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THE QUENCHING ACTION OF PLUTONIUM
AND IRON ON THE FLUORESCENCE OF URANIUM IN
SODIUM FLUORIDE PHOSPHORS

by

G. N. WALTON
G. HUTTON
J. A. W. DALZIEL

A.E.R.E. C/R 966

ABSTRACT

The effect of plutonium and iron on the fluorescence of uranium in sodium fluoride melts illuminated by UV light, has been measured over a wide range of concentrations.

The transmission of sodium fluoride to UV light at different wavelengths shows that sodium fluoride alone, and also when containing iron, has no absorption bands. Sodium fluoride containing uranium has a wide absorption band in the UV. Iron, however, has a strong quenching action and it is proved that iron does not quench by light absorption. It is also shown that the spectrum of the enhanced fluorescence of uranium does not change in the presence of small amounts of iron and it is concluded that the initially excited states of uranium, and not the metastable fluorescent state, are subject to quenching by iron.

Merritt's theory for uranium fluorescence is amplified with reference to Förster's theory of resonance transfer, and the experimental quenching curves are interpreted on the basis of energy transfer and light absorption. The distance of energy transfer is calculated to be of the order 100\AA . Förster's theory is criticised in that it fails to predict self-quenching.

The absence of detectable fluorescence in plutonium compounds is discussed.

A.E.R.E. Harwell
30th July, 1952

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1. INTRODUCTION

The purpose of this report is to study the fluorescence of uranium in a flux of sodium fluoride⁽¹⁾ containing plutonium. Iron was found to simulate plutonium, and this was used for more extended measurements.

(a) Absorption and Fluorescent Spectra of Uranium

The absorption and emission spectra of uranyl compounds has been attributed to the U-O bonds in the UO_2^{++} ion and the spectra of certain crystalline uranyl salts at low temperatures has been worked out in full detail on this basis⁽²⁾. Absorption lies in the region 3400 - 5000 Å and arises from electronic excitations from the vibrational levels of the ground state to those of several higher states. Emission lies in the region 4700 to 6000 Å and arises from a single electronic shift from bond vibrational levels in the first excited state to those of the ground state. After removing the exciting light the emission shows phosphorescence and decays exponentially with time constants of the order 10^{-4} secs. Dicke (2, pg. 42) points out that "the mechanism of the change from the various excited levels to the initial state of the fluorescence has never been studied in detail. There is little doubt that it is caused by interaction with the crystalline field." The excess energy is probably transformed into heat and the transfer must be rapid in comparison with the time of fluorescent decay of the metastable state.

(b) Comparison of Plutonium and Uranium

The plutonyl ion PuO_2^{++} , apart from nuclear differences, only differs from the uranyl ion UO_2^{++} in possessing two additional electrons which it is usually suggested lie in the inner 5f shell. As pointed out by Kroger (3, pg. 52) it might be expected that fluorescent effects would arise from the plutonyl ion itself, both by analogy with the uranyl ion, and by analogy with rare earth ions which have 4f electrons. In solution, plutonyl compounds absorb light over a similar spectral region to uranyl compounds. This absorption has been attributed to Pu-O-bond vibrations analogous to the U-O bond vibrations⁽⁴⁾. There is for plutonium an additional high absorption peak at 8300 Å which is attributed to excitation of the 5f electrons, by an analogy with the 4f absorption peaks in rare earth solutions⁽⁴⁾. However no fluorescent emission spectrum analogous to that for uranium has been found for solutions or crystals of plutonyl compounds, although an extensive search has been made by G. R. Price⁽⁵⁾. Conditions investigated included those of fluoride and carbonate melts similar to those in which the enhanced fluorescence of uranium is observed. The U^{4+} ion shows no fluorescence and in fact appears as a quencher of UO_2^{++} fluorescence, and the stable form of plutonium under some conditions is Pu^{4+} . However Price took account of all the common forms of plutonium including PuO_2^{++} during his measurements. Again no fluorescence due to plutonium has been observed in the experiments here reported, although no search has been made under conditions different from those under which uranium can be measured.

Recently J. K. Dawson⁽⁶⁾ has found that magnetic susceptibilities of certain PuO_2^{++} compounds favour the 6d and not the 5f configuration for the extra electrons. This destroys to some extent the similarity between UO_2^{++} and PuO_2^{++} , and between plutonium and the rare earths, and makes the absence of fluorescence less unexpected. The absorption peak at 8300 Å however remains.

The absence of fluorescence suggests that excited states of plutonium ions are not metastable, or that they can transform their energy into heat more rapidly than they can transform it into light. As shown below plutonium is a highly efficient quenching agent for uranium fluorescence (it falls into the "strongest interference"

class in the classification suggested by Zebroski and Newton⁽⁷⁾, and this may be precisely because it can transform absorbed light into heat rapidly.

(c) The Comparison of Uranium Phosphors with other Phosphors

Pringsheim⁽⁸⁾ places fluorescent melts containing traces of uranium "rather in the class of impurity activated phosphors." The latter include the fluorescent effect of thallium in potassium chloride crystals, of traces of chromium on the colour development of rubies and other gems, and the effect of impurities on the "short" fluorescence of zinc sulphide. This analogy has not been formerly emphasised, but many similarities appear.

The outstanding similarity is that a very small trace of impurity causes a marked effect throughout the whole of the base material. The colour of natural rubies is due to chromium or manganese in amounts of the order of 1 p.p.m. in otherwise colourless alumina. A second similarity is that the effect becomes less marked as the concentration of the impurity becomes appreciable. The linear relationship between fluorescence and uranium content of melts ceases to hold for amounts greater than about 20 p.p.m. and fluorescence decreases above about 2% (see Figure 12 and Ref. 17). Similarly the linearity of fluorescent quantum yields of thallium in potassium chloride drops above concentrations of 1%, and of the fluorescence of bismuth in calcium sulphide above 50 p.p.m. (Ref. 8, pgs. 589, 591). When the base materials are removed and only the pure salts are considered the fluorescence per atom becomes relatively small in UO_2F_2 and $TlCl$ and almost nil in chromium and bismuth salts.

Details of the spectral bands also show similarities. The ruby absorption and emission spectra have the same appearance as those of uranyl salts. They both have a long absorption spectrum with a short overlapping fluorescent spectrum which appears mirrored round a high peak. Spectral bands shift radically in intensities at different wavelengths from those of the pure salts to those of fused melts. As stated above the emission of uranyl solutions is mainly between 4700 and 6000 while that of uranium in sodium fluoride does not extend below 5300 and continues into longer wavelengths (8 pg. 498). For thallium chloride, while the absorption bands for the pure salt, for the solution in concentrated halide, and for the crystal phosphor, are all in the same region (3 pg. 55), the fluorescent emission shifts from a vague maximum at 3700 Å from the pure material to the region of 4500 and 4900 Å in the alkali halide phosphor.

(d) Migration of Excitation Energy

N. Riehl (Ref 11, pg. 135) in his paper on "New Results with Zinc Sulphide" shows that activation energy can be transferred from atom to atom in a luminescent material. In zinc sulphide activated by 100 p.p.m. of copper and irradiated by α particles, nearly 100% of the kinetic energy of the α particles is finally converted into light which has the copper atom spectrum, while most of the kinetic energy must have been delivered initially to the zinc and sulphur atoms in the path of the α particle. Similarly in excitation with ultra violet light the fluorescent quantum yield is sometimes claimed to be nearly quantitative⁽⁸⁾. Riehl states "the energy sent in is absorbed by the whole zinc sulphide lattice, and only after this is it transferred to the bodies which are capable of shining, i.e. to the activating atoms".

i) Excitation of Base Materials

In recent literature it appears that two theories for the migration of excitation energy are being developed. The earlier is called the exciton effect as discussed by Frenkel in 1936⁽¹²⁾,

by Goodeve (11, pg. 135, 13), and more recently by Seitz⁽²¹⁾. Apker and Taft and others^(22, 27) have recently claimed direct evidence for the exciton effect in the irradiation of alkali halide crystals with U.V. light. The energies of the photo electrons produced have been measured and they appear in two groups, one attributed directly to U.V. light quanta, and the other attributed to excitation of the crystal lattice, i.e. to "excitons". It might be expected that this effect in alkali halides would be very relevant to uranium fluorescence in sodium fluoride. The solids used by Apker and Taft, were potassium and rubidium bromide and iodide in which "F" centres⁽²¹⁾ had been specially induced and which show light absorption bands in the U.V.

Experiments have been made to find out if pure sodium fluoride melts prepared as in measurements of uranium fluorescence show any light absorption bands. The light from an iron spark was transmitted through a flake of fused sodium fluoride held against the slit of a spectrograph. The intensities of the lines transmitted compared with those of the spark direct (as described in the experimental section below), are plotted in Fig. 1. The sodium fluoride was almost opaque and the exposure necessary for the transmitted light was about 200 times longer than that for the untransmitted light. Nevertheless Figure 1 shows that there are no absorption bands. The light is evidently reduced by scattering i.e. multiple refraction and reflection in the mass of crystals, and only a small fraction diffuses through. At lower wavelengths the multiple refraction would be expected to be greater than at higher wavelengths and this would give rise to the small apparent absorption at low wavelengths as shown in Fig. 1. Thus there is no mechanism by which the light can cause excitation of the sodium fluoride lattice by itself. When uranium is present it might be supposed that the light energy is fed into the lattice via the uranium ions as "active centres". If enhancement were due to such a "feeding" effect it should over some range be dependent on the uranium concentration squared, and it is difficult to see how the linear relationship observed experimentally, (Fig. 12) arises. Also if enhancement was associated with excitation of the base material itself, it would be expected to be very dependent on the type of base material, whereas in fact it is not restricted to sodium fluoride melts but also occurs in borax beads, phosphate and carbonate melts, with relatively minor alterations. We conclude that excitation effects in the base material are not relevant to uranium fluorescence.

ii) Resonance Transfer

Merritt in 1926⁽¹⁷⁾ suggested that enhanced fluorescence of diluted uranyl ions is due to the fact that the uranyl ion is isolated in the fluoride lattice and does not lose excitation energy except by fluorescence or by transfer to a neighbouring quenching atom or ion. A recent theory called "resonance transfer" has been reviewed by J. Franck and Livingstone⁽¹⁴⁾ and by E. J. Bowen⁽¹⁵⁾. Direct evidence is found in the fluorescent light from mercury vapour containing small amounts of sodium vapour, where it is the latter that emits light absorbed by the former. A similar effect is observed in anthracene crystals containing small amounts of naphthalene. Further evidence is obtained from the concentration depolarisation of polarised light by fluorescent dyes in solution which appears to be explicable only by supposing that the energy has migrated through several molecules randomly distributed. The effect is distinguished experimentally from the mere absorption and re-emission of fluorescent light by a study of the extinction coefficients involved.

It does not yet appear whether "excitons" and "resonance transfer" are two aspects of the same phenomenon. In the theoretical treatment the former is regarded according to a very recent paper by Heller⁽²⁷⁾ as an interaction between the excited centre and electrons in the lattice surrounding it, whereas the latter is an interaction between different centres with matched, or nearly matched, energy levels.

Förster^(16,19) has discussed the resonance transfer effect theoretically. His theory has not been published outside the German literature, and a brief summary is given in Appendix 1.

Experiments have been made to find out if such a theory is relevant to the quenching effects observed in uranium fluorescence. Figure 6(a) compares our results for the apparent self quenching by uranium, with the quenching by iron. Quenching sets in over the same concentration range but the initial slope shows that iron is more efficient at quenching than is uranium. Figure 2 shows different exposures of the iron spark spectrum, first alone, then through sodium fluoride containing 830 p.p.m. of uranium (0.01 Molar) and again through sodium fluoride containing an equal weight of iron (0.04 Molar). The uranium melt spectrum shows high absorption in the U.V. below 4000Å° (together with some enhancement in the visible at 5500Å° due to fluorescence). While it was not possible to obtain absolute values for the extinction coefficient it does appear that light absorption by uranium might be sufficient to explain the self quenching shown in Figure 6; which is the conclusion reached by Merritt⁽¹⁷⁾. The sodium fluoride containing iron, however, shows no such comparable absorption in the U.V. or in the visible. Thus while iron quenching is initially greater than uranium self quenching, iron light absorption is much less than uranium light absorption, and this is proof that iron quenching is not due, as was formerly supposed by Price⁽¹⁾, to light absorption.

Ferric chloride and sulphate in solution show very high absorption in the U.V. below 3600Å° . Fluoride ions, however, complex iron and decolourise ferric solutions. Figure 3 shows a comparison of the absorption in ferric sulphate solutions at a concentration of 0.018M as obtained in a spectrophotometer, with and without added sodium fluoride solution. The latter suppresses the U.V. absorption (prior to fluoride precipitation) to very low wavelengths and this supports the evidence of Figure 2 obtained with the spark spectrum transmitted through fluoride melts.

Figure 6 is again significant in that increasing concentrations of both plutonium and iron quench some of the fluorescence, but not all of it. If the quenching were due to a mechanical effect such as increased light scattering by crystal size reduction, or to a chemical effect of a compound formation, no such sharp change in slope in the concentration quenching curve would be expected. A possible explanation is that the maximum solubility of the iron in the flux is reached at the point of inflexion. However the melts only began to appear inhomogeneous during fusion at very much greater concentrations of quencher. No inhomogeneity could be seen at the lower concentrations when melts were examined between slips of quartz in a polarising microscope, (which might be expected to show up any non cubic crystalline phase). We propose the explanation that some excited states of uranium are quenched, while others are not quenched. Figure 4 shows the spectrum of the mercury lamp used in the fluorimeter and Figure 5 shows the transmission curve for the U.V. filter used. These show that several wavelengths may be involved in the initial excitations between 3000 and 4000Å° .

Experiments were made to see if the quenchable states could be identified. Quenching must occur either during the lifetime of the initially excited states, or during the lifetime of the fluorescent states. If it is some of the latter transitions that are quenched and some that are not quenched, then the quenching agent must alter the fluorescent spectrum, an effect that has previously been reported for some elements⁽²⁴⁾. Figure 7 shows the fluorescent spectra of 100 μ gs of uranium in sodium fluoride melts, in the absence of iron and in the presence of 25, 100, and 1,000 μ gs of iron. No significant alterations in line positions or intensity could be proved using a densitometer, apart from alterations in overall intensity which appear in Figure 7. Figure 8 shows superimposed densitometer records from closely matched exposures. There may be a slight reduction in the green end of the spectrum relative to the red when very large amounts of iron are present, but it is a negligible effect in comparison to the overall reduction in intensity. We conclude that iron quenches by enabling some of the initially excited states of uranium to drop down to the ground state by energy transfer without stopping at the metastable state, while other initially excited states cannot so readily transfer their energy, if at all, and continue to give rise to the metastable fluorescent state.

2. QUANTITATIVE TREATMENT OF FLUORESCENCE AND QUENCHING IN URANIUM PHOSPHORS

Normally uranium fluorescence F is interpreted as a linear function of the concentration C_u of uranium atoms present^(1, 17, 18). The starting equation is of the form

$$F = I_0 \phi_q \phi_a \quad (6)$$

where I is a proportionality factor depending on the intensity of incident light, ϕ_q is a quenching coefficient arising from the interference of neighbouring uranium atoms with each other, or with quenching atoms, and ϕ_a involves the light absorption of the melt as the uranium or quencher concentration C_q varies.

For instance Bruninghaus⁽¹⁸⁾ has

$$\phi_q = e^{-k' C_u}$$

and Merritt⁽¹⁷⁾ has

$$\phi_q = e^{-k' C_u}$$

$$\phi_a = \frac{1}{k'' + C_u}$$

and Price⁽¹⁾ who was the first to consider theoretically quenching by ions other than uranium, has

$$\phi_q = 1 \text{ (for the range of concentration he considers)}$$

$$\phi_a = \frac{1 - e^{-k''(C_u + C_q)}}{k''(C_u + C_q)}$$

These authors make no allowance for different effects at different wavelengths and in fitting these equations to experimental curves for the dependence of fluorescence on concentration they conclude that the factor ϕ_a due to absorption is the important effect over the range 10 to 2000 p.p.m. and ϕ_q the interference effect is only operative above 2000 p.p.m. The equations also predict complete quenching as C_q rises (see Fig. 6c). In view of the transmission evidence

described above, these conclusions are not correct. Elaborating Merritt's equations by allowing for different effects at different wavelengths, and by including absorption and quenching by other ions as well as uranium, a general equation may be derived as follows:-

Let us consider a single excited uranyl ion in a melt containing a concentration C_u of uranyl ions and C_q of quencher ions. According to Forster's theory if a quencher ion is within a radius R_0 of the uranyl ion energy transfer may be frequent, and if outside, infrequent. To simplify (in accordance with Merritt) it may be supposed that a quenching ion inside a sphere of volume $\lambda^3 v_q$ surrounding the uranyl ion will cause complete loss of excitation of wavelength λ , and no loss will occur if the quenching ion is outside.

In unit volume the probability of one ion of q being outside a volume $\lambda^3 v_q$ is

$$1 - \lambda^3 v_q$$

and the probability of all quencher ions in a concentration C_q being outside is for a single sphere

$$(1 - \lambda^3 v_q)^{C_q} \\ = e^{-C_q \lambda^3 v_q} \quad \text{when } \lambda^3 v_q \ll 1$$

Similarly the probability of other uranium ions being outside a sphere of volume $\lambda^3 v_u$ is

$$e^{-C_u \lambda^3 v_u}$$

and the probability that neither uranyl ions nor quenching ions influence an excited uranyl ion is

$$e^{-C_u \lambda^3 v_u} e^{-C_q \lambda^3 v_q}$$

The number of uranyl ions in unit volume capable of fluorescing is therefore

$$C_u e^{-a} \tag{7}$$

where $a = C_u \lambda^3 v_u + C_q \lambda^3 v_q$

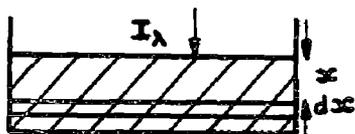
Next consider the incident U.V. light I_λ of different wavelengths λ . Assuming that the light is attenuated exponentially through the melt, the amount that penetrates to a depth x in the melt is

$$I_\lambda e^{-b_\lambda x}$$

where b_λ is the coefficient of absorption of the melt to U.V. light of wavelength λ . The fluorescence will be proportional to the amount of light absorbed by each uranium ion i.e. to

$$\lambda^\epsilon C_u I_\lambda e^{-b_\lambda x} \tag{8}$$

where $\lambda^\epsilon C_u$ is the coefficient of absorption by uranium.



The fluorescence $d_\lambda F_0$ from a thin layer dx thick of area A is then the product of the amount of light absorbed per ion (Equation 8) and the number of ions capable of

fluorescing (Equation 7) i.e.

$$d_{\lambda}F_0 = \lambda^{\epsilon_u} I_{\lambda} e^{-b_{\lambda}x} A d r c_u e^{-a}$$

The fluorescence may be absorbed in its passage through the melt to the surface with a coefficient b_f and the final fluorescent intensity $d_{\lambda}F$ is given by

$$d_{\lambda}F = d_{\lambda}F_0 e^{-b_f x}$$

$$\therefore d_{\lambda}F = A c_u \lambda^{\epsilon_u} I_{\lambda} e^{-a} e^{-bx} dx$$

$$\text{where } b = b_{\lambda} + b_f$$

If the samples are effectively infinitely thick

$$\begin{aligned} \lambda^F &= A c_u \lambda^{\epsilon_u} I_{\lambda} e^{-a} \int_0^{\infty} e^{-bx} dx \\ &= \frac{A c_u \lambda^{\epsilon_u} I_{\lambda} e^{-a}}{b} \end{aligned}$$

Now the absorption coefficient b will be the sum of that due to the scattering by the sodium fluoride P (practically independent of wavelength in the relevant region), that due to the concentration of uranium $(\lambda^{\epsilon_u} + f^{\epsilon_u})c_u$ and that due to the concentration of quencher $(\lambda^{\epsilon_q} + f^{\epsilon_q})C_q$ where the f^{ϵ} 's are the absorption coefficients for the fluorescent light (independent of the wavelength of the exciting light). For our final equation the total fluorescence F from all the different exciting wavelengths is therefore

$$F = A c_u \sum_{\lambda} \lambda^{\epsilon_u} I_{\lambda} \frac{e^{-a}}{b} \quad (9)$$

$$\text{where } a = c_u \lambda^{\nu_u} + C_q \lambda^{\nu_q}$$

$$b = P + (\lambda^{\epsilon_u} + f^{\epsilon_u})c_u + (\lambda^{\epsilon_q} + f^{\epsilon_q})C_q$$

Values of the absorption coefficients ϵ may be read from appropriate absorption curves. Values of λ^{ν} can only be surmised from the spectral regions in which the ions concerned are known to absorb and to lose excitation. This may be expressed by adapting Förster's theory:-

$$\lambda^{\nu_q} = \frac{4\pi R_0^3}{3}; R_0^6 \propto T^6 \propto \lambda^{\epsilon_u} \lambda^{\epsilon_q^2} \quad (\text{See Appendix 1})$$

$$\text{or } \lambda^{\nu_q} = K_q \sqrt{\lambda^{\epsilon_u} \lambda^{\epsilon_q^2}}$$

$$\lambda^{\nu_u} = K_u \lambda^{\epsilon_u}$$

} 10

where the K 's are constants for the ions concerned

Our transmission experiments suggest that when q represents iron

$$f^{\epsilon_u} = f^{\epsilon_q} = 0$$

$$\lambda^{\epsilon_q} = 0$$

v_q cannot however be zero for all values of λ and we can only conclude that while the fluoride ions prevent the ferric ions absorbing light, they do not prevent the ferric ions absorbing excitation from neighbouring uranyl ions in a fluoride lattice. In equation 10 $\lambda \epsilon_u^1$ will therefore be given values comparable to those for the absorption of light in the absence of fluoride ions i.e. as in ferric solutions.

In these circumstances equation 9 reduces to the following equations with the conditions shown:-

$$F = \frac{1}{P} C_u \sum_{\lambda} \lambda \epsilon_u I_{\lambda} \quad C_u \ll \frac{1}{V_u} \quad (11)$$

$$C_u \ll \frac{P}{\epsilon_u}$$

$$C_q = 0$$

i.e. proportional to C_u , where conditions shown hold for all values of λ ;

$$F = A \sum_{\lambda} I_{\lambda} \quad \frac{P}{\epsilon_u} \ll C_u \ll \frac{1}{V_u} \quad (12)$$

$$C_q = 0$$

i.e. independent of C_u ;

$$F = 0 \quad C_u \gg \frac{1}{V_u}$$

$$C_u \gg \frac{P}{\epsilon_u}$$

i.e. complete quenching at high uranium concentrations;

$$F \neq 0 \text{ if any value of } \lambda \epsilon_u \text{ or } \lambda v_u = 0$$

i.e. incomplete quenching at high uranium concentrations.

Fractional quenching ψ_u by uranium at high concentrations is given by:-

$$\psi_u = \left\{ \frac{\sum_{\lambda} \lambda \epsilon_u I_{\lambda} \frac{C_u}{P} - \sum_{\lambda} \lambda \epsilon_u I_{\lambda} \frac{C_u}{P + \lambda \epsilon_u C_u}}{\sum_{\lambda} \lambda \epsilon_u I_{\lambda} \frac{C_u}{P}} \right\}$$

$$\psi_u = \frac{\sum_{\lambda} \lambda \epsilon_u I_{\lambda} \frac{\lambda \epsilon_u C_u}{P + \lambda \epsilon_u C_u}}{\sum_{\lambda} \lambda \epsilon_u I_{\lambda}} \quad C_u \ll \frac{1}{V_u}$$

$$C_q = 0$$

Similarly fractional quenching by q is given by:-

$$\psi_q = \frac{\sum_{\lambda} \lambda \epsilon_u I_{\lambda} (1 - e^{-C_q v_q})}{\sum_{\lambda} \lambda \epsilon_u I_{\lambda}} \quad C_u \ll \frac{1}{V_u} \quad (14)$$

$$C_u \ll \frac{P}{\epsilon_u}$$

i.e. independent of C_u

Equation 14 reduces to:-

$$\psi_q = \frac{C_q \sum \lambda \epsilon_u I_\lambda \lambda^{\nu_q}}{\sum \lambda \epsilon_u I_\lambda} \quad C_q \ll \frac{1}{V_q} \quad (15)$$

i.e. proportional to C_q

$$\psi_q = 1$$

$$C_q \gg \frac{1}{V_q}$$

i.e. complete quenching

$$\psi_q \neq 1 \text{ if some values of } \lambda^{\nu_q} = 0$$

i.e. incomplete quenching.

Equation 9 thus may predict the fluorescence in all our experimental conditions. Some measurements have been made where both the uranium and the quencher concentrations are high, (i.e. outside the conditions of 14 and 15 when ψ_q is no longer independent of C_u) and again as shown below the approximate values predicted by equation 9 are obtained. By fitting the various curves, arbitrary values of A, an instrument proportionality factor involving the area of sodium fluoride exposed, P the light scattering of sodium fluoride relative to absorption by uranium, and the K factors of equations 10 may be evaluated. From the K factors the actual distance R_0 in the sodium fluoride over which energy is transferred, may be calculated.

3. EXPERIMENTAL

(a) The Fluorimeter

The measurements of the fluorescence of the uranium melts were made in a fluorimeter type 1080A which has been fully described previously⁽²³⁾. It consists of a U.V. lamp followed by a block filter (blue green) No. Chance OX1.

The light is focussed on to the sample and the fluorescent light after a further filter to remove reflected U.V. light, is measured in intensity by the response of a photomultiplier tube.

(b) Sample Trays

Samples were mounted in small platinum trays, 1" diameter and $\frac{1}{4}$ " deep which have also been previously described⁽²³⁾.

(c) Phosphor

Sodium fluoride was used for the phosphor. This has the disadvantage that it requires a high temperature for the fusion. Mixtures of alkali carbonates have a lower temperature of fusion but they tend to give a lower response in fluorescence⁽²⁴⁾, they are not easy to make homogeneous, a factor upon which precision has been reported to depend⁽²⁵⁾, and they deliquesce to give a variable response if cooled in the atmosphere⁽²⁴⁾.

Many brands of sodium fluoride give a high fluorescence when fused in the absence of added uranium. This appears due to (a) the presence of minute quantities of uranium in the fluoride and (b) to "white" fluorescence the cause of which is not yet clear although it can be seen with the naked eye. Brands that gave particularly low blanks were "Merck" brand Rahway N.J. (U.S.A.) and Baker and Adamson, Allied Chemical and Dye Corporation, N.Y. (U.S.A.) and these were used in all the experiments here reported. Varied sensitivity was

obtained for uranium fluorescence from different batches of sodium fluoride and figures were only comparable when measured with the same batch under the same conditions. The low blanks given by some brands may be due not only to low uranium content but also to a high quencher content which reduces the overall sensitivity in their use.

(d) Method of Heating

Where possible the fusions were done over a bunsen flame in a fume-hood. The sodium fluoride (600 mgs) was roughly measured onto the tray and heated until a clear melt was obtained, it was then set aside to cool on an asbestos board.

The fusion of high plutonium bearing melts in open trays is a health hazard which was overcome by using a muffle furnace in an enclosed glove box. The furnace consisted of two concentric silica tubes, the inner wound with Nichrome V resistance wire and the outer heavily lagged with asbestos.

It was found that samples heated in the furnace gave a lower fluorescence response than samples heated in an open flame. The response dropped steadily with the time of heating in the furnace. This effect was attributed to contamination by silicon from the silica tubes, which rapidly became corroded in use. It was overcome by lining the inner tube internally with a welded tube of 5/1000" platinum sheet. The temperature of the furnace was controlled by a thermocouple and a variac resistance. After heating up, the furnace was allowed to cool to a set reading corresponding to about 980°C. The samples were then heated one at a time for 2½ minutes (or the shortest time for homogeneous fusion) and cooled rapidly by standing the trays on an iron plate. By this means fair reproducibility was obtained.

(e) Treatment of Sample

In the initial experiments the synthetic uranium plutonium solutions, as nitrates in 4N nitric acid, were pipetted directly on to the cleaned trays and evaporated to dryness. The sodium fluoride was then added and fused. The resulting phosphors were often noticeably brown in colour and had a greatly reduced fluorescence, an effect which could possibly be due to attack on the platinum. Removal of the nitric acid by evaporating the stock solutions to fumes with sulphuric acid before adding to the tray effected an improvement. Reproducibility in the results was further improved by first fusing the sodium fluoride in the tray and then adding the aliquot of the sulphated uranium solution on top, drying, and finally refusing.

(f) Details of Transmission Experiments

Initial experiments were conducted using sodium fluoride melted between quartz slips, but the fluoride rapidly attacked the quartz and made the results of doubtful value. Thin films of potassium carbonate melts could be made in this way but the concentration measurements were all made in sodium fluoride and again comparisons would not have been useful. It was found that thin flakes of sodium fluoride containing definite concentrations of heavy metals could be made as follows:-

The fluoride and ferric or uranium sulphate in definite quantities were fused in a platinum tray in the usual manner until homogeneous. The melt was then broken up. A suitable piece of phosphor was melted on a thin piece of smooth platinum foil of small area (~ 1/2 cm²). On cooling the foil could be peeled away leaving an intact flake, about 1/2 mm thick. This was placed across a hole about 4 mms. diameter in opaque photographic paper and its corners fastened down with cellophane tape. Care was taken that the exposed part of the flake was as uniform in thickness as possible and that it

completely covered the hole.

An iron spark was run at 2.5 amps and 150 volts A.C. The light was focussed onto the slit of a medium grating spectrograph by a quartz medium focus lens. The spectra were photographed on fast panchromatic plates. Exposures were of the order 1 to 30 secs. for the spark alone and 1 to 30 minutes for the light after transmission through the sodium fluoride. The latter was placed right up against the slit.

After developing, the spectra were read in a Hilger automatic recording densitometer. The plates were calibrated by exposing to the light of the iron spark after transmission through a rotating logarithmic sector. The line densities were then measured in the densitometer under the same conditions as the densities on the sample plates were measured. The log of the intensity was plotted against the densitometer readings for selected lines along the spectrum. Separate characteristic curves were made in the regions 6200 to 4000, 4000 to 3000 and 3000 to 2500 Å°. Spectra of different exposures in which the unabsorbed parts were of about equal density were chosen for comparison. The differences of the logarithms of the intensities are plotted in Figures 1, 10 and 11. The log intensity scale is the same for each graph, but it is arbitrary and has been adjusted in Figures 10 and 11 so that zero corresponds to zero absorption.

(g) Details of Fluorescence Spectra Measurements

Platinum trays containing fluoride with varying quantities of iron and uranium were prepared in the usual way. The trays were then clamped facing the slit of a small prism spectrograph about 1 cm. away. A U.V. Woods glass lamp situated behind and at the side of the slit was then shone onto the tray and the spectrum of the diffused reflected light examined visually. The spectra were also photographed. Densitometer readings of the spectra were obtained and by choosing suitable exposures curves could be bracketed for the purpose of comparison as shown in Figure 8.

4. RESULTS

(a) Uranium alone

Table I shows a typical set of readings taken for a calibration run to determine the variation of fluorescence F with the uranium C_u of the melt. The readings were here taken on 6 separate trays, each tray being read twice in two different positions in the fluorimeter. The blank was read twice before addition of the uranium and subtracted in all measurements. The mean F of the N results for each quantity of uranium together with the standard deviation σ of the average of the two observations on each tray as given by

$$\sigma^2 = \frac{(F - \bar{F})^2}{N - 1}$$

is shown in Column 4. The variance \bar{y} , or root mean square fractional standard deviation is given at the foot of Column 4. Occasionally (1 in 60 in Table I) readings were found which were greater than 3 times the expected standard deviation from the mean and these were rejected.

Table II shows a similar set of data taken throughout a much greater range at high and low sensitivities. The detailed observations are not here recorded, but the standard deviations calculated as for Table I are shown.

(b) Plutonium Quenching

Tables III to VI show results similar to those given in Table I but here different amounts of plutonium are also present. The figures in Tables III and IV were obtained using the furnace with an exposed silica tube. Those in Tables V and VI were obtained with a platinum lined furnace. Each figure is again the mean of the observations on 6 trays. In Table VI the low reading obtained for 200 μ gms. of plutonium in the absence of added uranium shows that the plutonium was not appreciably contaminated with uranium. The same batch of plutonium was used throughout.

The figures in each Table, including the two sets in Table II were obtained at different periods over several months and as the sensitivity of the instrument changed, either by change of lamp or alterations in its position or intensity, or by alteration of the EHT to the photomultiplier tube, the tables must be compared by referring to the fluorescence of a fixed quantity of uranium in the absence of quencher.

(c) Iron Quenching

A further set of figures was obtained using iron as a quenching agent instead of plutonium. Solutions of ferric alum in approx. 0.5N sulphuric acid were made up and pipetted with uranyl sulphate in amounts of 0.05 to 0.5 mls. and measured as in the procedure given for plutonium. Results obtained are given in Table VII. Each column represents a run and the figures are adjusted horizontally for sensitivity by the readings of a standard solution measured with each run. The percentage quenching calculated from Table VII is shown in Table VIII.

(d) Saturation of Photocell

The manner in which the uranium fluorescence reaches a maximum as concentration increases could be due to a saturation effect in the photocell. This was checked by cutting down the light from the U.V. lamp with a pin-hole opaque disc placed in front of it. The total fluorescence was reduced by a factor of more than 10 but the same fluorescence curve was obtained with altering uranium concentration as that obtained with the full U.V. light, showing that the effect was not due to photocell saturation.

(e) Infinite Thickness of Sample

In the theoretical section we have assumed that the sample was infinitely thick to light. This point can be checked experimentally. If there is no loss of light with increasing thickness of melt, the fluorescence should be proportional to the amount of uranium and independent of the amount of sodium fluoride. If the melt is infinitely thick to light, the fluorescence should be proportional to the concentration of uranium. Figure 9 shows the fluorescence of 1 μ gm of uranium in different amounts of sodium fluoride. The fluorescence is nearly proportional to the reciprocal of the amount of sodium fluoride i.e. to the uranium concentration. This is not precisely true and we conclude that in some parts of the tray e.g. at the edges and in the middle the melt is not always infinitely thick to light. This would be a marked effect for small amounts of sodium fluoride, but it appears that infinite thickness may be assumed for the amounts used in our experiments.

(f) Graphs and Numerical Deductions

The results in Tables I and II are plotted in Figure 12 to show the fluorescence in the absence of quencher. The reduction in fluorescence after the maximum confirms previous work^(17,18). The

values of Tables V and VII are plotted in Figure 13 to show the reduction of fluorescence with different amounts of iron and plutonium. Although the points for plutonium are rather scattered they confirm that at low uranium concentrations a linear relationship between fluorescence and uranium content holds in the presence of different amounts of quencher.

Figures 6a, b and c shows the percentage quenching by different concentrations of quencher at fixed concentrations of uranium.

In Figures 12, 13 and 6 the full lines are the theoretical curves as given by Equation 9 using the values for the various terms as set out in Table IX. The relative intensity of the lamp at different wavelengths (col. 2, Table IX) has been obtained from the densitometer plot of Figure 4, using plate calibration curves as previously described. The intensities were multiplied by the width of the lines measured in mms. on the densitometer chart so as to give the integral of the total amount of light in any wavelength region. The continuum in the region of 3341 \AA° was measured in the same way and added to the 3341 \AA° line intensity which considerably augmented the total light in this region. The percentage transmission of the U.V. light filter (col. 3, Table IX) is obtained directly from Figure 5. The product of columns 2 and 3 gives I_{λ} in column 4. Relative values of $\lambda \epsilon_{\text{U}}$ (col. 5) are read direct from Figure 10. Absolute values of $\lambda \epsilon_{\text{Fe}}$ (col. 6) were obtained from the absorption of ferric iron in solution as given in Figure 3. To obtain the quenching curves the value for 3650 \AA° had to be reduced from that of the full line to the value shown by the dotted line. This reduction appears permissible because 3650 \AA° is at the skirt of the absorption peak and we are in any case extrapolating from light absorption in aqueous solutions to energy transfer in fluoride melts.

The parameters used to fit the graphs are:-

A which is obtained from the limiting value of the fluorescence at its maximum value (Figure 12, Eqn. 12),

P which is given by the linear slope of the curve in Figure 12 before uranium absorption arises (Eqn. 11).

K_{U} is obtained from the uranium concentration at which fluorescence drops off after the maximum (Figure 12, Eqns. 10 and 12), an effect that cannot be due to light absorption.

K_{Fe} is obtained from the initial slope of the quenching curve (Figure 6b, Eqns. 10 and 15).

5. DISCUSSION

Merritt's theory even as elaborated above is clearly over simple and no good agreement between theory and experiment can be expected. The laws that hold for transparent media have been applied to a diffusing medium where they are unlikely to be true. In Equation 9, b and in turn P depend on the light scattering properties of sodium fluoride melts and it is almost certainly this factor that is responsible for the very variable results that are obtained for different conditions of fusion.

As shown in Figures 6 b and c, the quenching action of plutonium is very similar to that of iron, except that the initial slope is steeper. This indicates that plutonium absorbs energy over the same range as iron, but more readily. The absorption spectra of PuIV in aqueous solutions is suppressed by fluoride ions, and in the absence of fluoride both PuIV and PuVI light absorption rises steeply in the region of 3500 \AA° like that for iron⁽²⁶⁾. Assuming that the transfer

is analogous to iron the value of K_{Pu} is 190 litres/gram mole and the substitution in Equations 9 and 10 gives the curve in Figure 6c. From the values of K_U , K_{Fe} , and K_{Pu} the calculated values of R_0 (Equation 10) are shown in Table X (converting from litres per gram mole to cubic angstroms per atom). This is the distance at which removal of activation from a uranium ion by a neighbouring ion becomes as probable as removal by internal deactivation to the metastable fluorescent state. The figures in Table X may be compared with the value of 60 \AA^0 for acriflavine to rhodamine⁽¹⁶⁾, "100 \AA^0 or more" for transfer between chlorophyll molecules⁽¹⁴⁾ and values between 120 and 400 \AA^0 for transfer in mercury vapour⁽¹⁰⁾. It would be expected that transfer might occur over greater distances in a rigid crystal lattice than in solution, or in organic crystals, where loosely bound electrons arise.

The low values for uranium transfer are interesting. In Förster's theory the neighbouring uranium atom would accept the activation energy of the initially activated atom and itself be fluorescent so that the total fluorescence is not reduced, i.e. in Equation 3 (Appendix 1) where "1" and "2" are both uranium

$$\eta_1 + \eta_2 = \eta$$

The suggestions of Goodeve and Frenkel^(13,12) appear more adequate i.e. that loss of energy occurs in the transfer process itself. This can arise if there is a change in the mean position of nuclei in excitation as indicated in

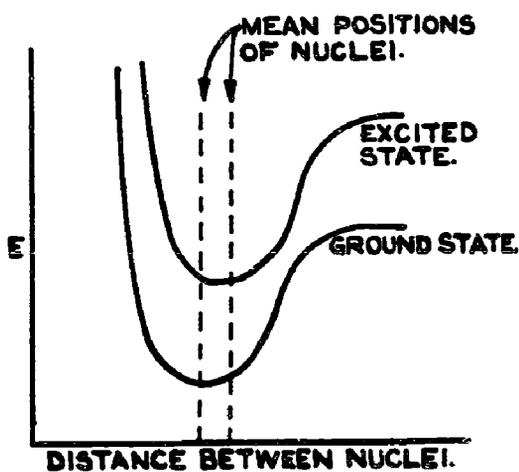


DIAGRAM 1.

Diagram 1, because some of the energy would be lost at each transfer as kinetic energy of motion (heat). Then the greater the number of transfers (TF in Förster's theory) the greater would be the probability of quenching. Förster's Equations 3 and 4 (in Appendix 1) do not predict this, but reach a constant value as TF increases, and therefore cannot predict self-quenching. Thus our values for R_0 suggest speculation that self quenching only arises when the distance between neighbouring uranium atoms is sufficiently small for very frequent transfers to occur, whereas quenching by other ions occurs at larger distances when a single transfer can occur

during the life-time of the excited state.

Table XI⁽²⁸⁾ shows information available on the quenching ability of other elements. These have been arranged to show the order of the amount of initial quenching per atom. It might be expected that factors other than those considered in this report such as changes in mutual solubility, enter in when the less sensitive elements after say copper, are involved. For instance, enhancement by aluminium and antimony has been reported⁽²⁴⁾. This report predicts that elements with U.V. absorption spectra spreading into the visible would tend to produce nearly complete quenching, whereas those with high U.V. absorption, but no absorption in the near visible, would give high initial quenching, but incomplete quenching as the concentration rose. At the bottom of Table XI the first 12 elements as far as the evidence suggests are arranged in order of their ability to quench completely, and it is noteworthy that the elements at the end of this list include those with absorption that spreads into the visible, whereas silver and lead which are colourless in the visible, head the list,

6. CONCLUSION

Evidence has been produced to prove that iron does not quench by a light absorption process. The alteration of fluorescence with concentration is explicable by assuming that iron and plutonium quench some excitations, but not others, by radiationless energy transfer, while uranium causes self quenching initially by light absorption and at higher concentrations by energy transfer. Other elements may quench by U.V. light absorption, by fluorescent light absorption, or by energy transfer, and the original equation of Merritt has been developed to meet these possibilities.

7. ACKNOWLEDGEMENTS

The experimental assistance of Miss M.A. Jones and Mrs. I. Milner, the advice and help of Dr. Gillieson and the Spectrographic Group, and conversations with Dr. E.J. Bowen, Mr. A.A. Smales and Dr. W. Wild are acknowledged with thanks.

8. REFERENCES

- (1) G.R. Price, R.J. Feretti, S. Schwartz, A.E.C.D. 2282
The Microfluorimetric Determination of Uranium.
- (2) Dicke and Duncan. Spectroscopic Properties of Uranium Compounds
McGraw Hill 1950.
- (3) G.A. Kröger. Aspects of the Luminescence of Solids. Elsevier 1948.
- (4) Betts and Harvey, J. Chem. Phys. 16, 1089, 1948.
Absorption Spectra of Hexavalent Plutonium.
- (5) G.R. Price, M.D.D.C. 1666. Fluorescent studies of Plutonium,
Neptunium and Americium.
- (6) J.K. Dawson, Private Communication.
- (7) E. Zebroski and T.W. Newton, M.D.D.C. 443. Fluorescence
Analysis for Uranium.
- (8) P. Pringsheim, Fluorescence and Phosphorescence, Interscience 1949.
- (9) Cornell Symposium, 1946. Solid Luminescent Materials.
- (10) Buhl. Z. Phys. 109, 180, 1938.
- (11) Faraday Society Discussion 35, 1939. Luminescence.
- (12) Frenkel. Physik Z. de Sow. 1936, 9, 158. On the Absorption of
Light. The Trapping of Electrons and Positive Holes in
Crystal Dielectrics.
- (13) Goodeve and Kitchener. Trans. Far. Soc. 1938, 34, 902.
- (14) Franck, J. and Livingston. Rev. Mod. Phys. 21, 505, 1949.
Migration of Excitation Energy.
- (15) E. J. Bowen, Symposia of the Soc. Exp. Biology V 1951, Pg. 152
Resonance Transfer of Energy between Molecules.
- (16) Förster, J. Ann. Phys. 2, 55, 1948.
- (17) Merritt, J. Opt. Soc. Am 12, 613, 1926.
- (18) Bruninghaus. C.R. 149, 1375, 1909.

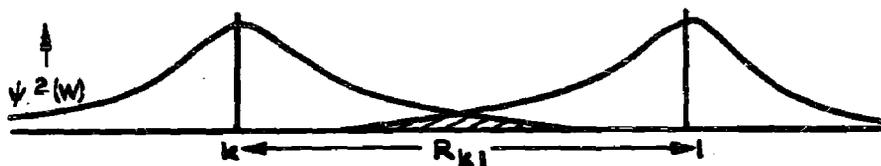
- (19) Förster, T.Z. Naturforsch, 4, 321, 1949.
- (20) Potteril, Walker and Weiss, Proc. Roy. Soc. 156A, 561, 1936.
- (21) F. Seitz, Revs. Modern Physics 18, 384, (1946)
- (22) L. Apker and D. Taft. Phys. Rev. 81, 698, 702, 1951.
- (23) Harwell Catalogue No. 3-7/5483.
- (24) S. Jacobs CRL 4E/54. A Study in the Determination of Uranium by measuring its Fluorescence.
- (25) M.E. Fletcher. T.E.I. 130 Oct. 1950.
- (26) Connick. The Transuranium Elements IV - 14B Pg 559. Spectrophotometric studies of Plutonium in Aqueous Solutions.
- (27) Heller and Marcus. Phys. Rev. 84, 809, 1951. A Note on the Propagation of Excitation in an Idealised Crystal.
- (28) A.A. Smales, Private Communication.

APPENDIX 1

SUMMARY OF FÖRSTER'S THEORY OF RESONANCE TRANSFER (16), (19).

Förster gives a complex mathematical treatment of the transfer of energy between excited centres, of which these are the main features.

The wave function $\psi(w)$ of a molecule or ion excited with energy w , in theory spreads to infinity and the probability $\psi^2(w)$ of finding the energy decreases as the distance from the excited centre increases. In Förster's theory, if there is another centre which can receive excitation energy of the same value w , then the probability of the excitation energy passing from one centre to the other is a function of the amount of overlap of the wave functions (i.e. of the distance between the two centres) and of the degree to which the energy levels of the two centres match each other.



The idea is applied to fluorescence as follows:-

$\rho_k(t)$ is defined as the probability of a fluorescent centre k possessing its activation at time t after activation; and F_{kl} as the number of transfers of activation from centre k to centre l in unit time; F_{lk} as the number of transfers back again; and τ the mean life of centre k . In the absence of transfer,

$$\frac{d\rho_k(t)}{dt} = -\frac{1}{\tau}\rho_k(t) \quad \rho_k(0) = 1$$

$$\rho_k(t) = e^{-\frac{t}{\tau}}$$

$$\frac{1}{\tau} = \frac{1}{\tau_s} + L \quad \text{where } \frac{1}{\tau_s} \text{ is the probability of fluorescence in unit time, and } L \text{ is the probability of losing activation by radiationless processes.}$$

In the presence of neighbouring atoms l the fundamental equation is

$$\frac{d\rho_k(t)}{dt} = \sum F_{kl} \{\rho_l(t) - \rho_k(t)\} - \frac{1}{\tau}\rho_k(t). \quad F_{kl} = F_{lk} \quad (1)$$

The three terms on the right in this equation represent the rate of arrival of activation from neighbouring l atoms, less the rate of loss of activation to neighbouring l atoms, less the rate of loss by an internal process (as fluorescence or heat). The summation is for all the l atoms surrounding atom k . The fluorescent efficiency is given by

$$\eta_k = \frac{1}{\tau_s} \int_{t=0}^{t=\infty} \rho_k(t) dt \quad (2)$$

In the simple case of an initially excited atom 1 in the presence of an unexcited atom 2 Förster integrates (1) and (2) and obtains

$$\eta_1 = \eta \left\{ \frac{1 + \tau F}{1 + 2\tau F} \right\} \quad \eta_2 = \eta \left\{ \frac{\tau F}{1 + 2\tau F} \right\} \quad (3)$$

where η is the fluorescent efficiency when no transfer is possible. These equations show that when $TF \ll 1$ (few transfers during the mean life) there is low interaction and the energy effectively stays with each centre, when $TF \gg 1$ the energy is with centre 1 for part of the time and with centre 2 for part of the time, and the fluorescent of each is reduced.

In applying Equation 3 he considers ξ which is the average number of 1 atoms inside a small volume v .

$$\xi = N^1 c v = N^1 \frac{v}{V}$$

where N^1 is Avogadro's number, c is the concentration of 1 and V is the total volume per mole. The probability of an atom of 1 lying outside a volume v is then

$$\left(1 - \frac{v}{V}\right)^{N^1} = e^{-\xi}$$

Applying (3) the total fluorescence quenching for all atoms is

$$\eta_1 = \eta \int_0^{\infty} \frac{1 + TF}{1 + 2TF} e^{-\xi} d\xi \quad (4)$$

where the integration is for all the different sized little volumes v .

Now in Equation 4, F , the number of transfers in unit time, is itself a function of the distance between k and l (i.e. of ξ). This function is worked out from wave mechanical considerations in which the following appear to be the main steps. The probability of transfer is a function of the square of the combined wave function for the two centres

$$\text{i.e. } F_{kl} = \int_{w=0}^{w=\infty} \left| \psi_{kl}(w_k \cdot w_l) \right|^2 dw$$

i.e. $\psi_{kl}(w_k \cdot w_l)$ depends on the volume in which the energy is spread i.e. on $\frac{1}{R^3}$, and Förster eventually arrives at

$$F_{kl} = \frac{1}{\tau_0} \left(\frac{R_0}{R_{kl}} \right)^6$$

where R_{kl} is the actual distance and R_0 is a critical distance "at which the energy transferred falls below the activation energy". This high power dependence on radius justifies the sphere of action pre-supposed in Merritt's theory of quenching. R_0 is a function of the energy levels concerned and is connected with the extinction coefficients $\epsilon(w)$ of the fluorescent and absorption spectra by an equation of the type

$$R_0^6 \propto \int_{w=0}^{w=\infty} \epsilon'(w) \epsilon''(w) dw$$

(i.e. the greater the overlap of the spectra at each value of w , the greater the number of transfers).

Förster does not develop the theory for quenching in crystalline materials, but applies it to quenching in solution. He illustrates it by the action of rhodamine on the fluorescence of acriflavine solutions, for which he calculates the value of R_0 to be of the order of 60 \AA^C from absolute units.

TABLE I
FLUORESCENCE AND URANIUM CONTENT

Uranium present in μgms	Fluorimeter Readings $F \times 10^4$ above blanks ($< 10^2$)						Mean \bar{F}	Standard Deviation σ
0.2	0.44 0.45	0.64 0.61	0.58 0.60	0.83 0.81	0.64 0.62	0.62 0.58	0.617	0.119
0.4	1.0 1.0	1.1 1.2	1.3 1.3	1.0 1.0	1.2 1.1	1.0 1.1	1.125	0.107
0.8	2.3 2.3	2.1 2.2	1.9 2.0	2.4 2.3	2.2 2.2	1.8 1.7	2.117	0.220
1.2	2.5 2.5	2.9 3.4	3.1 3.0	3.6 3.5	3.0 3.2	3.2 3.2	3.091	0.344
1.6	4.4 4.6	4.3 4.4	4.1 4.4	4.2 4.0	4.2 4.2	4.0 4.1	4.24	0.16
2.0	5.4 5.2	5.7 6.0	5.1 5.6	5.4 5.5	5.6 5.9	{4.1} {4.0}	5.64	0.23
2.4	7.0 7.0	7.4 7.7	6.3 6.7	6.3 6.6	6.8 6.8	6.1 6.4	6.76	0.47
2.8	7.2 7.1	5.8 5.9	7.4 7.5	7.0 6.8	7.1 7.6	7.3 7.8	7.04	0.62
3.2	9.4 9.2	9.8 10.2	9.3 9.8	10.3 8.6	10.3 9.5	8.8 9.9	9.51	0.40
3.6	10.5 9.9	8.3 9.7	11.0 10.0	9.6 11.5	9.7 8.6	9.6 10.5	9.91	0.67

$$\gamma = \left\{ \frac{1}{10} \frac{\sigma^2}{\bar{F}^2} \right\}^{\frac{1}{2}} = .095$$

Bracketed Readings rejected because $\bar{F} - F > 3 \times \bar{F} \times \gamma$

TABLE II

FLUORESCENCE AND URANIUM CONTENT

Uranium present μgrms	Number of trays measured	Mean Fluorimeter Readings	Standard Deviation	Number of Trays measured	Mean Fluorimeter Reading	Standard Deviation
		$\bar{F} \times 10^4$	σ		$\bar{F} \times 10^4$	σ
.05	6	.208	.025			
.10	6	.474	.030			
.15	6	.607	.046			
.20	6	.881	.096			
.25	6	1.03	.122			
0.5	6	1.54	.164	6	0.0627	
1.0	6	3.61	.39	6	0.0978	
1.5	6	5.57	.76			
2.0	6	7.56	.34			
2.5	6	9.53	.33			
5.0	6	17.7	2.1	6	0.528	
10.0	6	31.8	4.6	6	0.99	
15.0	6	45.9	4.5			
20.0	6	55.0	6.5			
25.0	6	61.3	4.1	6	1.70	.28
50				10	3.22	.25
100				4	4.56	.21
200				4	6.49	.16
500				8	8.02	.68
640				10	9.24	.40
800				10	9.37	.59
800				6	9.10	.80
900				6	9.6	1.0
1000				6	9.0	.6
2000				6	6.7	.8

γ

.106

.082

TABLE III

QUENCHING BY PLUTONIUM (Silica Furnace)

Uranium Present μgms.	Readings in the Presence of Plutonium x 10 ⁴			
	0 μ gms. Pu	5 μ gms. Pu	10 μ gms. Pu	20 μ gms. Pu
0.6	1.41 ± 0.21		0.93 ± 0.28	0.811 ± 0.13
1.2	2.79 ± 0.24	2.67 ± 0.27	2.50 ± 0.17	1.93 ± 0.14
2.4	5.51 ± 0.75	5.49 ± 0.3	4.50 ± 0.40	3.37 ± 0.31

γ = 0.137

Result on one tray outside 3γ and rejected.

TABLE IV

QUENCHING BY PLUTONIUM (Silica Furnace)

Uranium Present μgms.	Readings in the Presence of Plutonium, μgms. of Pu x 10 ⁴					
	0	5	10	20	30	40
2.0	5.70 ± 1.20	5.47 ± 1.14	3.30 ± 1.27	4.00 ± 0.7	3.20 ± 0.43	3.30 ± 0.35

γ = 0.22

TABLE V

QUENCHING BY PLUTONIUM (Platinum Furnace)

Uranium Present μgms.	Readings x 10 ⁴ μgms. of Plutonium		
	0	10	20
0.50	2.6 ± 0.1	2.0 ± 0.1	1.5 ± 0.2
0.75	3.7 ± 0.3	2.4 ± 0.2	2.4 ± 0.2
1.00	4.6 ± 0.1	3.5 ± 0.2	3.6 ± 0.4
1.25	6.5 ± 0.3	4.2 ± 0.4	3.7 ± 0.3
1.50	7.9 ± 1.6*	4.9 ± 0.1*	3.1 ± 0.5*
1.75	8.3 ± 0.6	5.9 ± 0.4*	4.5 ± 0.4*
γ	0.15	0.10	0.17

*Change in U.V. lamp. Alteration in sensitivity allowed for.

TABLE VI

QUENCHING BY PLUTONIUM (Platinum Furnace)

Uranium Present $\mu\text{gms.}$	Readings $\times 10^4$ $\mu\text{gms. of Pu}$				
	0	50	80	200	1000
0				$0.043 \pm .001$	
1.0	4.4				approx. 2
2.0	5.4	2.55 ± 0.4			
2.4	6.5		2.88 ± 0.3		
2.8	7.6			3.18 ± 0.85	
3.2	8.6			3.32 ± 1.2	
3.6	9.7			3.32 ± 0.73	

TABLE VII

QUENCHING BY IRON

Weight Iron Present $\mu\text{gms.}$	Readings by 10^3				
	Weight of Uranium $\mu\text{gms.}$				
	0.5	1.0	10	100	
0	0.580 ± 0.27	1.11 ± 0.09	10.0 ± 1.5	46.0 ± 5.3	Normalised to Fig.12
5	$0.525 \pm .041$	0.949 ± 0.096	8.27 ± 0.55	41.8 ± 3.4	
10	$0.430 \pm .025$	0.778 ± 0.120	7.99 ± 0.77	38.0 ± 2.8	
25	$0.385 \pm .053$	0.675 ± 0.092	5.46 ± 0.42	34.7 ± 5.2	
50	$0.272 \pm .016$	0.553 ± 0.060	4.98 ± 0.37	32.9 ± 2.4	
100	$0.246 \pm .048$	0.462 ± 0.059	4.75 ± 0.40	26.3 ± 2.1	
500	$0.160 \pm .023$	0.322 ± 0.026	3.94 ± 0.10	24.0 ± 3.0	
1000*		0.242 ± 0.060		21.1 ± 2.5	

*Separate phase of iron oxide beginning to appear

TABLE VIII
PERCENTAGE QUENCHING BY IRON

Weight of Iron Present μgms.	Weight of Uranium μgms.			
	0.5	1.0	10	100
5	9.48	14.8	17.3	9.1
10	25.8	30.4	20.3	17.4
25	33.5	38.5	44.0	24.5
50	53.1	52.1	50.2	28.3
100	57.6	58.6	52.6	42.8
500	72.2	71.0	60.6	47.8
1000		78.3		54.2

TABLE IX
NUMERICAL TERMS FOR EQUATIONS 9 AND 10

λ A°	Relative Intensity of light from Lamp (Fig. 4)	% Transmission of U.V. Filter (Fig. 5)	I_λ	$\lambda \epsilon_u$ (Figure 10)	$\lambda \epsilon_{Fe}^i$ (Fig. 3) (Ref. 20)
3021	0.196	1	0.20	1.3	2500
3125	0.342	5	1.71	1.1	2000
3341	0.296	30	8.9	0.8	300
3650	0.560	55	30.8	0.28	.003
4046	0.520	1	0.52	0.15	0

$A = 0.26 \times 10^4$ (Instrument Factor)

$P = 8.4 \times 10^{-4}$ (Extinction of sodium fluoride relative to ϵ_u , calculated for molar concentration of uranium).

$K_u = 11$ (litres per gram molecule of uranium).

$K_{Fe} = 45$ (litres per gram molecule of iron).

Weight of melt 0.6 grams

Volume of melt 0.21 mls.

TABLE X

DISTANCE OF ENERGY TRANSFER CALCULATED FROM QUENCHING CURVES
(Equations 9 and 10)

λ A°	R ₀ in Anström Units		
	Uranium - Uranium	Uranium - Iron	Uranium - Plutonium
3021	18	100	160
3125	17	94	150
3341	15	65	105
3650	10	16	26
4046	6	< 5.5	< 9

Distance Na⁺ - F⁻ in ionic cubic lattice 2.3A°

TABLE XI

QUENCHERS (Reference 28)

Element	Amount necessary to cause 10% quenching moles x 10 ⁻⁷	Amount necessary to cause 50% quenching moles x 10 ⁻⁷	Ratio of 50% to 10%
Ag	0.1	50	500
Pb	0.1	5	50
Co	0.2	2	10
Ni	0.2	20	100
Cr	0.2	2	10
Pu	0.2	4	20
Au	0.25	7.5	30
Pt	0.25	5.	20
Mn	0.4	2.	5
Th	0.75	7.5	10
Fe	1.0	20	20
Cu	<u>1.6</u>	<u>8</u>	<u>5</u>
Zn	4.0	20	5
Ti	10	100	10
Mg	20	260	13
W	25		
NO' ₃	50	300	6
CLO' ₄	50	150	3
Mo	100		
Sr	110		
Ca	230	3400	15
SiO ₂	350		
Ba	360		
BO'' ₃	1400	9800	7
Li	3000		

4th Column Order Ag Ni Pb Au Pt Pu Fe Th Co Cr Mn Cu
 " " Value 500 100 50 30 20 20 20 10 10 10 5 5

APPARENT ABSORPTION, $\log \frac{\text{INTENSITY OF IRON SPARK}}{\text{INTENSITY THRU NaF}}$

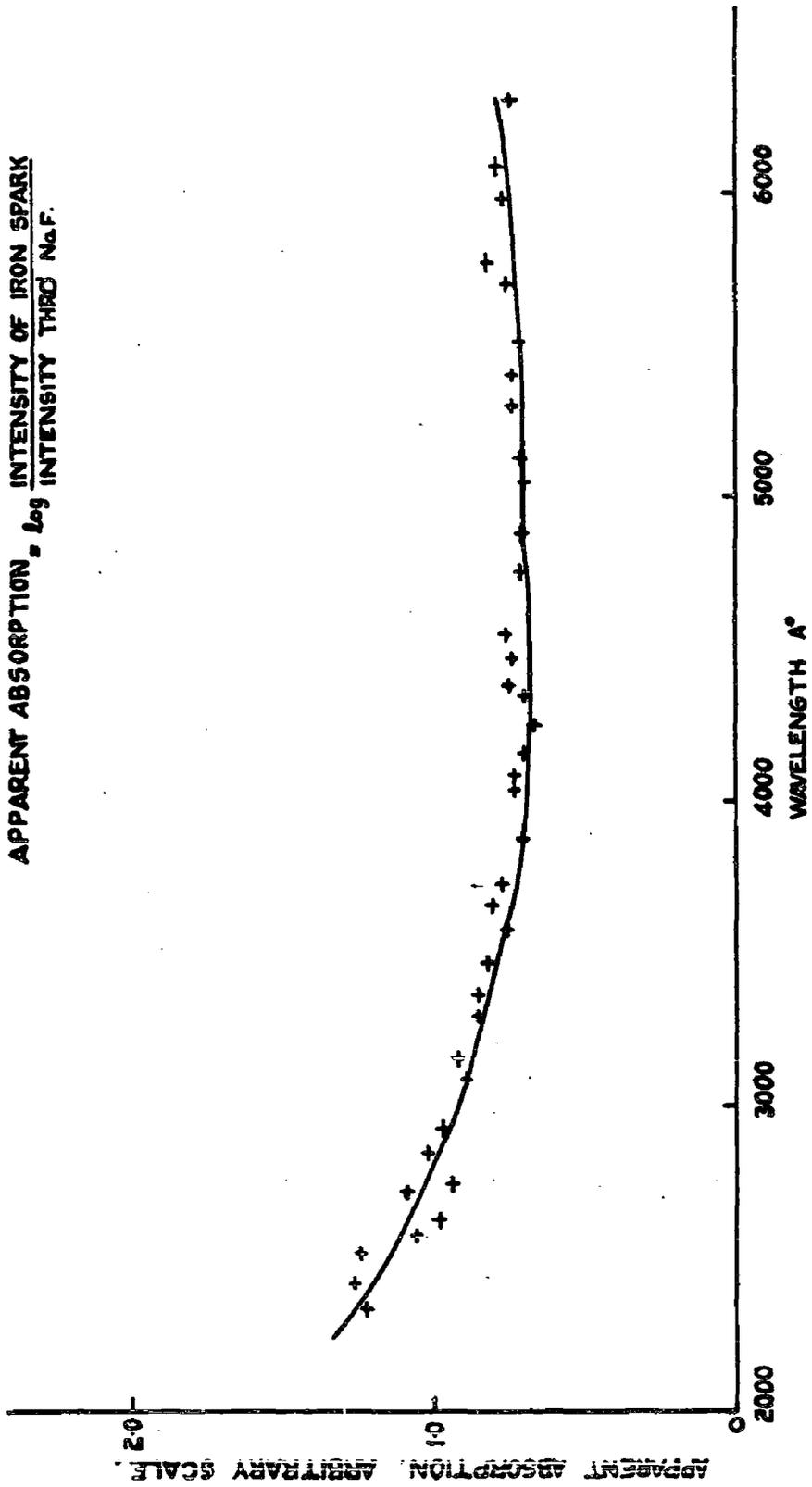


FIG. 1. SCATTERING OF LIGHT BY SODIUM FLUORIDE.

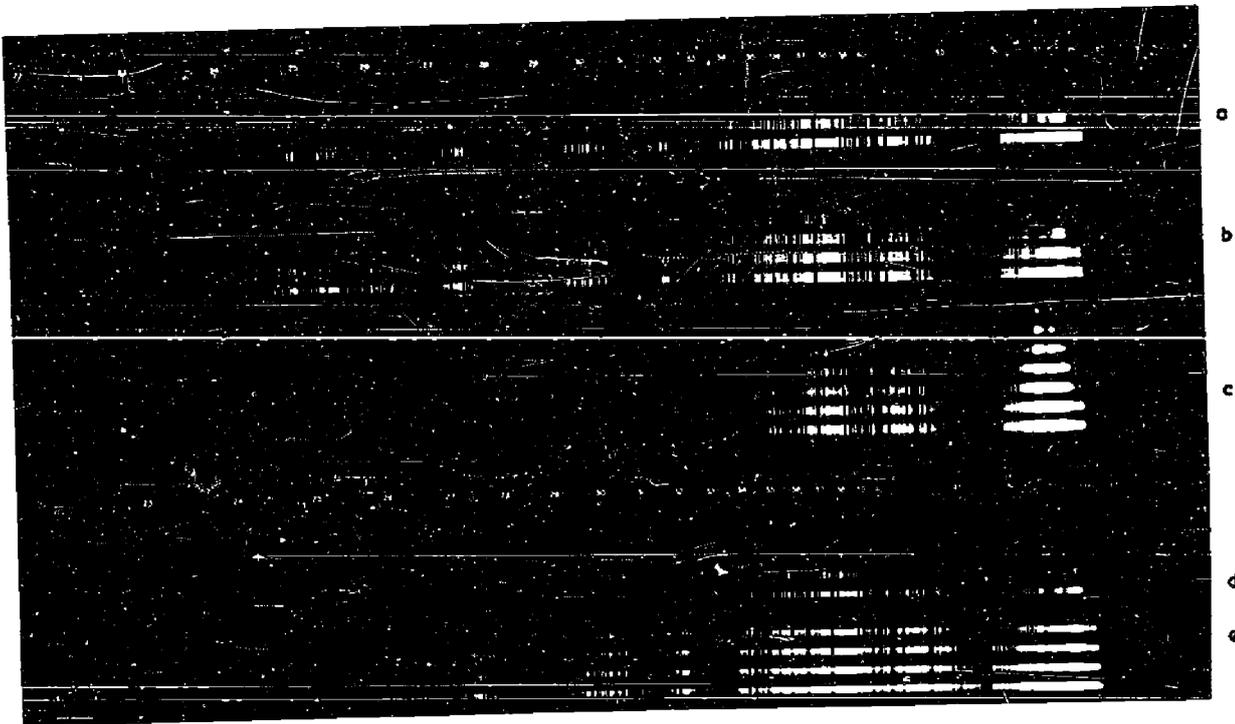


FIG. 2. Transmission of Iron Spark Spectrum.

- (a) Iron Spark Alone.
- (b) Through NaF containing iron 830 ppm.
- (c) " " " Uranium 830 ppm.
- (d) Iron Spark Alone.
- (e) Through NaF.

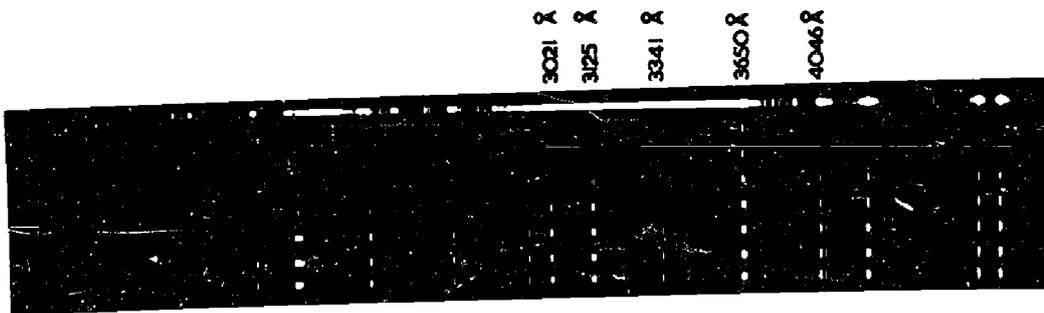
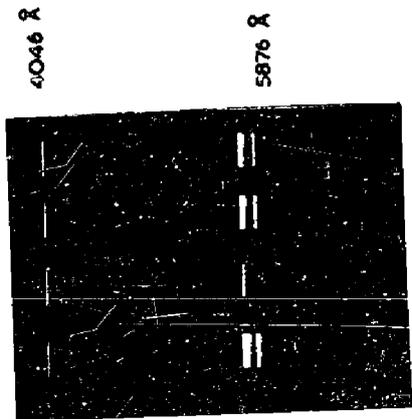


FIG. 4. Mercury Lamp Spectrum.



100 microgrms U.	25 microgrms Fe.	15 mins exp.
"	"	"
" 100	"	" 20 "
" 1000	"	" 40 "
" 0	"	" 10 "

FIG. 7. Fluorescence Spectrum from Surface of NaF

(a) ALONE.
 (b) WITH SODIUM FLUORIDE.
 STRENGTH 0.005 M.
 SPECTROPHOTOMETER CELL 1 CM.

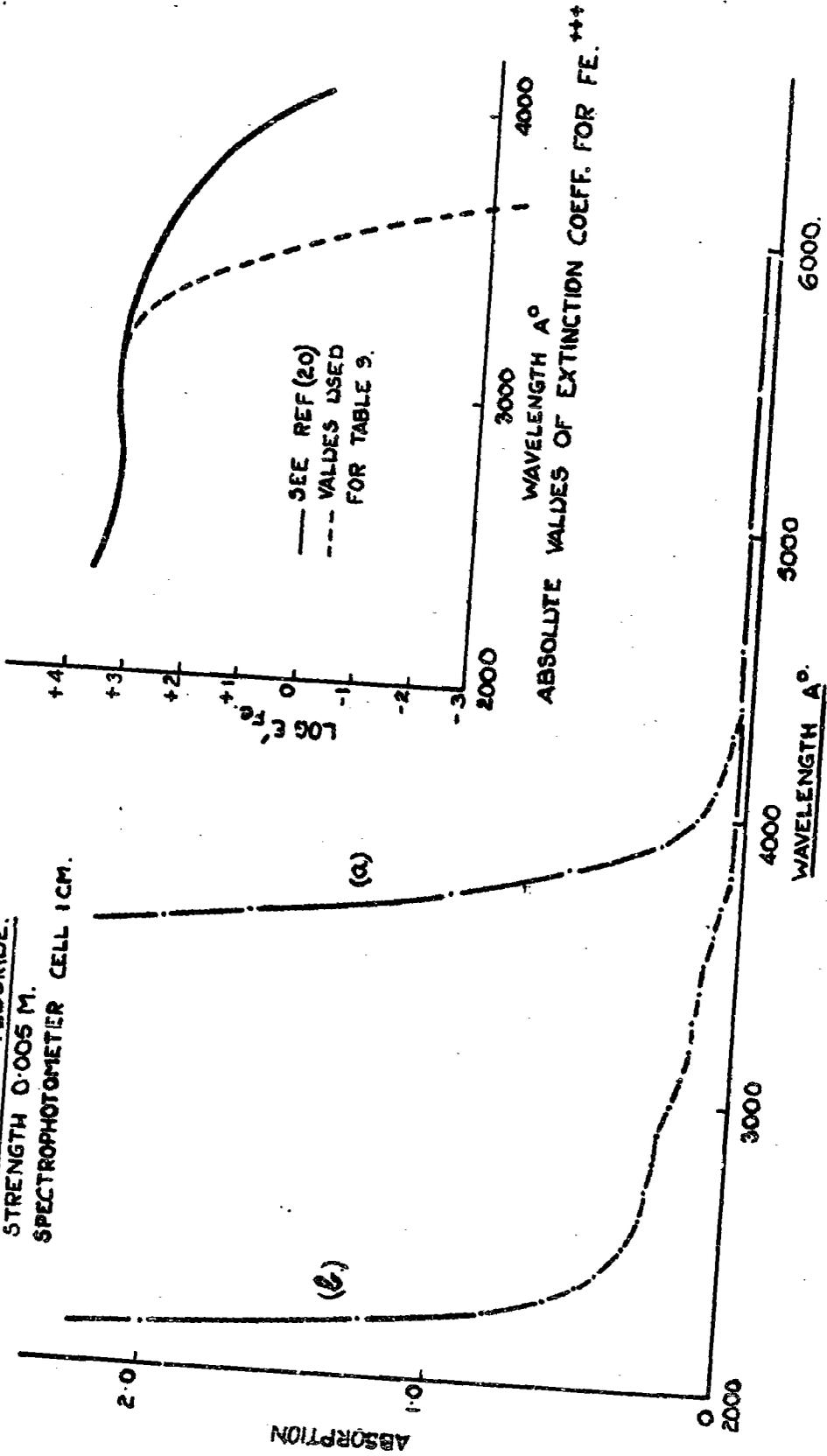


FIG. 3. ABSORPTION OF LIGHT BY FERRIC SULPHATE SOLUTIONS.

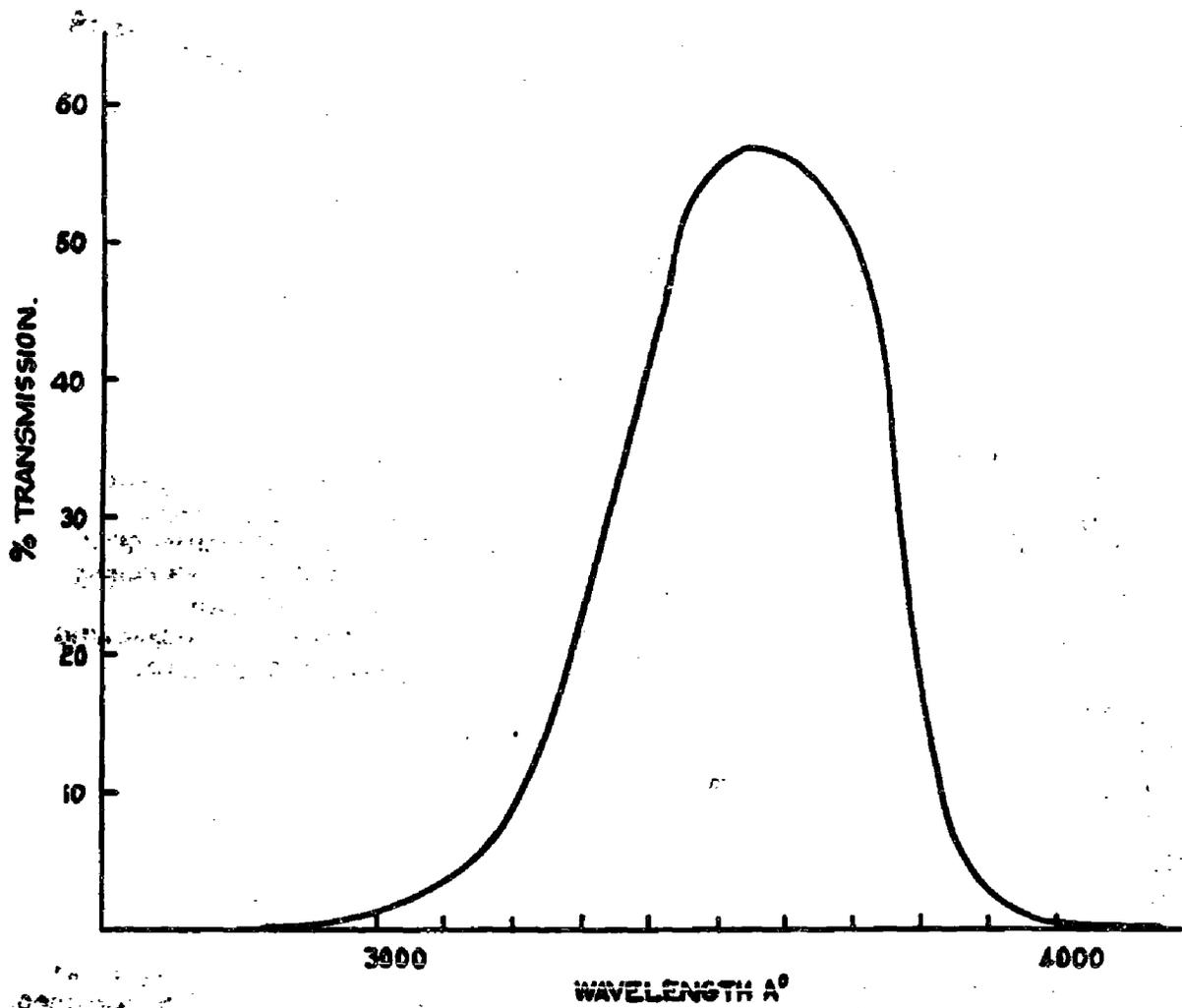


FIG.5. TRANSMISSION CURVE OF UV FILTER IN FLUORIMETER.

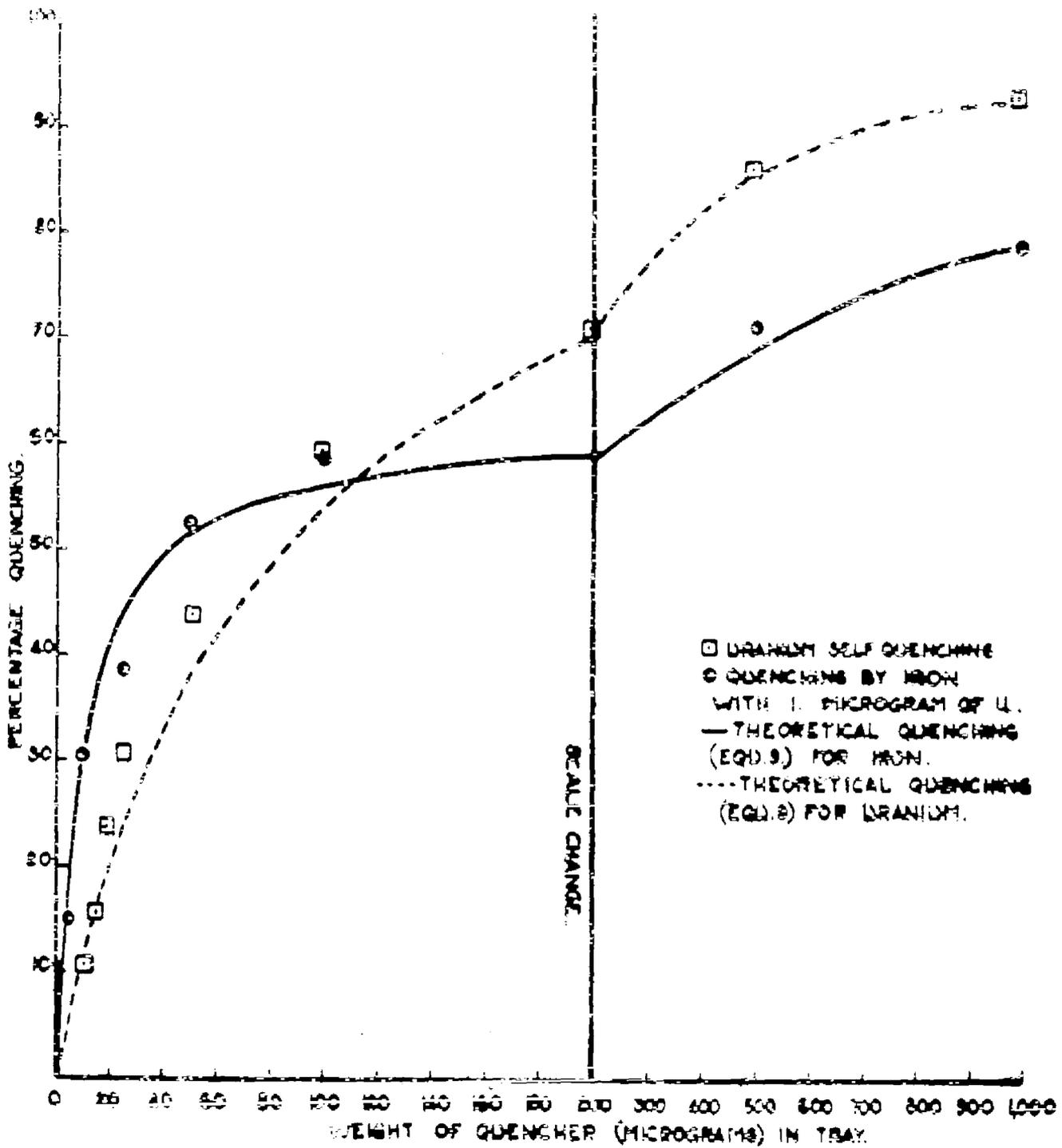


FIG. 66) QUENCHING BY IRON AND SELF QUENCHING BY URANIUM COMPARED.

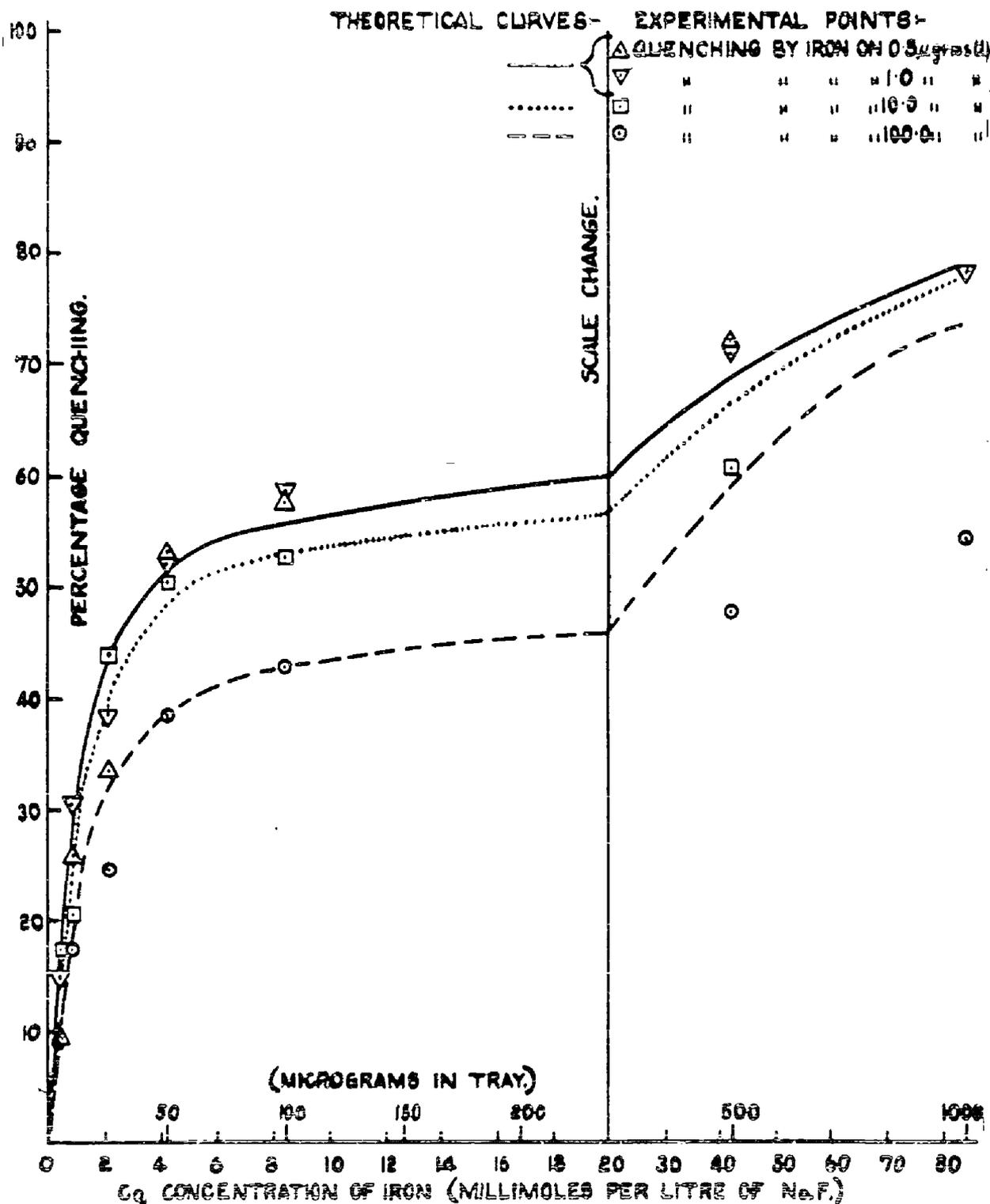


FIG. 6(E) QUENCHING BY IRON.

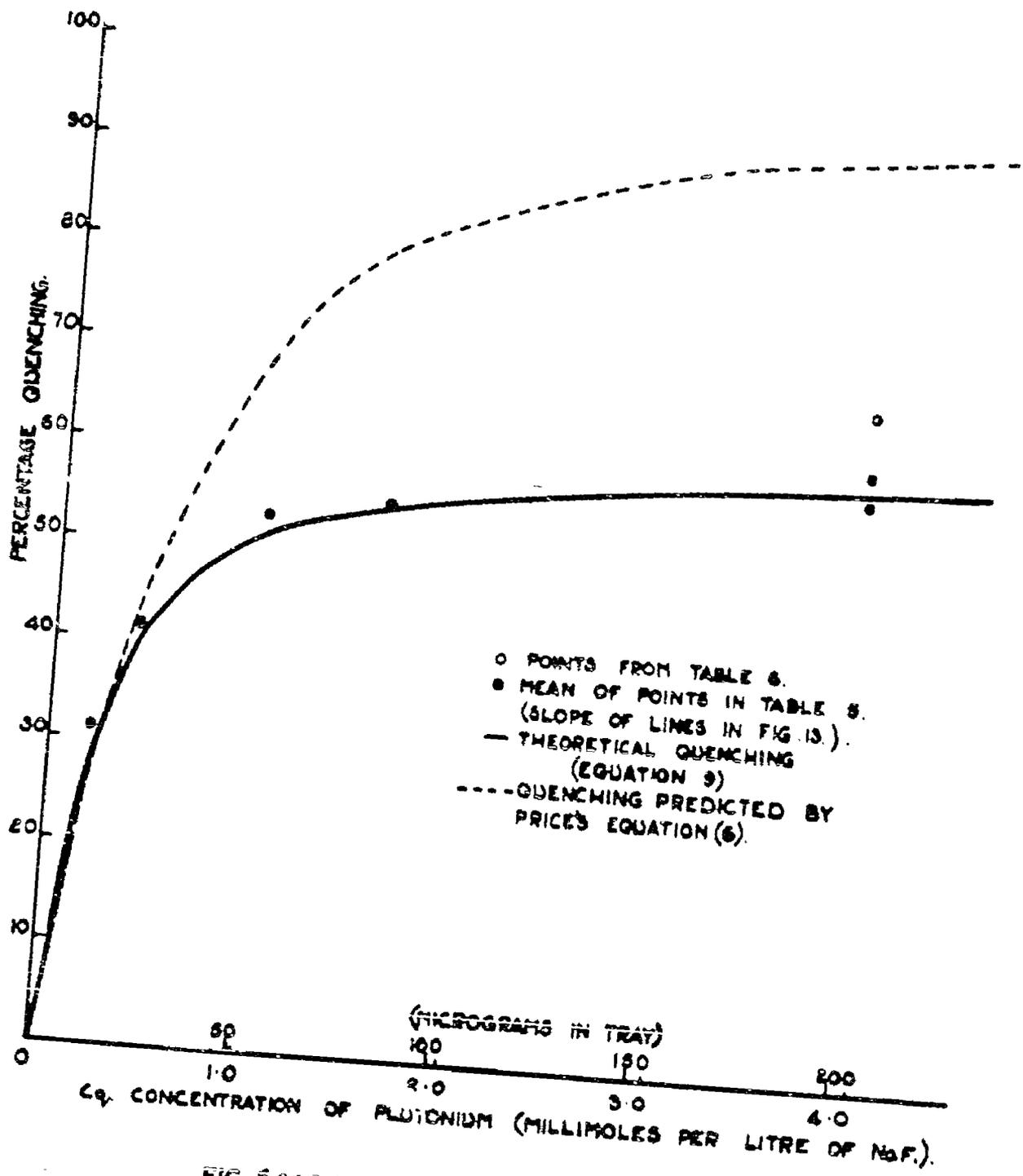


FIG. 6. QUENCHING BY PLUTONIUM.

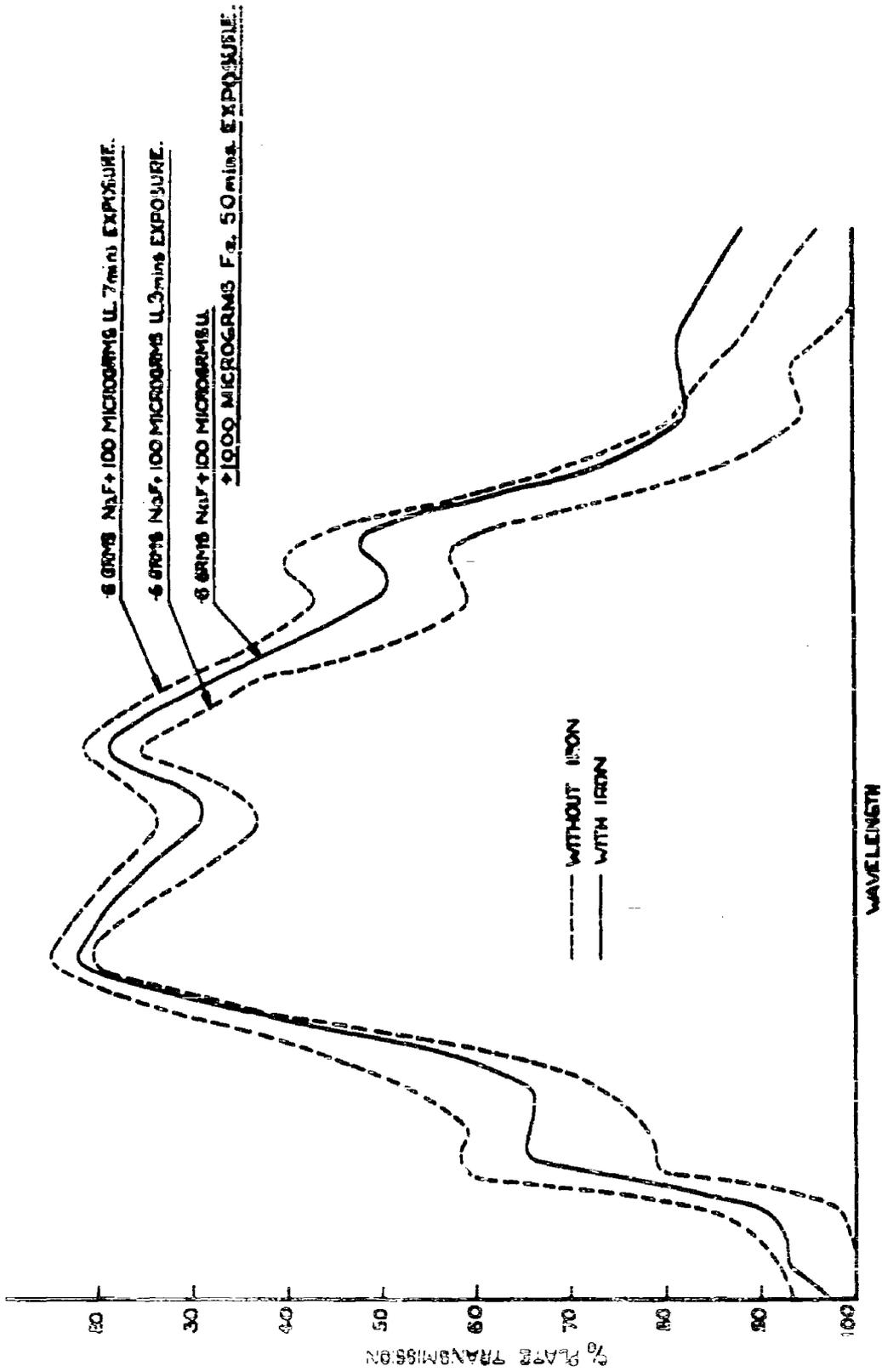


FIG. 8. DENSITOMETER READINGS OF FLUORESCENT SPECTRA

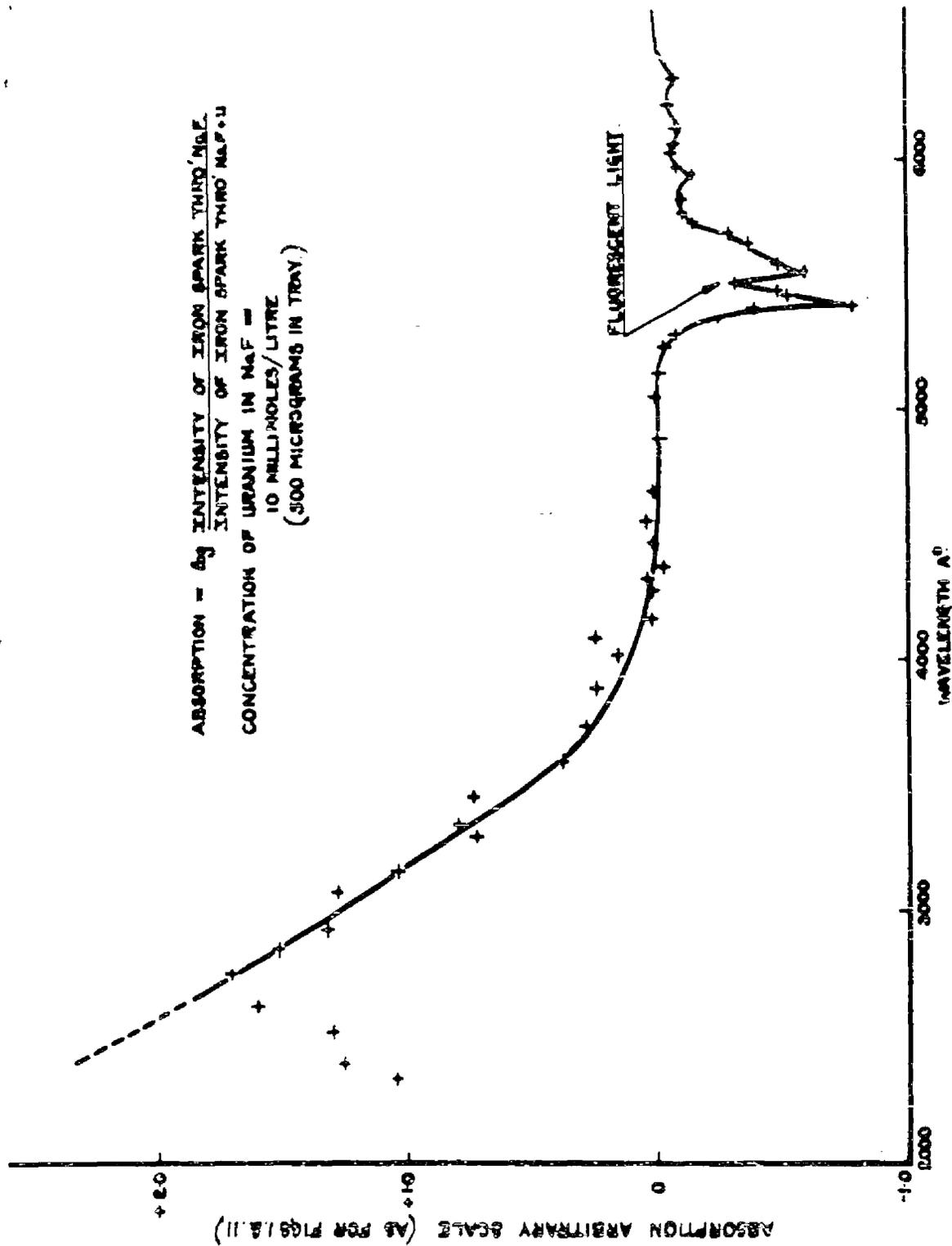


FIG. 10. ABSORPTION BY URANIUM IN SODIUM FLUORIDE.

FIG. II.

ABSORPTION = $\frac{I_0 - I}{I_0}$ INTENSITY THRO' NaF.
INTENSITY THRO' NaF + Fe.
CONCENTRATION OF IRON IN NaF =
42 MILLIMOLES / LITRE
(500 MICROGRAMS IN TRAY)

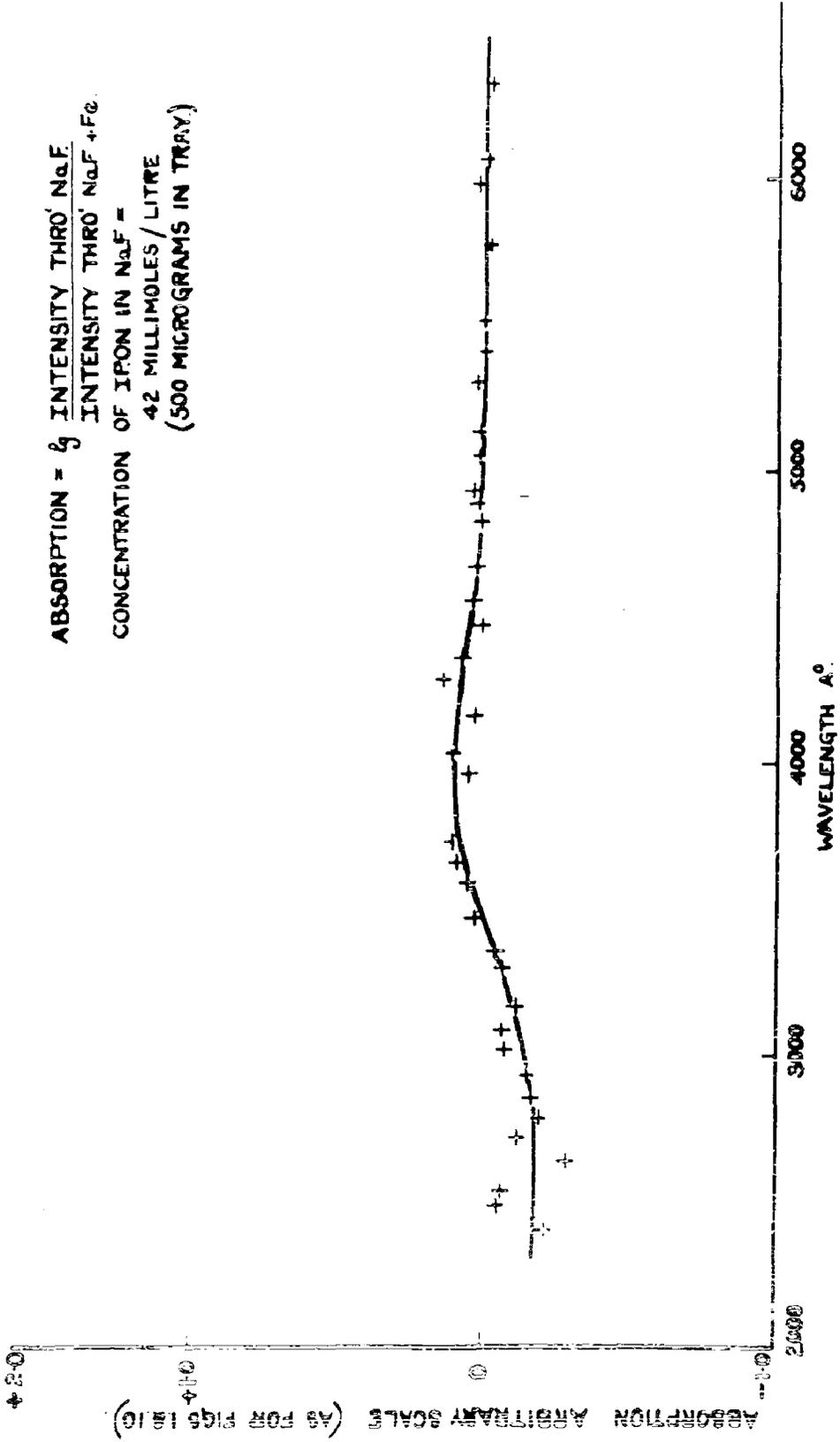


FIG. II. THE EFFECT OF IRON ON THE APPARENT ABSORPTION OF LIGHT
IN SODIUM FLUORIDE.

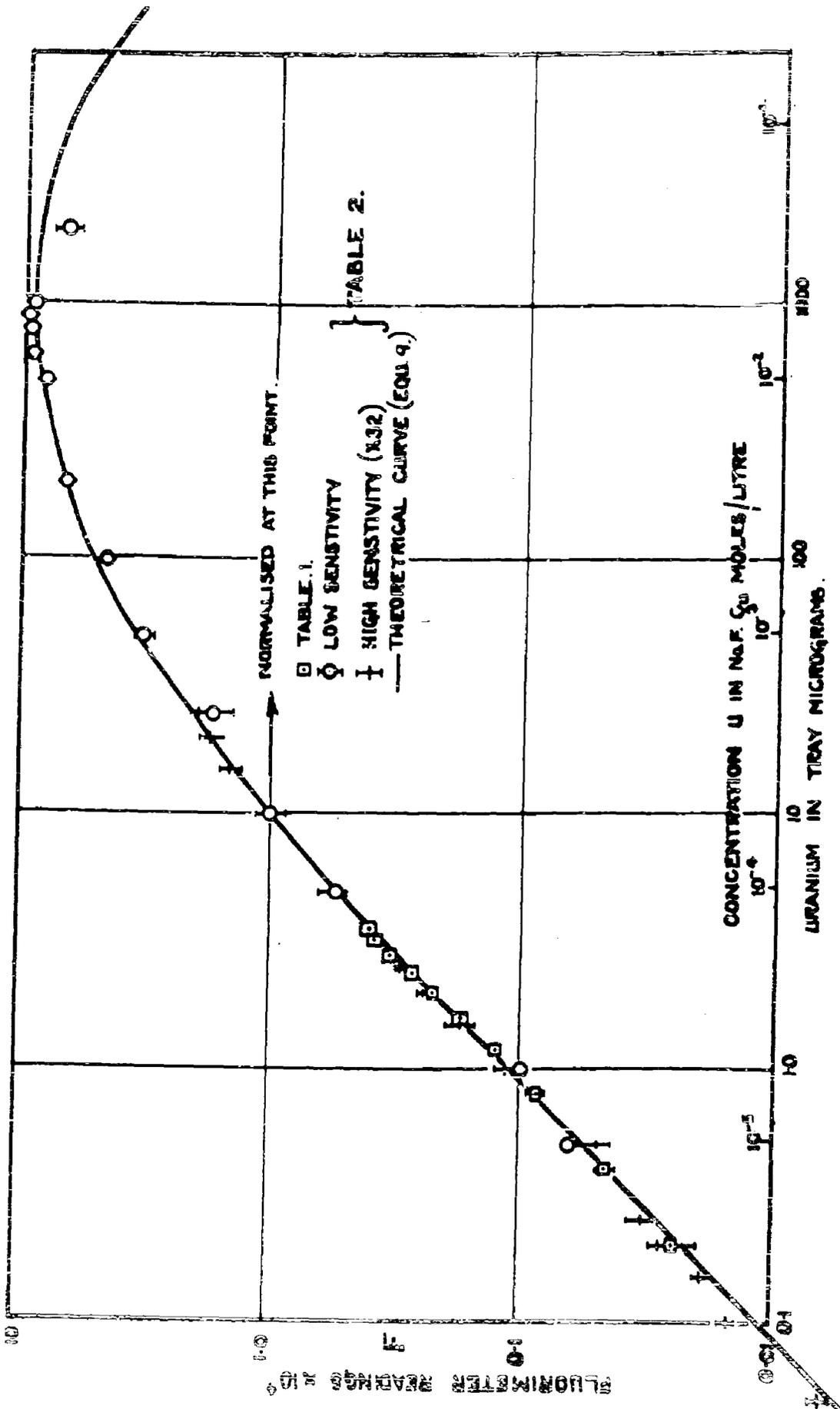


FIG. 12. FLUORESCENCE AND URANIUM CONCENTRATION.

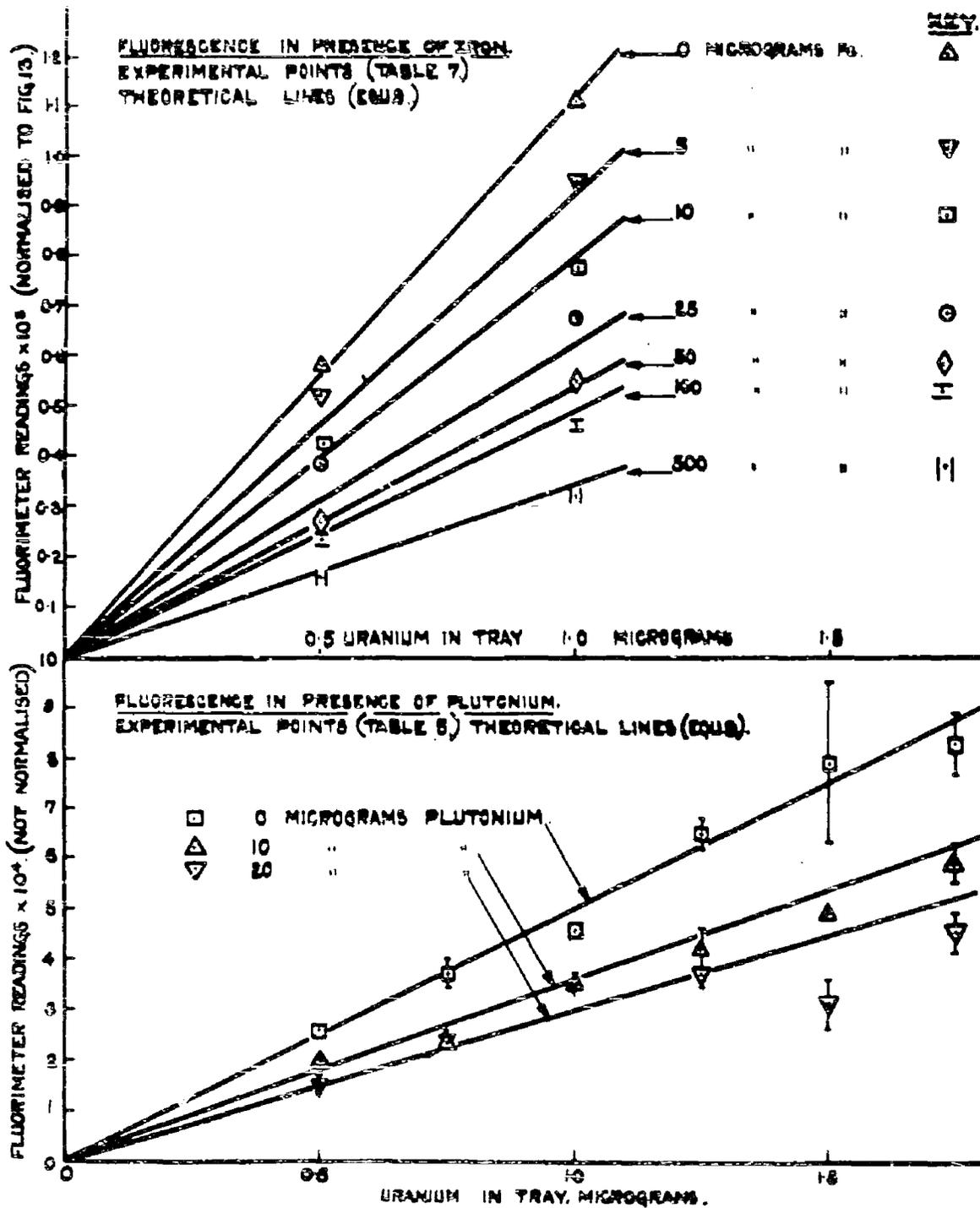


FIG. 13. FLUORESCENCE IN PRESENCE OF FIXED AMOUNTS OF QUENCHER



*Information Centre
Knowledge Services*
[dstl] Porton Down
Salisbury
Wiltshire
SP4 0JQ
22060-6218
Tel: 01980-613753
Fax 01980-613970

Defense Technical Information Center (DTIC)
8725 John J. Kingman Road, Suit 0944
Fort Belvoir, VA 22060-6218
U.S.A.

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Date of Search: 28 May 2009

Record Summary: AB 15/2489

Title: The quenching action of plutonium and iron on the fluorescence of uranium in sodium fluoride phosphors

Availability Open Document, Open Description, Normal Closure before FOI Act: 30 years

Former reference (Department) AERE C/R 966

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