The micro-estimation of uranium by the counting of alpha-particle tracks in photographic emulsions

Robson, Alec

Robson, Alec (1949) *The micro-estimation of uranium by the counting of alpha-particle tracks in photographic emulsions*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/9183/

"THE MICRO-ESTIMATION OF URANIUM BY THE COUNTING OF ALPHA-PARTICLE TRACKS IN PHOTOGRAPHIC EMULSIONS"

ALEC ROBSON

DECEMBER, 1949

DEPARTMENT OF SCIENTIFIC & INDUSTRIAL RESEARCH

DORLAND HOUSE

14-16 REGENT STREET,

LONDON, S.W. 1.

19.1.50

Telephone: Whitehall 9788

3/1/5785

L.S. 14B

The Secretary begs to return the enclosed report on (A. Robson) work carried out by a student under your supervision while in receipt of a grant from this Department.

Prof. F. A. Paneth F.R.S.
Londonderry Laboratory for Radiochemistry.
University of Durham.
South Road,
Durham.

CONTENTS.

I. THE MICRO-DETERMINATION OF URANIUM.

In the determination of the ages of rocks and meteorites by the well-known radioactive methods it is necessary to estimate the amounts of uranium and thorium, and of either helium or lead, present in these rocks. Uranium is present in such small quantities as to demand micro-techniques for its estimation. Of the three methods available for the micro-determination of uranium two are direct methods, and the third an indirect method based on the assumption that radioactive equilibrium exists between the uranium and its decay product radium. A brief account of these three methods is given here in order to appraise their advantages and disadvantages, and to indicate that an independent method for uranium estimation, affording the same sensitivity but with greater accuracy, would be of use in the solution of certain radioactive problems.

A full bibliography of chemical and radiochemical methods for the estimation of uranium, on both the macro-scale and the micro-scale, can be found in a recent review by C.J.Rodden (1).

The Fluorometric Method.

When uranium compounds are exposed to ultra-violet light they become fluorescent, and the fluorescence may be intensified by fusing the uranium with solids such as borax or sodium fluoride. This fluorescence was made the basis of a method for the estimation of microgram quantities of uranium by F.Hernegger and B.Karlik (2). Standards of known amounts of uranium fluxes of a constant amount of sodium fluoride were prepared, and the fluorescence of these standards compared with that of an unknown amount of uranium treated in exactly the same manner.

Good results have been obtained by visual comparison in instruments from which all extraneous light is excluded, and specimens differing by less than 5 per cent in uranium content can be clearly distinguished. For visual comparison a range of standard of 10^{-7} g. to 2×10^{-6} g. of uranium is recommended, but this depends on the instrument used. Instruments incorporating photo-electric cells for measuring the fluorescence give much better results than the visual method, and quantitative measurements can be made down to 10^{-9} g. with an accuracy of about 5 per cent. The minimum quantity of uranium detectable by this method is said to be 10^{-11} g.

Of all the methods available for the estimation of traces of uranium this is by far the most sensitive. It suffers, however, from the disadvantage that before fluxing with the standard amount of sodium fluoride the uranium must be extracted from all other elements in a very pure state. Traces of many elements interfere with the amount of fluorescence of the fused uranium disc, causing it to be either quenched of enhanced. Although uranium may be separated from many interfering elements by extracting its nitrate from solution with organic solvents, such as ether, the danger of contamination when such small quantities are being handled is very real indeed.

W.D.Urry's Radiochemical Method.

This method, devised and developed by W.D.Urry (3), for the estimation of traces of uranium in rocks, is based on the rate of emission of alpha-particles from the isotopes U238, U235 and U234. The rate of alpha-particle emission is directly proportional to the amount of uranium present.

The uranium is separated from all other radio-elements by co-precipitation with iron and aluminium, which are precipitated from a boiling solution as hydroxides by carbonate-free ammonia. The precipitate, which may contain traces of co-precipitated hydroxides of other non-radioelements is dried, ignited and weighed.

From a suspension of this finely-ground

precipitate in alcohol uniform "thin layers" are prepared, and the rate of alpha-particle emission from the layers determined in an ionisation chamber.

Now the rate of alpha-particle emission from the layer is not the same as that from the uranium present, since the layer has a finite thickness, and consequently some alpha-particles will not reach the surface or will fail to travel the minimum distance in the ionisation chamber to record an alpha-particle pulse.

The alpha-particles emitted per hour by each element will be given by:-

$$c = C\beta(1 - sm) \qquad (1)$$

where c = the mean count per hour,

C = the mean number of alpha-particles emitted per hour by U238,

m = the weight of the "thin layer",

β = the ratio of the number of alpha-particles counted to the number which would be counted in all directions,

and s = a parameter which is a function of

(i) the mean range of alpha-particles in nitrogen,

(ii) the minimum distance an alpha-particle must travel in the chamber for detection

(iii) the area of the "thin layer",

(iv) the stopping power of the layer for alpha-particles,

and (v) the density of the "thin layer".

The ratio of the number of alpha-particles emitted from U234 to the number emitted from U238 is 1.00 since these are members of the same radioactive series and in equilibrium. The ratio of U235 to U238 is 0.046. Thus equation (1) above becomes

$$c = C\beta\ (2.046 - sm)$$

The ratio β is 0.50 for flat surfaces, but it is taken as 0.48 when corrections are made for the depth of the containing dish and the area of the layer.

$$\text{Hence,}\quad c = C\quad (0.982 - (\beta s)\ m)$$

The term s can be eliminated by measuring c for two or more values of m.

A test of the method is provided by measuring independently the amount of radium associated with the uranium, and applying the relationship

$$N_{U238} = \frac{\lambda_{Ra}}{\lambda_{U238}} N_{Ra}$$

In use the method has not proved very sensitive but is suitable for estimating uranium contents of the order of micrograms per gram of rock. 10^{-6}g. of uranium can be measured with an accuracy of 30 per cent. For rock specimens whose uranium contents are less than a microgram per gram, the following method has proved much more sensitive and has been widely applied.

The Indirect Method by Determination of Radium.

This method in its various modifications has been widely applied to the determination of uranium in rocks and meteorites, and to the determination of the radium content of natural waters and ocean sediments. If it can be assumed that there is radioactive equilibrium between uranium and radium in the specimen under examination, then the uranium content can be estimated by measuring the amount of radium present and applying the relation:

$$N_{Ra}\lambda_{Ra} = N_{U238}\lambda_{U238}$$

Radium may be accurately determined by collecting and measuring its decay product radon, which is an inert gas. This is the emanation method of H.Mache, St. Meyer and E.Schweidler (4) and many modifications have been made to the technique by W.D.Urry (5), R.D.Evans (6) and others.

The essential steps in the method are:-

(i) The radon must be competely removed from its parent radium.

(ii) It must be transferred without contamination into an ionisation chamber, and the ionisation measured.

(iii) The apparatus must be calibrated by using a known amount of radon from a radon standard.

(iv) The alpha-particle pulses generated in the ionisation chamber must be automatically recorded as they are produced.

Various methods have been used for removing radon from its parent radium. Two of these involve fusion techniques, the radon being removed from the radium in situ by direct fusion of the rock sample or by fusing it with carbonate. Another method is to bring the whole of the rock specimen into solution and remove the radium from the solution by co-precipitating it on barium sulphate. The sulphate precipitate is filtered off, fused with sodium carbonate and brought into solution with hydrochloric acid. This solution is then sealed off until the radon can attain radioactive equilibrium with the radium.

The radon is carried into the ionisation chamber in a stream of radon-free nitrogen, until the pressure in the ionisation chamber has reached a standard, usually a few mms. of mercury above that of the atmosphere. It is advisable that the radon should have as few taps as possible to negotiate before entering the chamber since it is susceptible to absorption on tap grease.

Because of the decay of the radon whilst in the ionisation chamber and the growth of its decay products, some of which emit further alpha-particles, a time of about three hours is allowed to elapse after the radon has entered the chamber before counting is commenced. It is necessary to count for long periods of time, because of the statistical fluctuations in the emission of alpha-particles, and some sort of automatic recording device is essential.

A careful calibration of the apparatus using reliable radium standards must be carried out before attempting the estimation of unknown radium samples, and frequent re-calibrations are necessary to ensure the satisfactory working of the apparatus.

This method in the hands of a careful and experienced worker is capable of giving very good results. Its chief disadvantage lies in the fact that the technique is complicated, and the snags are many for the unwary and the inexperienced. The equivalent amount of uranium which can be estimated by this method is 10^{-8} g. withan accuracy of about 5 per cent.

Although the first and third of the methods described here for the micro-determination of uranium are very sensitive and of good accuracy they possess certain operational disadvantages which have been indicated above. With the advent of the new Nuclear Research Emulsions in which the tracks of alpha-particles can be easily detected and counted under high power magnification a new method of recording the rate of emission of alpha-particles has presented itself. The research undertaken by the author has been concerned with the development of sensitive and accurate methods for the detection and estimation of uranium by the Photographic Method.

THESIS

presented in candidature for the degree of

DOCTOR OF PHILOSOPHY

of the University of Durham

by

ALEC ROBSON, B.Sc., A.R.I.C.

entitled

" THE MICRO-ESTIMATION OF URANIUM BY THE COUNTING OF ALPHA-PARTICLE TRACKS IN PHOTOGRAPHIC EMULSIONS. "

Being an account of the work carried out at the Londonderry Laboratories for Radiochemistry, Durham University (Durham Division) during the period 1947 - 1949 under the direction of Professor F.A. Paneth, Ph.D., F.R.S.

II. THE PHOTOGRAPHIC METHOD.

Early in 1911 C.T.R.Wilson (7) had succeeded in photographing the tracks of single alpha-particles in his cloud chamber. This achievement probably inspired M. Reingamum (8) to attempt the production of similar tracks in a photographic emulsion, and he succeeded in showing that an alpha-particle in its passage through the emulsion rendered developable the silver halide grains along its path. Although O.Mügge (9) was the first to discover the phenomenon in 1909, and correctly attributed it to the radioactivity of the mineral zircon to which the emulsion was exposed, he did not identify the series of dots forming the tracks with the passage of alpha-particles. S.Kinoshita (10) also showed in 1910 that alpha-particles could render silver halide grains developable, but he failed to detect any tracks as such due to the fact that the alpha-particles he used impinged on the emulsion at angles differing from the normal by only a few degrees.

The findings of Reingamum were confirmed in 1912 by W.Michl (11), who measured the track lengths and number of grains per track for alpha-particles of different ranges. From his experiments he computed the range in air of the alpha-particles from polonium to be 3.8 cm., in good agreement with the value of 3.77 cm. given by Geiger.

The first dark-field photograps of alpha-particle tracks in photographic emulsions, published by W.Makower and H.P.Walmsley (12) in 1914, reveal tracks consisting of a few widely-spaced grains, making it difficult to distinguish either the beginning or the end of a track from the "background fog" of the emulsion. Michl published drawings of his tracks which were very much like these.

A further advance in technique was made in 1927 by L.Myssowsky and P.Tschishow (13), who prepared plates with emulsion coatings greater than 50μ in thickness in order to register longer tracks.

Important contributions were made during the years from 1931 to 1935 by H.Wambacher and M.Blau (14) (15), and by A.Jdanoff (16), in the development of proton-sensitive emulsions, and in attempts to produce emulsions of small grain size, with small gaps between the constituent grains in a track. These experiments met with only partial success as the photomicrographs published by Jdanoff reveal tracks with large grain spacing and seemingly indterminate length. However, a certain degree of discrimination between alpha-particle and proton tracks was achieved.

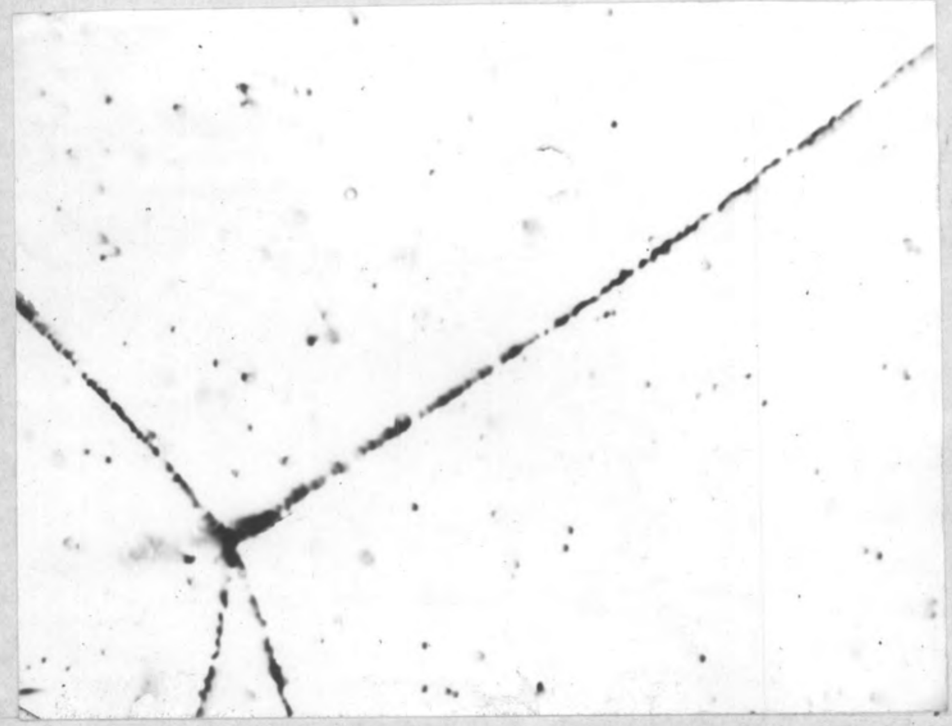
Before great strides could be made in the application of the photographic technique to problems involving nuclear particles of vastly different ionising powers, for which it seemed particularly suited, it became clear that photographic emulsions possessing the following properties would have to be developed.

(i) The "background fog" consisting of hundreds of thousands of single grains per sq. cm., revealed in unexposed plates on development, would have to be considerably reduced. Although the most careful precautions were taken in the handling of plates, all light being rigidly excluded and all the solutions used in processing carefully filtered, the "fog" persisted. It most probably arose from the chemical treatment of the emulsion, but possibly by the action of cosmic rays or by gamma radiation from any radioactive substances in the vicinity of the emulsion. Mechanical shock was also said to be a cause of "fog".

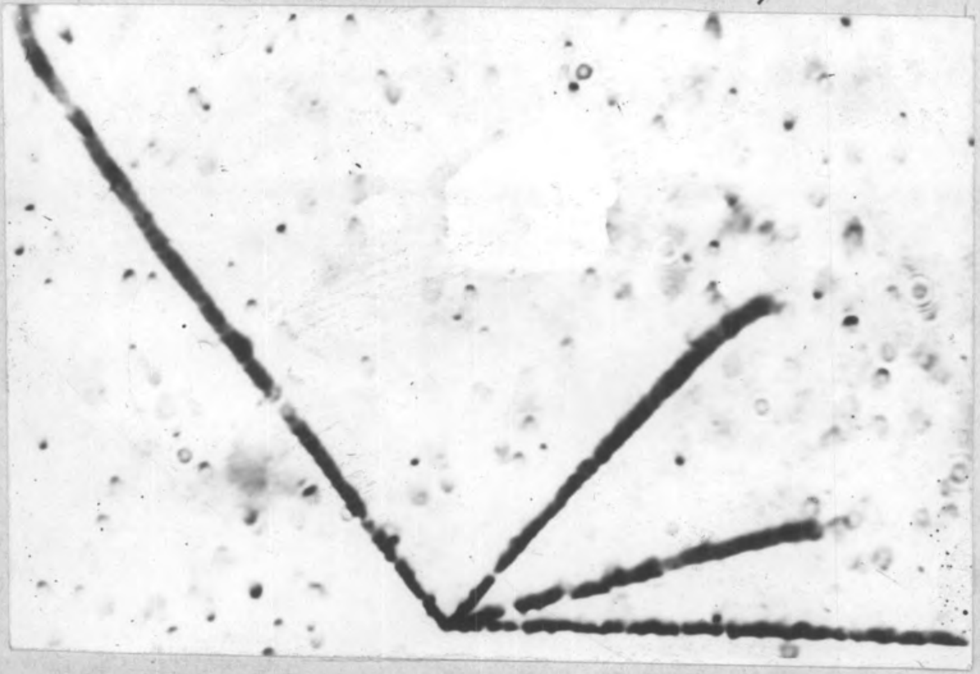
(ii) Greater definition of tracks would be necessary. A reduction in grain size and an increase in the number of developed grains in track would give greater definition, and to ensure this the halide content of the emulsion would have to be increased.

(iii) Emulsions clearly revealing the differences in ionising power between different charged particles, such as alpha-particles and protons, would be required.

(iv) A range of plates with emulsion thicknesses varying from tens of microns to some hundreds of microns



Thorium-X Star. The long track is due to the alpha-particle from Thorium-C'.
(Magnification about 2500x)



Radium Star produced by four successive alpha-particles emitted from a single Radium nucleus.
(Magnification about 2800x)

would be needed.

Recent Advances in Photographic Emulsions.

In 1946 C.F.Powell, G.P.S.Occhialini, D.L.Livesey, and L.V.Chilton (17) produced a new photographic emulsion for the detection of fast charged particles which had greatly improved properties over those used hitherto, The development of this emulsion undoubtedly owed much to the admirable work of the research staff of Ilford Ltd.,. It contained 80 per cent by weight of silver bromide, which was about eight times the normal quantity, but in spite of this large increase in halide content the "back-ground fog" of the emulsion was much less than that of the "half-tone" emulsions formerly used. The photomicrographs of alpha-particle and proton tracks obtained by using the new emulsion were excellent: the tracks being clearly defined, and the "energy resolution" being much greater than anything previously achieved. Spacing between grains was very small indeed, enabling range measurements to be made with fair accuracy, and the detection and counting of alpha-particle tracks under high power magnification was a comparatively simple matter, even though some of these tracks "dipped" steeply in the emulsion.

Some photomicrographs of alpha-particle tracks prepared by the author are shown here. The emulsion used is the Ilford Type C2 Emulsion, which is very similar to that used by Powell and his collaborators. The curvature of some of the tracks is due to shrinkage of the emulsion in drying after processing.

The preparative details for a number of new emulsions with silver halide contents of 80 per cent and more, are given in a very useful paper by P.Demers (18). Demers worked independently of Powell et alii, and the grain sizes of his emulsions are somewhat smaller than theirs the grain diameters varying between 0.1μ and 0.2μ. The qualities which he considers necessary in a Nuclear Research Emulsion are essentially those outlined here.

An Appreciation of the Photographic Method.

The development of photographic emulsions with the qualities indicated in the foregoing section has enabled the Photographic Method to assume prominence among the methods available for the investigation of the properties of nuclear charged particles. Even prior to 1946, however, the photographic technique had a wide application in the realm of nuclear physics, although many physicists voiced serious objections to it on the grounds of the inferior qualities of the emulsions and the severe limitations these imposed on the experimental data obtainable. A full account of applications of the method up to 1941 can be found in a review by M.M. Shapiro (19).

At the present time the method is being used in a great variety of experiments in nuclear physics and radiochemistry. Physicists the world over are finding the new Nuclear Research Emulsions an indispensable tool in their researches into the phenomena produced by cosmic rays. In the hand of C.F.Powell and his collaborators (20) (21) (22) the method has led to significant discoveries regarding the production and decay of mesons, and in determinations of the masses of these particles. A determination of the disintegration constant of uranium has been made by H.Yagoda and N.Kaplan. (23) using the photographic method and is in good agreement with the value obtained by other methods. E.Broda (24) has initiated a search for unknown alpha-particle emitting elements by loading photographic emulsions with solutions of many elements of atomic number less than that of bismuth. These are but three examples of the many ways in which the new Nuclear Research Emulsions are being used to help in solving chemical and physical problems.

The chief advantage the method has over other methods used for detecting nuclear charged particles lies in the continuous sensitivity of the photographic emulsion. Exposures may be made for long periods of time without the need of supervision by the research worker, provided adequate precautions are taken. The plates are cheap, easy to process, and when processed provide the investigator with a permanent record of his experiment which he can examine at his leisure. The absence of background in the emulsion, too, is a great advantage, for although tracks may be observed in unexposed plates, due to radioactive impurities in the emulsion or in the plate backing, they are very rare indeed.

Against these advantages, however, must be offset the following disadvantages. The examination of even a small area of plate under high power magnification, especially where measurements of track lengths have to be made or large numbers of tracks counted, is a long and tedious business. A microscope with binocular vision is essential, if long observation is necessary, in order to avoid eye-strain, and the observer must take a quarter of an hour's rest every hour. A further disadvantage of the method is due to the fading of the latent image in the emulsion. The latent image of a particle track, produced in the emulsion at the beginning of a long exposure, may partially or totally fade before the plate is developed; consequently no track will be seen by the observer on examination. This loss of tracks due to fading can seriously limit the useful exposure time of an emulsion. The amount of fading varies considerably with experimental conditions, and the type of emulsion used, and is of such importance that much research work has been done to investigate the conditions affecting it.

III. THE FADING OF THE LATENT IMAGE IN PHOTOGRAPHIC EMULSIONS.

It has been known for many years that the latent image of an alpha-particle track in a photographic emulsion may undergo serious fading if the development of the emulsion is delayed for more than a few days. With the old type emulsions the rate of fading of the latent image was observed by M.Blau (25) to be rapid, and J.Landa (26), also using old type emulsions, found that the rate of fading of the latent image was influenced by the conditions of humidity, temperature or vacuum under which the emulsion was stored. With the advent of the new Nuclear Research emulsions, and their consequent wide application in nuclear physics and chemistry, many workers have studied the phenomenon. In view of the importance of the fading factor in experiments involving exposures of long duration, as in the measurement of low levels of alpha-particle activity, the following short review of recent experimental work in the field is presented.

Recent Work.

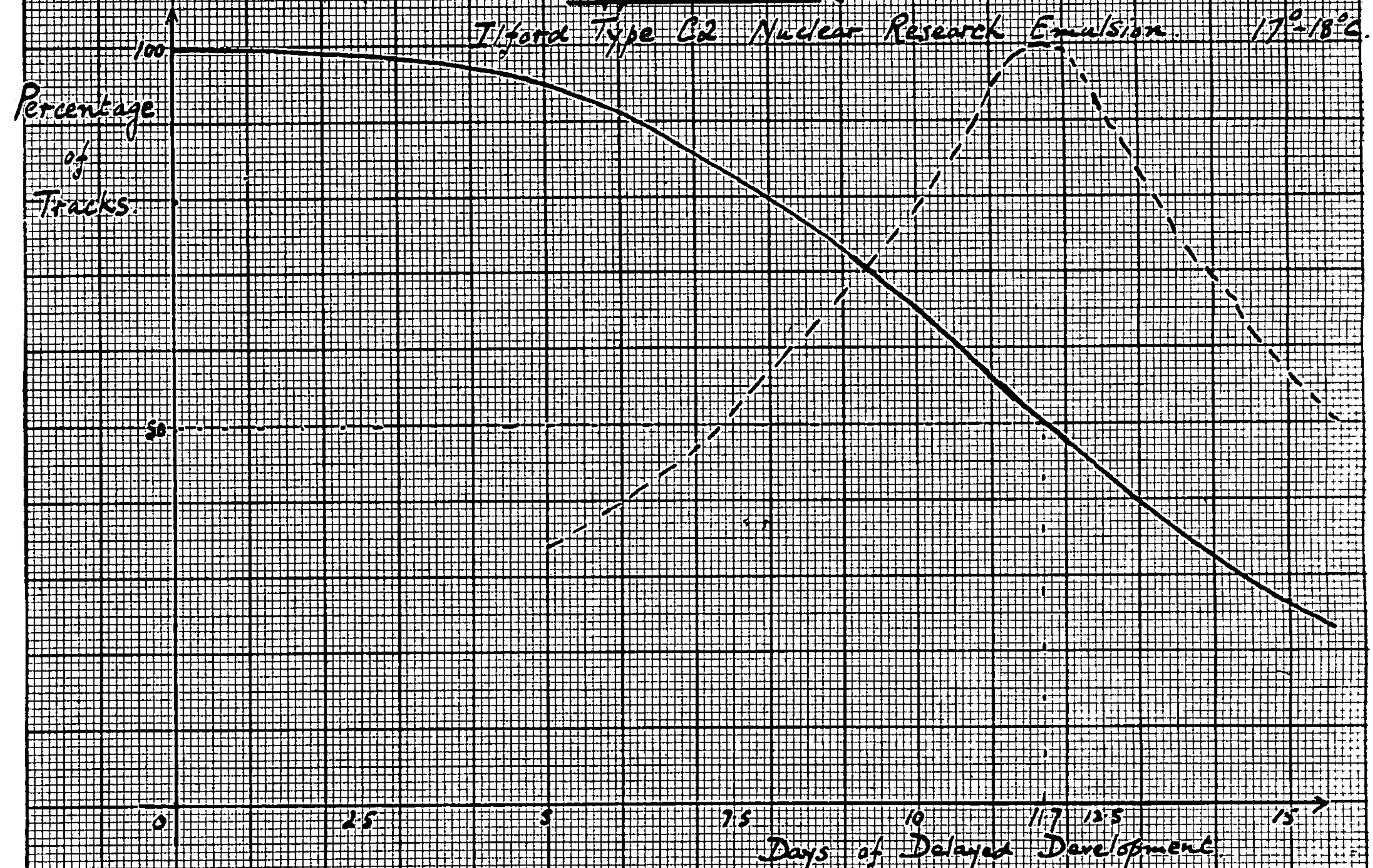
H.Yagoda and N.Kaplan (27) have shown that temperature, humidity and the presence of hydrogen peroxide have a pronounced effect on the rate of fading of the latent image. They exposed plates coated with new types of Eastman NTA emulsions to a flux of 5000 alpha-particles per sec. per cm^2., using as alpha-particle source a thin film of equilibriated barium-radium sulphates separated from the emulsion layer by 1 mm. of air. The photographic densities of the images formed by delayed development, and of the control developed immediately after exposure, were measured on a recording densitometer. The amount of fading was computed by them as a fractional loss in grain density. Under normal storage conditions they found that after 40 days there had been only 40 per cent fading, and they published photographs to show that an alpha-particle track was still recognisable as such after this time interval. However, in an atmosphere saturated with water vapour at 35°C. total fading of the latent image occurred in a few hours, whereas storage of the emulsion over freshly-distilled water caused no fading of the latent image. The hydrogen peroxide concentration of the atmosphere was found to accelerate fading appreciably, and after storing emulsions for 24 hours over 3 per cent hydrogen peroxide at 25°C. the latent image was completely obliterated. After loading the emulsions with borax or lithium sulphate it was found that the fading action of hydrogen peroxide was inhibited. These authors put forward a hypothesis suggesting that in situ production of hydrogen peroxide by the action of highly ionising alpha-particle radiation on the water in the emulsion was the cause of the fading.

In 1948 W.A.Lamb and F.W.Brown (28) also used Eastman NTA emulsions to study the effect of temperature on the rate of fading of the latent image, exposing their emulsions to a source of Po^{210} alpha-particles. However, instead of computing the fractional loss in grain density as did Yagoda and Kaplan, they estimated the loss in track counts for varying conditions of exposure. The results they give are only semi-quantitative, but show that at 0°C. there is only about 10 per cent loss in track count, whereas at 40°C. there is 50 per cent loss after 30 days.

In 1949 R.Coppens (29) (30) made a more detailed study of the influence of humidity, temperature, and the loading of emulsions with borax, on the fading of the latent image. He used both Ilford B1 and C2 Type emulsions, and electrolytically deposited Polonium or pulverised pitchblende as his alpha-particle source. If the percentage number of tracks per field is plotted against the time of delayed development in days a curve of characteristic shape is obtained - the control being reckoned as 100 per cent. A whole series of curves having this characteristic shape has been obtained for different storage conditions of the exposed plates. The shape of this curve clearly shows that the rate of fading is not a linear function of the time of delayed development. The track count remains approximately constant for a time, which varies with the conditions of

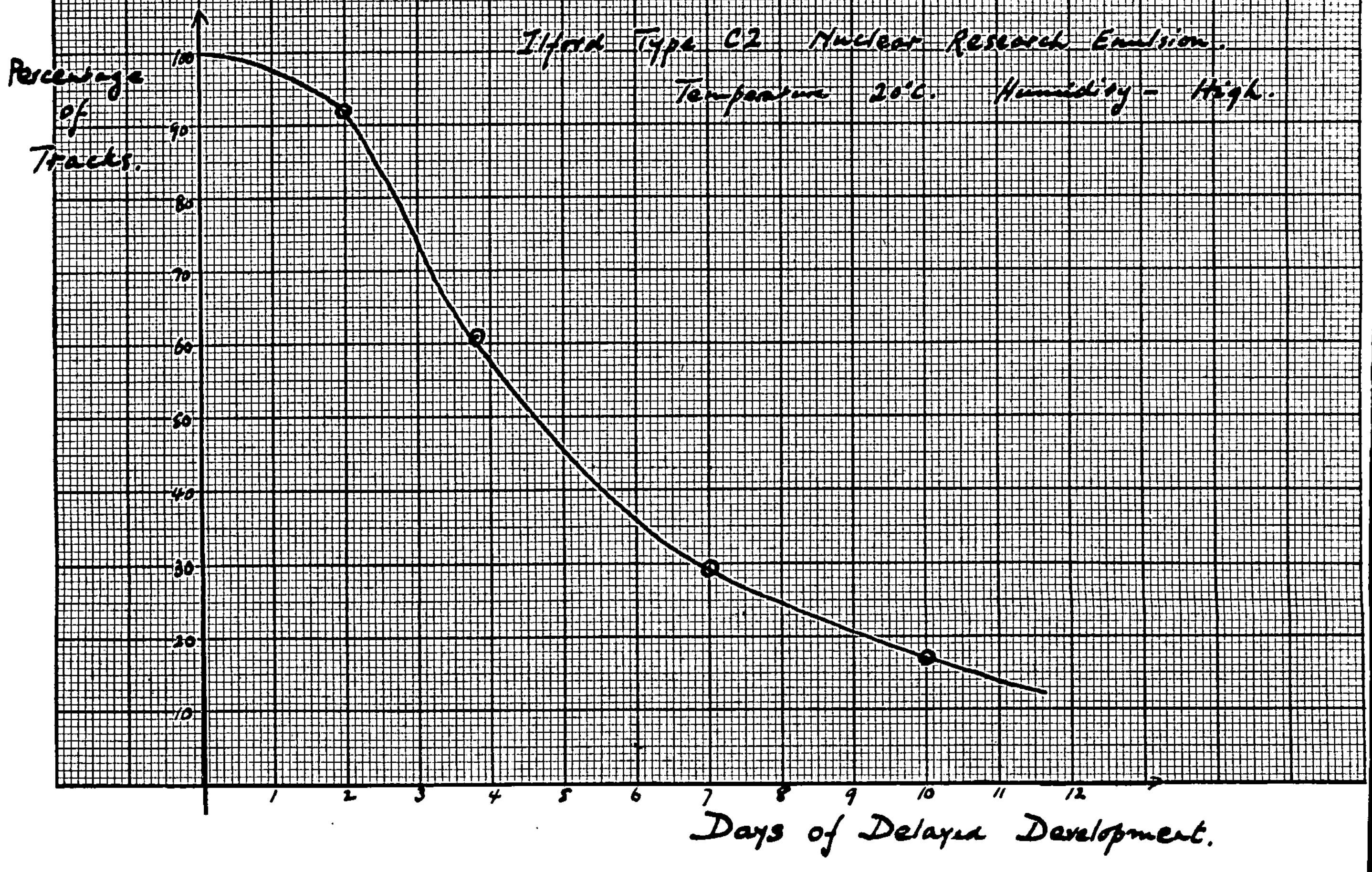
Coppens' Curve (29).

Ilford Type C2 Nuclear Research Emulsion. 17°-18°C.



Ilford Type C2 Nuclear Research Emulsion.

Temperature 20°C. Humidity - High.



storage, then decreases rapidly, and finally tends slowly towards zero. A typical curve taken from Coppens' results is shown opposite. Underneath this curve is a dotted curve showing the number of tracks having "lives" between t-dt and t+dt plotted against the time of delayed development t. This curve is of the Gaussian type, and shows a maximum for a time T, which is the most probable "life" of the latent image of a track. Coppens claims that this curve may be represented by the equation

$$n = Ke^{-\frac{(t-T)^2}{\rho^2}}$$

where K and ρ are constants.

The factor T/ρ is a constant for a specific type of emulsion being 5/3 for Ilford Type C2 emulsion. An experimental curve obtained by the author is shown underneath that of Coppens. This was obtained using Ilford Type C2 emulsion, with a piece of uranium as alpha-particle source. The magnification used for counting was 1425, against a magnification of about 400 used by Coppens, but the curves have substantially the same shape. Sufficient tracks were counted per plate to give a statistical counting deviation of only 1 per cent.

This fading experiment was carried out during a heat wave in July 1949, when the temperature and humidity were very high. Coppens has shown that such conditions cause acceleration of the fading of the latent image, but if the emulsion is immersed in a solution containing between 10 g. and 50 g. of borax per litre for 10 minutes, before exposure to the alpha-particle source, then no fading of the latent image occurs for periods up to 50 days of delayed development.

Later work by G.Albouy and H.Faraggi (31) confirms all the foregoing observations and throws light on other factors influencing fading. They show that the pH of the gelatin in the emulsion can influence the rate of fading, and when emulsions are immersed in solutions which are appreciably acid, that is solutions whose pHs are less than 2, the rate of fading is accelerated. The author can confirm this observation qualitatively, for in the course of the present work emulsions were immersed in solutions of uranium at pHs less than 2 and the fading of the tracks observed was quite considerable. Albouy and Faraggi found that in the presence of dry oxygen the rate of fading was much greater than in the presence of dry air or nitrogen, but that the rates of fading in all three cases were less than the fading rate in moist air. These experiments also revealed that the rate of fading at the top of the emulsion was greater than at the bottom. In seeking for mechanism to explain the influence of the various factors mentioned on the rate of fading of the latent image these authors discount the hypothesis suggested by Yagoda and Kaplan, on the grounds that the amount of hydrogen peroxide produced by the ionising power of alpha-radiation on the water in the emulsion is not sufficient to cause a detectable amount of fading. The mechanism which they propose is the oxidation of silver according to the following equation:-

$$2\,Ag + O + H_2O = 2\,Ag^+ + 2OH^-$$

They claim that the experimental data support such a mechanism and argue briefly as follows.

(a) A rise in temperature causes an increase in the rate of fading, and this is to be expected since a temperature rise will accelerate the oxidation reaction.

(b) High atmospheric humidity and temperature cause the emulsion to swell and thereby increase its water plus oxygen uptake. Such conditions have been shown to markedly increase the rate of fading.

(c) A low pH will favour the above reaction whereas a high one will retard it. It is claimed that the retarding action of borax and sodium carbonate on the rate of fading is due to the fact that these solutions have high pHs.

Conclusions.

It is clear from the experimental evidence available that the factors influencing the fading of the latent image in Nuclear Research emulsions are as summarised below.

(i) An increase in temperature causes an increase in the rate of fading, a decrease in temperature retards it.

(ii) Water vapour in the presence of oxygen causes rapid fading, but in the absence of oxygen water causes no fading at all. In a dry atmosphere of oxygen fading is appreciable, but not so rapid as in the presence of water vapour.

(iii) In a dry inert atmosphere, such as dry nitrogen, the rate of fading is very slow.

(iv) In vacuo there is no appreciable fading after many days delay in development.

(v) A low pH accelerates fading: a high pH retards it.

(vi) The rate of fading depends upon the type of emulsions, its grain size, and the pH of the gelatin.

(vii) If an emulsion is immersed in a solution containing 10g. of borax per litre for 10 minutes, and allowed to dry before exposure to an alpha-particle source, then there is no detectable fading of the latent image after periods of delayed development up to 50 days.

(viii) The presence of oxidising agents in the atmosphere other than oxygen, such as hydrogen peroxide, causes very rapid fading.

The mechanism of fading is not fully understood, although there can be no doubt that it is due to the oxidation of active centres in the emulsion. The mechanism suggested by Albouy and Faraggi is according to the equation:

$$2\,Ag + O + H_2O = 2\,Ag^+ + 2\,OH^-$$

Employing this mechanism all the factors affecting the rate of fading can be satisfactorily explained except the inhibiting action of salts such as borax, sodium carbonate and lithium sulphate. The explanation that the inhibiting action of these salts is due to the high pHs which they give in gelatin can hardly be valid, since the inhibiting action of borax is greater than that of sodium carbonate although its pH is smaller, and the pH of lithium sulphate is very little greater than that of the untreated emulsion. However, it may well be that the solubility of oxygen in aqueous gelatin containing a high concentration of these salts is very much less than its solubility in water alone, and a decrease in the amount of oxygen taken up by the gelatin would certainly retard the rate of fading.

In view of the large number of factors influencing the rate of fading of the latent images of alpha-particle tracks, it is practically impossible in an experiment involving the continuous exposure of an emulsion to weak source of alpha-particle activity to obtain an accurate estimate of the number of tracks lost due to fading. Therefore, it is advisable to store emulsions during long exposures under such conditions that the number of tracks lost due to fading will be negligible. The following methods would seem to be the most satisfactory.

(a) Store the plates in a vacuum desiccator, and keep the desiccator in a refrigerator. There is a danger in using this method that the emulsion will come away from its glass backing.

(b) Store the plates in a desiccator in an inert atmosphere.

(c) Treat the plates before esposure with a solution containing about 10 g. of borax per litre, and store them under normal atmospheric conditions, or in a refrigerator.

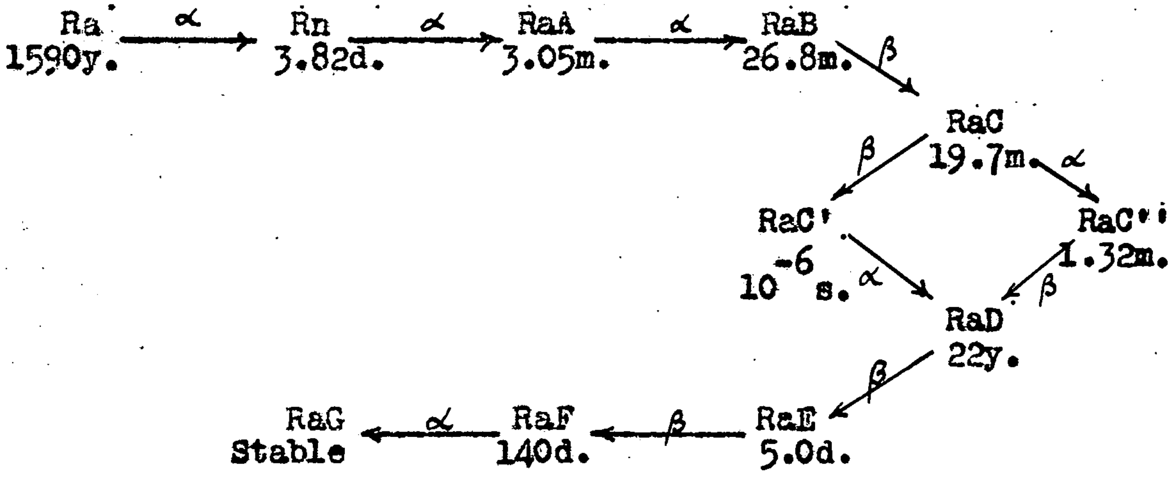
The author has used method (c) with satisfactory results in some recent work.

IV. THE ATTEMPTED ESTIMATION OF RADIUM BY THE PHOTOGRAPHIC METHOD.

Since very small amounts of radium are easily and quantitatively removed from solution by co-precipitation with a few milligrams of barium sulphate, which may subsequently be brought into a solution of very small volume, the following method of estimating radium by the photographic method was attempted. This method, if successful, would have been independent of standard solutions of radium, but dependent on uranium standards.

Method.

A small drop of solution containing a known amount of uranium is mixed with a drop of radium solution of known volume, from which all the disitegration products of radium have been removed, and the mixed solutions allowed to penetrate a piece of Nuclear Research emulsion. After a measured time of exposure, and subsequent development, examination of the emulsion under the microscope reveals both single alpha-particle tracks and "stars". The single tracks are formed by alpha-particle emissions from the uranium isotopes U238, U235 and U234, and by the alpha-particles emitted during the disintegration of radium atoms to radon atoms. The stars are formed by successive alpha-particles from single radium nuclei, as indicated in the radium series of radioactive elements shown below.



(Abbreviations:- y = years, d = days, m = minutes, s = seconds.)

The stars are mostly three-branched and four-branched, since radium-D has a long half-life and consequently the chance of an alpha-particle from radium-F appearing is small, but one five-branched star has been observed.

A track count of a certain number of fields of view of the emulsion is carried out, care being taken that it should be representative of the whole of the emulsion, and the numbers of single tracks and stars noted. From the disintegration constants of radium and radon it is possible to calculate the ratio of single tracks to stars given by the radium. This ratio is given by:-

$$\frac{\text{Number of radon atoms present after time } t}{\text{Number of radon atoms disintegrating in time } t}$$

The number of radon atoms produced in time t is $No_{Ra}\lambda_{Ra}t$ where No_{Ra} is the number of radium atoms present initially. Let this number be N_1.

The number of radon atoms present after time t is given by:

$$No_{Ra}\frac{\lambda_{Ra}}{\lambda_{Rn}}\left(1 - e^{-\lambda_{Rn}t}\right)$$

Let this number be N_2.

Thus the ratio $\dfrac{\text{Single Tracks}}{\text{Stars}} = \dfrac{N_2}{N1 - N_2}$

Using these formulae, therefore, the number of single tracks due to radium may be calculated, and hence the number of tracks due to the uranium may be had by subtracting this value from the total single alpha-particle track count. Now the concentration of uranium present in the original drop is known, and so by using the disintegration constants of radium and uranium it is possible to calculate the radium concentration.

Experimental.

Before work with mixed solutions of uranium and radium could be started it was necessary to discover whether the calculated ratio of single tracks to stars produced by radium would be given by track counts in a photographic emulsion.

Solutions of radium varying in concentration from 2 x10^{-10}g. Ra/ml. to 10^{-11}g. Ra/ml. were used. All radon was removed from the solutions before immersions were made by passing nitrogen through for 5½ hours, during which all disintegration products of radon had time to decay completely. The plates were given exposure times varying with the strengths of the radium solutions used, and track counts of the numbers of single tracks and stars were made. A Cooke microscope was used to count the tracks, an oil immersion objective with a magnification 95x being employed in conjunction with an eyepiece magnifying 10x, giving an overall magnification of 950. The ratios of single alpha-particle tracks to stars for the different exposure times were calculated and compared with those obtained by track counting. The results appear in Table 1.

<u>Table 1</u>.

Exposure Time in days.	Calculated Ratio Single tracks/Stars.	Found Ratio Single tracks/Stars.
1	10.74	11.0 ± 1.5 15.0 ± 2.3
2	5.36	8.2 ± 1 8.1 ± 1
4	2.49	5.3 ± 1
7	1.15	3.26 ± 0.2 3.29 ± 0.2

The reasons for the wide differences between the calculated ratios and those found experimentally were considered to be among the following.

(a) All the disintegration products of radium may not have been removed before the plates were immersed.

(b) Some of the radon formed may have escaped from the emulsion before disitegrating, or alternatively may have diffused within the emulsion.

(c) Radioactive impurities emitting single alpha-particles may have been present in the radium solution used.

These possible sources of error were investigated in the order given above.

(a) Inorder to ensure the complete romoval of all the disintegration products of radium the solution was treated as follows. A few milligrams each of barium chloride, lead acetate and bismuth nitrate were added to the solution, which was acidified with a few drops of glacial acetic acid. Hydrogen sulphide gas was passed through the solution until the precipitation of the sulphides of bismuth and lead was complete, when the precipitates were removed by centrifugation. These sulphides carry down with them as co-precipitated sulphides all the disintegration products in the radium series after radon. Excess hydrogen sulphide was removed by passing nitrogen through the filtrate, and the solution made neutral to litmus by adding caustic soda dropwise. One drop of glacial acetic acid was added and nitrogen passed through the solution for six hours. Emulsions were immersed in this solution, and after processing they were track counted. No appreciable difference in the single track - star ratio was found.

(b) In order to test the possibility of the escape of radon from the emulsion a plate was immersed in a concentrated radium solution, dried, and a second emulsion placed on top of it so that the two emulsions were face to face. After development the second emulsion showed many single tracks, but no stars, indicating that radon did not diffuse from the first emulsion into the second, although the possibility of it escaping through the narrow air gap between the two emulsions could not be ignored. Accordingly, an experiment in which any radon which escaped from the emulsion would be collected and estimated was performed for the author by Mr.E.R.Mercer of the Radiochemistry Department. Two pieces of plate were immersed in a solution containing about 1.6×10^{-9}g. Ra/ml. for 10 minutes, washed briefly, and allowed to dry. One of these was placed inside a small glass vessel, from which all air was swept in a stream of radon-free nitrogen, and sealed off. The vessel was stored for about a month to permit any radon which may have escaped to come to equilibrium with the radium in the emulsion. The gas in the vessel was then carried into an ionisation chamber in a stream of pure nitrogen, and the radon estimated by its rate of alpha-particle emission. After a measured time of exposure the second piece of plate was developed and track counted. From the track count an estimate was made of the amount of radium per unit volume taken up by the emulsion. These measurements revealed that approximately 20 per cent of the radon formed escaped from the emulsion.

If the ratio of single tracks to stars found by track counting is corrected for the loss of 20 per cent of radon there is still a big discrepancy between the calculated ratio and the observed one. Corrected ratios for various times of exposure are shown in Table 2. in which only the mean values of parallel experiments are shown. (Cf. Table 1)

Table 2.

Exposure Time in Days.	Calculated Ratio Singles/Stars.	Found Ratio Singles/Stars corrected for 20% loss of Radon.
1	10.74	10.0 ± 1.5
2	5.36	6.35 ± 1
4	2.49	4.7 ± 1
7	1.15	2.4 ± 0.2

It is almost certain that these further discrepancies are due to the diffusion of radon within the emulsion. Moreover, the escape of radon is probably not constant, and varies with changes in humidity and temperature.

(c) The different alpha-particle emitting elements present in a Nuclear Research emulsion may be identified by their track lengths, which can be measured to the nearest micron. However, since the difference between the calculated and observed single track - star ratios was shown to be due to the escape of radon from the emulsion and its diffusion within it, no thorough search for extraneous alpha-particle emitting impurities was made.

Conclusion.

The method outlined here for the estimation of radium by a photographic method has been shown to be unworkable owing to the escape of radon from radium loaded emulsions.

V. THE PHOTOGRAPHIC ESTIMATION OF URANIUM BY THE IMMERSION METHOD.

In 1947 E.Broda (32) (33) investigated the uptake of uranium by Ilford Type C2 Nuclear Research emulsions immersed in solutions of uranyl acetate under different conditions. From the results of a series of semi-quantitative experiments he assessed the influence of the following factors.

(1) Time of washing of the emulsion after immersion.
(2) Temperature of the immersion bath.
(3) Time of immersion.
(4) Concentration of hydrion - pH.
(5) Concentration of neutral salt.
(6) Concentration of heavy metal ion - Pb^{++}.

Broda found that the time of washing of the emulsion after immersion could be varied within wide limits without affecting the uptake of uranium. A small increase in the temperature of the immersion bath caused a relatively large increase in uptake, as evidenced by the fact that between 3°C. and 32°C. the uptake increased three-fold. The velocity of uptake decreased rapidly with time of immersion until the emulsion became apparently saturated with uranium. From the track counts he obtained Broda showed that the emulsion took up much more uranium per unit volume than the concentration of uranyl ion in the solution, and even allowing for the swelling of the emulsion during immersion it was clear that most of the uranium was being adsorbed. The pH of the immersion bath had a pronounced effect on uptake; from pH 1 to pH 2.6 the uptake was reasonable constant, but at higher pHs it increased rapidly with increasing pH. This increase in uptake with increasing pH Broda attributed to the hydrolysis of the uranyl ion. He found that at constant pH and constant temperature the uptake of uranium by the emulsion was a linear function of the uranyl ion concentration, except at very low concentrations - about 10^{-5}M. - when the uptake was greater than the linear relationship required. He further demonstrated that a high concentration of neutral salt can considerably reduce uptake, and that high concentrations of heavy metal ions such as Pb^{++}, whilst not markedly affecting uptake can cause serious desensitization of the emulsion.

Careful consideration of these findings pointed to the possibility of developing a method for the micro-estimation of uranium by the immersion technique. The method is simple, and is outlined below.

The Immersion Method.

A piece of Ilford Type C2 40μ Nuclear Research emulsion is immersed in a bath containing uranyl acetate, under known conditions of temperature and pH, for a measured interval of time. It is removed, washed free from excess acetate solution, dried, and stored in the dark for a known time. When fully processed and dried, a microscopic examination of the emulsion under high magnification reveals numbers of single alpha-particle tracks from U238, U235 and U234, all alpha-particle emitting isotopes of uranium. The number of tracks in a certain volume of emulsion is counted, and since uranium is taken up uniformly by the emulsion, the track density per unit time of exposure gives a direct measure of the amount. For the sake of uniformity the track counts are normalised to give the Average Track Count per Field of View per 10 Days Exposure, and this is hereafter referred to as the abbreviation A.T.C./F.O.V./10 days.

Since alpha-particles are emitted at random the number of alpha-particle tracks in each field of view will show statistical fluctuations, and the percentage statistical counting deviation will be given by $100/\sqrt{n}$, where n is the total number of tracks counted. The counting of alpha-particle tracks is a fatiguing and time-consuming task, and as large numbers of plates had to be examined, not more than 625 tracks per plate were counted, thereby giving a counting deviation of 4 per cent.

In order to develop the method as an analytical tool it was necessary to establish the relationship between the track count and the uranyl ion concentration under the most suitable immersion conditions. Therefore, all the conditions influencing the uptake of uranium which were investigates by

Broda were re-investigated, with the exceptions of (5) and (6) above.

Experimental.

A solution of uranyl acetate, free of all alpha-particle emitters except U238, U235 and U234, was prepared from uranyl nitrate. This salt contains a proportion of ionium, which stems from U234 by alpha-particle emission and itself emits an alpha-particle, so it was necessary to remove this contaminant. Crystals of uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, were shaken with a large volume of ether, the uranyl nitrate going into the ethereal layer and the ionium remaining in the aqueous layer formed by the water of crystallisation of the nitrate. The ethereal layer was removed, the ether carefully evaporated, and after washing with a little water the nitrate was evaporated to dryness. Successive small quantities of a mixture of glacial acetic acid and acetic anhydride were added to the nitrate, which was evaporated to dryness after every addition, until no further nitrous fumes were evolved. The residue, mainly uranyl acetate, was treated with glacial acetic acid until a negative test for nitrate ion was obtained from a test sample. The acetate thus prepared was dissolved in 5 per cent acetic acid. The uranium content of this solution was estimated by removing three 5 ml. samples from the solution, evaporating them to dryness in silica crucibles, and igniting them to constant weight of U_3O_8 over Meker burners above 850°C. The three weights agreed to within 0.2 per cent, and the solution was found to contain 21.25 g. of uranium per litre. From this standard all the uranyl acetate solutions used were prepared by dilution.

Before commencing experiments small pieces of Ilford Type C2 40μ plates, about 3 sq.cm. in area were cut with a diamond and cemented to microscope slides with Canada Balsam. This facilitated the experimental handling of the plates, and they were already mounted for microscopic examination. Moreover, the slides could be numbered for identification by scribing on the glass with a diamond.

During manipulation care was taken that the plates should not be contaminated, and all operations were carried out in dim red light. With a few exceptions immersions were made in blackened boiling tubes, which were clamped in a thermostat maintained at $25^{\circ} \pm 0.02^{\circ}$C. The time of immersion of a plate was reckoned from the time it was taken from the immersion bath to the time of its entry into the developing bath, and was measured by stop watch.

Emulsions were developed for 30 minutes, with intermittent rocking, in a solution containing one part of developer to three parts of water at 17°-19°C. The developer contained 2.2 g. of metol, 73 g. of anhydrous Na_2SO_3, 8.8 g. of hydroquinone, 48 g. of anhydrous Na_2CO_3 and 4 g. of KBr per litre. After development the plates were washed briefly in running water and immersed in a "stop bath" of 2 per cent acetic acid for 10 minutes. They were fixed in a fixing bath containing two parts of saturated $Na_2S_2O_3$ solution, one part of "acid hardener" and eight parts of water until the opaqueness due to silver halide had completely disappeared. Fixing was usually complete in 30 to 40 minutes. The "acid hardener" contained 50 g. of anhydrous Na_2SO_3, 75 ml. of glacial acetic acid and 100 g. of potassium alum per litre. After fixing plates were washed in a stream of running water for more than an hour. All the solutions used in processing were filtered before use, and when the developer began to show a pale straw colour it was discarded and a fresh supply prepared. Unfiltered solutions cause excessive background fog.

The pH measurements were made with a Cambridge Instrument Company pH meter which gave readings accurate to 0.02 pH. The pH of the buffered acetate-acetic acid solution was adjusted to the rquired value by the addition of small drops of 3N. HCl or 3N. NaOH.

The examination of the plates and the counting of the alpha-particle tracks were carried out using a 95x oil immersion objective in conjunction with a 10x eyepiece, giving an overall magnification of 950, and the area of each field of view was about 2.54×10^{-4}sq.cm.

The method of counting tracks was as follows. Fields of view were chosen in such a way as to cover an area representative of the whole emulsion surface, care being taken not to count near the edges of the emulsion, since track densities were always greater there than in the interior. Each field of view was searched slowly from left to right, the search being materially aided when the track density was high by fitting a squared grid into the eyepiece of the microscope. In this way it was possible to make an accurate count, no portion of a field of view being counted twice. It was the convention when counting to include tracks which appeared only partly within the field of view. The main errors in track counting may be sub-divided as follows.

(i) Errors due to non-identification of tracks, or the identification of spurious tracks.

(ii) Errors due to contamination of the emulsion, and to extraneous alpha-particle tracks originating in the plate backing of the emulsion. These may be classed as track background.

(i) From the experience gained in examining thousands of alpha-particle tracks it appears that the minimum number of consecutive grains required before a track can be identified as being due to the passage of an alpha-particle is about five or six. Yagoda (34) claims that tracks of residual range of 0.3 air-cm. can be differentiated from the background when a magnification of 1000x is used. Such a track would have a range of about 2 microns in the emulsion, and probably consist of five or six grains. Thus some alpha-particles emitted near the top or bottom of the emulsion may not leave sufficient grains to be identified as a track. In addition, tracks in the emulsion formed by alpha-particles emitted at angles normal to the surface may not be counted, since as the depth of focus is altered such tracks will only appear as persistent grains, and may easily be missed if the background fog is appreciable.

(ii) Examination of unexposed plates reveals very few background tracks, only about one track being seen per hundred fields of view. Besides these tracks, due to contamination of the emulsion in manufacture, several stars per plate may be observed which obviously have their origins in the glass backing of the emulsion. These are easily recognised as being spurious.

It is worthy of note that in cases where it was suspected that track counts were suspiciously high measurements of the emulsion thicknesses of the plates being counted have shown them to be much greater than 40μ. In one case an emulsion thickness 75 per cent in excess of this was measured. Pieces of emulsion used for immersion experiments were normally taken from the central portion of the Ilford Type C2 Nuclear Research plates used, in order to avoid the variation in emulsion thickness.

(1) Time of washing.

Five plates were immersed in a solution containing 7.4×10^{-4}g. of uranium per ml. for 30 minutes at pH 2.0 and 25°C. After immersion the plates were washed for 2 seconds, 30 seconds, 1 minute, 30 minutes and 1 hour respectively. They were given exposure times of 1 day, processed and track counted; and all of them gave an A.T.C./F.O.V./10 days within the limits 75 ± 3.

This indicates that within the counting deviation of 4 per cent the time of washing has no effect on the uptake of uranium by the emulsion.

The result agrees with that of Broda (32).

(2) Temperature of Immersion.

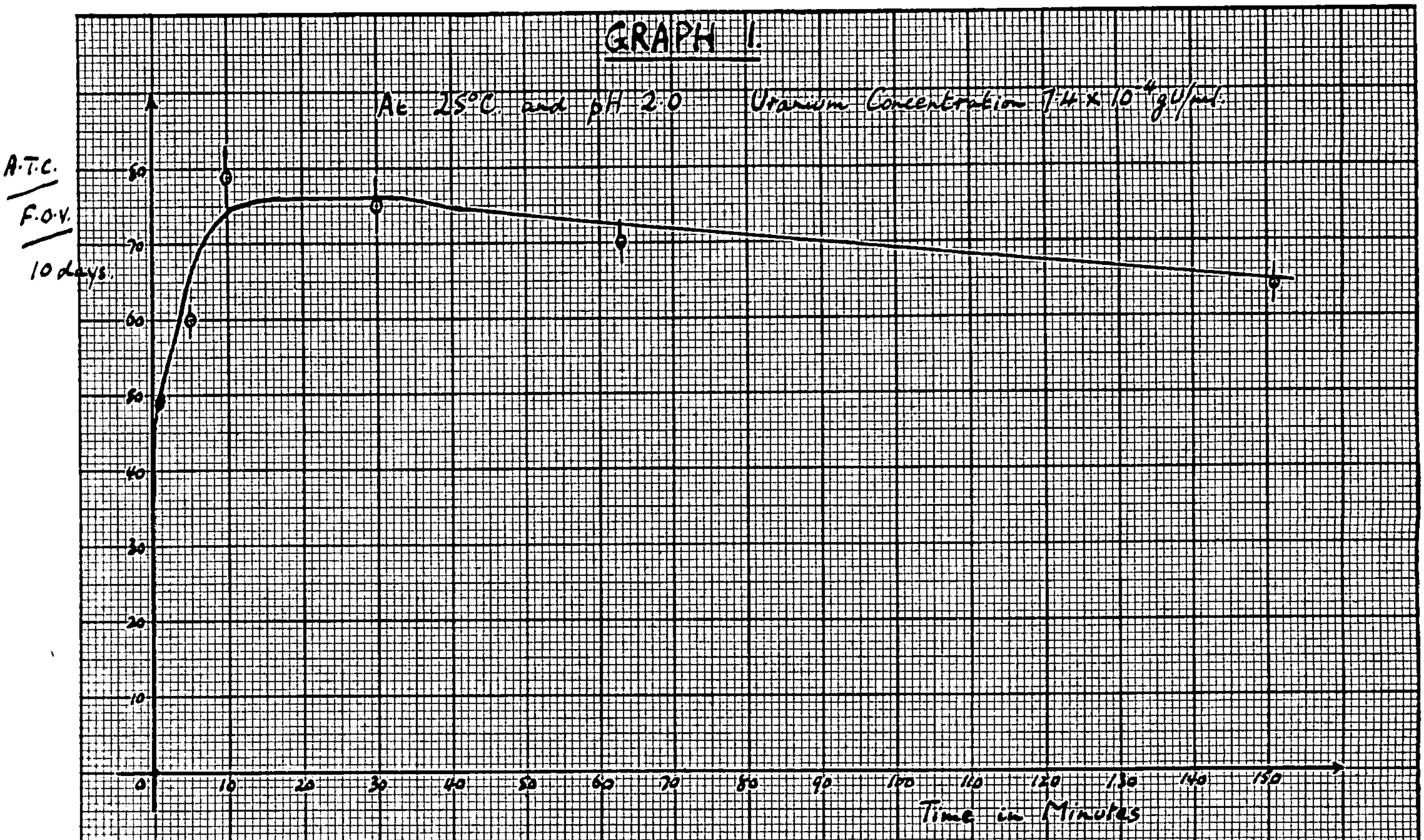
Plates were immersed in a solution containing 7.4×10^{-4}g. of uranium per ml. for 30 minutes at pH 2.0 and at temperatures of 20°c., 25°C. and 28°C. The immersions were carried out in duplicate, and the plates given exposure times of 1 day. The track counts are given in Table 3.

Table 3.

Temperature	20°C.	25°C.	28°C.
A.T.C./.F.O.V./10 days	45	74	122

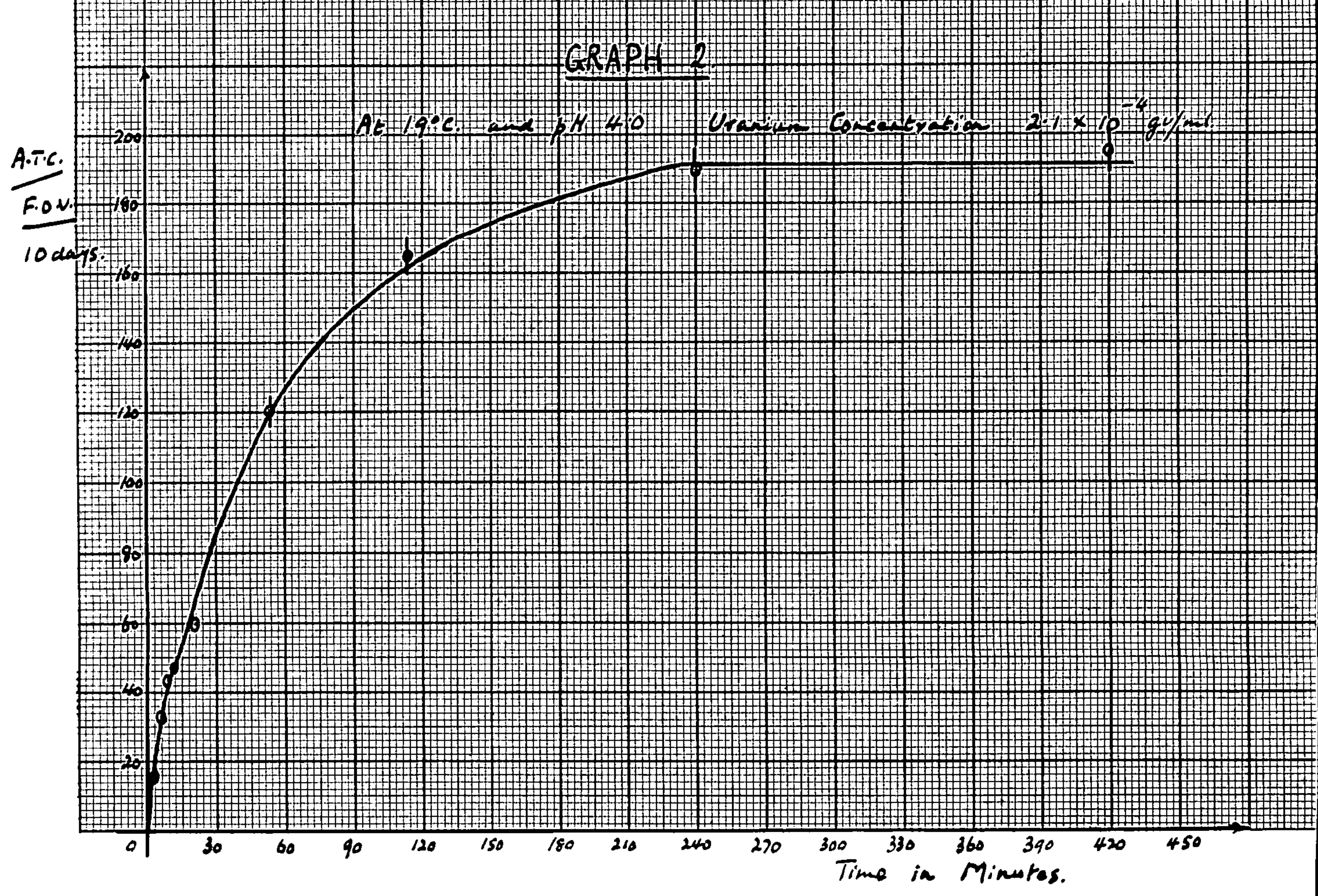
GRAPH 1.

At 25°C. and pH 2.0 Uranium Concentration 7.4×10^{-4} gU/ml.



GRAPH 2.

At 19°C. and pH 4.0 Uranium Concentration 2.1×10^{-4} gU/ml.



There is almost a three-fold increase in uptake of uranium over even this small temperature range, and therefore it is imperative to maintain the immersion bath at a constant temperature to obtain reproducible results.
This result confirms that of Broda (32).

(3) Time of immersion.

(i) The concentration of uranium, the hydrion concentration and the temperature of the solution were maintained at constant values, and the time of immersion varied. Immersions were made in solution containing 7.4 x 10^{-4}g. of uranium per ml. at pH2.0 and 25°C., for periods of 1 minute, 5 minutes, 10 minutes, 30 minutes, 63 minutes and 151 minutes. All plates were given an exposure time of 1 day.
Table 4 below shows the observed track counts for the different times of immersion.

Table 4.

At 25°C. and pH 2.0 Uranium Concn. 7.4 x 10^{-4}g.U/ml.

Time of Immersion in minutes.	1	5	10	30	63	151
A.T.C/F.O.V./10 days.	49	60	79	75	70	64

These results are used to plot Graph 1 opposite. The lines drawn through the points on the curve give a measure of the track counting deviation. It will be noted that the uptake of uranium by the emulsion increases rapidly with time of immersion, reaches a maximum value and then appears to decrease gradually. This indicates a tendency for the uranium to be slowly desorbed after an initial strong adsorbtion. The period of time over which the increase in uptake is rapid probably covers the period of swelling of the emulsion.

(ii) The above experiment was repeated using a solution containing 2.1×10^{-4}g. of uranium per ml., and making the immersions at pH 4.0 and 19°C. for the different times of immersion shown. Plates were given exposure times of approximately 1 day. The results are given in Table 5.

Table 5.

At 19°C. and pH 4.0 Uranium Concn. 2.1×10^{-4}g.U/ml.

Time of Immersion in minutes.	3	6	9	12	20	55	115	240	420
A.T.C./F.O.V./10 days	16	33	44	47	60	121	165	190	195

The figures from the above table are used to plot Graph 2. Since these immersions were made at room temperature they are comparable with those made by Broda and show the same trend towards saturation, but give no evidence of desorption as in Graph 1.

From the figures given in Table 4 the Average Track Count per day for a plate immersed in a solution containing 7.4×10^{-4}g. of uranium at pH 2.0 and 25°C. for 30 minutes is 7.5 tracks per F.O.V. Now, the area of each F.O.V. is 2.54×10^{-4} sq.cm. and the thickness of the emulsion is 4×10^{-3}cm., and so the volume of emulsion examined per F.O.V. is approximately 10^{-6}ml. From this it follows that the track density is 7.5×10^{6} tracks per ml. of emulsion, for each day of exposure. The amount of uranium required to give this number of alpha-particles in a day is 3.5×10^{-3}g. Thus the emulsion takes up about five times the concentration of uranium in the solution. Swelling of the emulsion will account for some of this, but there is no doubt that uranium is adsorbed.

(4) Concentration of hydrion - pH.

In this experiment all factors affecting uptake were controlled except the pH, which was varied within wide limits. Immersions were made in solutions containing 7.4×10^{-5}g. of uranium per ml. for 30 minutes at 25°C. The experimental results are given in Table 6.

Table 6.

At 25°C. Uranium Concn. 7.4×10^{-5}g.U/ml.

pH.	1.1	1.5	2.0	2.45	2.95	
A.T.C./F.O.V./10 days	1.07	4.8	8.0	22.7	60	

GRAPH 3

At 25°C. Uranium Concentration 7.4 × 10^{-5} gU/ml

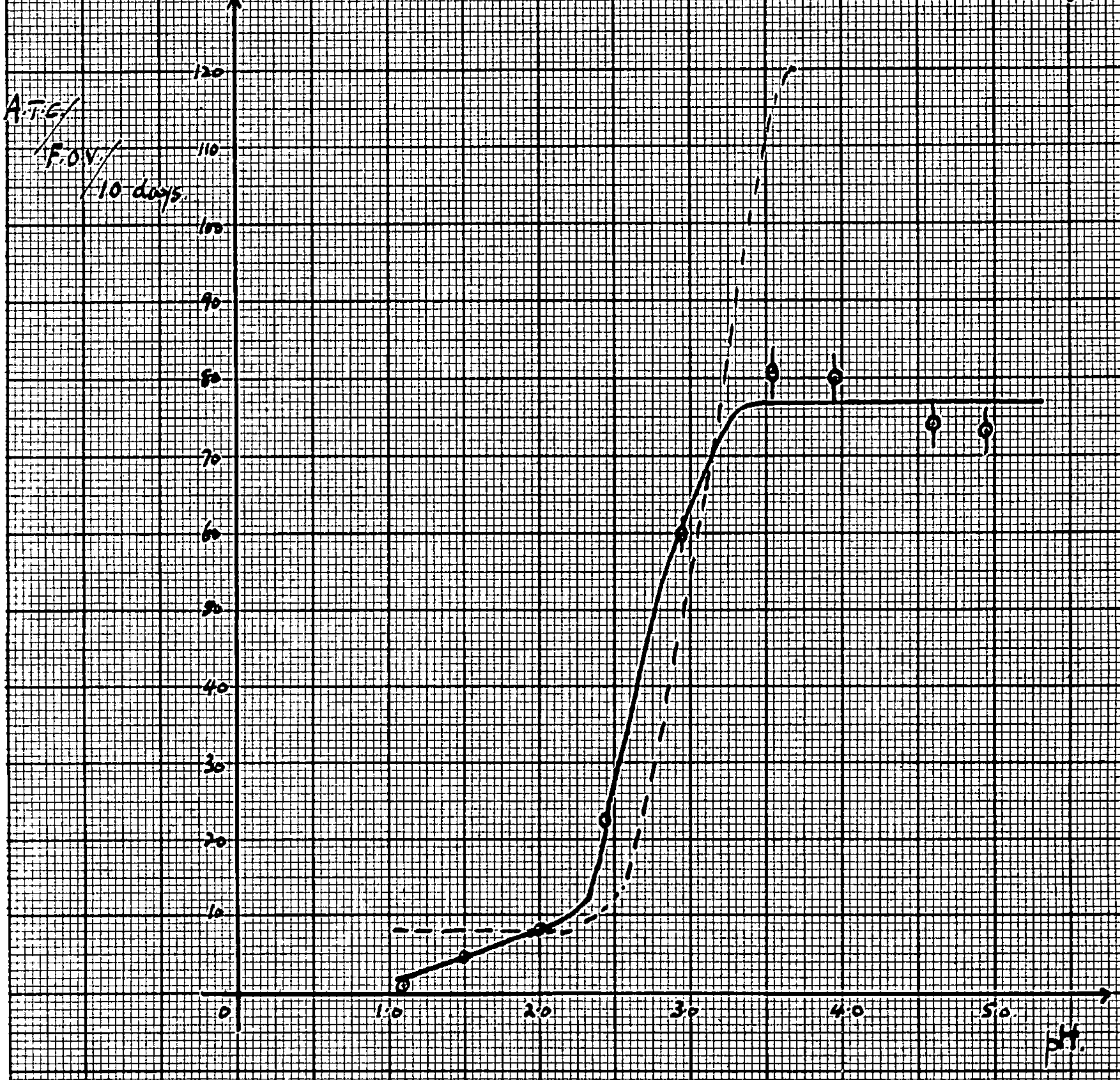


Table 6 (Continued).

pH.	3.55	3.95	4.60	4.95	
A.T.C./.F.O.V./10 days.	81	80	74	73	

The figures in Table 6 were used to plot Graph 3.

The gradual increase in uptake of uranium from pH 1.1 to pH 2.0 may not be real since at pHs below pH 2 there is considerable fading of tracks, which would make the track counts obtained too low. Moreover, as the plates immersed at pHs 1.1, 1.5 and 2.0 were given exposures of 13 days the track count loss may have been considerable. All other plates were given exposures of 1 day.

There is a rapid increase in uptake of uranium between pH 2.0 and pH 4.0 and it is thought that in this pH region the uranium is hydrolysed. After pH 4 the uptake of uranium is approximately constant, and here the uranium is undoubtedly fully hydrolysed.

The following figures, showing increase in uptake with increase in pH, are given by Broda (32).

pH (calculated)	1.0	1.6	2.0	2.6	3.1	3.7
Normalised track count ..	37	41	41	67	330	600

These figures have been used to plot the dotted curve which has been normalised to fit Graph 3 at pH 2. It will be noticed that the two curves are similar in shape, although Broda did not make immersions at pHs beyond 3.7 and consequently did not observe the plateau after pH 4. The solution he used contained 1.2 g. of uranium per litre, and in consequence his exposure times would be short. During short exposures the fading of the latent image due to high hydrion concentration would not be serious, and, therefore, the portion of the dotted curve (Broda's curve) from pH 1.0 to pH 2.0 probably represents the true uptake of uranium.

(5) Concentration of uranyl ion.

A careful study of the data presented in Tables 3,4, 5, and 6 led to the conclusion that the most suitable conditions for investigating the influence of uranyl ion concentration on the uptake of uranium by the emulsion were (a) an immersion time of 30 minutes, (b) a bath temperature of 25°C, and (c) pHs of 2.0 or 4.0. The uptake at pH 4.0 is approximately 10 times that at pH 2.0, and should give the more sensitive results, but the effect of uranyl ion concentration at both pHs was studied. Although it is in the region of pH 2 that small changes in pH bring about relatively large increase in uptake, it was decided to make immersions at this pH rather than at, say, pH 1.5, because of the effect of hydrion concentration on the fading of the latent image. An immersion time of 30 minutes at 25°C. was selected because after this time the emulsion is apparently saturated with uranium, which tends to be desorbed if the immersion is prolonged.

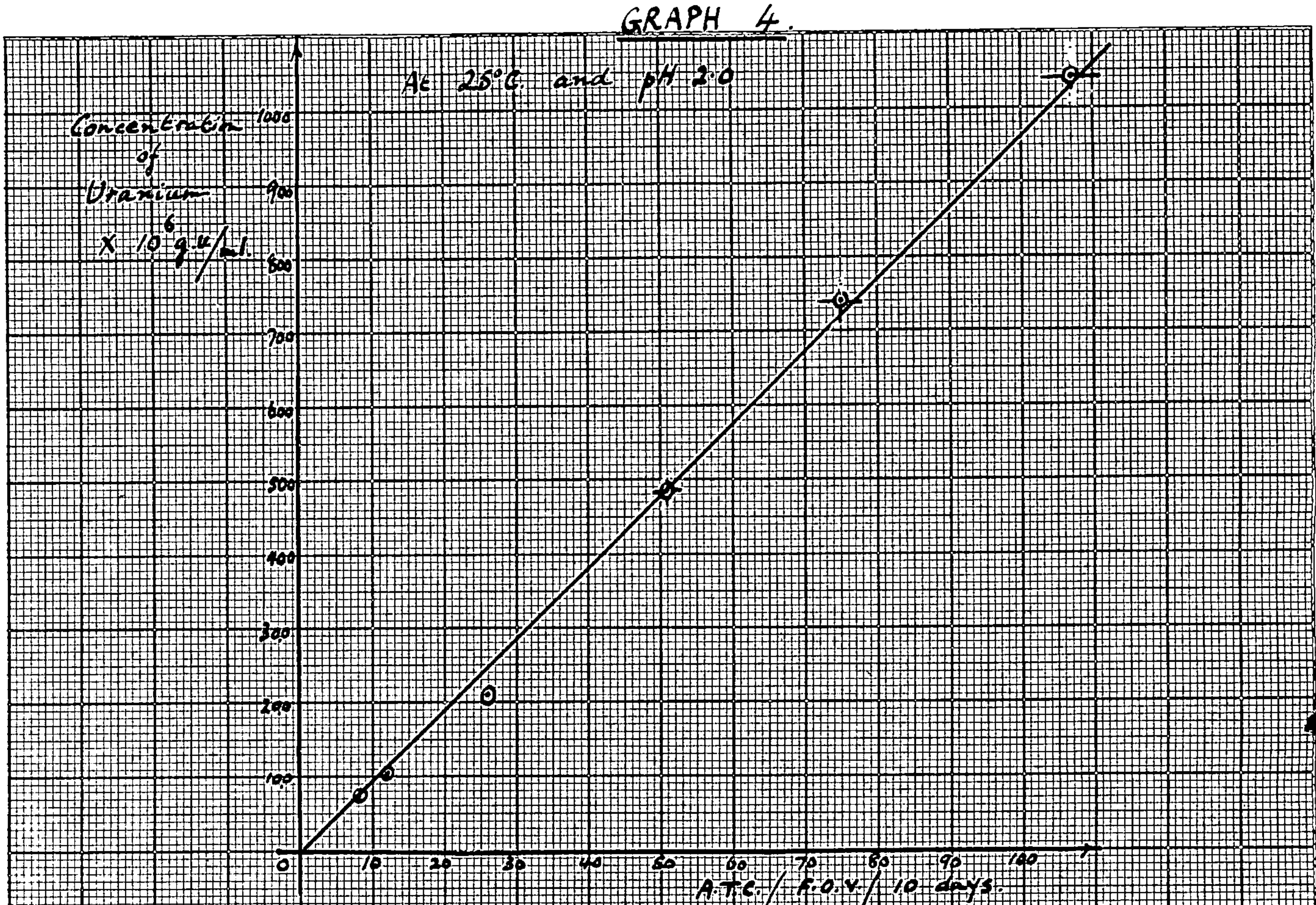
(i) Plates were immersed in uranyl acetate solutions of different concentrations for 30 minutes at 25°C. and pH 2.0, washed for 30 seconds, and stored in the dark for exposure times which varied according to the concentration of uranium. All immersions were made in duplicate and the results appear in Table 7.

Table 7.

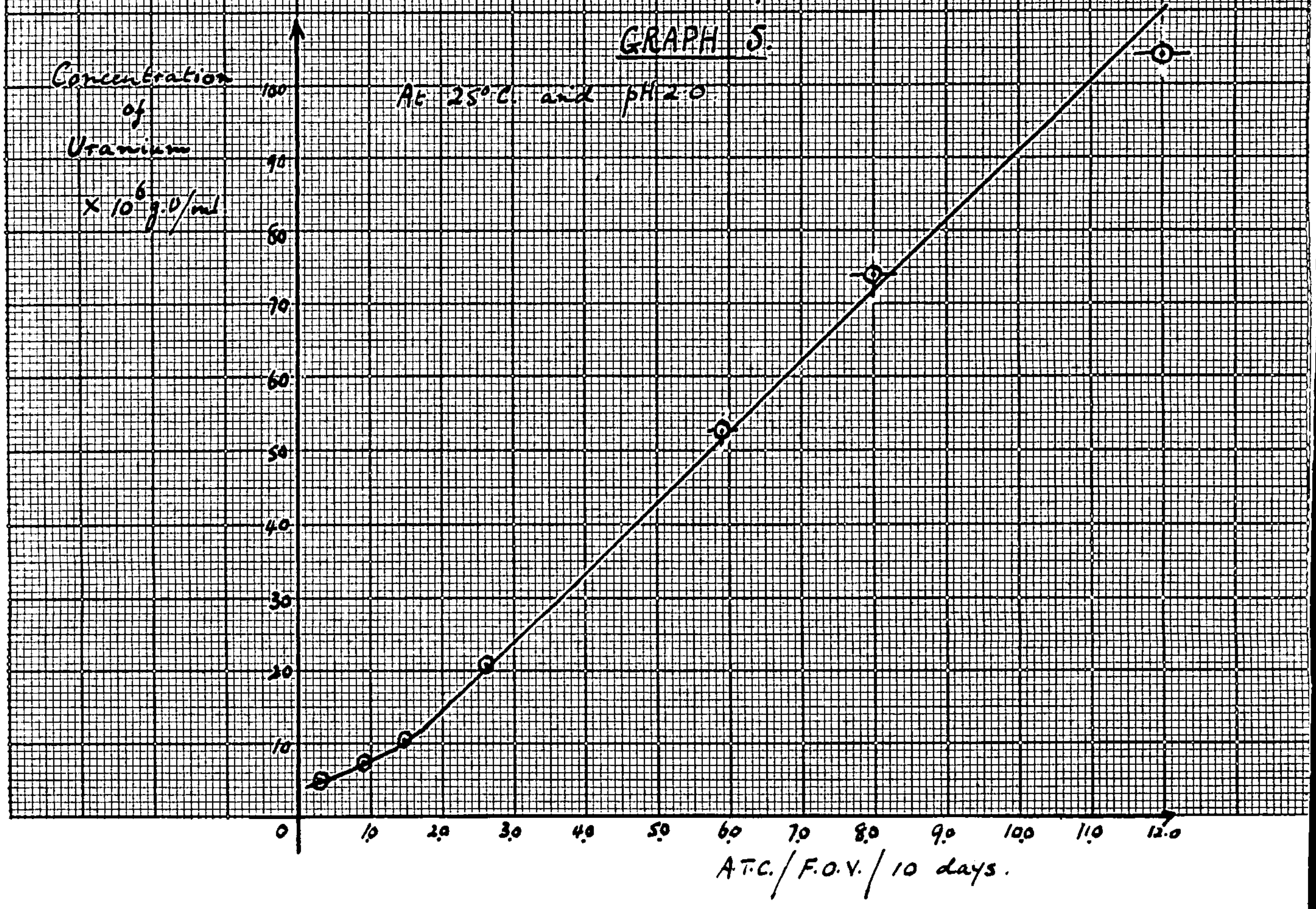
At 25°C. and pH 2.0 Immersion Time 30 minutes.

Concentration of Uranium x 10^6g.U/ml.	Time of Exposure in Days.	A.T.C./F.O.V./10 days.
1940	1	176
1040	1	107
740	1	75
484	1	51
210	3	26
104	7	12
74	11	8.0
52.5	6	5.9
21	13	2.6
10.4	29	1.45
7.4	35	0.89
5.0	36	0.26

GRAPH 4.



GRAPH 5.



(ii) Immersions were made inuranyl acetate solutions of different concentrations for 30 minutes at 25°C. and pH 4.0, washed for 30 seconds, and stored in the dark for varying periods of time. The track counting of these emulsions was carried out using a new microscope giving a magnification of 1425, and the area of each field of view was 1.41 x 10^{-4}sq.cm. The results are shown in Table 8.

Table 8.

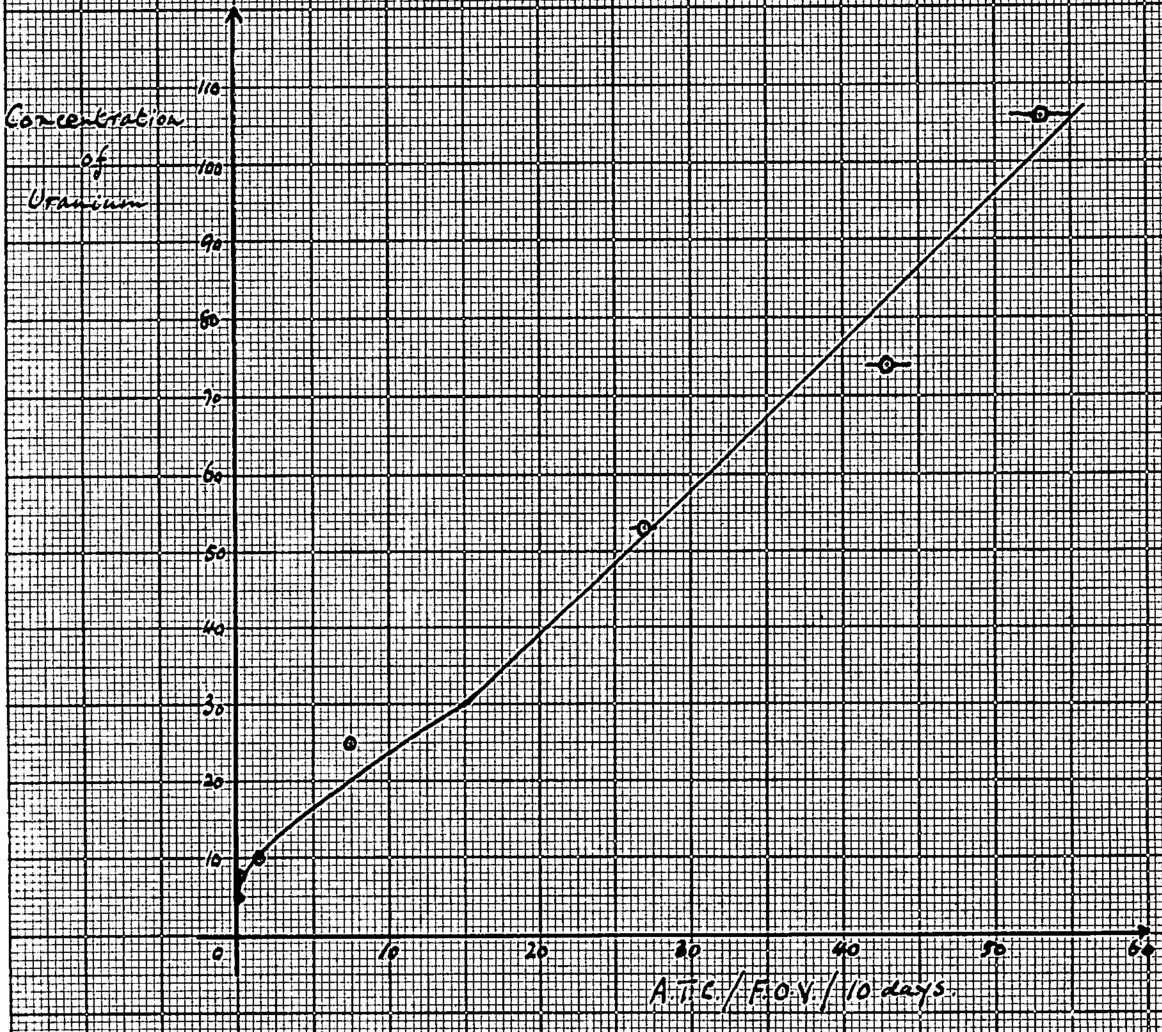
At 25°C. and pH 4.0 Immersion Time 30 minutes.

Concentration of Uranium x 10^6g.U/ml.	Time of Exposure in days.	A.T.C./.F.O.V./10 days.
106	1	53
74	1	43
53	1	27
25	4	7.6
10	4	1.6
7.4	18	0.24
5.0	18	0.17

The data from Tables 7 and 8 were used to plot Graphs 4, 5 and 6. The uptake of uranium by the emulsion is shown to be a linear function of the uranyl ion concentration

GRAPH 6.

At 25°C and pH 4.0



down to 10^{-5}g.U/ml., but at lower concentrations this is clearly not the case. Emulsions which were immersed in solutions of very low uranium content were given long exposures, and the examination of alpha-particle tracks in these emulsions revealed marked reduction of the grain densities. The data presented in Chapter III of this thesis show that during long exposures a considerable amount of fading of the latent track image can take place under normal atmospheric conditions. Unfortunately when these experiments were carried out the serious nature of this fading was not known, and no special precautions were taken during storage of the plates to prevent loss of tracks by fading. However, even allowing for a considerable amount of fading it is believed that the decrease in the ratio of the track count to the uranyl ion concentration shown in Graph 6 is real. For instance, the track count for a uranium concentration of 5×10^{-6}g.U/ml. at pH 4.0 is only the same as that for a similar concentration at pH 2.0, when it should be 10 times greater. The trend in Graph 5 may not be real, for although in this case exposure times were very much longer than those at pH 4.0 the decrease in the ratio of track count to uranyl ion concentration is not so pronounced.

Conclusions.

The experimental data show that for a standard time of immersion of 30 minutes at 25°C., and at pHs of 2.0 or 4.0, the uptake of uranium by Ilford Type C2 Nuclear Research emulsion is a linear function of the uranyl ion concentration for concentrations between 10^{-3}g.U/ml. and 10^{-5}g.U/ml. At lower concentrations of uranyl ion the linear relationship no longer holds. Because of the uncertainty of the experimental results in this region, due to loss of tracks by the fading of the latent image during the long exposures used, no reliance can be placed on the initial portions of the curves obtained.

With the knowledge now available of the factors affecting the fading of the latent image emulsions could be stored under conditions designed to prevent fading, such as those outlined in Chapter III. However, the track densities, even for long times of exposure, are far too small at very low uranyl ion concentrations to make the method of any use as an analytical method for the micro-estimation of uranium, and many hours would have to be spent in track counting to attain the accuracy required. It is possible that by using emulsions of much greater thickness, and making immersions at higher temperatures under similar conditions, the track counts could be enhanced, but the uncertainty of the true relationship between the observed track counts and the uranyl ion concentration would remain.

The Immersion Method could be used for the estimation of uranium in low grade ores, since very small pieces of plate can be cut from large plates and these would require much less than ml. of solution for complete immersion. However, a method for estimating uranium down to 10^{-8}g. with fair accuracy was needed, so attempts were made to develop methods of greater sensitivity. An account of these is given in the next chapter.

VI. THE PHOTOGRAPHIC MICRO-ESTIMATION OF URANIUM BY THE EXTERNAL SOURCE METHOD.

When a drop of uranium solution is delivered onto the surface of a Nuclear Research emulsion it will spread over the whole area, and after drying some of the uranium nuclei will have penetrated into the emulsion and the remainder be concentrated at or near the surface. The track count obtained from a representative area of the emulsion, after a known time of exposure, should give a measure of the amount of uranium present in the original drop provided the area of impregnated emulsion surface is known. An attempt was made to develop a method for the estimation of microgram amounts of uranium according to this procedure, but it was found that the solution had a strong tendency to overflow the edges of the emulsion. This was especially so when the drop consisted of uranium nitrate dissolved in quick-drying solvents such as an alcohol-water mixture or ether, which have low surface tensions. If comparatively large areas of emulsion were used in order to check this tendency the observed track counts per field of view were so small, with low concentrations of uranium, as to prohibit the use of the method; the number of fields of view which had to be counted to give the required counting accuracy being very large indeed. Moreover, there was some uncertainty as to the actual fraction of the uranium nuclei which remained on the surface of the emulsion, as this varied with changes in conditions of evaporation and led to inaccurate results. The method is recommended by H.Yagoda (35) in his recent book as being useful for the study of rare solutions, since only very small volumes of solution are required.

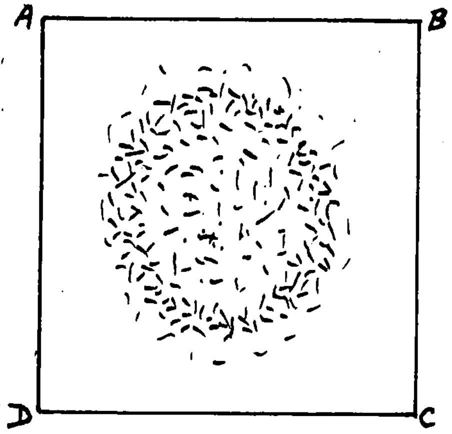
Instead of evaporating a small drop of solution on the surface of the emulsion the drop may be evaporated on a plane glass surface of small area, and this external source applied to the emulsion for the desired exposure time. In this way uncertainty as to the true time of exposure due to the time for the drop to evaporate is entirely eliminated. Providing the amount of uranium deposited is of the order of micrograms no corrections need be applied for source absorbtion of alpha-particles. Using this technique the method outlined below has been developed.

The External Source Method.

A measured drop of solution, containing a known amount of uranium, is delivered from a calibrated capillary micro-pipette onto the plane ground end of a glass rod of about 0.15 sq.cm. cross-section. The drop is slowly evaporated to dryness using a radiant heater, and the end of the glass rod clamped against a piece of Ilford Type C2 emulsion. After the desired exposure time the emulsion is processed, dried, and examined under the microscope using a magnification of 1425.

The deposit on the end of the rod is far from uniform, most of the uranium migrating to the edges of the drop during evaporation, and the track pattern revealed in the emulsion by microscopic examination is similar to that sketched in Fig. 1.

Fig. 1.



The high track density defines the edges of the deposit, and by means of the micrometers on the microscope, which enable the stage to be moved along the x and y axes, an area containing the whole of the tracks is measured. Such an area is ABCD in Fig. 1. The whole of the area ABCD is systematically track counted, commencing at A and traversing to B by moving the stage one F.O.V. diameter at a time. The distance AB is fixed so as to be an exact multiple of one F.O.V. diameter. At B the stage is moved so that a distance along BC greater than one F.O.V. by 18 microns is covered. This avoids the possibility of any track being counted twice. The track counting of the emulsion is resumed, traversing from N to A.

All tracks start at the emulsion surface making the track counting easier than in the case of immersed emulsions, and tracks having their origins within the emulsion are not counted. Such spurious tracks are very few. Should a track appear only partly within a field of view it is counted if its emulsion surface end appears within the field of view.

Account is kept of the number of fields of view counted and of the total track count. The area of one F.O.V. is 1.41 x 10^{-4} sq.cm., and so the area of emulsion counted is computed. It is assumed that the average track density in the unexamined portion of the emulsion is the same as that of the track counted portion, and although the distribution of tracks is very heterogeneous this is a reasonable assumption. Hence the total number of tracks is estimated.

A.F.Kovarik and N.I.Adams (36) give the rate of emission of alpha-particles from the isotopes U238, U235 and U234 as 25.01 x 10^{3} alpha-particles per second per gram of uranium. Thus 10^{-6} g. of uranium emits 2160 alpha-particles per day. If a source of uranium containing exactly one microgram is deposited on a plane glass surface and placed against a photographic emulsion, at the end of one day's exposure 1080 tracks should be registered. This number is, of course, subject to statistical fluctuations, since alpha-particles are emitted at random.

Using this figure the number of tracks expected from the uranium deposit on a rod is calculated.

In order to test the method various sources of uranium, from 10^{-6}g. of uranium to 5×10^{-8}g. of uranium, were deposited on the plane ground ends of glass rods and applied to pieces of Ilford Type C2 emulsion. The observed track counts were then compared with the calculated values.

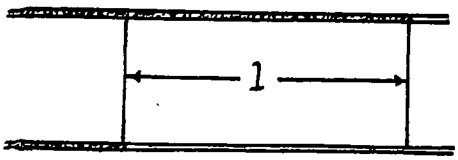
Experimental.

The uranium solutions used in these experiments were prepared from the uranyl acetate standard purified for use in the Immersion Method.

The capillary micro-pipettes were manufactured from soft glass tubing in the following way. A short length of about 7 mm. bore glass tubing was drawn out into capillaries of about 0.5 mm. bore, and these were cut into 10 cm. lengths. The cross-sections of the capillaries were inspected under the microscope, and those with non-circular cross-sections were discarded. The bores of the capillaries were examined microscopically along their entire lengths at intervals of 0.5 cm. and those showing variations in bore greater than 0.5 per cent were discarded. Only two out of about forty capillaries thus prepared and inspected came up to these requirements. Fine tips were drawn on the ends of these, and they were cleaned in aqua regia, washed and dried.

The micro-pipettes were calibrated for capacity by weighing the mercury in different lengths of capillary. This provided a further check on the uniformity of bore, and indicated the approximate delivery per cm. to be expected. Liquids are taken up in such pipettes by capillary action, and delivered by placing the tip of the pipette against the surface of the receptacle and expelling the liquid from the pipette by gentle blowing with the mouth. The expelled liquid will form a drop around the tip of the pipette and when sufficient has been delivered the tip of the pipette is withdrawn sharply from the drop. In this way liquid is delivered without creeping round the tip of the pipette. The technique requires practice but it is easily acquired. Using this method the delivery per cm. of the micro-pipettes was determined by delivering measured lengths of concentrated H_2SO_4, and titrating the acid against N/100 KOH with phenolphthalein as indicator. The acid was delivered onto thin glass cover slips and these dropped into distilled water in the titration vessel. The lengths of acid delivered were measured with a centimetre rule fitted with a vernier, and reading to 0.1 mm. In no case was the full volume of acid in the micro-pipette expelled, since this would have introduced errors due to the narrow tip, but measurements of the lengths delivered were made according to Fig. 2.

Fig. 2.



1 is the length of liquid delivered.

Typical results of such a calibration are given in Table 9.

Table 9.

Length of 36.6 N. H_2SO_4 delivered.	Mls. of 0.806 N/100 KOH used.	Volume of 36.6 N. H_2SO_4 $\times 10^3$ ml.	Delivery of pipette per cm. $\times 10^3$ ml.
2.32 cm.	18.05	3.97	1.71
3.46 cm.	25.65	5.84	1.69
2.40 cm.	18.81	4.14	1.72
4.73 cm.	36.66	8.06	1.70
1.91 cm.	14.60	3.21	1.68

From these figures the capillary micro-pipette delivers $1.70 \pm 0.02 \times 10^{-3}$ ml./cm.

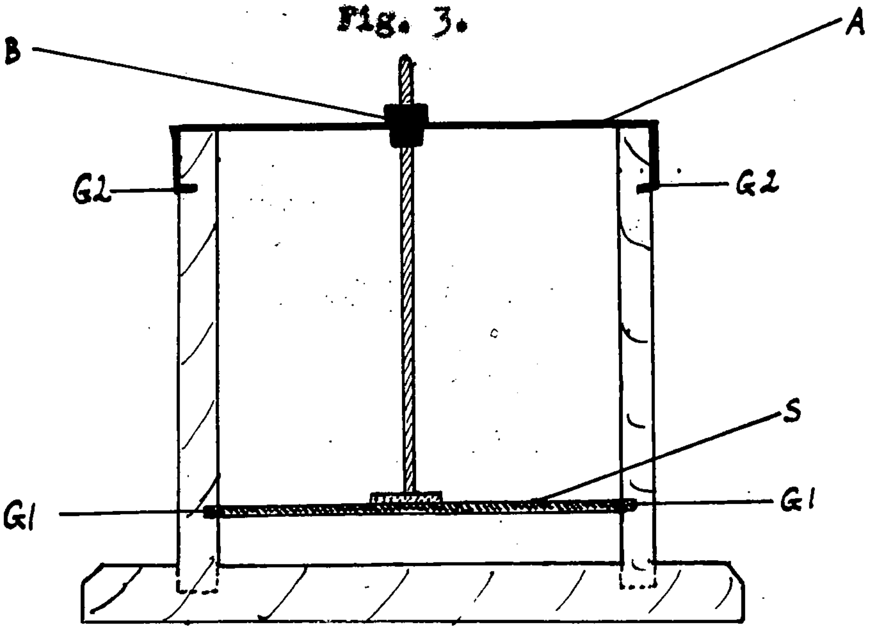
The capillary micro-pipettes thus prepared and calibrated were carefully labelled and stored in clean test tubes with cotton wool to protect the tips.

The glass rods with plane ground ends were prepared from ordinary Pyrex glass rod as follows. The rod was cut into 12 cm. lengths, and one end of each length trimmed with a mechanical grinder until it was about 4 mm. square. This end was ground mechanically with various grades of grinding powders until it was plane, the final grinding being done with moist alumina.

Small pieces of Ilford Type C2 plates were cut and cemented to microscope slides before use, as described in Chapter V.

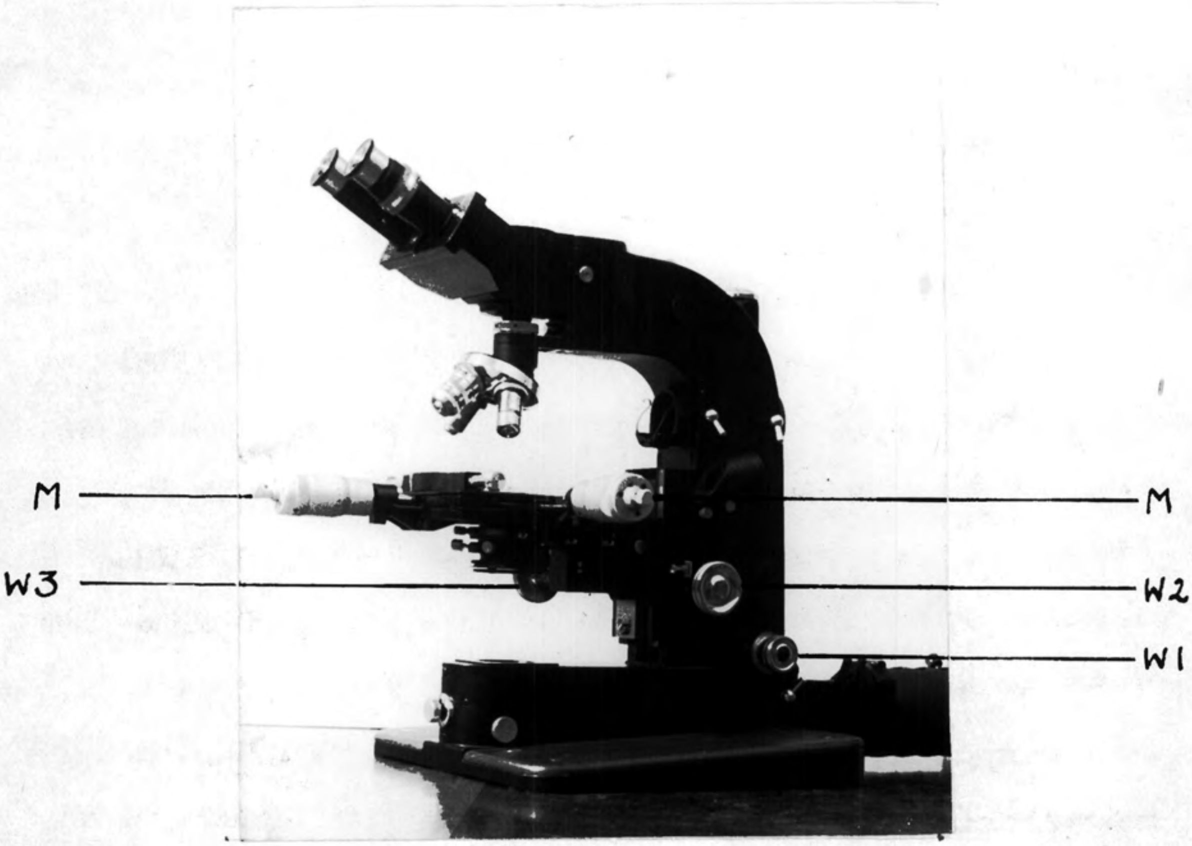
The camera used for holding the uranium deposit against the emulsion is illustrated in Fig. 3.

Fig. 3.



The apparatus consists of a wooden base about 9 inches by 5 inches, in which two 3½ inch wooden uprights are set. The microscope slide S is held in position by two horizontal grooves G1, along which it can be moved as required. Two more horizontal grooves G2, cut near the tops of the uprights, allow an aluminium slotted bar A to be moved into position above the microscope slide. A brass screw B, bored to take the glass rod, passes through the slot in the aluminium bar with its head resting against it, and when the glass rod has been set in the required position on the emulsion surface a brass nut clamps the screw in position. Thus the rod is supported vertically, and the only weight pressing on the emulsion surface is that of the rod itself. Examinations of rods held in this way against emulsion surfaces show that there is no visible air gap between the end of the rod and the emulsion. In practice care must be exercised in setting the ends of the glass rods against the emulsion surfaces, otherwise these may be damaged and some of the deposits rubbed off the rods. The apparatus is covered with a light tight box for the duration of exposures. Half a dozen exposures may be made in the camera at the same time.

The emulsions were processed after exposure according to the method given in Chapter V.



Nuclear Research

Microscope

The microscope used for examination of the emulsions and for track counting is shown in the photograph opposite. It was specially designed for work with Nuclear Research emulsions, being constructed by Cooke, Troughton and Simms Ltd., on the suggestion of Dr.Rotblat of Liverpool University, and has certain distinctive features.

By means of the two micrometers M the stage of the microscope can be moved along the x and y axes so that examination of an emulsion can be made anywhere within an area of 6.25 sq.cm., but to examine an area larger than this the position of the plate on the stage must be altered. The micrometer screws may be read accurately to 1 micron. The wheel W1 enables the oil immersion objectives to be racked up and down very slowly in making a thorough search of the full depth of an emulsion, and it carries a scale graduated in microns. Thus, with the aid of the micrometers and the fine-focussing adjustment fairly accurate measurements of track lengths can be made. The wheel W2 racks the whole of the stage and substage into position beneath the objective, and wheel W3 adjusts the substage. The binocular eye-pieces can be moved to the distance between the eyes of the observer, and prevent undue eyestrain during observation. Measurements of the angles between tracks can be made by fitting the goniometer provided to the eyepiece. Numerous other eyepiece attachments are available.

The microscope has a built-in illuminating system with a variable diaphragm for regulating the light intensity, and colour filters to aid observation. The best conditions of illumination for track counting were obtained by adjusting the illuminating system to give optimum illumination with the diaphragm fully open, and then inserting the green colour filter and closing down the diaphragm until the light intensity was just sufficient for clear observation. Emulsions were counted at a magnification of 1425. When traversing along the x axis the right hand micrometer screw was moved a distance of 1.34 x 10^{-2} cm. after the track counting of each F.O.V., which was the diameter of one F.O.V.; and on reaching the edge of the area to be counted the stage was moved a distance of 1.62 x 10^{-2} cm. along the y axis by means of the front micrometer screw. Track counting was then resumed, traversing along the x axis again until the opposite edge of the area was reached. In this way the whole of the area was examined. . . Usually this area was about 0.3 sq.cm., and approximately 65 per cent of this was actually track counted, the other 35 per cent being assumed to have the same average track density.

No corrections were made to the estimated counts for the background count of the emulsion, as this only amounted to about 1 track per 100 F.O.Vs. Normally fewer than 2000 F.O. were counted, and so the maximum background would be 20 tracks. Most of these background tracks have their origins inside the emulsion and were consequently not counted.

(i) Experiments under normal conditions.

Exposures were made using sources containing amounts of uranium from 5.77×10^{-6}g. to 7.5×10^{-8}g., and for time intervals calculated to give sufficient tracks to make the statistical counting deviation small. All plates were not exposed over the same time interval, and, therefore, there were variations in climatic conditions, notably of humidity and temperature; but all exposures were made during the winter months.

The results of these exposures are given in Table 10.

Table 10.

Weight of Uranium $\times 10^8$g.	Exposure Time in Days.	Counts Observed.	Percentage Counting Deviation.	Alphas per g.U per sec.	%age of 2.50×10^4.
577	1	5960	1.3%	2.40×10^4	96%
247	0.92	2295	2.1%	2.35×10^4	94%
93.5	2.33	2230	2.1%	2.37×10^4	95%
50.5	11.92	5880	1.3%	2.27×10^4	91%
23.4	3.79	877	3.4%	2.26×10^4	90.5%
7.52	11.92	925	3.3%	2.36×10^4	94.5%

All the values obtained for the rate of emission of alpha-particles from uranium are low compared with the value of 2.50 x 10^4 alphas per second per gram of uranium given by Kovarik and Adams (36). It will be seen from the last column of Table 10 that two of the determinations, made with weak sources and given fairly long exposures, are about 9 per cent too low. Allowing for a 1 per cent error in the weights of uranium used, and taking into account the counting deviation, these values are still seriously low.

The following were considered as being possible reasons for the low track counts obtained.

(a) Loss of some of the deposit of uranium by sputtering during the evaporation of the drop of solution.

(b) Loss of uranium from the glass rods during manipulation.

(c) Loss of uranium by the solution overflowing the edges of the glass rod during evaporation.

(d) Loss of tracks due to fading.

(e) Loss of tracks by failure to recognise and count same.

Of these (a) and (d) were thought to be the most likely sources of error, since the ends of the glass rods were carefully waxed around their perimeters to prevent the drop from running over the edges, and no overflowing was observed. The deposit adhered very firmly to the end of the rod, and only extremely careless handling could rub it off. With the experience gained in recognising and counting alpha-particle tracks the number of tracks missed in counting was considered to be very small. No precautions were taken to avoid fading as the exposure times were not very long, but recent work, to which reference has already been made in Chapter III, has shown that fading can be appreciable even in short exposures.

In view of this further exposures were made using borax loaded emulsions, which have been found to conserve the latent track image for periods of delayed development up to 50 days.

(2) Experiments with borax loaded emulsions.

Some pieces of Ilford Type C2 emulsion were immersed in a solution containing 10 g. of borax per litre for 10 minutes and allowed to dry. Exposures were made using these emulsions and amounts of uranium varying from 4.76×10^{-6} g. to 4.54×10^{-7} g. Care was taken to evaporate the drops of solution very slowly using a radiant heater.

The results of these exposures are presented in Table 11.

Table 11.

Weight of Uranium x 10^8 g.	Exposure Time in Days.	Counts Observed.	Percentage Counting Deviation.	Alphas per g.U per sec.	%age of 2.50 x 10^4
476	1.77	9030	1%	2.48 x 10^4	99%
138	2.02	2980	1.8%	2.48 x 10^4	99%
81.2	4.56	4030	1.6%	2.51 x 10^4	100.4%
45.4	2.02	1000	3.2%	2.51 x 10^4	100.4%

From the figures in Table 11 it is clear that the method is a very good one for the micro-estimation of uranium, and could likewise be used to make an accurate determination of the disintegration constant of U238. There is no fading of the latent track image in borax loaded emulsions stored under ordinary atmospheric conditions for periods up to 50 days, and therefore the method should be workable down to 10^{-8} g. of uranium.

Conclusions.

The External Source Method for the micro-estimation of uranium outlined above will compare very favourably with other methods. Microgram amounts can be estimated with an accuracy of 3 per cent and 10^{-8}g. with an accuracy of 6 per cent. The value for the rate of emission of alpha-particles from the isotopes U238, U235 and U234 in naturally occurring uranium obtained by this method is 2.48×10^4 alpha-particles per second per gram, in very good agreement with the value obtained by Kovarik and Adams (36) using the alpha pulse counting method.

The method should prove suitable for the estimation of the uranium contents of low grade ores and minerals. Attempts have been made to apply the method to the estimation of uranium in magnetites. An account of this work is given in Chapter VII.

VII. THE APPLICATION OF THE EXTERNAL SOURCE METHOD TO THE MICRO-ESTIMATION OF URANIUM IN MINERALS.

It is essential in using the External Source Method that the deposit of uranium on the end of the glass rod should be "weightless". Corrections cannot be made for the source thickness unless this is uniform. Therefore, in applying this method to the estimation of the uranium content of minerals and rock specimens the uranium must be extracted from them in a pure, carrier-free state.

The uranium content of minerals is usually of the order of a microgram of uranium per gram of mineral, and W.D.Urry (3) has shown that such a small amount of uranium can be quantitatively removed from solution by co-precipitation with the hydroxides of ferric iron and aluminium, using carbonate-free ammonia as precipitant. Following the preliminary separation of uranium in this way it must be quantitatively removed from the carrier iron and aluminium. It is well known that uranyl nitrate can be removed from aqueous solutions containing a high proportion of neutral nitrate by extraction with ether, but the partition coefficient for the extraction is low. Linstead et alii (37) have shown that under similar extraction conditions tetrahydrosylvan (2-methyl tetrahydrofuran) has a much bigger partition coefficient for uranyl nitrate.

With the above facts in mind it was decided to use the following procedure in an attempt to extract uranium quantitatively from minerals in a pure, carrier-free state.

(i) The whole of the mineral specimen to be analysed for uranium, about 1 gram, is brought into solution.

(ii) Ferric hydroxide, and other co-precipitated hydroxides, are precipitated from the solution by the addition of carbonate-free ammonia. Should the mineral contain iron or aluminium, as in beryls and magnetites, no ferric iron carrier is added to the solution; otherwise about 10 milligrams of ferric iron are added as ferric chloride.

(iii) The precipitated hydroxides are dissolved in the minimum amount of nitric acid, the solution adjusted to about 50 per cent nitrate concentration with ammonium nitrate, and extracted with successive equal volumes of tetrahydrosylvan until the extraction of uranium is complete.

(iv) The combined tetrahydrosylvan extracts are evaporated to dryness, and the residue taken up in 5N. nitric acid and evaporated to a small drop about 0.02 ml. in volume. This drop is taken up in a capillary micro-pipette and delivered onto the end of a glass rod, where it is slowly evaporated to dryness.

Before adopting this procedure preliminary experiments were carried out to test the extraction efficiency of tetrahydrosylvan under different extraction conditions.

Experimental.

The tetrahydrosylvan was fractionally distilled before use, and the fraction coming over between 78.3°C. and 78.9°C. was taken.

During extractions made with tetrahydrosylvan from solutions containing 50 per cent ammonium nitrate and 5 per cent nitric acid the acid attacked the organic solvent, and on slow evaporation of the tetrahydrosylvan after extraction it exhibited a strong tendency to explode! Care was therefore exercised in all extractions with the solvent, and the nitric acid concentration was kept at the absolute minimum, although extraction efficiency was much greater with the acid in the solution. The pHs of all acid solutions to be extracted were adjusted to about pH 3, that is to the yellow colour given by thymol blue indicator, and then 1 small drop of concentrated nitric acid added. The very slow evaporation of the tetrahydrosylvan from these extracts on a hot water bath proceeded smoothly, and left behind a minimum of brown resinous matter, probably a polymer. This was easily destroyed by treatment with 5N. nitric acid.

The efficiency of the extraction of uranium from uranyl acetate solutions by tetrahydrosylvan was first investigated.

Extraction of uranium from uranyl acetate solutions.

1 ml. of uranyl acetate solution containing 2 micrograms of uranium was run into a 10 ml. centrifuge tube fitted with a ground glass stopper, and 1 ml. of 80 per cent ammonium nitrate and 1 small drop of concentrated nitric acid added. This solution was extracted with four 2 ml. amounts of tetrahydrosylvan, the solution being agitated for 2 to 3 minutes after each solvent addition, and the aqueous and organic layers being separated after agitation by centrifugation. The tetrahydrosylvan layers were withdrawn, combined and evaporated to dryness in a 10 ml. crucible over a hot water bath. The visible residue of brown polymer was destroyed by slow evaporation to dryness with 5 N. nitric acid, and the invisible residue of uranyl nitrate taken up in dilute nitric acid. This acid solution was slowly evaporated to a small drop of about 0.02 ml. volume, and the drop transferred onto the end of a glass rod by means of a capillary micro-pipette. The crucible was washed with a small amount of dilute nitric acid, which was taken down to small volume and also transferred to the end of the glass rod. These drops were evaporated to dryness and the uranium determined by the External Source method.

The results of several such extractions show that uranium can be extracted with an efficiency approximating to 100 per cent.

Extraction of uranium carried down by ferric iron hydroxide.

To a solution containing 2 micrograms of uranium about 10 milligrams of ferric iron, as ferric chloride, were added, and the volume made up to 150 ml. with distilled water. The solution was heated to boiling point and a concentrated solution of carbonate-free ammonia added dropwise until the smell of ammonia fumes indicated the presence of excess. The solution was maintained near the boiling point for 10 minutes, and then set aside for half an hour. The precipitate was removed by centrifugation, dissolved in the minimum of concentrated nitric acid, transferred to a 10 ml. centrifuge tube and the volume adjusted to 2ml. with distilled water. 2 ml. of 80 per cent ammonium nitrate were added, the solution adjusted to pH 3, using thymol blue as indicator, and then one small drop of concentrated nitric acid added. This solution was extracted with four equal volumes of tetrahydrosylvan and the combined extracts treated as previously described.

The results of three extractions carried out in this way were very unsatisfactory, only 31 per cent, 34 per cent and 37 per cent of uranium being extracted.

The reasons for the low amounts of uranium being extracted are believed to be among the following.

(a) Incomplete removal of uranium from the solution by adsorption on ferric hydroxide.

(b) Loss of alpha-particle tracks due to the fact that a certain amount of iron was extracted with the uranium, and caused source absorbtion of alpha-particles.

(c) Incomplete extraction of uranium with tetrahydrosylvan.

Further extractions were made using a double extraction technique, the extract from the first tetrahydrosylvan extraction being redissolved in nitric acid and the whole extraction procedure repeated in order to reduce the amount of iron which came out with the uranium. Six extractions with equal volumes of tetrahydrosylvan were made in both cases instead of four. The percentage amounts of uranium extracted by this procedure, as measured by the track counts obtained, were still between 30 and 40 per cent.

It is possible that some of the uranium was adsorbed onto the walls of the crucible used for evaporation of the tetrahydrosylvan extracts, although the crucible was carefully rinsed with nitric acid in order to avoid this.

In spite of the fact that the extraction procedure was very unsatisfactory it was decided to attempt the estimation of uranium in a specimen of magnetite, and check the result against a similar determination made by the estimation of radium in the sample.

The estimation of uranium in magnetite.

About 1 gram of magnetite, finely ground to pass 200 mesh, was accurately weighed out into a platinum crucible. A few drops of hydrofluoric acid were added and a fairly vigorous reaction ensued. When it had subsided a few more drops of acid were added, and the crucible warmed gently until fumes ceased to be evolved. This was repeated until about 3 ml. in all of hydrofluoric acid had been added. Concentrated sulphuric acid was then added dropwise and the crucible heated to drive off the fumes of hydrogen fluoride produced. This procedure was repeated until further additions of sulphuric acid failed to produce fumes. In this way the small amount of silica in the magnetite was removed. The residue was fused with 6 grams of anhydrous fusion mixture - sodium and potassium carbonates - over a Meker burner for about half an hour, and the fused mass, when cool, dissolved in the minimum of dilute nitric acid. There was no residue. Since magnetite is mainly Fe_3O_4 this solution consisted chiefly of the nitrates of iron, sodium and potassium. It was heated to boiling point, and carbonate-free ammonia added dropwise with constant stirring until it was in slight excess. All the iron in the solution was precipitated in a finely-divided form, and was kept at the boiling point for about 10 minutes before being set aside for half an hour.

The precipitate was separated by centrifugation, dissolved in the minimum of nitric acid and evaporated to dryness. The residue was dissolved in about 5 ml. of extremely dilute nitric acid, and the solution divided into two 2.5 ml. portions. these were extracted according to the double extraction method previously described, and the combined residues from the extractions transferred to the end of a glass rod so that the uranium could be estimated by the External Source method.

The results of two such uranium estimations are given here.

	Analysis 1.	Analysis 2.
Weight of magnetite taken	1.056_7 g.	1.123_8 g.
Exposure time of emulsion (days)	3.34	3.83
Estimated number of tracks ...	1060	1630
Amount of uranium (grms.)	3.0×10^{-7}	3.9×10^{-7}
Weight of uranium per gram of magnetite.	2.8×10^{-7}g.	3.5×10^{-7}g.

An indirect determination of the uranium content of this magnetite, by measuring its radium content, was made by Mr. E.R.Mercer of the Radiochemistry Department, and a value of $8.9_7 \times 10^{-7}$g. of uranium per gram of magnetite obtained. Comparison of this value with those obtained above shows that the extraction of uranium from the magnetite is still only 30 to 40 per cent efficient.

Conclusions.

The procedure described here for the extraction of amounts of uranium from 10^{-6}g. to 10^{-7}g. from aqueous nitrate media is very unsatisfactory. Whilst tetrahydrosylvan is much more efficient than other solvents for extracting uranyl nitrate from concentrated nitrate solutions, it is not an easy liquid to handle because of its tendency to erupt with explosive violence when heated at temperatures above its boiling point.

Other solvents could be tried in the extraction, such as ether or hexone, which may not extract iron together with uranium. It is possible that the partition chromatographic technique devised by Linstead and his collaborators (37) might prove of use in the separation of the uranium before its estimation by the External Source method.

REFERENCES.

(1) C.J.RODDEN, Analytical Chemistry, 21, 327 (1949)

(2) F.HERNEGGER and B.KARLIK, Sitzber. Akad. Wiss. Wien. Math. Naturwiss. Klasse, 2b, 103, 148 (1938)

(3) W.D.URRY, Am.J. Sci., 239, 191 (1941)

(4) H.MACHE, ST.MEYER, and E.v.SCHWEIDLER, Weiner Anz., 16, II (1905)

(5) W.D.URRY and C.S.PIGGOT, Am. J. Sci., 239, 633 (1941)

(6) R.D.EVANS, Rev. Sci. Instruments, 6, 99 (1935)

(7) C.T.R.WILSON, Proc. Roy. Soc. London, 85, 285 (1911)

(8) M.REINGANUM, Physik. Z., 12, 1076 (1911)

(9) O.MÜGGE, Central. Mineral., 71, 114,142(1909)

(10) S.KINOSHITA, Proc. Roy. Soc. London, 83A, 432 (1910)

(11) W.MICHL, Sitzber. Akad. Wiss. Wien. Abt. 2a, 121,1431 (1912

(12) W.MAKOWER and H.P.WALMSLEY, Proc. Phys. Soc. London 26A, 261 (1914)

(13) L.MYSSOWSKY and P.TSCHISHOW, Z. Physik., 44, 408 (1927)

(14) H.WAMBACHER, Sitzber. Akad. Wiss. Wien. Abt. 2a, 140 271 (1931)

(15) M.BLAU and H.WAMBACHER, Sitzber. Akad. Wiss. Wien. Abt. 2a, 141, 617 (1932)

(16) A.JDANOFF, J. phys. radium, 6, 233, (1935)

(17) C.F.POWELL, G.P.S.OCCHIALINI, D.L.LIVESEY and L.V.CHILTON, J. Sci. Instruments, 23, 102 (1946)

(18) P.DEMERS, Can. J. Research, A25, 223 (1947)

(19) M.M.SHAPIRO, Revs. Modern Phys., 13, 58 (1941)

(20) C.F.POWELL, G.P.S.OCCHIALINI, and C.M.G.LATTES, Nature, 160, 453 (1947)

(21) C.F.POWELL, G.P.S.OCCHIALINI and C.M.G.LATTES, Nature, 160, 486 (1947)

(22) C.F.POWELL and S.ROSENBLUM, Nature, 161, 473 (1948)

(23) H.YAGODA and N.KAPLAN, Phys. Rev., 72, 356 (1947)

(24) E.BRODA and K.JENKNER, Nature, 164, 412 (1949)

(25) M.BLAU, Sitzber. Akad. Wiss. Wien. Abt. 2a, 140,623 (1931)

(26) J.LAUDA, Sitzber. Akad. Wiss. Wien. Abt. 2a, 145,707 (1935)

(27) H.YAGODA and N.KAPLAN, Phys. Rev., 73, 634 (1948)

(28) W.A.LAMB and F.W.BROWN III, Phys. Rev., 74, 104 (1948)

(29) R.COPPENS, J. phys. radium, 10,11 (1949)

(30) R.COPPENS, J. Phys. radium, 10,57 (1949)

(31) G.ALBOUY and H.FARAGGI, J. phys. radium 10, (1949)

(32) E.BRODA, J.Sci. Instruments, 24, 136 (1947)

(33) E.BRODA, Nature, 160, 231 (1947)

(34) H.YAGODA, Radioactive Measurements with Nuclear Emulsions, p. 124, John Wiley and Sons, Inc., New York.

(35) H.YAGODA, Ibid., p. 129

(36) A.F.KOVARIK and N.I.ADAMS, J. Applied Phys., 12, 296(1941)

(37) R.P.LINSTEAD, F.H.BURSTALL and T.V.ARDEN, J.C.S. In the press.

SUMMARY.

The work described in this thesis was undertaken to develop an accurate method for the micro-estimation of uranium. There is a need for such a method, since the accurate estimation of amounts of uranium between 0.01 micrograms and 1 microgram is an essential step in the well-known radioactive methods for the age determinations of minerals and meteorites.

With the exception of the fluorometric method, the methods in present use for the micro-estimation of uranium are based on the rates of alpha-particle emission from radium and uranium. The recently developed Nuclear Research Emulsions have presented the scientist with a means of recording the rate of emission of alpha-particles, which is not subject to the mechanical breakdown or electrical interference prevalent in the electronic instruments generally used for the purpose. Microscopic examination of such an emulsion, after exposure to an alpha-particle source and subsequent development, reveals the presence of tracks, consisting of closely-packed silver grains, which are clearly visible at a magnification of 200 and can be easily and efficiently counted at a magnification of 1000.

The application of this Photographic Method to the quantitative estimation of low levels of alpha-particle activity is limited only by the amounts of alpha-particle

emitting impurities incorporated in the emulsion during manufacture, and by the rate of fading of the latent track image in the emulsion. The former is very small indeed, and the latter can be eliminated for exposures up to fifty days bystoring the emulsions under suitable conditions. These conditions are those of very low temperature and humidity, and the absence of any oxidising agent.

An attempt to estimate uranium indirectly, by the estimation of radium by the photographic method, was unsuccessful. It was an essential part of the method that the number of radium "stars", produced in the emulsion by four successive alpha-particles emitted from one radium nucleus, should be accurately counted. This proved to be impossible due to the fact that a high proportion of the radon produced by the radium in the emulsion escaped before disintegrating, and hence the number of "stars" counted was too small.

The photographic estimation of uranium by the Immersion Method was investigated. The normal method of loading an emulsion with an alpha-particle emitting element is to immerse it in a suitable solution of the element for a period of about 30 minutes, rinse it briefly in tap water, and allow it to dry. In this immersion method the element is taken up uniformly by the emulsion. The uptake is influenced by the solute concentration, the pH of the solution, the time of immersion and the temperature of the immersion bath. The uptake of uranium by the emulsion from uranyl acetate solutions at controlled pHs of 2.0 and 4.0, a standard immersion time of 30 minutes and at a temperature of 25°C. was investigated. It was found that for concentrations of uranium between 10^{-3}g./ml. and 10^{-5}g./ml. the uptake of uranium, as measured by the observed track count, was a linear function of the uranyl ion concentration, but that at concentrations lower than 10^{-5}g./ml. the relationship between the uptake of uranium and the uranyl ion concentration was uncertain. The track counts obtained for the lower concentrations were inaccurate due to loss of tracks by the fading of the latent track image.

Amounts of uranium from 10^{-6}g. to 10^{-8}g. were accurately determined by the External Source Method. The uranium to be estimated was deposited on the plane ground end of a glass rod, about 0.15 sq. cm. in cross-section, and this was firmly clamped against a piece of photographic emulsion for a measured time of exposure. After development the whole of the area of the emulsion occupied by the tracks was counted, and from the estimated track count the amount of uranium was determined. With exposures made under ordinary atmospheric conditions it was found that a small percentage of tracks was lost due to fading of the latent image, but emulsions loaded with borax prevented this track loss. Using this method 10^{-6}g. of uranium can be estimated with an accuracy of 3 per cent, and 10^{-8}g. with an estimated accuracy of about 6 per cent.

In using the External Source Method it is essential that the uranium deposit should be "weightless", as no corrections can be applied for source thickness because this is not uniform. Therefore, in applying the method to the estimation of uranium in minerals the uranium must be extracted in a carrier-free state. Attempts were made to remove the uranium from magnetite by adsorption on ferric hydroxide, dissolving the hydroxide in the minimum of nitric acid, and extracting the uranium from this solution with tetrahydrosylvan. However, only 30 to 40 per cent of the uranium was extracted.

Thus the application of the above method to the estimation of uranium in magnetite has proved very unsatisfactory. However, when an extraction procedure which gives 100 per cent extraction is devised, the method should give results which will compare verynfavourably with those obtainable by any other method.

ACKNOWLEDGEMENTS.

I wish to expres my deep gratitude to Professor F.A.Paneth, Ph.D., F.R.S. for the privelege of being allowed to work under him at the Londonderry Laboratories for Radiochemistry, for the encouragement which he has given throughout the course of this work, and for the benefit of his wide knowledge and experience in the field of radioactivity.

It is a pleasure to record my sincere thanks to Mr.G.R.Martin, B.Sc., A.R.C.S. for the keen and sustained interest he has shown in this research, and for the sound advice he has at all times so freely given.

I acknowledge my debt to Mr.E.R.Mercer, B.Sc., for his assistance in certain parts of the analytical work.

Finally, I should like to thank the Department of Scientific and Industrial Research for a maintenance grant without which this work could not have been done.

Alec Robson.