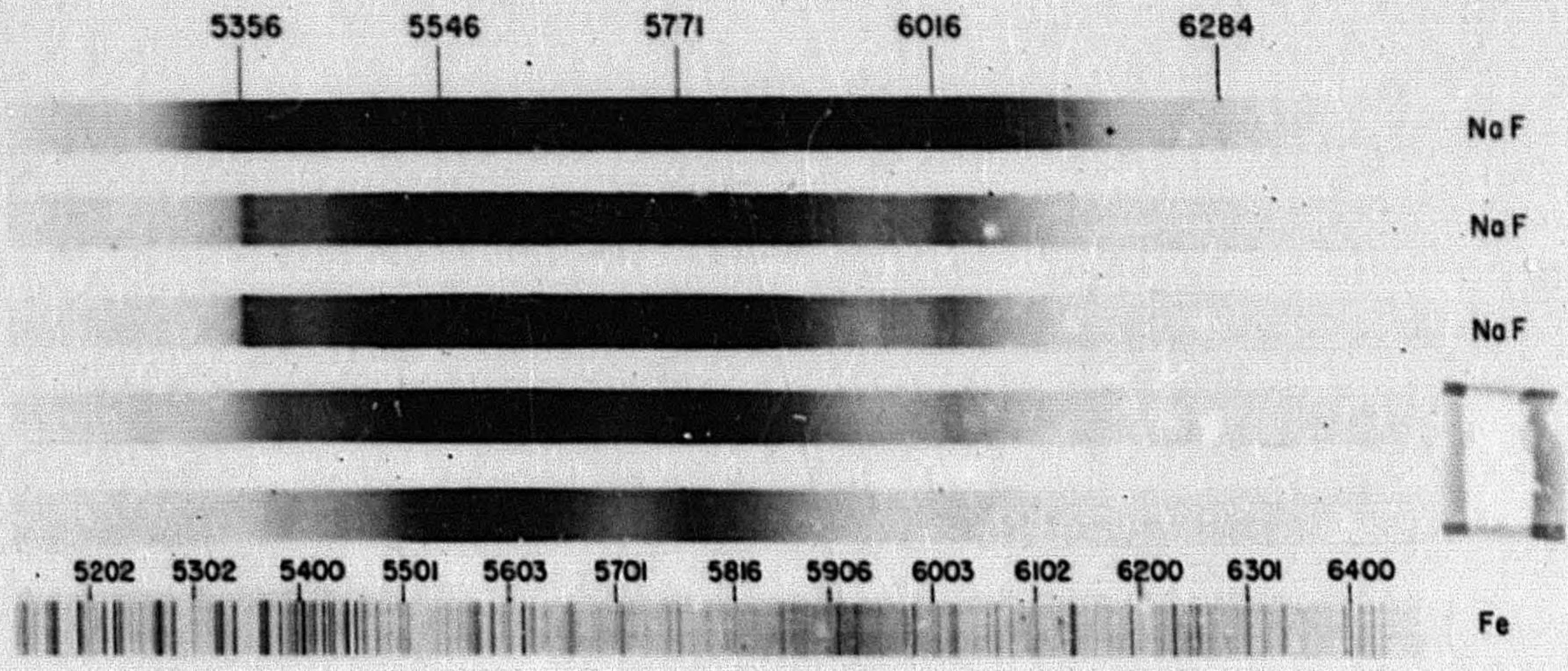

FIG.2 - FLUORESCENCE OF URANIUM IN SODIUM FLUORIDE AND

fluoride concentration is 55 times as great as in the other. This shows that the uranium must have a very strong affinity for fluoride.

The wavelengths in Angstrom units of the five principal bands are as follows: 5356, 5546, 5771, 6016, and 6284. The frequency intervals in wave numbers are, in order: 639, 705, 703, 709 cm^{-1}.

A study of the excitation spectrum of NaF-U was made, using a Beckman Spectrophotometer as light source, and measuring the fluorescence with a multiplier phototube. The intensity of the irradiation was measured by means of a Weston Photronic Cell that had previously been calibrated for relative spectral sensitivity against a thermopile. It was found that with a tungsten filament lamp as light source, the slit had to be opened so wide to obtain sufficient intensity, that results were greatly in error. Therefore the inner tube of an A-H4 mercury arc was mounted in the Beckman housing. Even with this, results were doubtful except at 365 mμ and 334 mμ. The relative spectral sensitivity found was as follows: 436 mμ, 1(?); 405 mμ, 2(?), 365 mμ, 15; 334 mμ, 17; 313 mμ, 550(??).

Figure 3 is a calibration curve, which demonstrates a linear relation between uranium concentration and fluorescence intensity over a remarkably wide range. Further data on this calibration are tabulated in Section 3.5.

An attempt was made to detect phosphorescence "frozen in" at low temperatures by immersing several NaF-U preparations at the 0.1 μg to 1 μg range, beneath the surface of liquid nitrogen. The phosphors were irradiated one hour by an unfiltered quartz mercury arc, and then an additional 10 minutes through a filter of copper sulphate solution. They

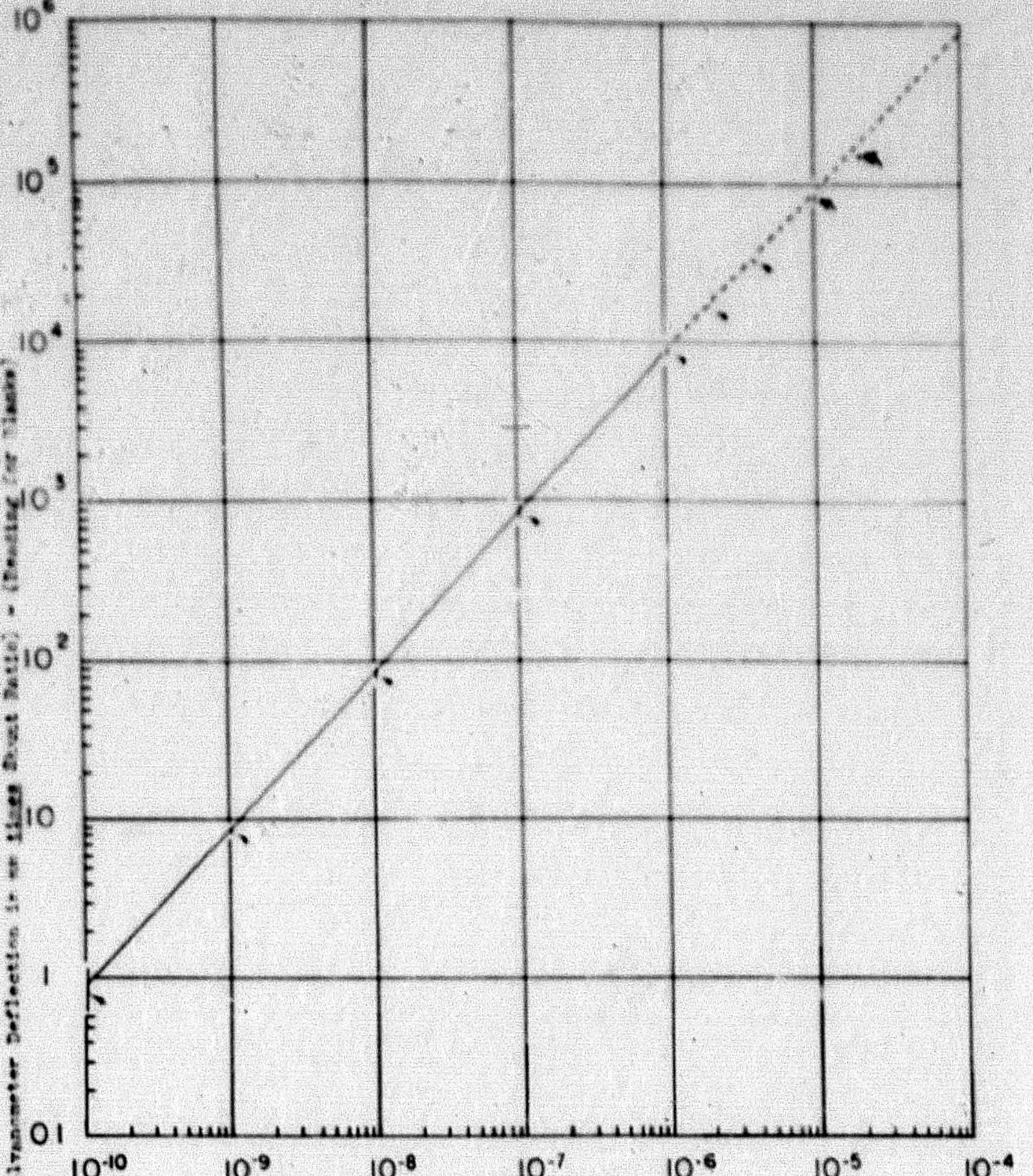

Fig. 3 - Calibration curve for Fluorophotometer Model IV

were removed from the liquid nitrogen in a perfectly dark room, and warmed to room temperature either gradually or by a hot plate. With dark adapted eyes, no trace of light could be seen.

3.7 Experiments on General Procedure. The principal experiments on general procedure have been concerned with fusion techniques, fusion materials, and dish styles.

Dishes have in the main been fused in open flames, as mentioned in Section 1.1 and as will be described further in Section 4.7. When NaF dishes are fused in a muffle furnace, they ordinarily emerge colored yellow or brown as a result of dissolved platinum. If they are covered while they fuse, this does not occur. Dishes fused in a muffle furnace while covered, have very large, clean crystals, but unfortunately the fluorescence is extremely low until the dish is refused uncovered in a flame.

When NaF is fused in contact with air, a considerable amount reacts to yield titratable base. At the same time, a gas is liberated that etches silica plates covering a dish. Quantitative information on the free base produced was obtained by dissolving sodium fluoride in water, measuring the pH, and then titrating with 0.1110 N HCl to a final pH of around 5.9 (the solution was too buffered for an indicator to be used successfully)*. Results are shown in Table 2. All samples were dissolved in 50 ml of water. These results indicate that each gram of NaF stove fused in dishes by the usual procedure increases in titratable base content by approximately 0.8 milliequivalents. Dishes fused while covered increase in titratable base by a much smaller amount.

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* These titrations were done by Mrs. Hespelhorn

TABLE 2

TITRATABLE BASE IN FUSED AND UNFUSED SODIUM FLUORIDE

Sample	Method of Fusion	Weight in Mg	Inital pH	Ml of HCl Added	Final pH
1	(unfused)	646	7.9	1.04	5.88
2	"	633	7.8	0.9	5.9
3	Hand	952	9.85	3.61	5.91
4	"	911	9.88	3.55	5.82
5		873	9.82	3.05	5.88
6	Stove	1006	10.22	8.9	5.90
7	"	1006	10.12	7.34	5.90
8	"	999	10.0	6.77	5.88

Stove fused dishes are always whiter and more opaque than hand fused dishes. A hand fused dish refused on the stove assumes a "stove-fused appearance," but this change cannot be effected in the opposite direction. Therefore the difference in appearance is presumably related to the increase in alkali, which has the effect of turning the flux into a mixture. All fusion mixtures yet tested show even whiter appearance than stove fused NaF. Presumably this is because the constituents of the fusion material are insoluble in each other at room temperature, and therefore the crystals break up on cooling. A substance crystallizing in the same form as sodium fluoride and mutually soluble with it might give a more transparent result, but according to a theory of Tobolsky on "Solid Solutions of the Alkali Halides"(51) such a substance may be difficult to find because the lattice constant of sodium fluoride is quite different from all other alkali halides containing a common ion.

Most dishes of our regular size, fused exposed to air are found covered with brown spots on the platinum, after the disc is removed. These spots are associated in position with bubbles that appear in the molten flux. Spectrographic analysis has shown that these spots are mainly composed of platinum, presumably coming from the action of the alkali. A small amount of iron is also present in them. Dishes fused tightly covered, and shallow dishes such as Neuman uses, do not show much of this stain.

A great variety of fusion materials have been tested. In all of these the fluorescence is reduced, though in most cases only slightly. High carbonate mixtures, are strongly hygroscopic, besides having undesirable behavior in regard to specificity and quenching, as will be described later. Mixtures containing lithium always attack the platinum too much, giving a red disc; no attempt has been made to test them in an inert atmosphere. Mixtures containing potassium are hygroscopic. Mixtures with sodium chloride have no particular disadvantages, other than the change in optical properties. A mixture of 90% sodium fluoride with 10% sodium carbonate (hereinafter referred to as the "10%" mixture) has proved quite satisfactory in analytical use

Experiments to determine the effects of different fusion times and of repeated fusions have so far yielded inconclusive results. The only pronounced change in fluorescence that has been found to occur as a result of slight variations in fusion technique, comes when a dish is not quite completely remelted by a hand method, and then allowed to cool slowly; with sodium fluoride, this results in larger crystals, and enhances the fluorescence slightly.

3.3 Specificity.

(a) Experimental. The six elements, cadmium, columbium, erbium, neodymium, tantalum, and zirconium, mentioned in Section 2.4 as fluorescing in NaF or in high carbonate mixtures have been tested in this laboratory. One quarter milligram of neodymium oxide and of tantalum pentoxide, and 0.2, 0.1, and 0.05 mg of trivalent erbium were each fused in NaF and examined in a fluorophotometer with the optical system used for uranium analyses. In none of these was fluorescence found that should be considered significant. All of the dishes had about as much fluorescence as 0.001 μg of uranium; under the conditions of the experiment the blanks were approximately this value also. The highest fluorescence was given by the 0.2 mg of erbium, which read as high as 0.004 μg of uranium. This much fluorescence would be produced by contamination with uranium amounting to about 0.002% by weight, which is a thoroughly plausible value. Visually all the dishes appeared to give the typical uranium fluorescence; no spectroscopic examination was made.

A number of dishes were prepared containing 0.1 mg of zirconium in sodium fluoride. These all gave readings in the neighborhood of 8 (1 μg of uranium = about 10^4). Some of the phosphors were examined visually through a Zeiss hand spectroscope, and the faint fluorescence appeared to be definitely due to uranium.

Columbium was tested more thoroughly than the proceeding elements, because with those there were no claims of fluorescence in NaF under near ultraviolet light. A solution of columbium was made by dissolving the pentoxide in concentrated sulfuric acid with strong heating, and dishes were prepared containing 47 µg, 94 µg, and 470 µg. The most careful work was done at the 94 µg level. Here five columbium dishes read, respectively, 1.8, 2.1, 9.2, 1.9, and 1.8; the two blanks were 1.1 and 1.9. The mean difference between the two groups (excluding the 9.2, which is without question contamination), if it were statistically significant, would amount to less than 0.0007% uranium impurity in the columbium pentoxide. Dishes at all three levels were examined visually and with a hand spectroscope; no qualitative difference could be seen between columbium dishes and blanks.

Cadmium was investigated in two fusion materials.

Spectroscopic and spectrographic study showed the fluorescence to be a continuum streching from violet to red, with its maximum at about 560 mµ. Fluorescent samples were tested for "frozen in" phosphorescence by the procedure described for uranium in Section 3.1; no such phosphorescence was observed. In NaF and in the "10%" mixture, no evidence of cadmium fluorescence was found. The results of one experiment are shown in Table 3.

TABLE 3

THE FLUORESCENCE OF CADMIUM IN FLUORIDE FUSION MATERIALS

Fusion Mixture	Micrograms of Cadmium	Fluorophotometer Reading	
		After 1st Fusion	After 2nd Fusion
10%	25	2.5	2.0
	25	2.2	2.0
	25	2.3	2.3
	0	2.0	2.0
	0	2.0	1.5
NaF	25	2.1	2.0
	25	2.0	2.1
	25	1.9	1.7
	0	1.6	2.0
	0	1.7	1.8

ment that it had become overheated and had dissolved platinum.

The other dishes were first stove-fused, and then refused by hand. In the case of the first fusion with NaF, there is a significant difference between cadmium dishes and blanks; this difference would amount to only 0.0001% uranium in the cadmium.*

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* The difference between first and second fusions for the "10%" and NaF dishes is due to the dishes not having been read immediately after the first fusion; this gave them time to "rise."

(b) Discussion. From the experiments just described, it is concluded that no element besides uranium has been shown to give detectable luminescence in NaF or "10%" mixture under the conditions of the recommended analytical procedure. This does not mean that no such interfering element will ever be found; quite possibly, for example, one of the rare earths still untested would give detectable fluorescence. It seems likely that the rare earths still untested showed no detectable fluorescence because they did not absorb the ultraviolet light or because their emitted fluorescence was not of a wavelength that passed through the filters. Since rare earth absorption bands are remarkably narrow, it is not surprising that a light source supplying almost entirely 365 mμ light should fail to be absorbed by rare earth ions; with an iron spark as light source, quite a different sort of behavior might have been found.

The cadmium luminescence found in high carbonate mixtures, from its susceptibility to heat treatment and from the nature of its spectrum, would appear to be a typical case of "impurity luminescence". Why it did not exhibit "frozen in" phosphorescence is not known.

3.4 Sensitivity and Blanks.

(a) Experimental. The sensitivity of our method depends directly on the cleanliness of the platinum dishes. As an example of what can be accomplished when the dishes are extremely clean, data from the calibration shown in Figure 3 will be presented. At the 10^{-4} µg level (really 0.000103 µg), there were six dishes; and six blanks were prepared at the same time. Each sample was read once in the dish in which it was fused. The six blanks read:

0.8, 0.8, 0.9, 0.9, 0.9, and 1.0.

The 10^{-4} µg dishes read:

1.5, 1.6, 1.7, 1.8, 1.9, and 2.0.

For the blanks, the mean is 0.88, the standard deviation is 0.08, and the coefficient of variation is 9%. For the 10^{-4} µg samples, the mean is 1.75; the standard deviation, 0.19; and the coefficient of variation, 11%. The difference of means between uranium dishes and blanks is 0.87, and the standard error of the difference is 0.18 scale division or 2×10^{-5} µg of uranium or 21% of the difference of means. From these data it will be seen that the sensitivity we claim (for determination -- not just for detection) is considerably greater than the sensitivity claimed by any other worker.

The amount of uranium that may be present in the fusion material is indicated by the data in Table 4 (1 µg of uranium would have read about 10^4). The results show that it is of extreme importance to exercise care in selecting fusion materials. From the data on the General Chemical Company product, one might guess that the uranium contamination of chemical companies in the United States is increasing, and that it will soon become increasingly difficult to buy satisfactory sodium fluoride. All the analyses reported in this paper have been made with General Chemical Company Lot No. 37 material, but this is no longer on the market. A synthetic

TABLE 4

URANIUM CONTENT OF SODIUM FLUORIDE

Brand of Sodium Fluoride	Readings	Mean
Gen. Chem. Co., Lot No. 37	1.0, 1.1, 1.2	1.1
Gen. Chem. Co., Lot No. 46	1.4, 2.2, 2.4	2.0
Gen. Chem. Co., Lot No. 47B	6.0, 6.6, 6.9	6.5
Harshaw, Lab. Sample No. 307-43	12.5, 12.1	12.3
Merck, No. ".74082, 42573"	37.0, 38.5, 73.5	50
Baker's Analyzed, No. 122443	100, 120	115
Baker's Analyzed, No. 9943	200, 210	205

sodium fluoride made as will be described in Section 4.6 is less pure than the Lot No. 37 material to the extent of about 10^{-4} µg of uranium per 0.3 g of sodium fluoride. Thus it will be somewhat less satisfactory than the commercial product for analyses at the 10^{-4} µg level, though at the levels where most analyses are run it will be quite satisfactory. The contamination of sodium carbonate (needed for preparing the "10% mixture) is not likely to be a problem.

The fluorescence of uranium phosphors increases on standing; this phenomenon is referred to as "blank rise". Its absolute magnitude has been found to be independent of the uranium content, and therefore it is due to the growth of a new luminescence rather than to a change in the conditions to which the uranium is exposed. The rate of increase is affected by temperature, being two or three times as great at 100°C as at room temperature. At slightly higher temperatures, the increase becomes still faster, but somewhere between 300 and 500° an opposite effect sets in, and the luminescence tends to decrease. This decrease, like the increase, is reversible, and it is possible to make the same preparation rise and fall in luminescence an indefinite number of times. The rate of increase is fastest immediately after fusion, and gradually becomes slower as time passes.

That the new luminescence is connected with moisture absorption has been indicated by an experiment in which seven "tapped out" NaF blanks were read in a "black dish" before and after being left for 21 hours either exposed to the room air or in a desiccator containing anhydrous magnesium perchlorate. (The desiccator was not evacuated.) The three phosphors exposed to the atmosphere each increased in luminescence from 300 to 400%; the four blanks in the desiccator each increased by between 20 and 50%. A very slight increase in weight, of the order of 0.5 mg per dish in 24 hours, also occurs after fusion.

The spectrum of the new luminescence has been studied both visually and photographically in Lot No. 37 NaF. For the visual work, the same Zeiss hand spectroscope was employed as was used for the experiments described in the preceding section. For the photographic studies, a very fast spectrograph was constructed by combining the hand spectroscope with a miniature camera of approximately 2 in. focal length.* "Super XX"

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*This camera was loaned to the author by Mr. J. W. Britain.

panchromatic film was used, and very long exposures were made in a darkened room. In both the visual and the photographic work, luminescence was excited by a General Electric C-H4 lamp equipped with a filter to pass mainly 365 mμ light. Visually the luminescence appeared to be a continuum stretching from about 490 to 610 mμ, with the cut-off much sharper at the long wave length end than at the violet end. Unfused NaF showed a luminescence that appeared to be exactly the same, only stronger. A photograph of the spectrum of unfused NaF however, showed, in addition to the continuum, two fairly narrow bands at about 520 and 600 mμ respectively, and a faint trace of a very broad band with its maximum at approximately 470 mμ. This is shown in Figure 4b; Figure 4a shows a mercury arc spectrum and 4c shows NaF-U, both photographed with the same equipment. It has thus far proved impossible to observe these bands visually, even using the same sample that was employed for the photograph. The reason for this discrepancy is not known, unless it is due to a visual error caused by the spectral sensitivity characteristics of the human eye, or unless a reversible change was produced in the preparation by the heating that occurred during its four hour exposure to an intense light source. It is impossible to repeat the photograph because the camera is no longer available.

Different brands of unfused NaF give different amounts of luminescence. Thus, a dish full of unfused Lot No. 37 material reads about 80, the Harshaw NaF described in Table 4 reads over 100 before fusion, and the specially synthesized material reads about half as much as the General Chemical Company product. Similarly, the different brands give different rates of "blank rise," the laboratory-made material increasing less rapidly

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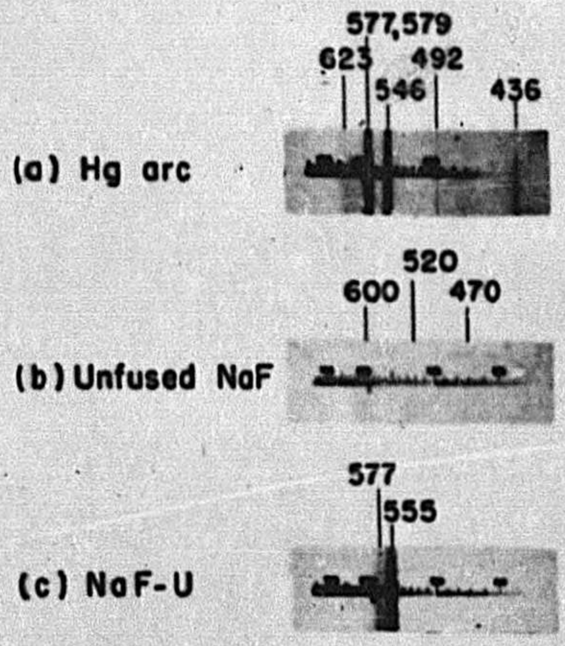

FIG. 4. FLUORESCENCE OF UNFUSED SODIUM FLUORIDE.

than the Lot No. 37. Other experiments have indicated that the rate of increase is affected by fusion conditions and by previous heat treatment. Thus, annealing for several hours at 500°C can cause a significant decrease in the rate of subsequent "rise," and conditions of fusion that give a finely divided powder seems to cause faster increases. Blanks fused in a muffle furnace while covered "rise" extremely slowly. Moistening the fused preparation with a small amount of water, followed by drying, causes a slight immediate increase; but the blank while wet does not have a greatly enhanced luminescence. When blanks that have "risen" are kept for several days in an evacuated desiccator over Anhydrone, no decrease in readings results.

(b) Discussion. The fluorescence of unfused NaF and of aged NaF blanks appears to be in many ways similar to that described for "wetted white solids" by Ewles and Martin.(52) They found that many alkali halides and other white salts gave bluish luminescence that was apparently due to the presence of water as an activating impurity. In all cases, prolonged heating destroyed the luminescence, but pumping-out had no effect. The luminescence spectra in all these materials were similar, and showed maxima at 462, 520, 568, and 610 mμ; except for the band at 568 mμ, this is very much like the NaF spectrum photographed. Apparently in the case of NaF, a trace of water diffuses into the fused preparation and is very tenaciously adsorbed. The diffusion seems to be facilitated by lattice imperfections.

This behavior of water is reminiscent of an effect found by Clement in many alkali halides.(53) He prepared strongly luminescent alkali halide phospors by subliming activator salts (such as TlCl) in vacuo on to a layer of alkali halide, and then heating. The activation process apparently involved diffusion into the crystal lattice, since lower temperatures were required for activation as the lattice constant of the alkali halide increased, and as the size of the activator molecule decreased. According to this interpretation, NaF would be difficult to activate because of its very tight crystal structure, but water would be a potent activator because of its small size. One wonders why water alone of all impurities tested causes luminescence in NaF. A profitable working hypothesis might be that substances that diffuse into an already formed lattice become situated more favorably for luminescence than do substances present in the flux as it crystallizes.

3.5 Accuracy. Some information on the accuracy of our work was given in Section 2.5 in the description of the Rochester study. In these analyses we employed NaF and fusions were made by hand. Twenty-seven of the thirty samples were run in duplicate, one in triplicate, and two in quadruplicate. All phosphors were read in a "black" dish in the Model III Fluorophotometer.(54) The accuracy of our results is shown in a figure in which the values we reported are plotted against the actual concentrations as listed in the Wantman and Tiedeman paper.(29) In this work the estimated standard deviation of repeated duplicate measurements on a single sample was 2.5% of the mean, while the standard error of the difference between actual and obtained values was 9.1%. Data on precision of determinations in stove-fused preparations read on the Model IV Fluorophotometer are given in Table 5.

TABLE 6

PRECISION OF URANIUM DETERMINATION

μg of U Added to Dish	Number of Samples	Mean Reading $\bar{x}$	Mean minus Blanks $\bar{x} - \bar{x}_B$	$\frac{\bar{x} - \bar{x}_B}{\mu g \text{ of } U}$ times 10^3	Standard Deviation of Readings, σ	$\frac{\sigma}{\bar{x}}$, in %	$\frac{\sigma}{\bar{x} - \bar{x}_B}$ in %
First Lot							
(Blanks)	6	0.88	- -	- -	0.076	8.6	- -
0.000103	6	1.75	0.87	8.4	0.187	10.7	21.4
0.00103	6	9.62	8.74	8.4	0.49	5.1	5.6
Second Lot							
(Blanks)	6	0.93	- -	- -	0.082	8.8	- -
0.0103	6	85.7	84.8	8.2	5.42	6.3	6.4
0.103	6	869	868	8.4	54.7	6.3	6.3
1.03	6	8.94×10^3	8.94×10^3	8.7	387	4.3	4.3
Third Lot							
2.06	3	16.8×10^3	16.8×10^3	8.2	295	1.7	1.7
4.12	3	32.7×10^3	32.7×10^3	8.1	2080	6.4	6.4
10.3	3	81.0×10^3	81.0×10^3	7.9	6000	7.4	7.4
20.6	2	148×10^3	148×10^3	7.2	0	0	0.0

It was from these data that Figure 3 in Section 3.1 was plotted. All phosphors were read in the original dish. No values at all were discarded. The procedure used was the standard one for routine work of ordinary accuracy except that the dishes were cleaned exceptionally well, and no more than a dozen were fused together on the stove at the same time.

A number of experiments have been run in an attempt to find ways of improving accuracy and precision. The most significant benefits have been obtained by improving the optical conditions by eliminating variations in reflection from the dish bottoms and by decreasing the scattering and reflection in the flux. In hand fused NaF with little colored impurity present, the variance is reduced as much as ten-fold by "tapping out" the disc and placing it in a black, non-flucrescent dish (a surface of freshly heated cupric oxide or of graphite, for example) . This technique has the disadvantage that discs not infrequently break in the "tapping out" process. Moreover, in cases where the scattering is large or the absorption strong, as when fusion mixtures or stove fusion is employed or when colored impurities are present, this "tapping out," though the disc is now less likely to break, becomes of smaller benefit, since less light gets through to the bottom. But this does not mean that the variance is decreased; if anything it is increased by the processes that interfere with the light's reaching the bottom. The remedy here is to reduce the thickness of the disc. Preliminary experiments with shallower dishes,

have indicated that this produces a substantial improvement in precision. Moreover, the smaller dishes fuse more easily, and there results less discoloration of the bottoms by platinum deposition. They do, however, have the disadvantage that it is more difficult to "tap out" from them.

3.6 Quenching.

(a) Experimental. Figure 3 illustrates the effect that dilution has on quenching. Aqueous solutions containing uranium plus quencher were diluted progressively, and aliquots were withdrawn at various dilutions and analyzed by hand fusion with NaF. The "Fe-U" curve illustrates the behavior of a solution containing ferric iron and uranium in a ratio of 1000 to 1 by weight. The "mixed quencher" contained equal amounts by weight of aluminum, bismuth, calcium, chromium, copper, iron, lead, and magnesium, with uranium added to give a ratio of total quenching metals to uranium of 72 to 1 by weight. It is seen that as the solutions become more dilute, the curves approach asymptotically the calibration curve for pure uranium. This is a direct demonstration of the feasibility of the dilution method of treating quenching. The points plotted are the means of from two to four separate determinations; Table 6 gives data indicating the degree of reproducibility in the measurements. In this work the power supply voltage was such that 1 µg of uranium read, when unquenched, 3.3×10^3. ϕ was calculated by the equation:

$$\phi = \frac{A}{B + UC}$$

where A is the photometer reading for the sample; B, the reading for blanks without quencher; U, the micrograms of uranium in the sample; and C, the photometer reading expected for 1 µg of uranium.

The basic premise of the "spiking" method of analysis, it has already been stated, is that quenching is independent of uranium concentration. The graphs in Figure 6 demonstrate that this is true over a very wide range

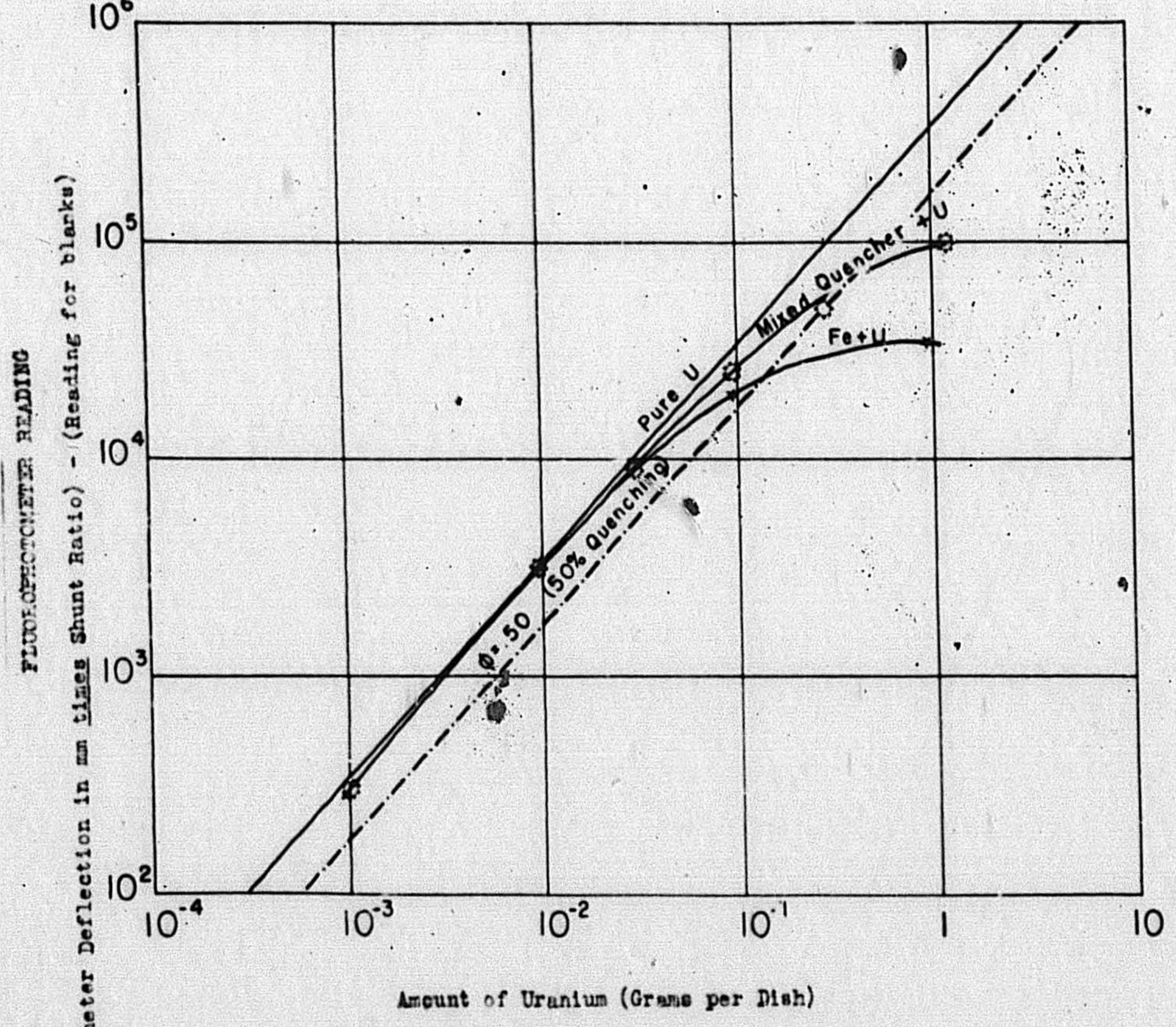

Fig. 5. Variation of fluorescence with dilution

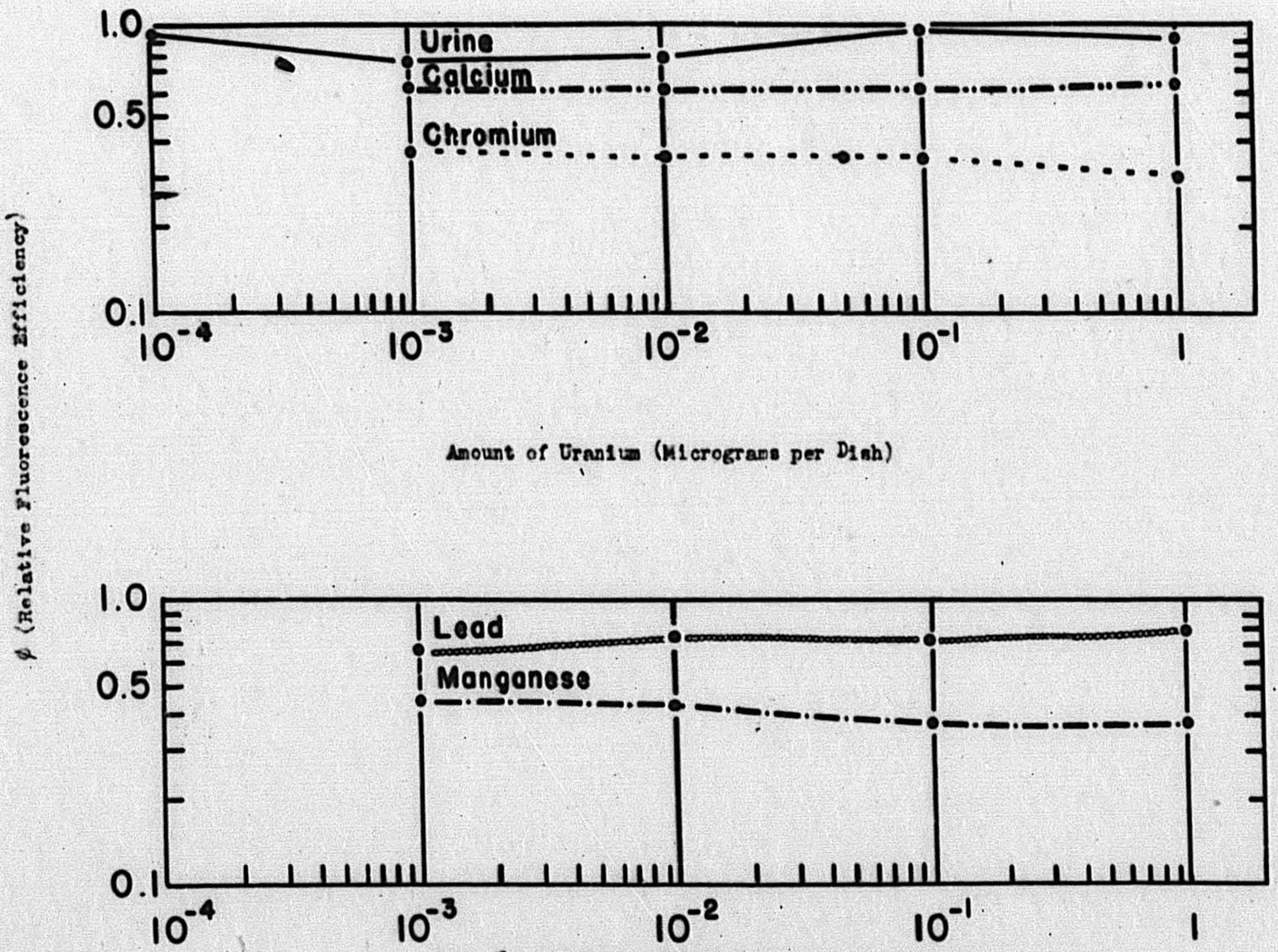

Fig. 6. Relation between ø and amount of uranium

TABLE 6

VARIATION OF FLUORESCENCE WITH DILUTION

Quencher	U Conc., μg/Dish	No. of Samples	Mean Photometer Reading	ϕ	Coefficient of Variation of ϕ
Iron	1.0	3	33.7×10^3	0.101	20.2%
	0.10	3	21.4×10^3	0.64	31.6
	0.010	3	3.28×10^3	0.98	5.1
Mixed Quencher	1.0	4	48.6×10^3	0.29	11.9
	0.30	2	48.4×10^3	0.48	1.1
	0.10	4	25.2×10^3	0.75	2.5
	0.030	2	8.88×10^3	0.87	1.2
	0.010	4	3.20×10^3	0.95	10.3
	0.0010	4	300	0.90	17.5

of uranium concentrations. They show that, as the uranium concentration varies by a factor of a 1000 or more, the quenching (as measured by ϕ) remains constant within experimental error. The points plotted are mean values. The data in Table 7 furnish additional information. In the last column the significance of the regression coefficient is given as probability, in per cent, that such a behavior may be due to chance. The only significant regression is that of manganese, and it signifies merely that we did not randomize in that experiment. It should be noted that this shows an increase in quenching with increase in uranium concentration.

TABLE 7

RELATION BETWEEN $\underline{\phi}$ AND AMOUNT OF URANIUM.

Quencher	mg Quencher per dish	Fusion Material	Fusion Method	No. of Samples	Mean ϕ	Coefficient of Variation of ϕ	Regression Coefficient, ϕ vs. µg of U	Significance of Regression Coefficient
Calcium	2.5	"10%"	Stove	8*	0.62	6.9%	+ 0.04	50%-10%
Chromium	0.010	NaF B	Hand	7	0.33	9.3	- .0205	> 50%
Manganese	0.010		Furnace	8	0.40	9.2	- .0295	< 1%
Lead	0.20	NaF	Stove	24*	0.71	16.9	+ .0023	50%-10%
Urine	(0.10 ml)	NaF	Hand	14	0.88	14.9%	+ .0221	50%-10%

* One value was discarded for statistical reasons.

The coefficients of variation of ϕ listed in the table were determined by treating all ϕ values alike regardless of the uranium concentrations to which they applied. It is seen that the degree of variability found when all uranium levels are treated alike is not significantly greater than what is found when unvarying amounts of uranium are studied. In Figure 6 the methods of plotting--using a log-log scale-gives equal emphasis to equal per cent variation in either variable.

Figure 7 summarizes data on various quenchers; some of the values here have been replotted from previous figures.

(b) Discussion. The shape of the curves in Figures 7 suggest, that the quenching is due mainly to light absorption. With quenching by chemical reactions, one would expect ϕ to approach zero rapidly when the quencher concentration reached a certain level. Instead, one finds the asymptotic relation shown, which is typical of quenching by light absorption when observation is

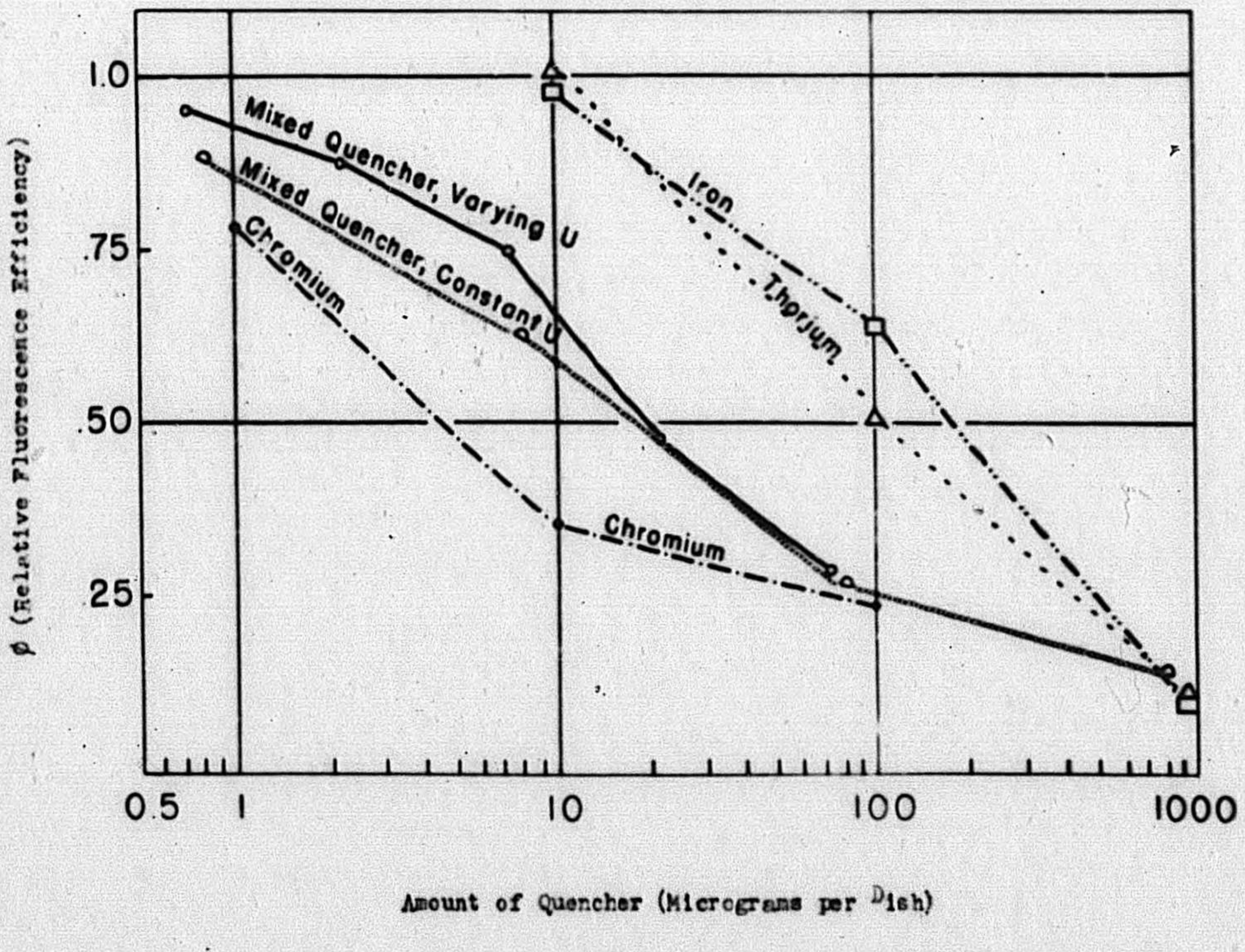

Fig. 7. Relation between ϕ and amount of quencher

from the same side as irradiation. A small degree of quenching occurs readily because the light transmitted to and from the bottom of the phosphor is reduced by a slight increase in optical density, but complete quenching by light absorption is very difficult to achieve because it requires an extremely high optical density in the uppermost layer of the phosphor. The following equation for quenching by light absorption was derived, making use of a number of simplifying assumptions:

$$\phi = \frac{1 - e^{-ha}}{ha}$$

Here <u>h</u> is the thickness of the disc, and <u>a</u> is the absorption coefficient.

4. Analytical Procedure

An outline of the general procedure was given in Section 1.1. The present section contains detailed instructions plus discussion of possible variations. The system described has been employed with little change since the spring of 1946, but it is expected that several changes in procedure, particularly in regard to dish shape and fusion technique, will be made during the next few months. It has seemed preferable to describe the thoroughly tested system rather than the possible future one.

4.1 List of Equipment. The quantities in the following list have been estimated for a laboratory with one or two full time analysts making routine determinations at maximum possible speed. It has seemed desirable to refer whenever possible to an actual commercial product, though it is not intended to suggest that the products described are necessarily more suitable than those of other manufacturers. Catalog numbers designated by "Cenco" or "Sargent" refer to the Central Scientific Company catalog J-141 and to the E. H. Sargent & Company catalog 50, respectively.

(a) Ordinary Equipment

2 doz. porcelain spot test plates, Cenco No. 18600.

1 doz. curved forceps, small, Cenco No. 53120.

1 doz. beakers, 50 ml.

1 doz. beakers, 150 ml.

1 doz. glass stirring rods.

1 or 2 doz. micro pipets; 100, 50, 20, 10 and 5 μl.

(Microchemical Specialities Company, Berkeley, Calif.)

(Where safety considerations permit, mouth pipets like Cenco No. 16325-A can be employed for greater speed.)

2 instrument cabinets, Cenco No. 12690.

4 instrument covers; two each of Sargent S-4945-A and S-4935-C.

6 pipet rests, porcelain, Sargent S-69845.

2 stainless steel spatulas, Cenco No. 18755-D.

2 Meker burners. (Where gas pressure is low, a blast Meker like Sargent S-12475, Size 4, may be necessary.)

1 pr. platinum tipped forceps, Model 139, American Platinum Works, Newark, N. J.

1 hot plate, electric, Cenco No. 16611-A.

1 drying oven.

2 reflector heat lamps, 250 watt.

1 platinum evaporating dish, 40 to 100 ml.

1 or 2 pairs didymium glass blower's glasses.

4 petri dishes, Cenco No. 44370-D.

4 crystallizing dishes, Cenco No. 14645-D.

1 doz. watch glasses, 125 mm diameter.

A supply of facial tissue, "wipes," folded paper towels, and writing paper in tablets.

Concentrated reagent grade acids: HCl, HNO_3, H_2SO_4, and HF.

Sea sand and steel wool.

Crucible tongs, soap, matches, equipment for washing pipets, etc.

(b) Special Equipment.

1 photoelectric fluorophotometer.

2 fusion material dispensers.

1 special high temperature stove.

A set of stock uranium solutions.

50 special platinum dishes.

A supply of fusion materials.

The fluorophotometer was described briefly in Section 1.1.

The fusion material dispenser (See fig. 9, sec. 4.6) is made from an 8 cm length of the graduated portion from a 10 ml graduated pipet (Cenco No. 16325-F), and a 10.5 cm length of glass rod that slides easily but not too loosely inside the tube.

The special stove (See fig. 10, sec. 4.7) is made from a Cenco No. 11085 Fletcher burner in the following way. The three vessels supporting lugs are sawed off, and a closely fitting brass ring is hammered down over the outside of the grid to prevent gas leakage. The gas inlet is replaced by a gas-air inlet, such as that from a Meker blast burner (Sargent S-12475, Size 2). An iron ring of not less than 15 cm inside diameter is mounted over the stove, and across the top of the ring are filed deep slots 1.6 cm apart to support several rows of parallel alundum rods of about 4 mm diameter.

To make the stock uranium solutions, one prepares (preferably in another building) a solution of uranyl nitrate in dilute HNO_3 with a uranium concentration close to 1.00 g/l. A portion is analyzed gravimetrically. With the remainder are prepared solutions of 10^{-2} and 10^{-3} times this concentration, in 1 or 2 M nitric acid. (More dilute solutions may occasionally be useful for such purposes as checking the linearity of a fluorophotometer.) Portions of the dilute stock solutions are poured into small bottles for use in pipetting.

The platinum dishes will be described in Section 4.4. The greater the number of dishes, the faster and more convenient is the work; the quantity recommended (50 dishes) would be necessary in a laboratory where one worker was expected to perform 80 analyses per day.

The fusion material will be discussed in Section 4.6.

4.2 Cleanliness. Experience has repeatedly shown that the uranium contamination problem is more serious than most analysts are ready to believe, and for analyses at high sensitivity, the most scrupulous attention to cleanliness is essential.* If possible, the work should be done in a locality where no large amounts of uranium are being handled, and in a building in which no one works with macro amounts of uranium. Where these conditions cannot be met, it is essential (and where they can be met, it is advisable) to keep everything protected from atmospheric dust as much as possible. Instrument cabinets, instrument covers, watch glasses, petri dishes, crystallizing dishes, and facial tissue are all useful for this purpose. At Chicago, when work is done in uncontaminated buildings, it has proved safe to assume that distilled water; reagent grade hydrochloric, nitric, and sulfuric acids; thoroughly washed glassware and platinum (provided that uranium has not been "baked" into the platinum by heating); and sheets of paper torn from the inside of a tablet or freshly removed from a box of tissue are clean.

In the recommended procedure for uranium analysis, opportunities for contamination are reduced by keeping the necessary manipulations few and simple. Uranium contamination is dangerous from the time of the final rinsing of a dish to the end of fusion; contamination introduced into the dish but not fused in is easily rinsed off, and any contamination occurring after fusion is complete will not be noticed because it will be comparatively non-fluorescent. Because of their small size, the dishes are very easy to keep covered, and similarly the accessory equipment is small and easy to protect from contamination. In all important analyses, except at high levels under optimum working conditions, it is necessary to include blank dishes to determine whether contamination has occurred. Whenever the requirements of the experiment are such that complete randomization is not needed, it is desirable to separate to some extent extremely low level samples from the highest levels. Tests have shown that with careful work, blanks and 1 μg dishes can be run alternately without noticeable contamination, but nevertheless, since the analytical method covers a hundred thousandfold concentration range, it is wiser to avoid this situation when one is particularly interested in high accuracy at the 0.0001 μg level.

4.3 Preparation of Solution. Organic samples are usually ashed, by either a dry or a wet method; if of small bulk they are frequently ashed directly in the platinum dish. Solid inorganic samples are brought into solution in any standard way. If aqua regia or any other substance harmful to platinum is present in large amount in the solution, it should be removed by evaporation or by heating with sulfuric acid before transferring to the dish. Whenever possible, no purification of the solution is employed. When the ratio of impurity to uranium is so high that even after the maximum dilution permitted by the uranium content there is still present a large amount of quencher, it may be necessary to purify to some extent. Probably the most generally useful method of purification is by extraction of the uranium into an organic solvent; [redacted]

When large amounts of heavy metals are present, it is desirable to take as small an aliquot as the uranium concentration will permit in order to reduce damage to the platinum dishes, even when this is not required from the quenching standpoint.

4.4 Dishes. The size and shape of the standard dishes is shown in Figure 8. These are stamped from 20 mil platinum. When they become badly deformed, they are reshaped in the forming die.

The dishes are conveniently held and stored in spot test plates, and are transferred by means of the curved forceps. No identifying marks are made on them; it has proved more convenient to mark their locations on the spot test plate, and then always put them on and take them off the fluorophotometer and the stove in a definite order.

Methods of cleaning dishes are described in Section 4.9.

Preliminary work has indicated that shallow dishes may have important advantages in certain types of work. [redacted] Some are made from 0.0 5" foil, 7/8" by 3/4" and have a circular identification 7/16" in diameter and approximately 1/16" deep at the center. The shallow layer of flux gives less light diffusion and less quenching by light absorption, and the thinner platinum requires less heating, so that the platinum is

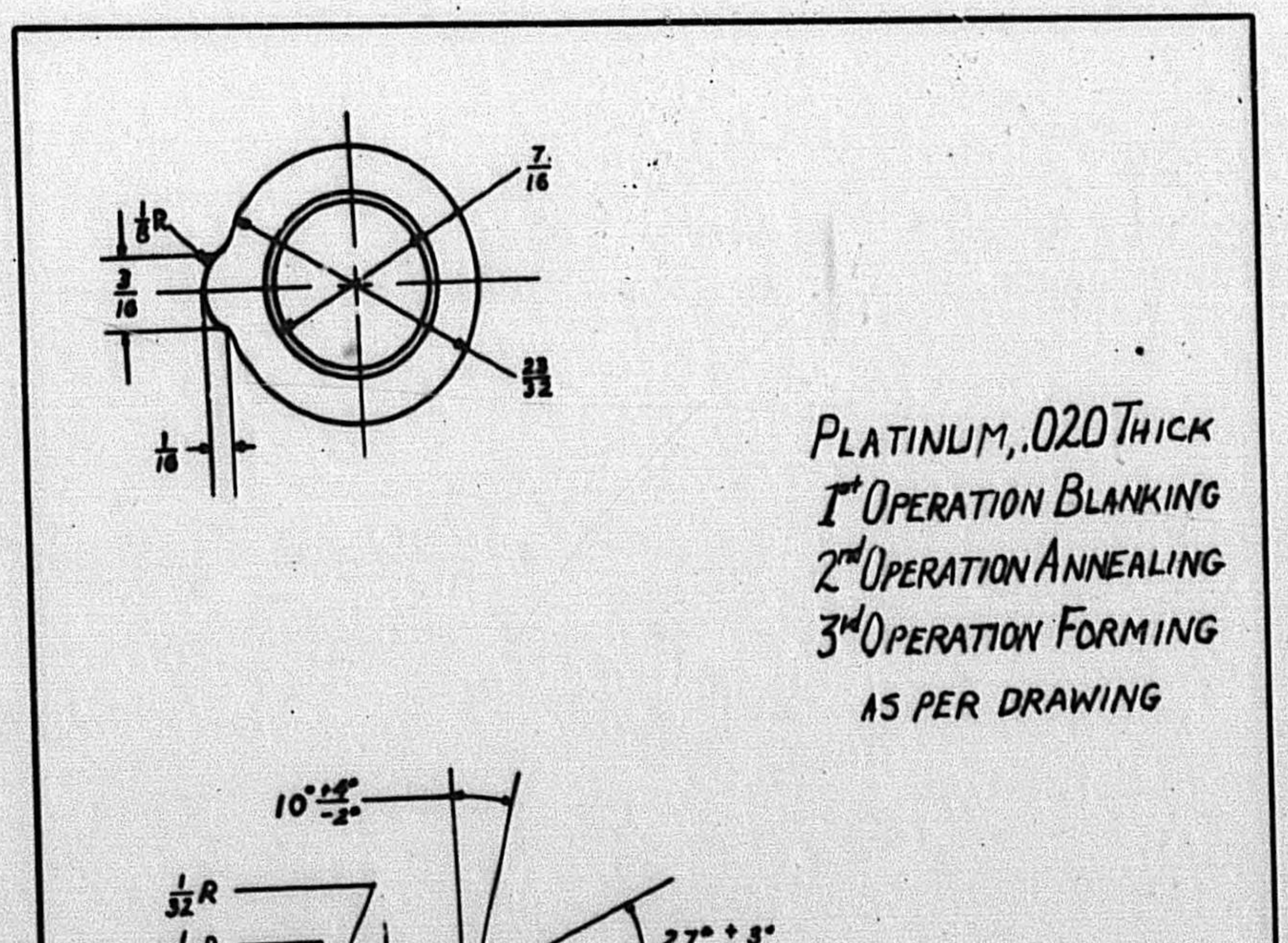

Fig. 8. The Platinum dishes

not discolored as much as with dishes of thicker material. Similar results are obtained with dishes of the same general shape, but made from 20 mil platinum and with smaller rims. However, it is difficult or impossible to "tap out" from these, and there seem to be other inconveniences in handling, so that we are not yet ready to recommend them.

4.5 Pipetting and Evaporating. If hand controlled pipets are employed, the most convenient volume to introduce into the dish is 100 µl; with this size sample it is possible to pipette with 1% accuracy without great care in setting levels and without rinsing. Smaller pipets require greater care, but their use may be simpler than making a dilution. The pipetted solution is evaporated by setting the spot test plate holding the dishes under a heat lamp. If the solution contains substances tending to froth or spatter slightly during evaporation, it is advisable not to have high level dishes on the same spot test plate with low level ones; with ordinary dilute aqueous solutions this precaution is not required.

After evaporation, the sample is treated in the dish by ashing briefly in a flame if it contains much organic matter, or by heating with concentrated sulfuric acid if it contains a high concentration of interfering anions. In heating with sulfuric acid in the platinum dish, it is important to evaporate to dryness before cooling, since the acid has a strong tendency to spread over the rim while the dish cools. With any solution, it is advisable to evaporate completely to dryness before adding sodium fluoride; failure to do this sometimes results in discoloration of the fused preparation.

4.6 The Fusion Material.

(a) Recommended Procedure. The two recommended fusion materials are specially pure sodium fluoride and sodium fluoride mixed with 10% of sodium carbonate (the "10%" mixture). A small amount of the powder is poured into the bottom part of a petri dish, which can then be kept covered by an inverted crystallizing dish. The dispenser is held in the right hand like a hypodermic syringe, and some of the powder is pressed into the tube with help from a spatula in the left hand. The spatula is then held flat against the end of the tube, and the plunger pushed down to compress the powder into a firm tablet. A final tablet volume of about 0.25 ml is desirable; more powder can easily be pressed in if necessary, while if the tablet is too large, the end is readily sliced off by using the edge of the spatula. The properly formed tablet is extruded directly into the platinum dish, as shown in Figure 9.

The "10%" mixture is chosen whenever the sample contains large amounts of non-volatile acidic substances. In NaF, compounds like aluminum oxide and silicon dioxide interfere by forming volatile fluorides that bubble up through the molten flux, but in the presence of a stoichiometric excess of carbonate no such behavior occurs. Carbonate fusion mixtures also are occasionally advantageous when "tapping out" is employed, since they have less tendency to break in this process than does NaF. They always crystallize from the molten state into finer particles than are formed with the pure fluoride; this makes them less transparent, which decreases the effects of quenching by light absorption.

For best results, the sodium fluoride used should contain not more than 5 parts per 10^{10} by weight, of uranium. If it proves impossible to purchase

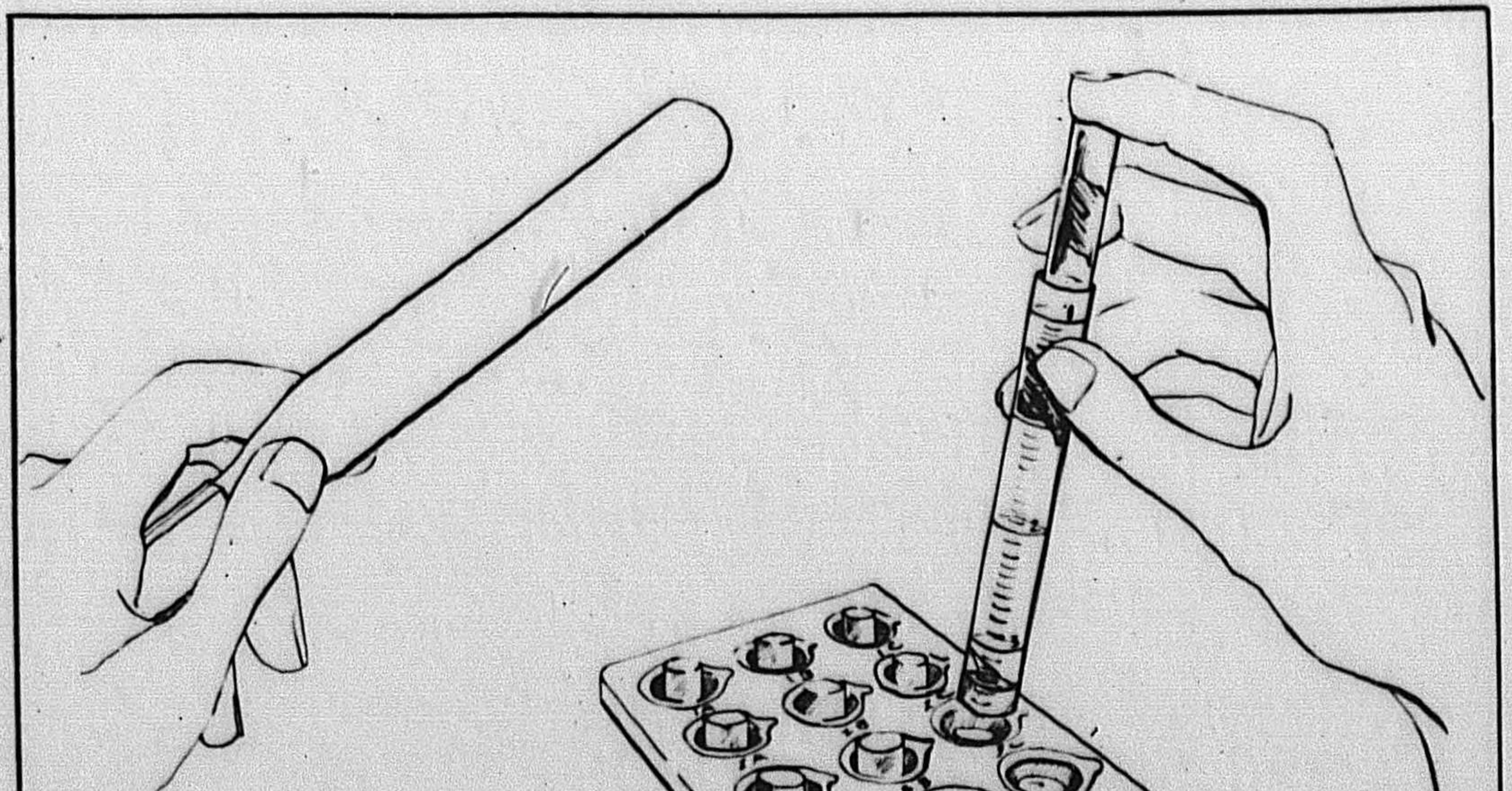

Fig. 9. Using the dispenser to fill the dishes

material this pure (see the data in Table 4, Sec. 3.4), satisfactory sodium fluoride can be synthesized with little difficulty. Hot, nearly saturated aqueous solutions of sodium bromide and potassium fluoride are prepared, with about a 10% stoichiometric excess of the latter. The potassium fluoride solution is filtered, and the filtrate added to the sodium bromide solution until a small amount of sodium fluoride precipitate forms, in order to remove any metals forming highly insoluble fluorides. The sodium bromide solution is then boiled briefly and filtered, and the filtrate is poured while hot into the main portion of the potassium fluoride solution. The precipitate of sodium fluoride is digested, washed thoroughly, collected, and dried. This work should not be done in a locality where uranium contamination is high. Some selection of starting materials in regard to brands and lots may be found necessary, but small amounts of uranium present will tend to remain in solution, since the uranyl ion is strongly complexed by fluoride.(3) If desired, the sodium bromide and potassium fluoride can readily be purified by crystallization.

4.7 Fusion Technique. The two methods in current use for fusing the NaF and the "10%" mixture are "hand fusion" and "stove fusion." The platinum dishes can be held in the flame of a Meker burner with the platinum tipped forceps, or they can be set on the stove with their rims resting on the alundum rod , as shown in Figure 10. The latter method is much the faster since as many as 40 dishes can be prepared at once, but in some cases the stove may be undesirable because of its loud noise and excessive heating effect. With a gas-compressed air flame, great care must be taken to avoid overheating. The thin, non-luminous flame resulting from an oversupply of air causes attack of the platinum by the flux; this is indicated

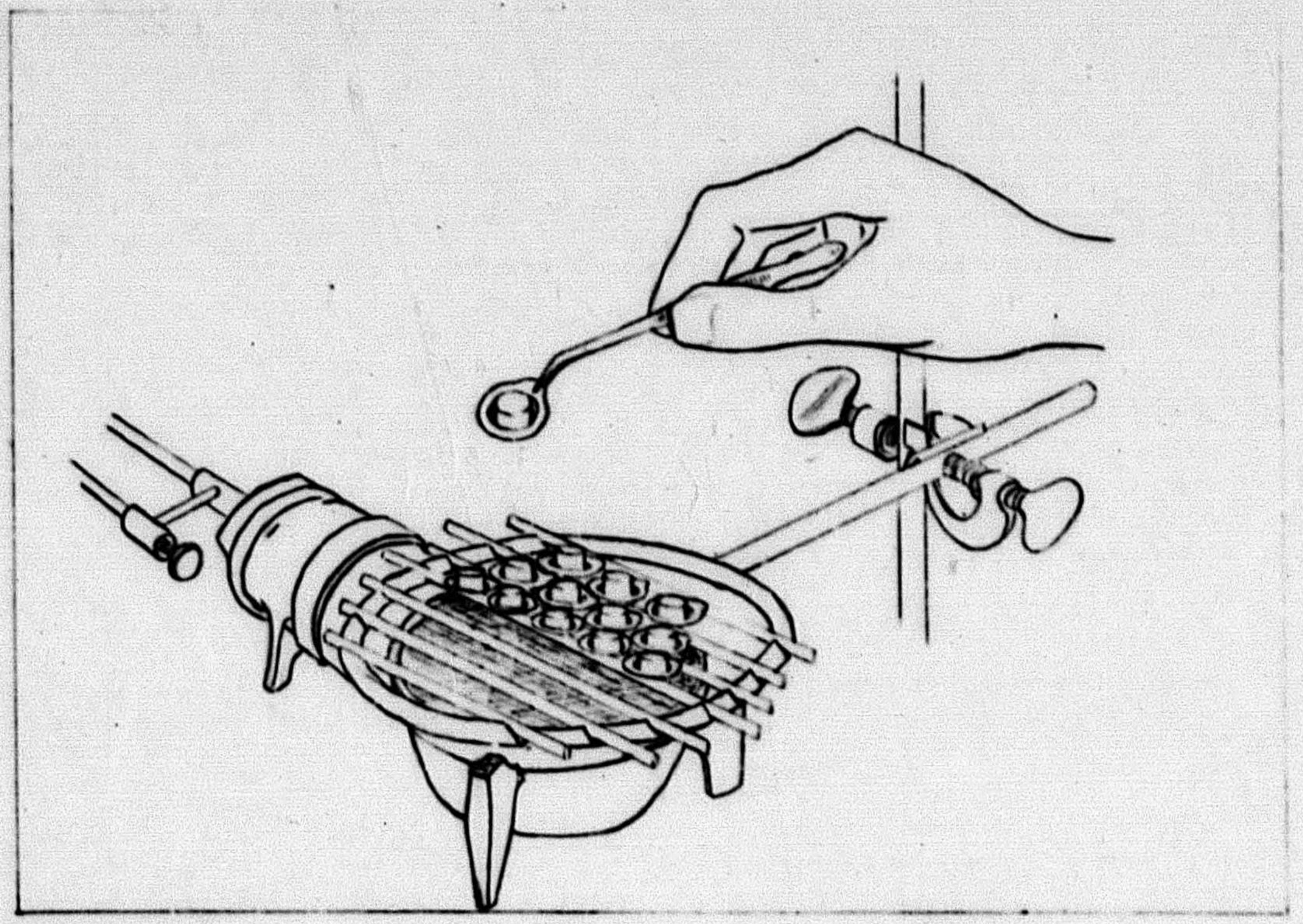

Fig. 10 The Stove

by a yellow, orange, or reddish brown color in the phosphor.

In hand fusions using the platinum tipped forceps a certain amount of manipulation is possible. When the NaF is molten and in a very hot dish, it tends to cling together, so that it is possible by tipping the dish to make the flux flow out on to the rim, pick up any particles stuck there, and then flow back into the center; but if the dish is withdrawn from the flame, the flux has a strong tendency to spread. In all cases, using either stove or hand fusions, it is important to make sure that the flux has been completely melted and that it has spread completely over the bottom of the dish. (In stove fusions one can make the flux spread by turning down the flame for a moment.) A pair of didymium glasses facilitates such observations.

The duration of fusion has not been found to be critical. With hand fusions, because of the time and labor involved, one usually holds the flux molten for 15 to 30 seconds after it has completely liquified; with stove fusions, 5 minutes is the standard fusion time. Long fusions are advantageous when cleaning dishes; and when oxidizable quenchers like ferrous iron are present a long fusion will insure that all samples have been brought to valence state equilibrium. Brief fusions are sometimes employed in very low level work to reduce the amount of contamination introduced from the dish. A marked enhancement of fluorescence is obtained when a fused dish is partially remelted and allowed to cool slowly; this occurrence should be avoided.

4.8 Preserving and Reading the Phosphor. The cooled dish can be put directly into the holder of the fluorophotometer, the reading taken, the average value of the blanks subtracted, and the difference multiplied by the proper calibration factor, to give the uranium content of the dish. Since impurities present in the sample being analysed frequently deposit on the bottom of the dish in fusion, to cause variation in the amount of ultraviolet and of fluorescent light reflected from the dish bottom, greater accuracy can be obtained by removing the phosphor from the dish in which it was fused and mounting it in a black, non-fluorescent dish. The effect of light absorbing substances on the dish bottom is more pronounced in NaF than in mixtures containing carbonate, and more pronounced in hand fused NaF than in stove fused.

Removing the phosphor is more conveniently done by "tapping out" by turning the dishes upside down in the spot test plate, grasping the bottom with the curved forceps, and tapping lightly a few times against the indentation in the plate. With NaF, stove-fused preparations usually drop out without trouble, but a hand fused one may break if it contains too little flux or is cooled too slowly. Also, the presence of impurities may have a marked effect on "tapping out"; for example, iron and columbium make the process more difficult, while with aluminum present the phosphor frequently falls out by itself. With fusion mixtures the "tapping out" procedure is almost invariably successful, except in the presence of large amounts of substances that collect at the bottom and stick to the dish.

If possible, because of "blank rise", dishes should be read immediately after the conclusion of fusion. Low level dishes that cannot be read immediately, are brought back to their original readings by heating strongly. The standard procedure is to heat for about 50 minutes in a muffle furnace at 500°C, or to heat on the stove or by hand to bright red incandescence.

Storage in a vacuum desiccator does not remove the necessity for reheating.

4.9 Dish Cleaning. The recommended procedure is to remove the flux by "tapping out", or by heating in concentrated sulfuric acid in a platinum evaporating dish. The dishes are then put in a small beaker and boiled for a few minutes in about 6 N hydrochloric acid, with occasional stirring to separate them from each other, and then they are boiled in a mixture of 10% concentrated hydrofluoric acid, 70% concentrated hydrochloric acid, and 20% water in a platinum dish. They are thoroughly rinsed, and dried on the stove. The dry dishes still on the stove are filled with NaF by the usual procedure, and then fused for about 15 minutes. They are then read in the fluorophotometer without "tapping out", and divided into groups according to the amount of fluorescence found. All dishes are washed with hydrochloric acid and dried as before, but the more contaminated ones are retreated as many times as is necessary to make their reading sufficiently low. In the case of particularly refractory dishes, and where foreign metals have alloyed with the platinum, cleaning with sea sand and steel wool and with nitric acid is recommended. Other procedures occasionally useful include fusion with pyrosulfate, and bathing the whole dish in a low melting fluoride-carbonate mixture in a platinum evaporating dish.

4.10 Correcting for Quenching. The two principal methods of treating quenching are dilution by taking a smaller aliquot, and 'spiking' by addition of a known amount of uranium to determine the magnitude of quenching so that it can be corrected for mathematically. Both of these methods depend upon the fact that, as was shown in Section 3.6, under proper conditions of analysis quenching is not a function of the uranium concentration.

Quenching should be expected whenever there is a large residue of solid matter in the dish after evaporation of the solution, the flux is not pure white after fusion, the bottom of the dish is strongly colored after removal of the phosphor, and whenever the amount of fluorescence found falls on the non-linear portion of the calibration curve (see fig. 3). The occurrence of quenching can be determined with certainty by "spiking" or by making a dilution and finding whether the fluorescence is proportional to the concentration. When the general composition of the sample is known within rough limits, one can predict whether dilution or "spiking" will probably be necessary. The data in Section 3.6 will be helpful here.

When there is reason to expect quenching, one should take as small an aliquot as the uranium concentration permits without reaching the level where the analysis becomes more difficult and less accurate. (Detection of 0.01 µg per dish is routine; 0.001 µg requires some precautions for best accuracy; at the 0.0001 µg level great care is necessary to obtain a standard error as low as 20%.) When the uranium concentration has been reduced as much as is expedient, and quenching is still found, it is necessary to "spike" the sample. For "spiking" one uses separate dishes, usually some that are too contaminated to permit their use in low level work. One microgram samples of uranium (If the uranium level in the sample is sufficiently low, use of a 0.1 µg "spike" will contaminate the dish less) are pipetted into these dishes and evaporated, and then portions of the unknown solutions are added, with precautions to avoid contaminating the solutions with the uranium in the dishes. Or, the order of addition can be reversed if care is taken not to contaminate the uranium solutions. After the solution in the dish has been re-evacuated, the flux is added and fused by exactly the same procedure as with the corresponding "unspiked" dishes. Results are evaluated by the following equation:

$$\mu g \text{ U in aliquot} = AS/(D-A) - B/C^{*}$$

Here A is the fluorescence reading for the "unspiked" sample, and D is the reading for the "spiked" sample. B is the average fluorescence reading of the unquenched blanks being run at the same time; and C, is the reading for 1 μg of uranium under the fusion conditions employed, and in the absence of quencher; and S is the number of micrograms of uranium in the "spike". In the equation it is assumed that the fluorescence of blanks is quenched in the same manner as uranium fluorescence. In order to decrease the effect of an error in the determination of A, it is advisable to keep the amount of uranium in the aliquot from the sample below 0.1 μg, if a 1 μg "spike" is used. The equation for the determination of ϕ from a "spiking" experiment is:

$$\phi = (D-A)/C$$

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[*] The corresponding equation for an ordinary analysis without spiking is:

$$\mu g \text{ U in aliquot} = (A-B)/C.$$

5. Discussion

The most interesting observation about the work that has been described is the unexpected complexity of the fusion process. It has repeatedly been found that factors one would expect to be important are unimportant, and factors that appear trivial have turned out to be crucial. Probably the best example of this is found in the formation of brown spots on the bottom of the platinum dish. Fifteen second fusions and thirty minute fusions, hand fusions and stove fusions, small amounts of flux or large amounts of flux, gradual heating or strong heating, heating from below or turning the flame down from above, dishes of 5 mil platinum or dishes of 20 mil platinum, all have little or no effect; but simply changing the depth of the dish by a factor of 2 gives a profound difference in the formation of brown spots.

In our last major report on the general analytical method, we listed certain problems to be worked on, including fusion in muffle furnaces and the construction of an improved fluorophotometer. Almost two years have passed, and both problems are still being studied, though at a considerably advanced stage.

What changes in methods and what increase in accuracy and speed will result from the work now in progress is impossible to predict. It is hoped that the accuracy and precision will improve very substantially. However, because of the long interval and because of the various reports from other laboratories which are not in agreement with our results, it has seemed best to publish at this time the material available.

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ANL-4002 ADDENDUM
Chemistry - General

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ADDENDUM TO "THE FLUOROPHOTOMETRIC DETERMINATION OF URANIUM"

by George R. Price, Renato J. Ferretti, and Daniel Williams

September, 1947

HEALTH DIVISION

Report Received: October 22, 1947
Issued: November 7, 1947

Operated by the University of Chicago
under
Contract W-31-109-eng-38

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ADDENDUM TO "THE FLUOROPHOTOMETRIC DETERMINATION OF URANIUM"

Work done by: George R. Price, Renato J. Ferretti, and
Daniel Williams

Written by: G. R. Price

Since the writing a brief study has been made of the effects of fusing uranium fusion materials in different types of atmosphere. The results appear to be so interesting and important that we think it worthwhile to report them now, even though the work is far from having been completed. In this paper we also list several miscellaneous additions and corrections and we suggest a number of studies that we believe should eventually be made.

1. Fusions in Various Gases

Equipment used was a resistance type tube furnace and an induction heater.* In all experiments the flux was contained in the usual platinum dish, so that with the induction heater the heat was generated by currents in the dish. In the room with the resistance furnace, thoroughly purified helium was available, while the induction furnace had the advantages of rapid heating and excellent visibility.

Sodium fluoride fused in the induction furnace in an atmosphere composed of the gases from the flame of a Meker burner had the appearance and gave (with uranium added) the fluorescence of a dish hand-fused in a Meker flame in the ordinary way. Sodium fluoride fused in either furnace in an air atmosphere (wet or dry) had the typical yellow-brown color

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*We are indebted to Mr. Sidney Gaarder for the use of the former, and to Dr. Robert Thorn for the latter.

found when dishes are fused in an air atmosphere in a muffle furnace. The brown color also appeared in dishes fused in an atmosphere of commercial oxygen, but it did not appear under any conditions when oxygen was not present, as in atmospheres of helium, carbon dioxide, and water. This means that the reason the yellow-brown color was always found in muffle furnace fusions was that the oxygen concentration in the air and the oxidizing strength of heated air is much greater than that of the so-called "oxidizing" flame.

Sodium fluoride dishes fused in a helium atmosphere were always completely colorless, and if they were cooled sufficiently slowly it possible to obtain clear discs that were single crystals. After fusion in helium, the bottom of the platinum dishes were always found to be clean in appearance. Sodium fluoride preparations containing uranium gave the same fluorèscence spectrum when fused in helium as when fused in a flame, even in one experiment where helium was employed that had been purified by passing through concentrated sulfuric acid, over hot copper turnings, through a phosphorus pentoxide tube, through two tubes full of hot uranium turnings, and through a liquid nitrogen trap. (The uranium in this and in all other experiments described here had been added to the dish as uranyl nitrate.) A single dish containing uranium in "10%" mixture was fused in the highly purified helium; this gave a fluorescence unlike any we had seen before. In addition to the usual bands found in the ordinary NaF-U preparation, this had two bands to the violet side of the 555 mμ band, that were approximately of the same intensity as the 555 mμ band. The result was that the disc was of a purer, less yellowish green than the usual dish. No further investigation of this phenomenon was made. A brief study of the reproducibility obtainable with the clear, single-crystal phosphors, showed that the precision of the fluorescence measurements was far lower than in the usual micro-crystalline dishes. (This, and all fusions described <u>infra</u> were made with the induction furnace.)

The brown color produced by fusion in the presence of oxygen can in most cases be removed by refusing in the absence of oxygen. A plausible hypothesis is that the yellow-brown is due to a platinum compound resulting from chemical interaction between the dish, the flux, and oxygen, and that the disappearance of the color on refusing under proper conditions is due either to volatilization of this compound or to its reduction. To test this, an experiment was performed with six sodium fluoride dishes containing no uranium. Four of these were fused in moderately damp oxygen to yield a yellow color, and the remaining two were fused in helium. Then two of the yellow dishes were refused in helium until they were white. All six discs were analyzed spectrographically for platinum.* No platinum was found in the two discs fused only in helium, while platinum was present in all the others. The difference between the two fused only in oxygen, and the two fused both in oxygen and helium was not significant.

With rapid heating, it was possible to obtain pure white dishes by fusing in an atmosphere of unburned Chicago cooking gas. (Chicago gas is a mixture of 45% coke oven gas and 55% natural gas. Composition is 0.1% of carbon dioxide, 1.5% of illuminant, 0.3% of oxygen, 2.6% of carbon monoxide, 26.2% of hydrogen, 54.1% methane, 7.8% of ethane, and 6.1% of nitrogen by volumetric analysis.) When the heating was too slow, a considerable amount

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*We are indebted to Mr. James Brody for this work.

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of carbon was deposited. Dishes containing uranium gave the usual fluoresence when fused in the unburned illuminating gas. In experiments with mixtures of air and illuminating gas, it was found that the ratio of air to illuminating gas controlled the tendency of the sodium fluoride to spread evenly over the dish. In pure illuminating gas, the molten flux usually formed a clump at the side of the dish. When air was added, the flux would spread over the entire dish bottom. If the air was then cut off, the sodium fluoride would immediately draw together again on the side of the dish. It was possible to repeat this procedure indefinitely. This experiment thus explains the observations regarding spreading of the flux that we reported in Sec. 4.7 of the main report.

It was reported that covered dishes fused in a muffle furnace were clear and colorless, but non-fluorescent. Another condition has been found that gives colorless non-fluorescent dishes, though not with very large crystals. This is fusion in a carbon dioxide atmosphere. Sodium fluoride dishes fused in carbon dioxide never have more than a weak fluorescence. As with the dishes fused, covered, this fluorescence can be brought up to normal by refusing under any conditions that oridinarily give fluorescence. Also, fluorescent dishes are quenched by refusing in a carbon dioxide atmosphere. A "10%" dish fused in carbon dioxide had the usual strong fluorescence. The following hypothesis was developed: that the CO_2 quenches by its acidity refusion causes volatilization of the CO_2 and thereby removes the quenching the "10%" dish was not quenched because it was too basic. The experiments summarized in Table 1, which were designed to test this hypothesis, showed that it was incorrect. The correct explanation of the quenching effect of carbon dioxide is not known.

TABLE 1
EFFECTS OF FUSION IN CARBON DIOXIDE ON THE FLUORESCENCE OF SODIUM FLUORIDE DISHES CONTAINING ONE MICROGRAM OF URANIUM

Conditions of Fusion	Fluorophotometer reading	Ml. of HCl/g of NaF to Titrate to pH 6.0
Fused in CO_2; annealed slowly	670	1.5
Fused in CO_2 twice	100	2.5
Fused in CO_2; refused in He	7600	1.7
Fused in exhaust gases from Meker flame	7100	3.5
Fused in flame exhaust gases; refused in CO_2	370	4.2

The production of titratable base seems to be correlated to some extent with the presence of water in the atmosphere. In several experiments in which the atmosphere was carefully dried, it was found that comparatively little titratable base was produced. Similarly, in one experiment in which a NaF dish covered loosely with a silica plate was fused in thoroughly dry air, there was no etching of the silica except at one point where it came in contact with the molten flux.

In most of the experiments, even in an atmosphere of helium, the usual bubbles were seen on the bottom of the platinum dish. In testing the hypothesis that these were due to gases mechanically trapped within the sodium fluoride, we found that breaking up the pile before fusion greatly decreased the number of bubbles. Breaking up the pile also decreased a very troublesome tendency of the sodium fluoride to creep over the rim of the dish when it melted in a helium atmosphere. (Thorough drying of the sodium fluoride likewise decreased this tendency.) Even when many bubbles were seen on the bottom of a dish fused in a helium atmosphere, the dish bottom would not be found to be discolored; and a dish fused first in air or in a flame exhaust and then refused in helium would have a clean bottom.

With a helium atmosphere in the induction furnace, it was readily possible to volatilize the sodium fluoride without apparent decomposition. In an experiment in which weighed amounts of sodium fluoride were boiled off from a dish containing uranium, and then repeatedly replaced with fresh sodium fluoride and boiled down again, it was found that little or none of the uranium volatilized.

F. Miscellaneous Additions and Corrections.

3. We wish to add to our survey of work at other laboratories by mentioning the excellent studies of E. Rona on uranium in sea water and

in marine organisms. Using a spectrographic method similar to that of Hernegger and Karlik, she achieved amazingly high precision. (Yr.Bk. Amer. Philos. Soc.--for 1943, 136-8 (1944); ibid for 1945, 143-144 (1946).

5. Study of a later lot of General Chemical Co. sodium fluoride has not indicated that the trend shown

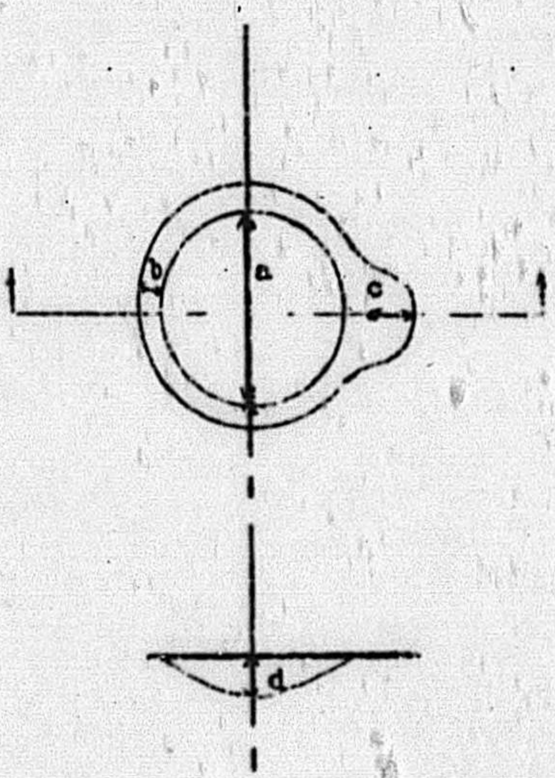
continuing.

6. In stove fusions in the deep style of platinum dish (as shown in Fig. 8. of the main report), it has been found that breaking the pile into smaller particles after it has been dispersed into the dish, results in the formation of fewer bubbles on the bottom of the dish and, consequently, a cleaner dish bottom. The hypothesis proposed is that the bubbles are ordinarily trapped under the pill and against the wall of the dish. In the shallow style dish, because of the gradual curvature and the absence of a vertical side wall, there is far less opportunity for such occlusion. The alternate hypothesis given on

7. More explicit instructions for "spiking" are desirable. The standard procedure is as follows. Take 4 dishes of identical shape, and pipet 1 µg of uranium into each of two of these, and evaporate to dryness. The unknown solutions should be sufficiently dilute so that not more than 0.1 µg of uranium is contained in the aliquot used. The

two "unspiked" dishes are pipetted first, and then one of the "spiked" dishes. The pipet is washed (unless it is unnecessary to avoid contaminating the unknown), and the remaining dish is pipetted. The usual number of blanks (depending on the sensitivity required) are included.

8. The question of the relative merits of shallow and deep dishes has not yet been settled nor will it be possible to obtain a final answer until the question of which fusion method to employ (hand, stove, or furnace?) has itself been settled. The style of shallow dish that we have standardized on is stamped from 10 mil platinum in the shape shown below.



a = 7/16"
b = 1/16"
c = 1/8"
d = 1/16"

Scale (2x)

3. Discussion

The most important consequence of the work described in this addendum is that it demonstrates the possibility of successfully fusing NaF and "10%" dishes in a muffle furnace. Use of a muffle furnace in fusion would be expected to have several advantages over stove fusion. There would be less noise, less heat liberated in the room, fewer contamination problems, and greater possibilities of precise control. What type of atmosphere to use in a furnace, cannot be decided without further work. It seems certain that use of an atmosphere of burned cooking gas would give all the advantages of fusion in an open flame, minus a few of the disadvantages. An atmosphere of pure helium, on the other hand, might prove very unsatisfactory under some conditions. Thus, if uranium were added to the dish in some form other than as a uranyl compound it might not fluoresce when fused in a helium atmosphere. Also, there might be trouble from other metals, not being in their highest oxidation states. For example, ferrous iron quenches more strongly than ferric, and manganese may cause fluorescence when it is in the plus two state. Finally, in a low oxygen atmosphere there is the problem of getting the sodium fluoride to spread properly. Some oxygen, then, is probably desirable in fusion, but too much oxygen will cause brown spots on the dish bottom, even when the concentration is not high enough to cause a yellow color in the flux. A possible solution may be to heat first in an atmosphere containing a fairly high amount of oxygen, and then finish the fusion in an atmosphere with no oxygen.

In addition to the problem of determining the proper oxygen content of the atmosphere, there is the question of what type of crystal structure to produce. One can obtain anything desired from a clear single crystal to the extremely fine white powder given by many fusion mixtures. In pure sodium fluoride, the fineness in crystal structure depends on the rate of cooling and on the decomposition (increase in base) occurring in fusion; the latter effect is not reversible by simply refusing. For work of high precision, one should certainly aim always to obtain the same fineness of subdivision, and probably the most satisfactory state is somewhere between the two extremes. With single crystal discs, much of the fluorescence is imprisoned within the crystal by total reflection and can escape only at cracks or other irregularities. This means that the intensity of fluorescence depends very markedly on the presence of a small number of imperfections, and the precision is consequently very poor. In discs with fine crystal structure, little ultraviolet light will penetrate to the bottom. This will be desirable to some extent in that it will eliminate the effects of spots on the dish bottoms, but it will have such undesirable effects as making the intensity of the measured fluorescence depend strongly on the thickness of the disc. When light goes through the disc with only a very slight diminution in intensity, a small change in the thickness of the disc or in the amount of light scattering will have little effect on the fluorescence, but when light penetrates only a short way into the disc, such small changes may produce pronounced effects. A simple method for roughly measuring the penetration of light into a disc is to read a "tapped-out" disc in a dish with blackened bottom and then in a dish with shiny bottom; the ratio of these two readings may prove useful as a correction factor. (Of course it is also an indicator of the presence of quenching by light absorption.)

Use of controlled atmospheres in fusion can also be used to throw some light on questions relating to the nature of the fluorescence in fluoride mixtures. For example, by fusion of uranium compounds containing no oxygen in an atmosphere completely without oxygen, one could learn more about whether or not the uranium in the NaF-U is in the uranyl form. The best choice of uranium compound for such an experiment--though not the easiest to use--would be the hexafluoride. Other possible studies of interest growing out of the work described in this paper include investigations of the quenching effects of carbon dioxide and fusion in a covered container, the unusual spectrum found in the "10%" dish fused in helium, and the absorption spectrum of uranium in the clear discs.