Studies on the radioactivity of terrestrial minerals and meteorites

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THESIS

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by

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Being an account of research carried out in the Londonderry Laboratories for Radiochemistry, Durham University, during the period October 1949 - July 1951, under the supervision of E.R. Mercer B.Sc., and the period July 1951 - July 1952, under the supervision of Professor F.A. Paneth F.R.S.

Studies on the Radioactivity of
Terrestrial Minerals and Meteorites.

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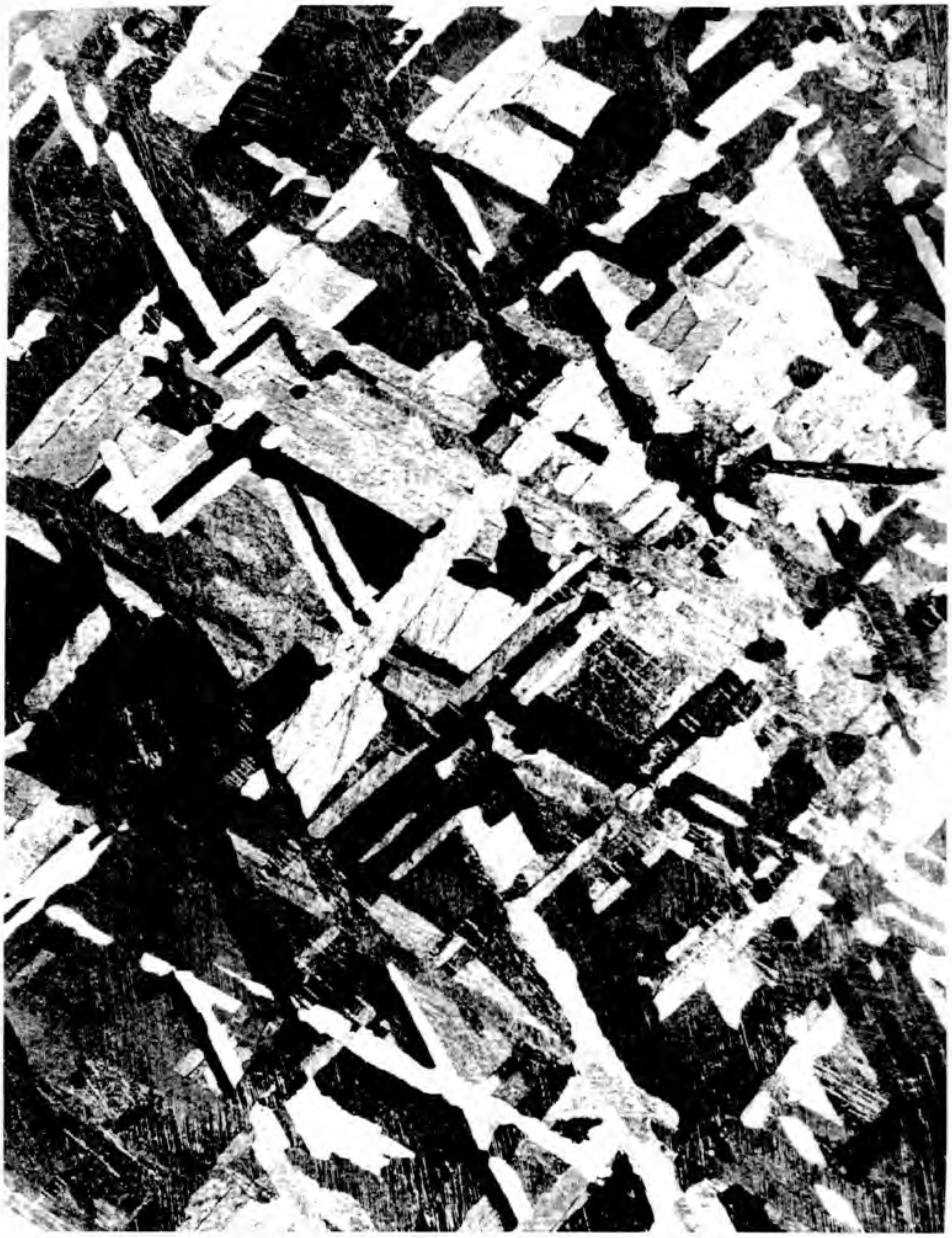


FIG 1

Chapter I: General Introduction

From 1928 to 1931 several papers on the ages of iron meteorites were published, based on analyses of their helium and uranium content (1). A new attempt to increase the accuracy of the age determinations was begun in 1937 and the main alterations and the results obtained were described in 1942 (2). The apparatus and techniques used were described in detail (3). Thorium as well as uranium results were obtained by determining the amounts of the rare gas members thoron and radon. Pulses were obtained from a gas ionisation-chamber containing thoron or radon and after suitable amplification the pulses were recorded photographically. When investigations were begun again in 1945 modern counting equipment was introduced. The radon-thoron method for the estimation of the two main radioactive series was adopted and developed further by the present author.

Improvements were made both in the manipulation of thoron and radon, and in the carrier procedures used to extract the parent activities. Useful results were obtained, in particular of the low age meteorites Savik, Ahnighito, and Muonionalusta.

However, new developments in the scintillation counting of α particles and in the fluorimetric determination of uranium showed the radon-thoron method to be relatively less efficient. An important corollary to this is that much more sample is needed for the radon-thoron method than for the new methods.

Blau and Dreyfus (4) used a zinc sulphide screen and a photomultiplier tube and measured the intensity of the current produced by an α source. Coltman and Marshall (5) showed that individual light flashes could be detected with good efficiency. Zinc sulphide phosphors can be obtained commercially which have a very low natural activity. This means that the measuring instrument using such a phosphor has a low background count (of the order of 1 count per hour) and consequently low activities can be estimated more accurately, even though the efficiency of the counter is less than that of the gas-counting ionisation chamber. In this way the lowest detectable amount of thorium was reduced from 4×10^{-7}g. to 1×10^{-7}g. (The "lowest detectable amount" has been calculated for comparable counting times, and represents the amount of activity whose standard deviation would be equal to ± 100%. Any less amount of activity would have even less accuracy, and such a result would have to be expressed as equal to, or less than, a certain limit.)

The fluorescence produced by uranium when present in a sodium fluoride matrix was referred to by Nichols and Slattery (6) and was used for the detection of uranium by Papish and Hoag (7). The method was developed for the quantitative determination of uranium by Hernegger (8)/and

and used for the measurement of uranium in sea-water by Hernegger and Karlik (9). This method is more sensitive than the radon method, reducing the lowest detectable amount of uranium from 4.8 x 10^{-8}g. to 6 x 10^{-9}g.

New radiochemical methods were needed for both these recently developed instruments. It was necessary to design procedures for the extraction and separation of the small amounts of uranium and thorium present in iron meteorites. These methods were developed by the author to permit a determination of both series to be made from the same sample. Ideas for an analysis of the radium content by scintillation counter as a check on the fluorimetric analysis of the uranium content did not lead to a suitable procedure. After extraction and separation of thorium the use of a repetitive source of ThB (and hence ThC) was proved possible. This increases the accuracy further, since a series of thorium estimations can be obtained from the same sample and a thorium figure calculated by taking the mean and computing the standard deviation in the usual way.

Using the relevant parts of the developed procedures, uranium results were obtained from some residue solutions of the radon-thoron method, thus affording a useful check.

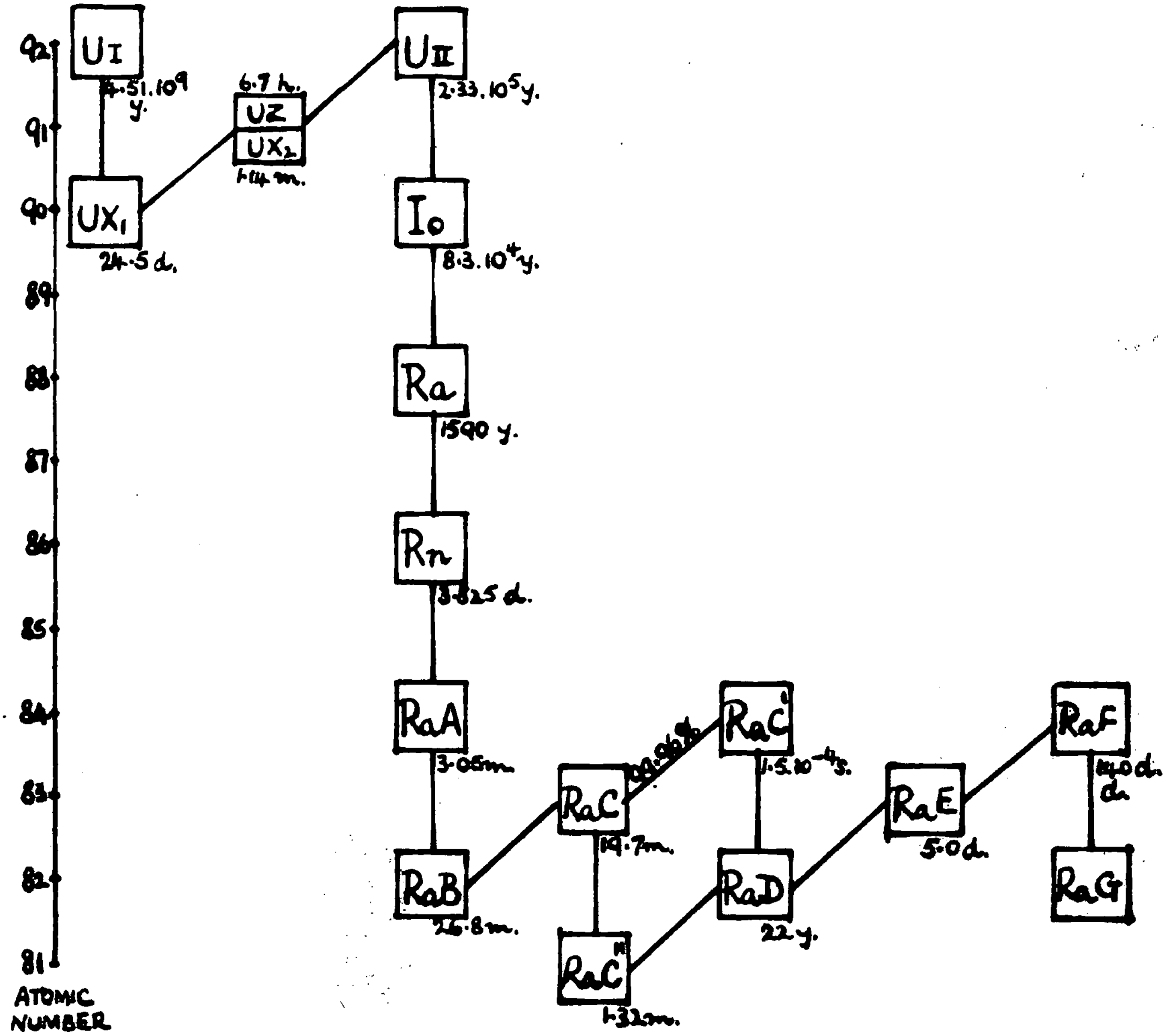
Many interesting carrier procedures were investigated both for the main methods and for the removal of the amounts of uranium and thorium present in the reagents used. In particular, series of tests showed that the choice of iron or zirconium as a carrier for thorium in the caustic soda-peroxide procedure had a great effect on the subsequent efficiency of separation of uranium and thorium. After exhaustive testing of procedure and reagent purity the meteorite San Martin was analysed for uranium and thorium. The results agreed fairly well with those obtained by earlier workers (2).

Most of the results obtained by this author relate to iron meteorites, only one meteorite, Beddgelert being outside this class. Beddgelert is a chondrite. The spectrographic and radiochemical analyses of this meteorite and their results are described in a separate chapter.

A general review of age determination by radioactivity has not been included here, since a comprehensive survey of the many methods in use is available (10). However, an interesting recent method of age determination of certain rocks is due to L.H. Ahrens (11) using Rb^{87} as the "geochronometer". The concentrations of rubidium and strontium, the decay product, can be determined with some success using a spectrographic method. The uranium contents of meteorites have been estimated by Davis (12) who used a vacuum fusion technique to liberate radon. His results agree with those of Paneth et al (2).

Figure 1 shows the sample of Savik (enlarged 1.5 times) which was analysed. A typical iron meteorite, Savik shows

Widmannståten figures that are clear and undeformed and there is no possibility of helium leakage.



Uranium Series

FIG 3.

Chapter II: The Radon-Thoron method

(i) Introduction

In this method of radiochemical analysis the two main helium producing radioactive series are estimated by means of their rare-gas members; the Th232 series (see Fig. 2) by thoron, and the U238 series (see Fig. 3) by radon. The U235 is not directly estimated but the determination of the U238 series affords an indirect estimation, since U235 is present in a fixed small ratio to U238. (U235/U238 = 1/139) (13).

The immediate parent of each rare gas is separated from the series and the thoron and radon collected and their activities assessed in a gas ionisation chamber. The two series are interrupted by carrier precipitation at Ra in the U238 series and at ThX (an isotope of Ra) in the Th232 series. Both these radioactive bodies are quantitatively brought down from a homogeneous acid solution by means of a precipitate of barium sulphate. The barium sulphate is converted to barium chloride. The solution obtained contains the thorium X and radium initially present and the thoron and radon can be easily obtained from this solution. Thoron (54.5 seconds half-life) is much shorter-lived than radon (3.84 days half-life) and so a method of counting each in the presence of the other has been devised. To estimate thoron a flow method is used. A flow of nitrogen carries the thoron into the ionisation chamber quickly

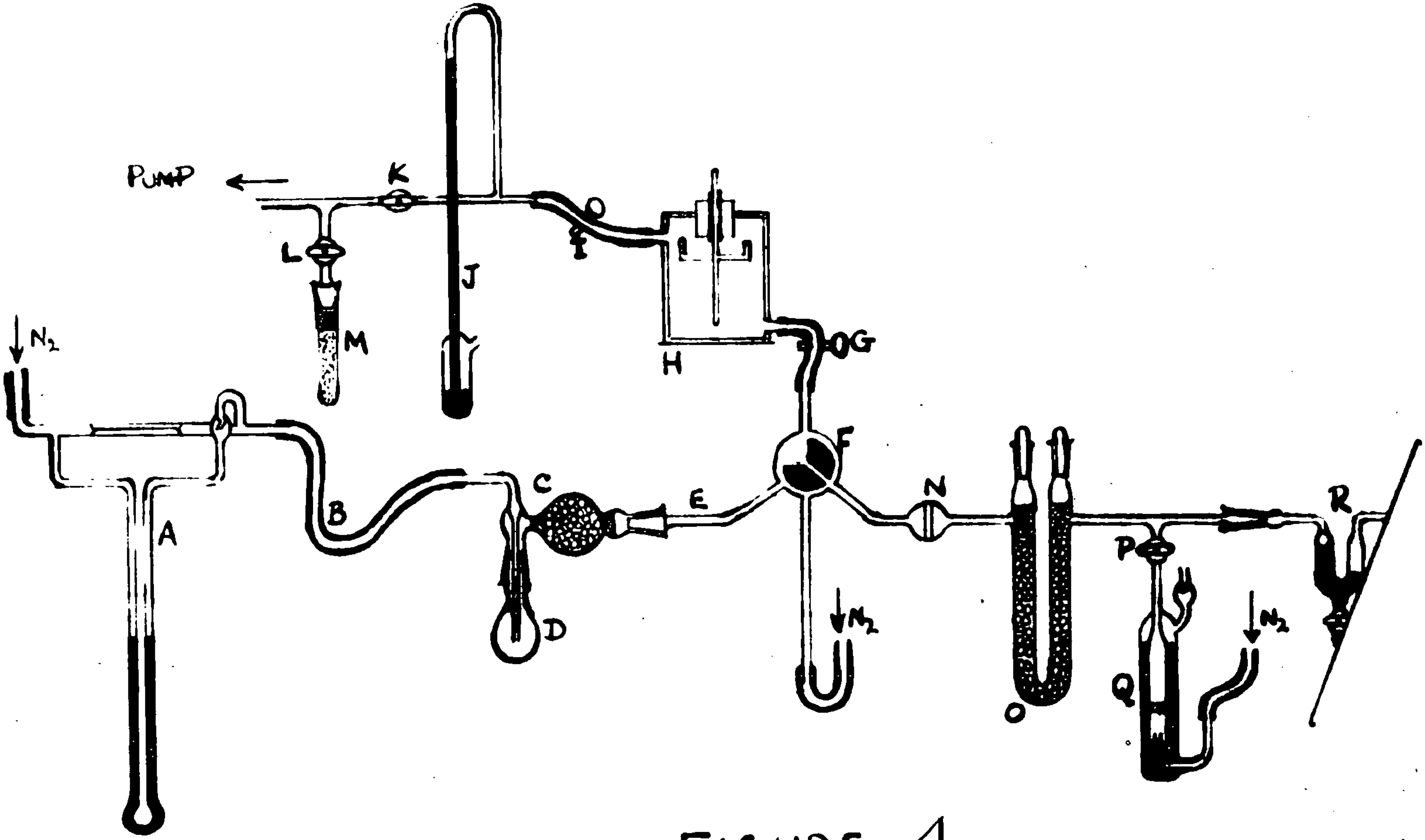


FIGURE. 4

enough for most of it to decay there and give rise to counts. Any radon present in this flow does not spend a long enough time in the chamber to contribute appreciably to the count. To estimate radon a static method is used. The ionisation chamber which has previously been evacuated is filled with the accumulated radon from the barium chloride solution.

The apparatus used for the manipulation of the radioactive gases is shown in Figure 4. The central point of the apparatus is the manifold F which can link the chamber system ending at G to any of three other systems. These are (a) the nitrogen line, (b) the thoron system ending at E and (c) the radon system ending at N. The pump lead from the chamber (H) system contains a charcoal trap M (stopcock L) which can be cooled in liquid nitrogen, and a stopcock K. The charcoal trap is used after a reassembly of the chamber system to clean the internal chamber surfaces, particularly the insulators, from absorbed water vapour. The manometer J indicates the pressure inside the chamber. Screw clips I and G clamp on to the rubber leads which conduct gas into or through the chamber.

For thoron determination the apparatus ABCDE is linked through F to the chamber system GH etc. The flow of nitrogen passes through a graduated differential manometer A, using mercury as the indicating liquid, and the rubber lead B to the thoron unit C whence it carries the thoron through E and F to the chamber. The thoron unit C. consists of a B 10 socket sealed into the top of which is a 1mm. bore tube. This tube leads the gas flow below the surface of the liquid in the bubbler D which has the corresponding B 10 cone. The gas is then dried by passing it through a bulb filled with KOH pellets.

For radon determinations the apparatus NOPQR is linked through F to the chamber system G.H. etc. N is a sinter disc to keep fibres etc. out of the chamber where they can cause insulator trouble. O is a large KOH pellet drying system. A stopcock P leads to Q which is a sinter disc nitrogen leak sealed off from the air by mercury. Nitrogen is fed directly underneath the sinter disc and when no demand for nitrogen is made by the system beyond P, it bubbles out through the mercury seal to the atmosphere. When the system beyond P is evacuated and needs to be refilled with nitrogen the opening of P calls on the supply and nitrogen passes through the disc and into the system.

Any possibility of introducing air by having an insufficient supply of nitrogen for the demand of the system is precluded by the surrounding mercury which, although sucked against the disc, cannot pass through it. The radon unit R is attached by cone and socket. The radon unit and its manipulation are described in detail later (see page 34).

(ii) The Ionisation Chamber and Electronic Techniques

The ionisation chamber was the one used by Jacobi (3) with a modified electrode assembly due to Mercer and Martin. The ionisation chamber is shown in Figure 5. A mild steel cylinder of 910 ml capacity, it has two tapered orifices for the flow of gas. The end faces have a circular groove into which the body of the cylinder fits. The fit is rendered vacuum tight with Everett's wax (Hard No. 1). The top plate has a thick section A which borders the cylindrical aperture into which fits the polystyrene insulator B and the central electrode assembly. The copper central electrode E has a concentric silica tube D fixed round it with high melting point Apiezon wax. This (D) insulates E from C the brass guard ring which is earthed. C is waxed on to D with Apiezon wax in such a way that the upper portion of D is untouched and its insulating properties preserved. The insulator B is turned on the lathe, so as to fit the aperture in A and is waxed in with Everett's wax. This wax has a low melting point and consequently does not crack or distort the polystyrene which would, of course, ruin its insulating properties. The central electrode assembly (C,D and E) is waxed into the cylindrical aperture of B, again using the low melting point wax. This is so to prevent the disarranging of the central electrode assembly which would ensue from the use of a higher temperature. Finally the top plate which is now fully

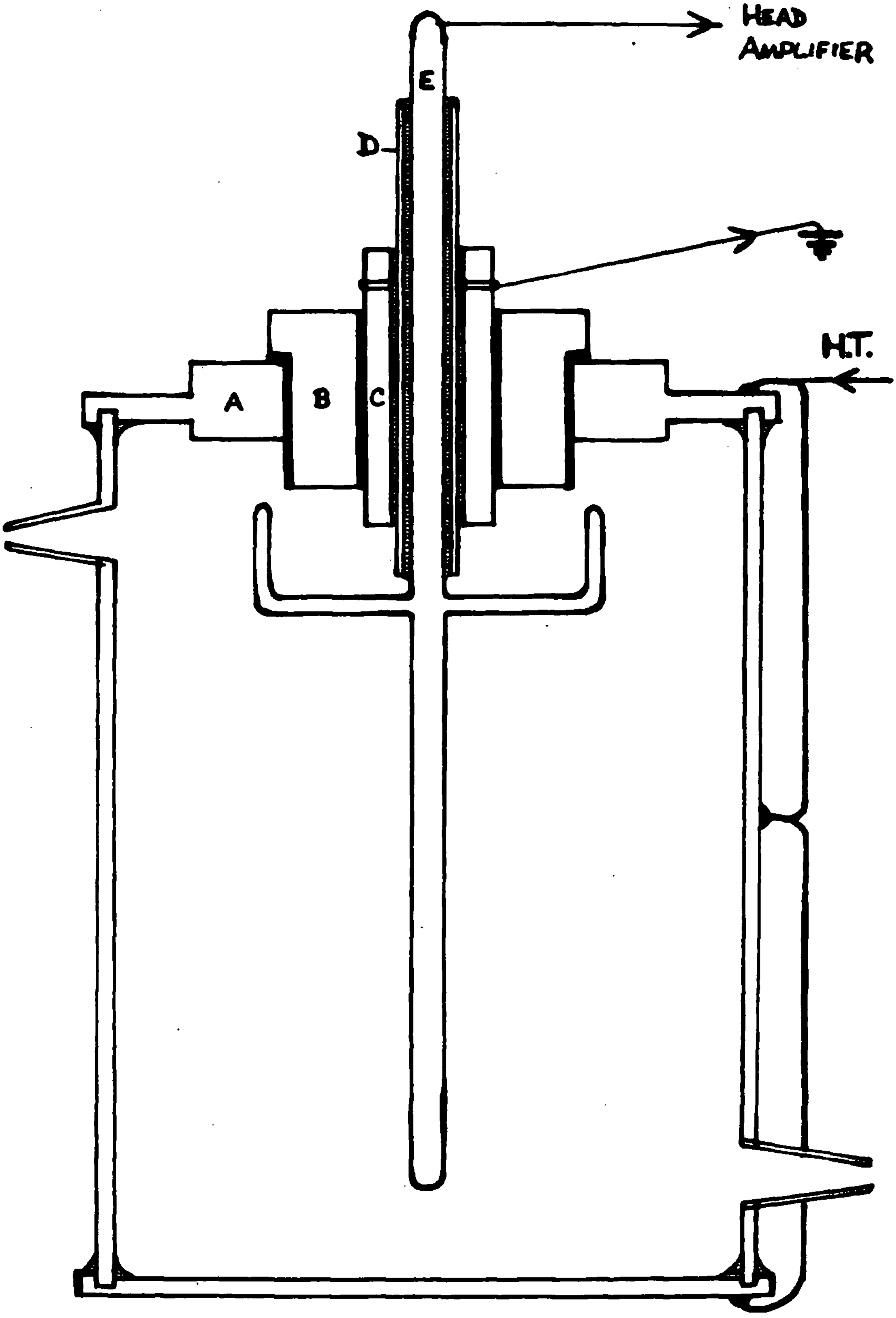


FIGURE 5.

assembled is fitted on to the body of the chamber and the joint waxed with the low melting point wax. The central electrode has an umbrella attachment which shields the internal insulators from the electric field. There are silver solder tabs on each of the three parts of the chamber. These are connected to the H.T. supply and in this way a uniform field is assured. The chamber is constructed of mild steel because this material has been found to have a low natural activity (14). As a further help to low background counts all internal metal surfaces were nickel-plated. It is to be expected that during the metallurgical processing of nickel by the carbonyl method much of the contaminating α activity will be lost.

As is shown in the block diagram (Figure 6) the ionisation chamber is housed in an earthed copper box (A) to screen the chamber from stray electromagnetic radiation. The lead from the potentiometer which taps off the required potential from the power supply is led into an annexe of the copper box (not shown) which surrounds and screens D. D is a smoothing circuit for the H.T. The chamber C rests on a sheet of neoprene to insulate it from the earthed box A. The electrical leads to and from the chamber passed through Pye plugs situated in the sides of A. Aerial-like loops in the wiring were avoided.

The chamber is maintained at a potential of -450 volts. The ionisation produced by an α particle is mobilised by the

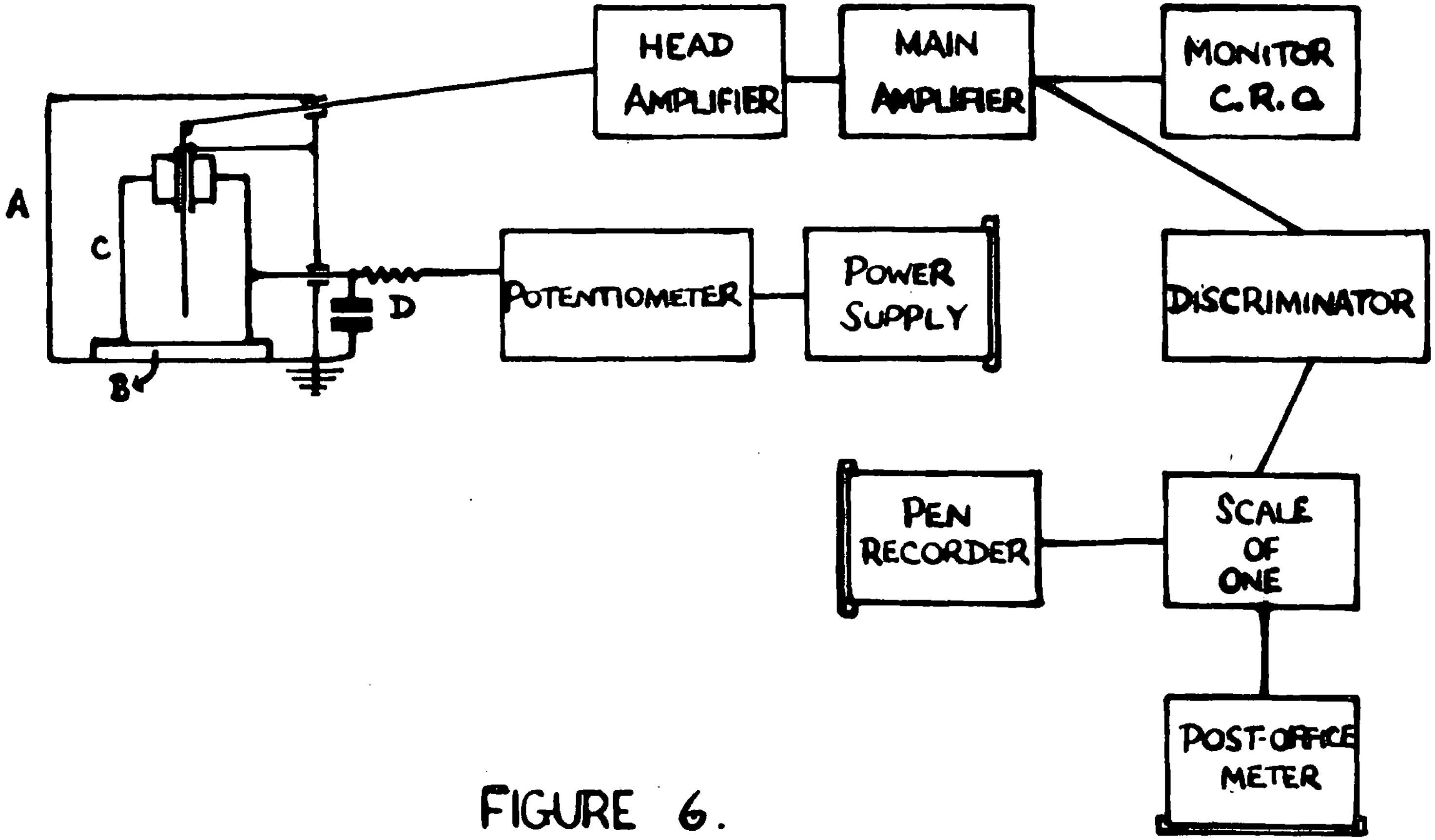

HEAD AMPLIFIER
MAIN AMPLIFIER
MONITOR C.R.O.
A
C
B
D
POTENTIOMETER
POWER SUPPLY
DISCRIMINATOR
PEN RECORDER
SCALE OF ONE
POST-OFFICE METER

FIGURE 6.

electric field and the electrons are collected by the central electrode. Negative going pulses are produced corresponding to the incidence of α particles. These negative going pulses are fed through a short length of polythene insulated cable to the first stage of a resistance-capacity coupled linear pulse amplifier, modified from the 'type 1002' amplifier built for the Atomic Energy Research Establishment, Harwell. The amplifier was constructed in two parts, a 'head amplifier' giving a gain of about 100 with a cathode follower output stage, connected through a fairly long cable to the main amplifier which gives a gain of circa 10^4.

In order to achieve adequate stability of gain the anode supply for the amplifier is electronically stabilised at 250 volts d.c. and the valve heaters, all connected in series, run from this same supply through a suitable series resistance. This also eliminates the introduction of 50 cycle ripple through cathode-heater interaction. The output from this amplifier is displayed on a cathode ray oscillograph for visual checking and fed also to a pulse amplitude discriminator, (based on a design by Cooke-Yarborough (15)). By suitable choice of the level of discrimination it could be arranged that pulses due to α particle ionisation in the chamber were passed to the recording mechanism whereas the random amplifier 'noise' was effectively rejected. Since the average rate of arrival of pulses is rarely greater than 1 or 2 per minute no electronic scaling circuit was normally used and the discriminated output was used directly to trigger a 'flip-flop' circuit driving a mechanical counting meter. The rather long resolution time (1/8 sec) of the mechanical meter had the advantage of making the whole system relatively insensitive to microphonic interference. This usually appears as a short damped train of impulses which in general can trip such a recorder only once whereas an electronic scaling circuit with much shorter resolution time would record a considerable number of spurious counts for each disturbance of this type.

A simple pen recorder connected in parallel with the mechanical meter provided a useful check on the reliability of the recorded pulses. The pen recorder consisted of a rotating drum bearing paper on which a pen or pencil described a continuous helix. A battery operated relay was attached to the scribing arm and the relay was operated when a count was registered on the mechanical meter. The pen was then attracted away from its normal path and formed a clearly visible mark. The resolving time of this device was much longer (½ sec) than that of the mechanical meter and so each count had not a corresponding mark. This meant that a straightforward 'count' could not be made from the trace avoiding portions, obviously recording breakdowns. However, its main use is that whereas the mechanical meter gives no indication of the arrangement of the counts in time, the pen recorder shows whether the counts are randomly distributed or whether many have occurred together. Since the activities measured are so low, it is very improbable that even groups of six or five will occur within a few seconds. When these large groups of counts are found in the trace, the run has to be discarded and the source of the trouble located. During normal laboratory working hours the cathode ray oscillograph was available for inspection and the actual rate of count could be checked periodically, but overnight the pen recorder was the sole means of checking whether or not a count was valid.

Typical sections of the trace of the pen recorder are shown in Figure 17. The lengths of the helix shown correspond to approximately 4 minutes. (a) Shows a low radon count with a small portion of the background on either side. This was taken as a valid count. (b) Shows a high rate of counting (circa 590 per hour). This was a radon calibration run, and was taken as valid since the frequency distribution of singlets, doublets, triplets, etc., is what one would expect. (c) Shows a low thoron count with no spurious additions. (d) Shows a count rendered invalid by much spurious counting. This actually occurred overnight and the mechanical meter simply recorded a high activity. The C.R.O. next morning showed that conditions were steady and that no breakdowns were taking place, but the pen trace shows that breakdowns took place, after which the counter regained stability.

By far the greatest single cause of trouble was the

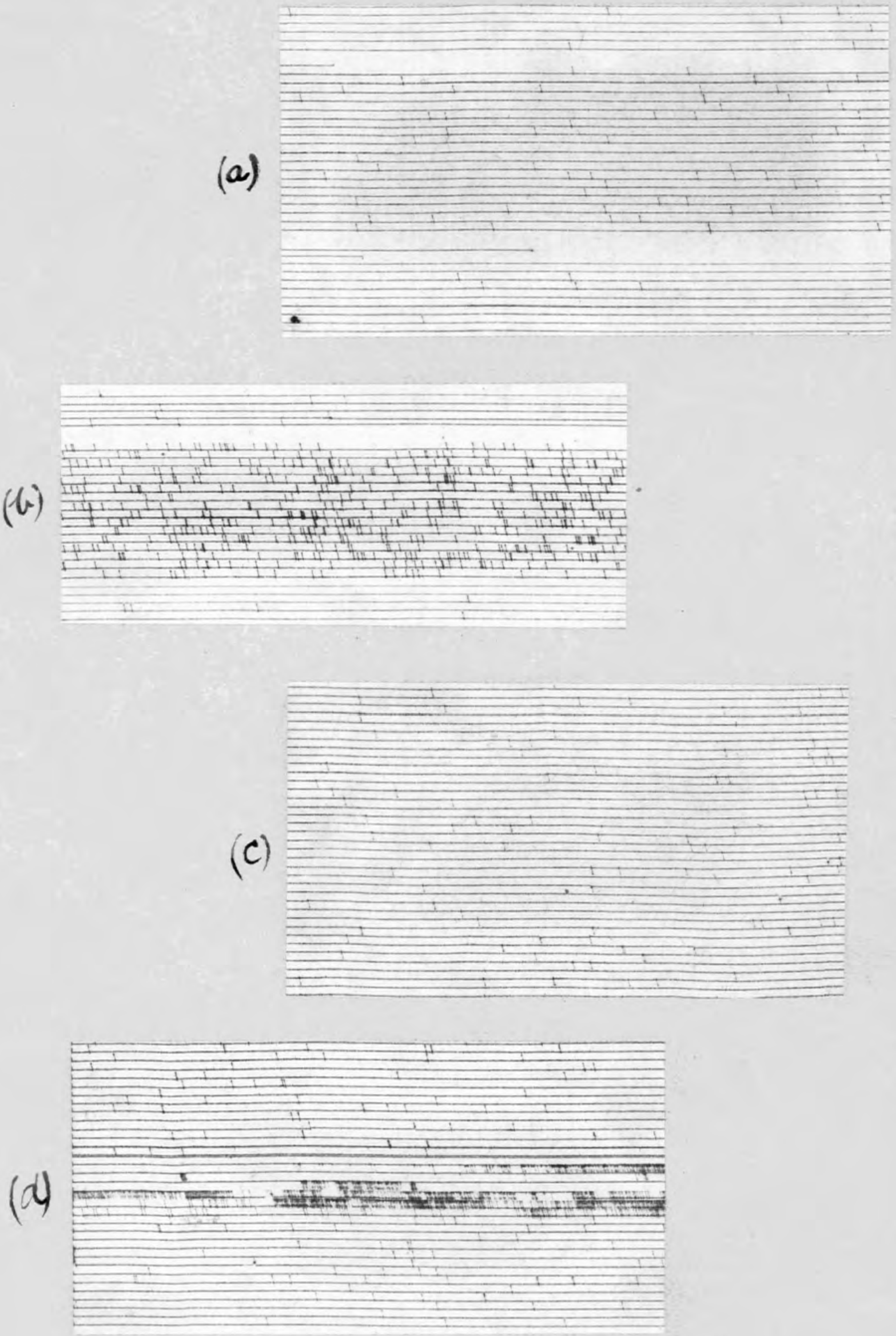


FIGURE 7

insulation system of the ionisation chamber. When spurious counting was tracked down to the chamber, it had to be dismantled. The polystyrene block was left in its seating in the top plate and the central electrode assembly removed, stripped down, and thoroughly cleaned and dried. The silica insulator was boiled for several hours in concentrated nitric acid, copiously washed, and dried. Meanwhile a very thin layer was turned off the insulating surfaces of the polystyrene block. The opportunity was taken to polish the internal surfaces of the chamber to remove any deposited activity. A carefully prearranged order of assembly was observed, so that no insulating surface was touched. After assembly the system had to be pumped out over charcoal cooled with liquid nitrogen. Some improvement in the incidence of insulator breakdown was found when as many as four 100-ml vessels of silica-gel were kept in the copper box which housed the chamber, and when the lid of this box was cork lined and firmly screwed down. A special brush was kept only for use on the insulators.

Originally the gas leads to and from the chamber were of stout capillary tubing terminating in B 10 cones which fitted the tapered orifices of the chamber. This system made the counter microphonic. Rubber leads were substituted which completely removed this trouble, and made the removal and insertion of the chamber much easier, since this type of lead could be easily waxed in. The rubber leads proved reliable, both in the electrical system, i.e. there were no breakdowns from the chamber via the rubber leads to the copper box, and in the gas system, i.e. they neither absorbed nor contributed to any activity.

(iii) Chemical Procedure

A brief test of the best reagent for dissolving an iron meteorite was carried out. 10 mgm. portions of Calvert No. 2 turnings were weighed out and treated with 10 ml. amounts of the reagents shown in the following table. The time was noted when no speck of meteorite was visible. The test was carried out at lab. temperature (circa 18° C).

Solvent	Time in hours	
5N HNO_3	0.14	
5N H_2SO_4 satd. with $K_2S_2O_8$	1.1	
10N H_2SO_4 " " "	1.6	
10N HCl	2.1	
$KCuCl_3$	4.0	
5N H_2SO_4	28.0	
1N HNO_3	120	
H_2O	120	rusting.
conc. H_2SO_4	120	metal still bright.

Of these attacks 5N HNO_3 was thought to be perhaps too quick, risking loss of material, and the conc. HCl (10N) attack was chosen as being reasonably quick and easily controlled. It was found that a prolonged HCl treatment could form a homogeneous solution of practically the entire meteorite sample.

So long as this solution was stable enough to allow the $BaSO_4$ precipitation to be carried out then the requirements for the extraction of the radium isotopes were fulfilled.

The small residue left from the HCl attack was generally resistant iron oxide and was very greatly reduced by treatment with hot concentrated HNO_3. The very small residue now remaining was sometimes siliceous in nature and this could be treated with HF and $HClO_4$ in a platinum dish. That the HCl solution was capable of holding up most of the silica present was shown by the fact that if too much H_2SO_4 was added to the meteorite solution, containing barium, a flocculent precipitate of silica was produced as well as the characteristic precipitate of $BaSO_4$. This occurrence did not interfere with the method, since the whole precipitate could be fused with alkali carbonate and the leached residue of $BaCO_3$ obtained in the normal way. Further, it was later found that a precipitation of silica from a HCl solution did not interfere with either uranium or thorium in that solution (see page 130).

Further attacks such as fusion with alkali carbonates or potash were available for persistent residues, but were seldom necessary. There is a danger in tackling a small residue with too much, and too great a variety of reagent. This greatly increases the 'blank' (i.e. the activity contributed by the reagents) which has to be subtracted from the meteorite run, much to the cost of the accuracy of the final figure.

Where more than one kind of attack was carried out it was found advisable to extract the various solutions with $BaSO_4$ separately. Then the $BaSO_4$ extracts could be combined for the rest of the procedure. After such a separate $BaSO_4$ extraction on the two main attacks of a Savik sample (conc. HCl and hot conc. HNO_3) the two mother liquors were combined for storage. (Extracted meteorite solutions were always stored since other data might be obtained from them). After an induction period a violent reaction took place which caused loss of some of the material. Since ethyl alcohol, which can be used to improve the liquid surface in centrifuge tubes, had been avoided for the very reason that it might engender such a reaction, it was surmised that the HCl solution must have contained some carbonaceous material. Sometimes the HCl attack of a meteorite resulted in a solution with a grease-like film of graphitic-looking material. Graphite is well known as a constituent of some iron meteorites, as is amorphous carbon(16).

After homogeneous solutions of the meteorite had been obtained (50 - 100 gm of meteorite were generally used) they were extracted in the following way. Approximately 100 - 150 mgms Ba as $BaCl_2$ had already been added to the sample before acid was added, to act as holdback carrier. This barium was precipitated by the addition of 25% H_2SO_4. The technique used was precisely that used for maximum recovery of $BaSO_4$ in quantitative analysis. Pyrex glassware was used throughout, since it has been shown that soda glass adsorbs radium isotopes from solution (2). The precipitate was separated from its mother liquor by centrifuging, and washed. It was then transferred to a platinum dish and fused with 10 - 15 times its weight of fusion mixture. The contents of the cool platinum dish were leached out with water and the $BaCO_3$ precipitate separated by centrifuging. The alkali carbonate mother liquor was discarded. The fusion was repeated to ensure that no $BaSO_4$ remained to interfere with the final solution of $BaCl_2$ obtained by dissolving the $BaCO_3$ in a little dilute HCl. This solution was transferred to a bubbler. These bubblers were of standard 30 ml capacity and the solution in them was kept at 15 mls for all runs. This was necessary to preserve the de-emanating conditions and dead space volume at standard values.

(iv) The Determination of Thoron

(a) Theory

The streaming method for thoron was first used by

Strutt (17) and later by Urry (18). Detailed expositions of the theory are given by Urry (19) and Koczy (20). A flow of nitrogen is maintained through the bubbler containing the thorium X obtained from the meteorite. The thoron atoms, after they are born, are swept out of the solution and into the chamber. No account is taken here of the time lag between the birth of a thoron atom and its entry into the nitrogen stream.

Let N_0 atoms of thoron be in equilibrium with the thorium X contained in the bubbler.

Then $N_0\left(1-e^{-\frac{\lambda v}{s}}\right)$ atoms of thoron die before reaching the chamber, where v is the volume of "dead space" (i.e. the volume between the surface of the liquid in the bubbler and the entrance to the chamber) and s is the rate of flow of nitrogen.

Hence $N_0 e^{-\frac{\lambda v}{s}}$ atoms of thoron reach the chamber.

If N is the number of thoron atoms decaying in the chamber of volume V, then

$$N = N_0 e^{-\frac{\lambda v}{s}}\left(1 - e^{-\frac{\lambda V}{s}}\right) \qquad \text{(I)}$$

The ratio N/N_0 is termed the 'recovery' of the apparatus and has its maximum when

$$s = \frac{\lambda V}{\log_e\left(V/v + 1\right)}. \qquad \text{(II)}$$

Combining equations (I) and (II).

$$\frac{N}{N_0} = \left(\frac{v}{V+v}\right)^{v/V} \cdot \frac{V}{V+v} \qquad \text{at optimum } S$$

Hence for a given relation of chamber to dead space volume the recovery of the apparatus can be calculated. In the following table a few values are given:-

V/v	100	20	5	1
Recovery %	94.5	81.8	59.6	25

The chamber volume is 910 mls. Originally the dead space was 64 mls. Fitted into the glass gas leads of the chamber were mercury controlled non-return valves. These were of use only in radon work when they closed up the chamber filled with nitrogen and radon to prevent the diffusion of radon to taps greased with apiezon where the radon would have been absorbed. When rubber gas leads were substituted for glass ones (see page 14) ordinary screwclips were clamped on to the rubber leads, which could close up the radon in the chamber. These prevented any absorption of radon on apiezon, but did not contribute to the dead space. In this and other similar ways the dead space was reduced to 40 mls.

Using the equations derived above the optimum flow rate and the recovery (N/No) can be calculated for each value of the dead space. This data is shown in the following table:-

Chamber vol. (mls)	910	910
Dead space vol. (mls)	64	40
Optimum S (mls/min)	255	217
Experimental S (mls/min)	104	220

N/No for opt. S (%)	77.	83
N/No for expt. S (%)	62.5	83

The recovery (N/No) for any radon carried into the nitrogen stream is 0.05%. Radon has such a relatively long half life (3.84 days) that the probability that any radon atom will disintegrate during the short time it spends in the chamber, is very small. To contribute a count of 10% of the thoron count the radium activity of the bubbler would have to be 200 times as great as the thorium X activity. A contingency of this nature is so remote that it can be disregarded, although a correction could be applied. Since the error of a thorium determination is rarely less than ± 30% a contribution of 10% would hardly be discernible. The recovery for any actinon (3.92 seconds half life) carried into the nitrogen stream is 16%. However, the U235 series is present only in small proportion (1/139) to the U238 series although the former series is 6.35 times as active as the latter. Apart from these considerations, the serious factor preventing any actinon contributing to the thoron count is the time lag between the birth of an emanation atom and its entry into the nitrogen flow. For actinon this factor would prevent very nearly all the actinon from reaching the chamber.

With the dead space at 64 mls and the flow rate at 104 mls/min, the average thoron calibration was 4.2 ± 0.3 counts per hour per microgram of thorium. With the dead space at 40 mls and the flow rate at 220 mls/min the average thoron calibration was 7.0 ± 0.3 cts. per hour per microgram of thorium. This is a much greater improvement than would be expected from the above table.

Thus the 4.2 ± 0.3 figure corresponds to a recovery of 62.5%. Increasing the recovery to 83% should increase this figure to 5.6 ± 0.4. The difference between this last figure and 7.0 ± 0.3 is most likely due to the increase in extraction of the newly born thoron atoms from the solution by the increased flow rate. This factor is not included in the calculations of recovery.

It is to be noted that 1 microgram of thorium gives circa 15 α particles per hour. Yet the thoron in equilibrium with 1 microgram gives only 7 α particles per hour by the thoron method. If we take into consideration the fact that this figure of 7 includes active deposit counts, the thoron count is only 5 α's/hour. Then we know that this is only 83% (by dead space calculations) hence the corrected count really is 6 α's/hour. Again the chamber counting efficiency and the recording efficiency will have lowered a given count by say 15%, and we can thus bring the count to 7.1 α's/hour.

We can now see that the various corrections we can apply cannot close the gap between theoretical expectation and the practical result. We have to assume that a time lag exists between the birth of a thoron atom and its entry into the flow of nitrogen. Even if we assume that the various corrections are too small we can only bring the practical figure to 9α's/hour. We can (very approximately) calculate this time lag, if we assume that the difference between the expected count (15α/hour) and the obtained count (9α/hour) is due to this phenomenon and a result of the order of 50 seconds is found. This is of the same order as the half life (54.5 seconds). In some later experiments it was shown (see page 112) that solutions of thorium X contained in open test-tubes do not lose any appreciable amount of thoron, which loss would vitiate any results dependent on estimation of the equilibrium amount of ThB produced. Hahn (21 p.197) states that because of its 54.5 sec. half life this emanation cannot be quantitatively expelled from solutions. However, Strassman (21 p.234), using barium palmitate preparations of ThX has obtained nearly 100% of the thoron from a preparation. Evans, et al (22) refer to the poor emanating power of ThX solutions. They calculate the emanating power of a typical solution to be 0.6. It is also interesting to note that Běhounek and Klumpar (23) found that a leaky vessel containing radium, mesothorium and radiothorium as salts gave off emanation which followed the typical radon active deposit decay curve with no evidence of thoron active deposit decay. From this author's work, it seems that after the birth of a thoron atom in a solution, on the average a period of time of the same order as the half life passes, before the thoron atom can be swept into the bubbles of the extracting gas stream.

Earlier workers have maintained the experimental flow rate below the optimum value (3). This was done to avoid using the drying agent up too quickly, and to avoid excessive spraying of the solution. However, it is possible to increase the quantity of drying material without increasing the dead space too much; actually only 1/3 to ½ of any increase in volume of the drying bulb will be an increase in dead space. A larger drying bulb for the thoron unit is included in the modified dead space of 40 mls. The second limitation imposed on high flow rates, i.e. excessive spraying, was subjected to a brief investigation.

The investigation into spray loss was carried out in the following way. When a thorium calibration was performed, a known amount of radium was added to the bubbler, which was not enough to interfere with the thoron count. After the thoron run of 12 hours, the bubbler was sealed into a radon unit and the radium estimated by the radon method. The average ordinary radium calibration was 190 ± 4 counts per hour per 10^{-12} gm. Ra. Taking this as 100% the special radium solutions which had been subjected to 12 hours bubbling (210 mls/min) gave the following recoveries:-

(a) 90.5 ± 3.2%　　(b) 97.0 ± 2.0%
(c) 96.8 ± 3.0%　　(d) 98.4 ± 2.0%
Mean 95.7 ± 2.5%

As a check on the maximum possible loss of solution by spraying, (c) and (d) had been weighed before and after the thoron run. The loss in weight as % for these two bubblers was

(c) 7.45%　(d) 7.31%
Mean 7.38%

This represents the loss by spray plus the loss by normal vaporisation of water. It was concluded that the loss of radium by spray was not excessive. Further, since errors on meteorite radon runs are never better than 10%, no correction factor need be applied for the small loss shown.

Finally an empirical investigation into the optimum flow rate for the reduced (40 ml) dead space was carried out, using a very strong thorium source. The results were plotted graphically and are shown in Figure 8. It can be seen that the count obtained flattens out into a plateau about the region of the optimum flow rate (220 mls/min.). The original flow rate is shown (104 mls/min). A further advantage in working at the optimum flow rate is obvious from the graph, since any variation

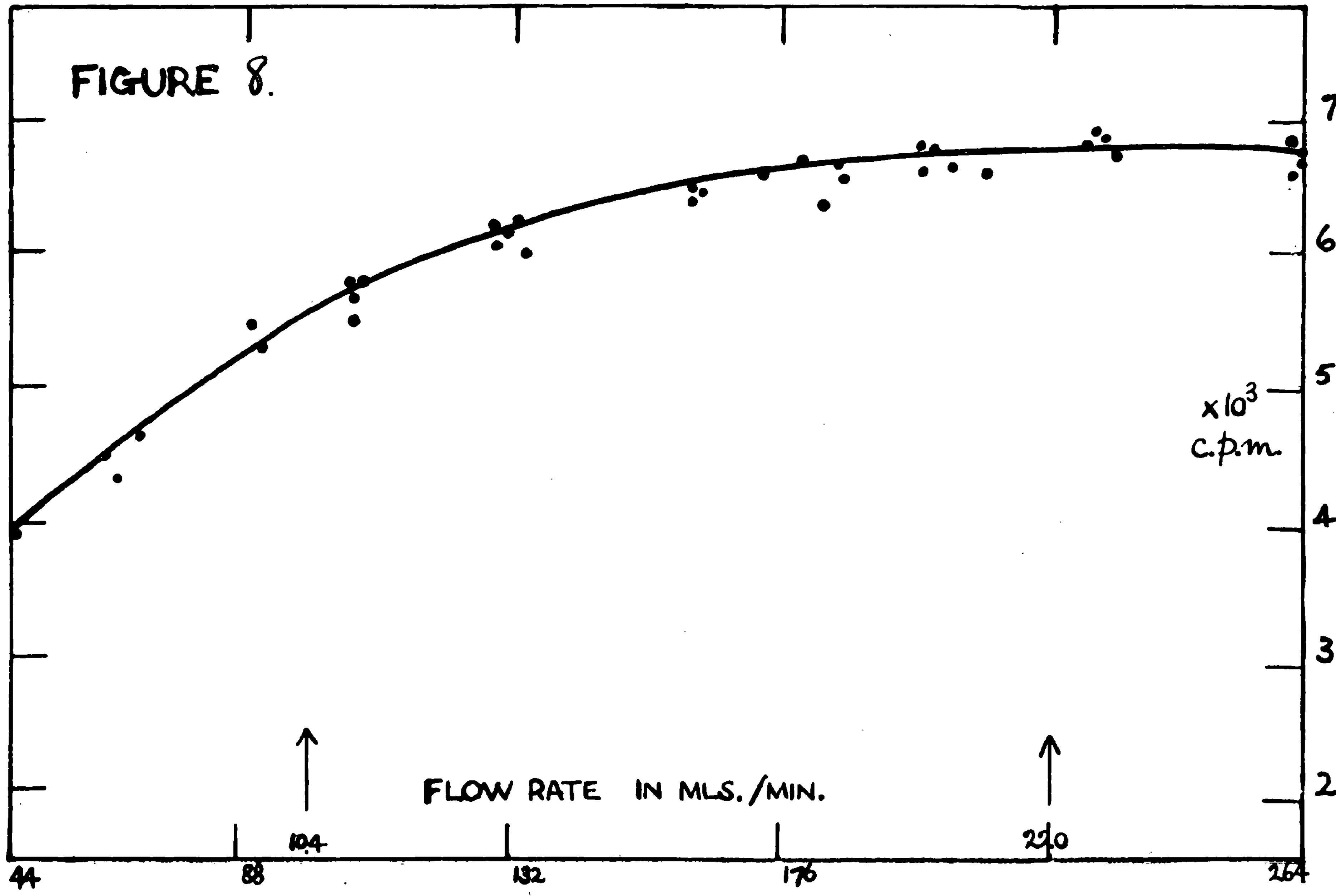


FIGURE 8.

in the flow rate over a considerable range would result in very little difference in the count obtained.

(b) Experimental Procedure

The nitrogen used as the carrier gas contained < 10 volumes per million of oxygen. This was necessary since oxygen would attach the electrons produced in the track of an α particle and delay their collection by the central electrode, thus encouraging ion recombination and also slowing down the rate of rise of the α particle pulses.

As a precaution against a build-up of pressure forcing the mercury of the flowmeter into the thoron unit and spoiling the run, an escape valve was inserted. This consisted of a narrow vertical tube filled with mercury, to the bottom of which passed a tube from the nitrogen line. If the pressure of nitrogen became slightly greater than that necessary to maintain the chosen flow rate, the excess nitrogen bubbled up through the mercury to the atmosphere.

When the chemical procedure has been completed and the bubbler has been filled to a standard volume (15 mls) the thoron run is begun. The thoron run has to be performed first since the separated thorium X has a half-life short relative to the radium. The thoron run can only be performed once. During the chemical procedure a background count is taken under standard conditions except that the bubbler D is empty.

Without interfering with the rate of flow of nitrogen, the sample bubbler, whose ground joint is greased with apiezon grease, is inserted into the socket of the thoron unit C (see Figure 4). The stream of nitrogen after bubbling through the solution passes through the manifold (F) and into the chamber (H). Immediately after the sample bubbler is in position, a Dewar flask filled with finely crushed ice is arranged round the bubbler D. This keeps the vapour pressure of the solution as low as possible during the 12-hour run and permits the use of a drying bulb of circa 4 cm diameter.

When the flow of nitrogen has passed for 15 minutes, all air introduced into the system has been swept through and the count is begun. After the 12-hour count, the whole thoron unit C is disconnected from the apparatus without interfering with the rate of flow of nitrogen. The bubbler is detached and stored for future insertion into a radon unit. Then the thoron unit is completely cleaned out, dried, refilled with KOH pellets, regreased and fitted with an empty bubbler. A background count is then taken for 12 hours after inserting the unit back into the apparatus, and ensuring that all air has been swept out of the system.

For thorium calibrations, a thorium solution was used which had been made up from a sample of thorium nitrate 40 years old. It could thus be assumed that all the members of the series had reached radioactive equilibrium. This thorium solution had been quantitatively analysed by the oxalate method and diluted suitably.

The thoron background count varied from 35 ± 2 to 40 ± 2 counts per hour, while the radon background count (static chamberful of gas) varied from 20 ± 3 to 25 ± 3. This implied that thoron was being produced in the cylinder and/or the leads bringing the nitrogen to the apparatus.

A U-tube packed with cotton wool was inserted in the nitrogen line just before its entry into the apparatus and the U-tube surrounded by powdered solid CO_2. This maintained the U-tube close to -78° C. Radon and thoron liquefy at approximately -62° C. An escape valve (exactly similar to the one already described) was inserted into the nitrogen line before the drikold-cooled U-tube in case a stoppage occurred and pressure built up. The background with the U-tube at lab. temperature was 34.0 ± 2.1 c.p.h. When the U-tube was surrounded with drikold this was reduced to 20.7 ± 2.0 c.p.h. The drikold only lasted 5 hours, and at least 12 hour counts are necessary. Overnight counting is essential for thoron runs and so the improvement could not be maintained without a device for maintaining the supply of drikold round the U-tube.

(c) The Assessment of the Count and its Error.

The many factors involved in the thoron count make any absolute method of assessment extremely difficult. The issue is resolved in this (and the radon) case by empirical standardisation. In a meteorite run the separated thorium X will decay during the chemical procedure and during its counting time in the bubbler. This means that the time of precipitation of the $BaSO_4$ has to be noted and a correction applied to the count obtained. It can be assumed that the decrease in count of the thoron in the chamber will follow the decay of the ThX in the bubbler. However, the $BaSO_4$ precipitate also carries down from a meteorite solution approximately 50% of the radiothorium present. Arrol (3) obtained this figure from a separate test using UX_1 as an indicator for thorium. This test was repeated by the author under the same conditions of concentration, temperature etc. as apply during a meteorite extraction and a figure of 48 ± 0.5% was found for the % of thorium isotopes present brought down on $BaSO_4$.

Arrol used this fact to make the assumption that since half the thorium X will be replaced as it disintegrates the thorium X in the bubbler will apparently decrease at only half its usual rate. The author has found that when the $BaSO_4$ precipitate which contains 48% of the radiothorium present is fused with fusion mixture and leached, 65 ± 1% of that radiothorium passes into solution (see page 121). Hence only 17% of the original radiothorium remains on the $BaCO_3$ precipitate.

The second fusion and leach will reduce this to only 6%. Thus only 6% of the thorium X in the bubbler is replaced as it decays.

That 65% of any radiothorium present in a fusion is leached off the subsequent $BaCO_3$ precipitate is not surprising, since thorium is known to form complex carbonates and the excessive amount of alkali carbonates present in the leaching of such a fusion would be expected to compete with the $BaCO_3$ present which would in other conditions carry down all the thorium.

When thoron decays in the chamber thorium A is produced, some of the disintegrations of which will be counted. Thorium A has a very short half life. (0.158 sec.) and approximately half of the thorium A counts will be lost in the resolving time of the recording instrument ($\frac{1}{8}$ sec.). Some at least of the thorium A atoms will have been collected on to one or other of the electrodes by the electric field and only half the ensuing radiation can be counted. Hence the probability of recording the disintegrations of thorium A is (approximately) 0.25.

The β -active thorium B which is then formed (10.6 hr. half life) will not have completely decayed during the counting period (12 hours). The α -active thorium C formed from ThB, has a half life of 60.5 minutes, and so for these purposes its decay can be taken to follow that of thorium B. Again only half of the radiation can be counted. Hence the probability of recording the disintegrations of thorium C is (approximately) 0.20. The 12 hour background taken immediately after the thoron run is averaged with the first background. In this way the undecayed active deposit is treated as an increase in natural background. The second background has always to be counted for the same time, i.e. 12 hours. Under steady conditions the first background can be counted as long as is convenient. The 12-hour count obtained from a thoron run is seen to be the result of several contributions, the extents of which are only approximately known.

However, if known amounts of thorium are analysed by the standard procedure used for samples, then a straightforward calculation of the thorium content of the sample is valid. The square root of the total count is taken to be the standard deviation of that count. For addition, subtraction, multiplication, division or averaging of counts with such standard deviations the usual rules for combining them are followed. These errors or standard deviations were generally large because of the generally low concentrations of uranium and thorium in meteorites, and the difficulty of obtaining large amounts of meteorite material for analysis. Their computation is, therefore, important.

The normal statistical treatment is complicated by the fact that two subsequent members of the disintegration series

(ThA and ThC) can contribute α particles to the total count. Those contributions will not be completely random but subject to a degree of correlation with those coming from the thoron. A rigorous treatment for the counting routine described would be complex, but the case considered below is a sufficiently good approximation.

Probabilities can be estimated for the recording of each of the three α particles which are altogether emitted. (E_1 for thoron, E_2 for thorium A, and E_3 for thorium C).

The average number of disintegrations recorded in a given time will then be

$N = n(E_1 + E_2 + E_3)$, where n is the number of actual disintegrations occurring within the chamber for the first member of the series, i.e. thoron.

Regarding these events, to a first approximation, as independent of one another, the variance of this number will be

$$n(1-E_1)E_1 + n(1-E_2)E_2 + n(1-E_3)E_3$$

The corresponding standard deviation is the square root of this, i.e.

$$\sqrt{n(E_1 + E_2 + E_3 - E_1^2 - E_2^2 - E_3^2)}$$

In addition to this source of uncertainty and quite independent of it, the number n will also be subject to random fluctuations with standard deviation $\sqrt{n}$ and the overall relative standard deviation will, therefore, be obtained by combining these two by the rule for the error of the product of two quantities.

$$\text{Total standard deviation} = \sqrt{\frac{1}{n} + \frac{n\,(E_1 + E_2 + E_3 - E_1^2 - E_2^2 - E_3^2)}{n^2\,(E_1 + E_2 + E_3)^2}}$$

$$= \sqrt{\frac{E_1 + E_2 + E_3 + 2E_1E_2 + 2E_2E_3 + 2E_3E_1}{n(E_1 + E_2 + E_3)^2}}$$

The absolute standard deviation on the observed count $N = n(E_1 + E_2 + E_3)$ will be:-

$$\sqrt{N} \quad \sqrt{\frac{E_1 + 2 \quad E_1E_2}{E_1}}$$

instead of the value $\sqrt{N}$ obtained in the normal, uncorrelated radioactive decay case. In general, of course, the absolute value of the E's are not known but, by making reasonable assumptions, plausible values can be obtained.

E_1 will approach 1 since only disintegrations occurring in corners and emitting α particles in an unfavourable direction will go unrecorded. E_1 is taken to be 0.9, E_2 and E_3 are reduced by two effects already discussed in the previous section. E_2 is taken to be 0.25, and E_3 to be 0.20.

Hence the standard deviation on a count of N disintegrations will be $1.27\sqrt{N}$.

In this discussion no account has been taken of the natural background of the ionisation chamber which is of the order of 30 counts per hour. When the counting rate due to thoron is small compared to this, the additional error introduced by the correlation effect discussed above is negligible, but becomes significant when the total counting rate is of the order of 2 x the background.

(v) The Determination of Radon

(a) Theory and Experimental Procedure

To determine the amount of radium present in the solution the bubbler is sealed into a closed system which can be freed of air. Here the radon grows with a period of half-growth of 3.84 days. After a suitable known time nitrogen plus radon is swept into the evacuated ionisation chamber, and the disintegrations of the radon counted. Opinion is divided as to the best method to adopt to sweep the radon out of the solution and into the chamber. Supported by the early work of Moran (24) Jacobi (3) (25) employs nitrogen or argon as a carrier gas and removes radon to within 1%. This carrier gas technique (using nitrogen) was employed in the work to be described here. However, Evans (26) claiming support from the early work of Boltwood (27) claims that only by boiling can the radon be removed quantitatively. This complicates his apparatus somewhat. The boiling technique has been used more recently (28).

Neither thoron or actinon can contribute counts in this static method. From the radon count the equilibrium amount of U238 is calculated, and from this an indirect estimate of the U235 series can be obtained.

After the thoron run has finished the bubbler D is transferred to a radon unit (see Figure 9). The B 10 cone of the bubbler is cleaned, coated with "sugar grease" (sucrose, glycerol and starch) and inserted into the B 10 socket of the radon unit. Unlike apiezon grease, this sugar grease does not absorb radon during the several weeks of growth. D is held firmly in place by means of a rubber band passing over the glass lugs on the radon unit and on D. From the internal seal a 1 mm bore jet projects below the surface of the liquid in D.

During this operation the two U tubes contain no mercury, this having flowed into the reservoir Y on taps X' and X" being opened. Then with these taps closed there is a free path from V to R via the liquid contained in the bubbler. A rubber lead carrying oxygen free nitrogen is attached to V and nitrogen is bubbled through the unit to free the system of radon and air and hence of any oxygen since this would later interfere in the ionisation counter. After ten minutes or so, the nitrogen lead is removed from V and applied to the top of

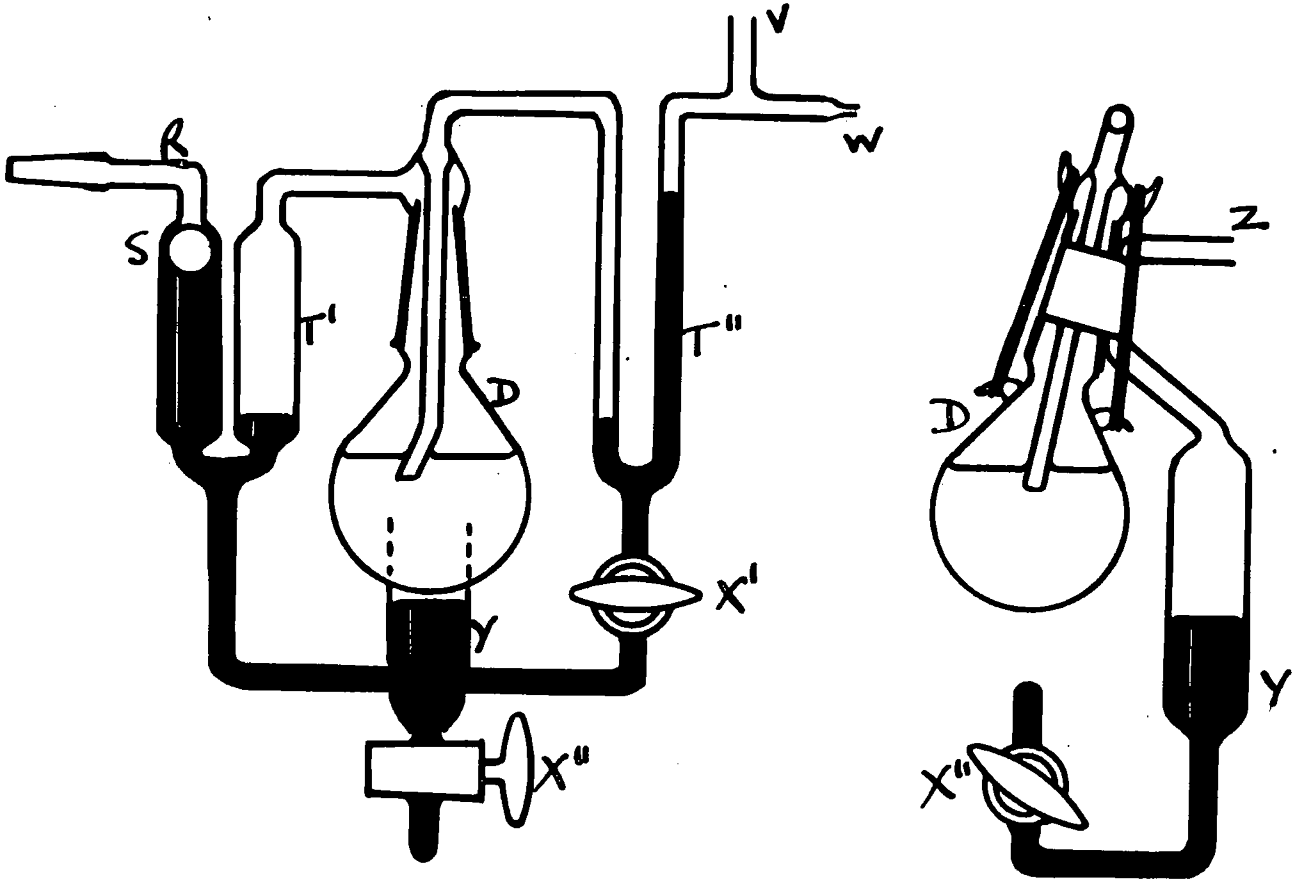


FIGURE 9.

of the mercury reservoir Z. Tap X' is opened, followed by a cautious opening of X". Mercury then rises into the two U tubes and taps X' and X" are closed, and the nitrogen supply removed from Z.

There now exists an internal closed system of nitrogen above the solution containing radium. This system is maintained for a known time and the fraction of the equilibrium amount of radon which has grown in that time is calculated and the necessary correction made to the count finally obtained. The closed system of nitrogen is at a pressure of a cm or two of mercury which is shown by the U tubes. If for any reason, e.g. failure of the sugar grease, the system should become open to the air this slight pressure will disappear and the U tubes will show this.

The ground joint (R) and the manifold (F) are greased with apiezon grease, since they must bear a vacuum. The radon bearing nitrogen passes both these regions very quickly and there is no risk of absorption of radon. When the radon unit has been fixed into the main apparatus nitrogen is bubbled against the sinter disc Q with tap P shut. The manifold F is arranged to connect pump and chamber with the 'radon side' of the apparatus. This situation is the one shown in Figure 3. The steel ball is pushed home into the ground socket by rising mercury and the mercury is prevented from going further by the ball (S). The entire radon side together with the chamber is then evacuated by the pump. With the pump shut off from the system, the constancy of the manometer J shows the absence of any leaks in the relevant parts of the apparatus, F is then operated to isolate the 'radon-side' of the apparatus. Tap P is then opened so that nitrogen leaks into the system through the sinter disc. The steel ball descends on the falling mercury until the U tubes are as before. P is then closed, F is opened and the evacuation repeated. After this has been repeated a third time any oxygen in the radon side has been flushed away.

The radon side is again isolated and filled with nitrogen from P until the U tubes of the radon unit are as before. During these latter procedures a nitrogen lead passes nitrogen from V to W so that the gas above the mercury in this side of the U tube is flushed free of air.

A small yellowish-white coal gas flame is arranged so that the jet of nitrogen flowing from W blows on to it. This streams the flame out and makes it blue. From then on the nitrogen flow from W must be maintained. If at any time in the subsequent operations it fails, the small flame burns upright and is yellowish-white. This device enables both hands to be free, yet making sure that no air enters. Another device (not quite so successful) was the double-reeded hole of a mouth-organ.

When nitrogen was streaming from W a particular note was sounded. If this stream stopped there was silence, and if air was sucked violently in, a note different from the first by a tone, was sounded.

The mercury in the U tubes is then slowly lowered by opening the taps the mercury flowing into the reservoir. There is now a clear passage for nitrogen through the apparatus and into the chamber. The evacuated chamber is closed from the pump and connected through F to the radon side. A steady stream of nitrogen carries the radon into the chamber, while W is watched to notice whether any air has been introduced. When J shows that the chamber has been filled to atmospheric pressure F is closed and the screwclips I and G are clamped down on the rubber leads to prevent absorption of radon by the apiezon grease. The radon unit is then removed and more radon grown for further analysis of the bubbler for radium. The potential is then applied to the chamber and the count is begun.

A great deal of trouble was caused by non-sealing properties of the steel ball (S) when the radon side was being evacuated. The mercury instead of being checked by the ball in its seating was able to flow slowly past. It was noted that finally small rusted areas developed, although the balls were of "stainless" steel. The leakage occurred with seemingly unattacked balls, and much time could be wasted when a radon run failed. The bubbler then had to be removed, the unit dismantled, the steel ball renewed and the radon growth restarted.

A technique was developed to make use of a radon unit with a leaky ball seal so that the radon (free of oxygen) could be swept into the chamber. One evacuation only of the radon side from the steel ball onwards usually gives a much reduced radon count for the run owing to the presence of oxygen. Hence it was obvious that a thorough cleaning of the radon side from any air which had been introduced was essential for a successful run.

The evacuated chamber was connected through F to the radon side and a sound steel ball seal, the radon side being filled with nitrogen at atmospheric pressure. The nitrogen distributed itself between the chamber and the radon side. The manometer J showed a pressure of 36 mm. With a typical leaky ball seal, nitrogen only passed to the chamber until J registered 24 mms pressure and then mercury began to leak past S, and F had to be turned off.

Thus with a leaky ball seal 2/3 of the gas in the radon side is passed into the chamber before the process has to be stopped. Then after F is closed the radon side can be refilled with nitrogen and the partial evacuation of the radon side repeated. Assuming the radon side completely filled with air then nine operations should reduce the level of oxygen to the lowest level obtained by the backing pump (0.01 mm). This level is the normal level for a successful sound ball-seal run. In practice, as a precaution, fifteen to twenty such operations were performed since they took little time.

Finally it was found possible to adjust P and F, the chamber being pumped, so that the mercury and the steel ball in the radon unit remained stationary. In this way a considerable flow of nitrogen could pass through the radon side and after ten minutes the radon side was sufficiently air free to enable a successful radon run to be performed. The steel ball was now redundant and radon units were made without the ball and socket seal. Radon calibrations performed by both these modifications of technique gave results in agreement with those obtained using the previous technique.

When the radon has been successfully swept into the chamber and the count begun the rate of counting rises for the first three hours while the active deposit grows to equilibrium. When this has been reached the count can be taken for a fixed time (e.g. six hours). However, for convenience in a normal day's laboratory work, the count was commenced soon after filling the chamber. The same technique was applied to standards. After the six hour count, the radon is pumped away. The chamber is filled with nitrogen and pumped out several times, before being filled with nitrogen for the background count. The next morning this background count is taken (usually three hours). By this time the radon active deposit, the longest lived of which is RaB (27m) has decayed and what is the second background for the first day's run can be used as the first background for the second day's run. In this way a sequence of radon runs can be established.

As a further convenience, a simple alarm clock mechanism was installed. This could be set after a radon run to operate the counting switch the next morning. The radon background could be started at 6 a.m. and a radon run started at the beginning of the normal working day at 9 a.m., or a longer background could be obtained. The background plus active deposit activity is never counted, although the active deposit grows and counts during the actual radon count. This is valid if the same conditions apply to the calibration run, of course, but the technique does mean that there is a degree of correlation to be considered for the count obtained, and this affects the error.

The cylinders of oxygen-free nitrogen were used not earlier than one month after they had been filled and so contributed no radon to the system. The radium standards used were those prepared by Jacobi (2) and standardised by the Vienna Radium Institute.

(b) The Assessment of the Count and its Error

As in the thoron case, there are many factors involved which make any absolute assessment difficult. The normal statistical treatment is complicated to the same degree as that for thoron. Thus there are two subsequent members of the disintegration series (RaA and RaC) which can contribute to the total count. The equations derived in the thoron case (page 33) are equally applicable for radon counting but the probabilities of recording each of the three α particles which are emitted (E_1 for radon, E_2 for RaA, E_3 for RaC) differ.

None of the half lives of the immediate descendants of radon are long enough or short enough to introduce any complications and we can take $E_1 = 0.9$, $E_2 = 0.5$, $E_3 = 0.5$. Hence the standard deviation on a count of N disintegrations will be $1.49\sqrt{N}$. Again this additional error is negligible for counts small compared to the background, but becomes significant when the total counting rate is 2X background.

(vi) Activity contributions from reagents

Any thorium present in reagents will be in equilibrium with the members of the series after radiothorium. A sample of the reagent after suitable treatment was extracted by $BaSO_4$ in the usual way. The $BaCl_2$ reagent could not be extracted efficiently in this way and the bubbler was filled to the required volume with a solution of a known amount of this reagent and a thoron run performed.

The thorium figures so obtained were not simply applied to meteorite results, since the analysis of each reagent for thorium involved the use of others. Some reagents (e.g. $BaCl_2$ and fusion mixture) contributed so little that the thorium content for each particular reagent could be easily found.

Reagent	Th content (10^{-8} gms Th)		Error	Amount Reagent
$BaCl_2$	≤ 72			per 200 mgms
H_2O (dist. once)	200	±	110	per litre
H_2O (dist. twice)	27	±	8	per litre
HCl conc.	183	±	35	per litre
Fusion mixture	≤ 155			per 500 gms) *
KOH	≤ 150			per 450 gms)
Iodine reagent	168	±	42	per 600 mls
HNO_3 conc.	312	±	124	per litre

*The limit shown, was attributable to the HCl used.

The thorum figures obtained for Beddgelert (see page 59) are the figures obtained by subtracting the reagent contributions as given above from the meteorite runs. However, since two errors are combined in this subtraction the error on the final corrected result is worsened. It is, therefore, an aim in this type of work to lower the contribution from the reagents as much as possible.

As can be seen from the table, one of the main reagents (distilled water) could be partially purified by redistillation. Concentrated HCl, on the other hand, proved resistant to purification by this means, redistilled HCl still containing approximately 180.10^{-8} g Th / per litre. In the case of both redistilled water and HCl it seems to be 'pick-up' from the glassware used which brings in the thorium, since the distillations were carried out at a very slow rate.

Radon runs were performed on the reagents and the equilibrium amount of uranium to produce this radon calculated. Actually the reagent's radium content is analysed by this method and this is likely to be very different from the uranium content. However, since meteorite results are expressed as uranium content, (equilibrium assumed to be established) the reagent results are similarly expressed.

Reagent	'U conc.' 10^{-8} g U.		Error	Amount of Reagent
$BaCl_2$	64	±	10	per 200 mgms
H_2O (twice dist.)	10	±	5	per litre
HCl conc.	150	±	7	per litre
Fusion mixture	580	±	31	per 500 gms
KOH	177	±	23	per 450 gm
Iodine reagent	158	±	10	per 600 mls
HNO_3 conc.	42	±	18	per litre

The results in the above table are due to each reagent alone. Again the figures obtained for Beddgelert (see page 59) were obtained by subtracting the reagent contributions as given above from the meteorite runs.

The levels of thorium and uranium shown by these reagents enabled the Beddgelert work to be completed but they were not low enough to permit iron meteorite analyses to be performed, since these have very low concentrations of uranium and thorium. Thus 50 grams of an iron meteorite which might contain 25.10^{-8} g Th and 25.10^{-8} g U would need circa 300 mls of conc. HCl to dissolve it. The acid would contribute 55.10^{-8} g Th and 45.10^{-8} g U. The result from such a run would have either a very large error or have to be expressed as a fairly high limit. An attempt was made to lessen these difficulties by purifying the reagents. Shaking the reagents with $BaSO_4$ was tried.(3) A slow exchange reaction between radium atoms in solution and barium atoms on the precipitate can be expected to take place.

Polythene reagent bottles were obtained to prevent any pick-up of uranium or thorium from glass. The three reagents most used (conc. HCl, H_2O, conc. HNO_3) were then subjected to the following treatment. 500 mls of each were placed in polythene bottles with approx. 2 gms of $BaSO_4$. This $BaSO_4$ had been prepared in the normal way and washed with distilled water for several weeks to free it of any trace of adsorbed Ba^{++} or $SO_4^{=}$. The polythene bottles were then shaken on a machine performing circa 280 oscillations/min, for varying lengths of time. The water used had only been distilled once. After one hour's shaking, followed by settling, separation, and thoron analysis of an extract of the combined reagents, the figure 130 ± 60.10^{-8} g Th was obtained. An exactly similar run, but with the shaking carried on for three hours gave the figure 110 ± 50.10^{-8} g Th. A further similar run, where the shaking was carried on for 12 hours gave the figure $\leq$ 40.10^{-8} g Th. The shaking with $BaSO_4$ had reduced the concentration of ThX in these reagents significantly.

To check these findings, fresh shaking experiments were conducted followed by radon analyses. The three reagents (conc. Hcl, H_2O dist., conc. HNO_3) were again shaken for known times and after settling, combined and extracted as for the thoron runs. After 12 hours shaking the mixture gave the result:- 80 ± 30.10^{-8} g 'U'. (The results are expressed as the corresponding amount of Uranium). After 44 hours shaking the mixture gave the result: $\leq$ 14.10^{-8} g 'U'. Fusion mixture was made up into a strong solution to enable this purification to be carried out. Barium chloride proved to be an exception in that it needed a longer shaking time. A strong $BaCl_2$ solution was shaken with $BaSO_4$ for varying periods of time. Samples of this solution containing 2 gms. of $BaCl_2$ were analysed for radon and gave the following figures (as corresponding uranium).

12 hours shaking	640 ± 35	10^{-8} g. U.
44 " "	570 ± 40	"
72 " "	≤ 15	"

In practice all the reagents were shaken with $BaSO_4$ for four or five days. Using reagents which had been purified from ThX and Ra in this way the 'blank' run of a meteorite analysis generally gave a count which was sufficiently low to enable a definite figure on the meteorite to be obtained.

(vii) Results of radon-thoron method on meteorites

The Beddgelert results are given in the section devoted to that meteorite. This was the only stone meteorite analysed, all the rest being iron meteorites, the results for which are given on page 59. Before this, however, a complete sample calculation is given to show how the figures and their errors are computed, for both thorium and uranium. A typical run was the analysis of a 111 gm. sample of Ahnighito. This sample was in perfect condition, showing clear Widmannstäten figures. The dissolving and $BaSO_4$ extraction of a meteorite has already been described. While some of these chemical procedures were being performed a thoron background was taken. In the special case of the first background where there is no active deposit activity the count can be prolonged beyond the usual 12 hours. This is useful since it lessens the error of the background estimate and hence of the run. With this particular sample, the first background was counted 36 hours and gave a total of 1,597 counts. The square root of this number is taken to be the standard deviation of the count and we deduce the background as $\frac{1597 \pm 40}{36}$ c.p.h. = 44.4 ± 1.1 c.p.h.

The Ahnighito $BaCl_2$ extract was then analysed for thoron. Precisely 24 hours had elapsed from the precipitation of the $BaSO_4$ to the beginning of the thoron count. The thoron count was carried on for 12 hours and gave a total count of 637, the standard deviation of this count being 25.2. Hence the thoron count = 53.1 ± 2.1 c.p.h. In an exactly similar manner the second background was found to be 42.1 ± 1.8 c.p.h. over a 12 hour period. Hence the mean background is

$$\frac{42.1 + 44.4}{2} \pm \frac{1.1 + 1.8}{2} \text{ c.p.h.} = 43.25 \pm 1.45 \text{ c.p.h.}$$

Hence the count due to the bubbler's contents

$$= 53.1 - 43.25 \pm \ 2.1^2 + 1.45^2$$

$$= 9.85 \pm 2.55 \text{ c.p.h. in excess of background.}$$

A correction had to be applied here for the decay of ThX during the source preparation time of 24 hours. The ThX had decayed in this time to 82.64% of the amount initially present. Hence corrected c.p.h. of the thoron source

$$= (9.85 \pm 2.55) \times \frac{100}{82.64} = 11.9 \pm 3.09 \text{ c.p.h.}$$

The whole procedure was then performed again with all the regents used in the same quantities but with, of course, no meteorite sample present. This run gives a 'blank' which can be subtracted from the above figure to give the thoron contribution from the meteorite alone.

In an exactly similar manner to the above calculation the contribution of the blank was found to be

5.4 ± 2.56 c.p.h. in excess of background.

Hence $6.5 \pm \quad 3.09^2 + 2.56^2 \quad = 6.5 \pm 4.0$ c.p.h. are due to the thorium from 111 gm Ahnighito.

The thorium calibration figure obtained by performing just such a run but with a known amount of thorium in the bubbler solution, in equilibrium with all its daughters, was 7.5 ± 0.3 c.p.h. per 10^{-6} g Th. Hence contained in 111 gm of Ahnighito there is

$$\frac{6.5 \pm 4.0}{7.5 \pm 0.3} \times 10^{-6} \text{ grams of thorium.}$$

Hence the thorium contained in 111 gm Ahnighito is

$$\frac{6.5}{7.5} \pm \frac{6.5}{7.5} \quad \frac{4^2}{6.5^2} + \frac{0.3^2}{7.5^2}$$

It can be seen that the error of the thorium calibration contributes in a very small way to the final figure which is

$0.866 \pm 0.533 \quad . \; 10^{-6}$ gm Th/111 gm Ahnighito

or $\underline{\underline{0.78 \pm 0.48}} \quad . \; 10^{-8}$ gm Th/per gm Ahnighito

The bubbler was then sealed into a radon unit and after a period of growth the radon was analysed in the way already described.

A background was counted before and, the day after, the radon run. The mean background was calculated in the same way as the thoron example and gave the figure 32.1 ± 3.27 c.p.h. The radon count gave a total count 312 ± 17.6 for 6 hours, hence c.p.h. = 52.0 ± 2.93. The count in excess of background is 19.9 ± 4.4 c.p.h.

In the same way the blank run was analysed and gave 4.1 ± 4.1 c.p.h. in excess of background.

Hence the count due to the meteorite

$$= 19.9 - 4.1 \pm 4.4^2 + 4.1^2$$

$$= 15.8 \pm 6.03 \text{ c.p.h.}$$

The figure for a radium calibration was 190 ± 4 c.p.h. per 10^{-12} g radium. Hence the radium content of the bubbler can be easily calculated and assuming that the U238 series is at equilibrium the corresponding uranium content can also be found.

Concentration of uranium in 10^{-8} gm. U/gm. Ahnighito,

$$= \frac{15.8 \pm 6.03}{190\ (\pm 4)} \cdot \frac{2.84 \cdot 10^{-6}}{111} = 0.21 \pm 0.08$$

The relative error of the radium calibration is so small that that it can be neglected.

TABLE OF RESULTS (RADON-THORON METHOD)

	NAME OF METEORITE	CLASS	HELIUM 10^{-6} cc/gm	WEIGHT (gm) of meteorite taken	URANIUM 10^{-8}gm/gm	THORIUM 10^{-8}gm/gm	AGE 10^{6} years
1	SAVIK	Om	< 0.0002	57 144 201	≤ 1.1 0.20 ± 0.05 * 0.22 ± 0.05 * 0.21 ± 0.04	≤ 1.1 ≤ 0.26 ≤ 0.21 ≤ 0.24	≤ 0.8
2	AHNIGHITO	Om	< 0.001	111 75	0.21 ± 0.08 * Contaminated	0.78 ± 0.48 ≤ 0.80	≤ 1.2
3	MUONIONALUSTA	Of	< 0.002	78 55	0.88 ± 0.13 Contaminated	1.10 ± 0.88 1.83 ± 0.96 1.46 ± 0.7	≤ 1.4
4	COAHUILA	H	0.1	52 71	≤ 0.5 Contaminated	≤ 0.93 ≤ 1.02	> 115
5	TREYSA	Om	26.5	41 64	0.70 ± 0.3 ≤ 1.6	5.9 ± 2.4 5.1 ± 1.2 5.5 ± 1.3	5200
6	TOLUCA (LONDON)	Om	20	53	0.86 ± 0.3	≤ 1.05	≥ 6600
7	TOCOPILLA			58	2.3 ± 0.3	1.9 ± 0.8	

Other meteorite results:- Beddgelert page 59 *Residue solutions page 124 San Martin page 152

Notes on the table of results

All are iron meteorites, - Om = Medium Octahedrite, Of = Fine Octahedrite, and H = Hexahedrite.

The results given in the uranium column are each the result of at least two radon runs on the $BaCl_2$ extract of the samples. Where more than one figure is given for a meteorite then the corresponding number of independent samples were so analysed. (Only one thoron run could be performed on each sample.) The weight of each sample analysed is given. That this weight has an important bearing on the accuracy is obvious, since the more activity to measure, the greater the accuracy in measuring it. The uranium results given by the fluorimetric method, obtained by Mr. Dalton, agree fairly well with the results by the radon method except for Ahnighito (see page 125).

In the case of Coahuila the sample is not big enough to obtain data other than limiting figures. There would never be any point in analysing any more 50 gm samples of Coahuila by the radon-thoron method. The difficulty is to persuade museum curators to part with sizeable portions of meteorites under their care, yet the radiochemical analysis of a single large piece (~100 gm) is much better practice than the repeated analysis of smaller (circa 50 gm) pieces. This is shown by the data on Savik.

Where a limiting figure is shown, its meaning is that at least 2/3 of an infinite number of future results from analyses of the meteorite would fall on or below the limit stated.

The entries 'contaminated' in the radon column mean that the radon count was alarmingly high and the runs were not regarded as valid. The three samples concerned were stored together and sealed off in radon units about the same time. A thorough investigation was made into all reagents, glassware, bubblers, radon units, etc., used, but the source of contamination could not be tracked down. Work was going on elsewhere in the department with large quantities of radioactivity, and it was conceivable that this might be the cause.

The age figures were calculated using either the simple formula, or for ages $> 10^8$ years the triangular nomograph. These are discussed in a separate section where a sample age calculation is given.

The helium values given in the table were determined by the following workers:-

1 and 2	Arrol, Jacobi and Paneth (2)
3 and 4	K.F. Chackett
5 and 6	P. Reasbeck

The helium content of Tocopilla (No. 7) has so far not been determined.

The results show the low level of natural activity present in iron meteorites. As in the results published in 1942 (2) (Table I) the thorium figures vary over a greater range than the uranium figures. However, because of the more refined techniques smaller concentrations have been determined than in previous experiments and in several cases small limiting concentrations below which the value of the content must lie.

The thorium content of Savik (≤ 0.24) is at least 10 times lower than that of Mt. Ayliff which was the lowest of the 1942 thorium figures. The highest thorium content, that of San Martin, was 8. This meteorite has been analysed using the new procedures and a value 10.4 ± 1.4 obtained (see page 156). The uranium figures fall mainly in the same range as before but the smallest measurable concentration has been lowered by a factor of 2, the least figure being that of Savik (0.21).

It is interesting to compare the average thorium and uranium contents which are of some value in assessing the overall activity of meteoritic matter.

	U	Th
1942 paper, average content	0.7	4.0
This work, average content	0.8 - 0.9	2.2 - 2.5

The ages obtained using the present results are spread over the same range as were the previous results. Those meteorites whose helium contents are limiting values are shown to be very young. (Savik, Ahnighito and Muonionalusta).

(viii) Beddgelert Meteorite

On September 21st, 1949, shortly after the work for this thesis was begun, a meteorite fell at Beddgelert in North Wales. Durham University obtained half of the approx. 800 gm meteorite for chemical and radiochemical analysis; the other half going to the British Museum.(29) The meteorite is classed as a black crystalline chondrite with 18% free metal. Photographs of the meteorite after cutting are shown in Figures 10 and 11. Figure 11 shows the dispersed metallic phase reflecting light while Figure 10 shows the chondrules visible in diffuse light.

The radiochemical analysis of a stone meteorite such as Beddgelert, combined with a helium figure can be used as age data if the stone is of a dense and hard structure and its temperature has always been low. These conditions are fulfilled in the Beddgelert stone which is very hard - it cuts glass easily - and of which we know definitely that after its fall its temperature was never raised. As is well known, the heating of a meteorite during its flight through the terrestrial atmosphere is confined to the crust. The helium method for age determination was therefore applied to Beddgelert. The chemical and radiochemical work carried out is described in this section.

A complete chemical analysis would have been both

FIG 10.

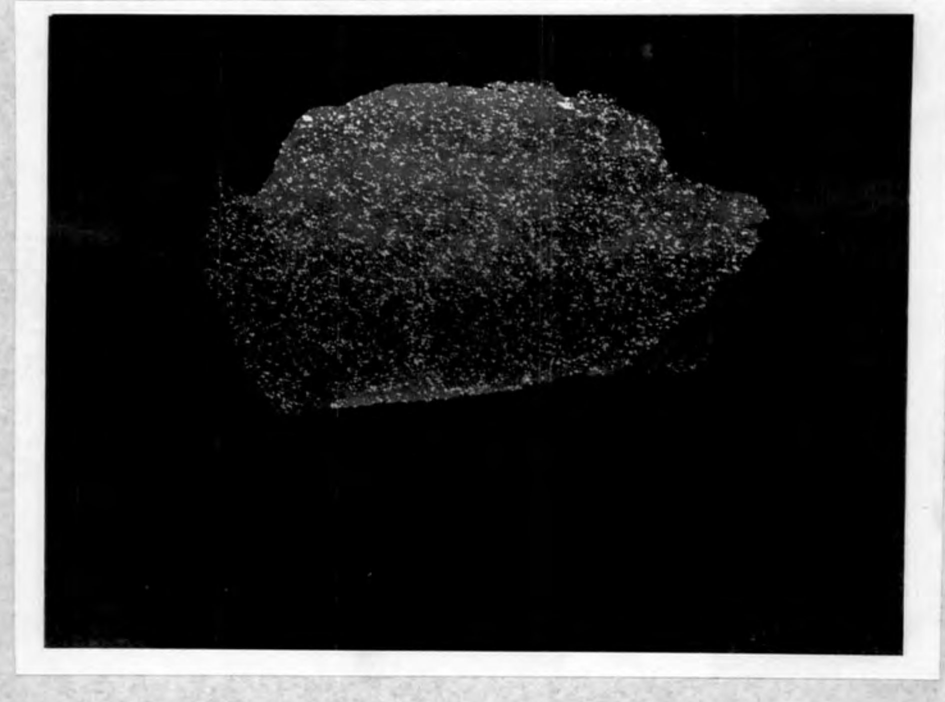


FIG 11.

arduous and time-consuming, but conclusions as to the composition of the meteorite can be drawn from qualitative spectrographic results. The spectrographic investigation was carried out with a Hilger Large Automatic Quartz Spectrograph (Littrow Type). For the range of 2800-4600 Å an Ilford Zenith plate was used under the following conditions: slit width 0.015 mm; Hartmann diaphragm; copper and graphite electrodes; air gap 3mm; current 4 amp; exposure time 30 secs. For the range 2200-2800 Å a Kodak B plate was used and the current increased to 7 amp., the other conditions remaining the same.

The analyses were carried out separately on a fragment from the interior of the meteorite, without any preliminary treatment, and on metallic nodules separated from the same fragment by KOH fusion, leaching, etc. The results are given in the following table. It will be noted that Ti, V, and Ba are present only in the untreated fragment.

Table I

	Fragment (untreated)	Metallic Nodules
Major constituents	Fe, Si, Mg	Fe, Ni.
Minor constituents	Cr, Mn, Na, Ca, Al, Ni,	Si.
Heavy Traces	Cu	Cu, Mg, Ca.
Traces	Ti, V, Co.	Cr, Co, Mn, Al, Na.
Slight Traces	Ba.	

The following table gives a rough quantitative estimate of some of the constituents of the untreated fragment based on comparison with iron lines. (Iron circa 60% of the total meteorite).

Table 2.

Element	Semi-quantitative estimate
Si and Mg	15% each
Ca, Al and Ni.	1.0 to 1.5% each
Cr and Mn	0.5% each
Ti	0.07%
V	0.015%
Co not more than	0.05%

An investigation was made to determine the best method for separating the stone and metal phases of the meteorite. Magnetic separation after grinding was a possible method, but because the metallic nodules were malleable it was difficult to achieve a clean separation. Attacking the meteorite with dil. HNO_3 only left 45% of the weight taken. It must therefore attack much more than the 18% of metallic nodules. This was confirmed by magnesium being found in bulk in the dil. HNO_3 solution, as well as iron and nickel. The metallic nodules were known to be mainly iron and nickel.

Fusing the meteorite with potash, followed by leaching, gave a reasonable separation. 18% of the weight taken was found in metallic nodules. A sandy redbrown precipitate was also formed which contained iron and magnesium. The KOH solution after acid treatment and boiling gave a precipitate of silica 32% of the weight taken.

Attacking the metal phase with iodine reagent was then tried. This method of attacking steels is dealt with at great length in the 7th and 8th reports of the Committee on the Heterogeneity of Steel Ingots of the Iron and Steel Institute. From the information given in these reports, a very simple method could be evolved for our purposes since we are not concerned with preserving the chemical identity of oxide or oxygen gas, inclusions etc. Taylor-Austin's report (39) showed that if 5 grams of steel turnings were stirred with iodine reagent consisting of 30 gm I_2, 25 g Kl, 120 ml H_2O, for 6 hours, at lab temperature, the steel would be entirely dissolved leaving non-metallic inclusions as residue.

Taylor-Austin's method was chosen and tested, using circa 1 gm of Beddgelert, previously ground in a pestle and mortar. To this sample was added 12 mls. of iodine reagent (more than sufficient for the iron phase) and the mixture was agitated vigorously by a magnetic stirrer. After each hour of stirring the residue was separated, washed with dilute Kl solution and weighed. After 3 hours the residue assumed a constant weight and a further 3 hours stirring made no change.

In performing a meteorite run, the stirring was carried on for more than 4 hours with the excess of iodine reagent recommended. When the residue had been separated from the solution the latter was simply diluted and extracted with $BaSO_4$ in the usual way, followed by thoron and radon analysis.

The 'iodine-insoluble' or silicate phase was alternately fused with fusion mixture followed by leaching, and attacked by HCl. After a few alternations , only a few mgms. of residue remained which dissolved in aqua regia. The alkaline leachings were combined, acidified, and extracted with $BaSO_4$ in the normal way. The acid attacks were combined and separately extracted with $BaSO_4$. The two $BaSO_4$ extracts were combined and after suitable treatment analysed for thorium X and radium.

Results:	**U** 10^{-8} g/gm	**Th** 10^{-8} gm/gm	**He** 10^{-6} cc/gm	**Age** in 10^6 yrs
Metal Phase	9.1 ± 1.0	12 ± 9		
	9.4	8.1 2.4		
Mean	9.1 ± 1.0	8.5 ± 4.9	2.8	210
Silicate Phase	10.0 ± 1.9	38.0 ± 16		
	12.8 ± 3.8	58.0 ± 13		
		29.0 ± 5		
Mean	10.8 ± 2.7	39.0 ± 8	30	1,240

While quantities of the order of 20 gm of meteorite had to be used for uranium and thorium analysis to obtain the accuracies shown, considerably less error in a He determination could be obtained using only a few tenths of a gram. It was not surprising, therefore, that variations found in the helium analyses should average out in the uranium and thorium figures. For an age calculation it would be necessary to determine U, Th and He in one and the same sample. Hence as preliminary figures only, it can be stated that the silicate phase seems to have solidified more than 1,000 million years ago, and the iron phase about 200 million years ago.

Chapter III Helium method of age determination

As the radioactive families of U238, U235 and Th232 decay, the α particles produced form helium gas. Provided the mineral or meteorite in which the decay takes place is a crystalline structure which has not suffered large-scale deformation due to weathering or heating, the helium is trapped. During millions of years or more, the helium grows to a measurable quantity, which can be extracted and determined. If the uranium and thorium concentrations are also determined then the time which has elapsed since the body assumed helium-tight properties can be found. This time is called the geological age.

If the simplifying assumption is made that the concentrations of the parents of the series have not appreciably decreased during the time that the helium was produced, then a direct ratio can be formulated.

Thus

$$\text{Age in yrs} = \frac{[\text{Helium}] \text{ in cc per gm of meteorite}}{11.6\ 10^{-8}.[U] \text{ in gm/gm} + 2.89.10^{-8}.[Th] \text{ in gm/gm}}$$

The factor 11.6 . 10^{-8} which operates on the uranium concentration makes no allowance for AcU present. This can be allowed for and changes the factor to 11.9 . 10^{-8} but it obviously makes only a small correction. (The above simple equation is sufficiently accurate up to ages of 10^{8} years).

For ages greater than a few times 10^8 years, however, the above simplifying assumption no longer holds, and a comprehensive equation has to be formulated to allow for the fact that the rate of helium production must have been appreciably faster than it is now. Making the assumption that there has been no loss or gain of any of the three relevant materials during the period considered an originally helium free material will have accumulated in a time t ending now a quantity of helium given by -

$$[He] = 8.\,[U^{238}]\left\{e^{\lambda_{238}t} - 1\right\} + 7\,.\,[U^{235}]\left\{e^{\lambda_{235}t} - 1\right\}$$
$$+ 6\,.\,[Th^{232}]\left\{e^{\lambda_{232}t} - 1\right\}$$

where the symbols in square brackets represent the numbers of atoms of the various nuclides found at the present time.

Starting from the analytical data this equation can be solved for t only by a rather tedious iterative process, and it is more convenient to use a graphical method.

F.R. Wickman (31) suggested the use of graphs for the computation of ages, since the error in reading from the graph is negligible compared with the other errors involved. A modification of this graphical method has been devised by G.R. Martin and has been used to calculate the ages given in this thesis. This is the triangular nomograph shown in Figure 12.

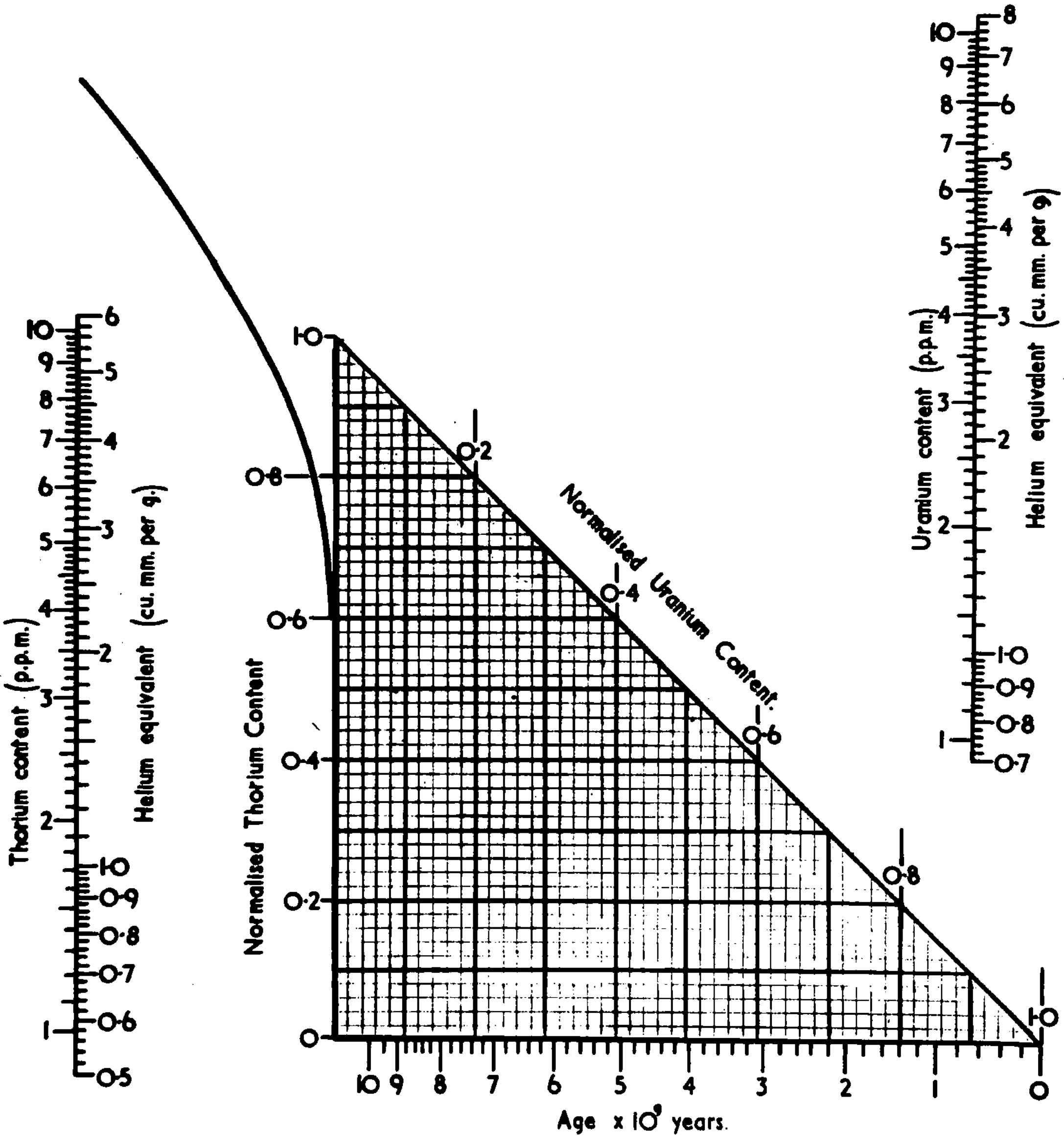

Thorium content (p.p.m.)
Helium equivalent (cu. mm. per g.)
Normalised Thorium Content
Normalised Uranium Content.
Uranium content (p.p.m.)
Helium equivalent (cu. mm. per g)
Age x 10⁹ years.
10 9 8 7 6 5 4 3 2 1 0
0 0·2 0·4 0·6 0·8 1·0

FIGURE 12.

Lines can be drawn running slantwise across the diagram representing equiage lines, the age being given for each in units of 10^9 years. Any point on the diagram represents a definite U - Th - He composition, and its associated age. In order to plot the three variables on a triangle of graph paper in this way it is necessary first to reduce them to some common unit. A convenient one is the volume of helium per gm. of material in the case of helium, and the potential volumes of helium which could be produced by the complete radioactive decay of the uranium and thorium in the case of the other two components. The sum of these three quantities is then used to divide into each to give the fraction of the total possible helium present as (a) helium gas, (b) 'undecayed' uranium and (c) 'undecayed' thorium.

The conversion factors are
1 μg of U per gm material ≡ 0.758 cu mm He/gm
and 1 μg of Th per gm material ≡ 0.579 cu mm He/gm,
when they are completely decayed.

The equiage lines on such a diagram are all straight and interpolation is a simple process. For convenience (see Figure 12) the envelope of these equiage lines has been drawn. When a point has been fixed in the diagram, the tangent from this point to the envelope passes through the age scale at the corresponding age.

Chapter IV Modification of the $BaSO_4$ extraction method

The chemical procedure of the barium sulphate method (see page 15) involving two carbonate fusions, leachings etc., was tedious. As well as being inconvenient the time taken to convert the carrier to a suitable form for thoron and radon assay wasted some of the thorium X which decays from the time of precipitation. The conversion to barium chloride allowing time for the $BaSO_4$ to digest etc., took at least 12 hours to perform. Further, this procedure involved a correspondingly greater risk of contamination than would a shorter technique. For these reasons some other carrier procedure was sought. The various attempts to find a new carrier procedure are described in this chapter and these descriptions are preceded by a brief survey of the results.

A study of various carrier procedures for radium (32) shows that a precipitate of barium carbonate is 100% efficient for the carrying down of radium from solution. If this method could be developed for meteorite solutions much time and effort could be saved. It proved impossible to precipitate barium carbonate simply with sodium carbonate or ammonium carbonate without creating conditions suitable for bringing down iron as hydroxide. As expected, a complexing agent for the iron was necessary and eventually proved practicable. However, when tartaric or citric acids were used as complexing agents several useful precipitates could not be employed. Oxalate precipitation proved inefficient for the carrying down of radium, so that oxalate as a complexing agent was also precluded.

Using salicylic acid as the complexing agent proved successful (but only at lab. temperature). Under alkaline conditions then possible, barium carbonate carried down 100% of the radium present. Before this method was found, several other ideas were considered. These are enumerated below.

1. The salting out of barium chloride by saturating the meteorite solution with HCl was a possible method. ($FeCl_3$ forms a complex with HCl). Considering the large bulk of $FeCl_3$ solution the technique when developed could be as involved as the $BaSO_4$ method and it was not investigated.

2. It was thought worth testing whether or not a precipitate of barium oxalate would carry down radium from a solution. Barium oxalate was precipitated by oxalic acid from a neutral solution containing iron and nickel and the precipitate was free from both Fe and Ni. Ammonium oxalate could also be used. In spite of large amounts of oxalate ion present, the solubility of barium oxalate (17 mgms/100 ml) seemed too great, and no radium was carried down. Calcium oxalate has a solubility of 1 mgm/100 ml. This also was precipitated from a solution containing radium but no detectable amount of radium

was found on the precipitate. This suggests a continuation of the oxalate solubilities down the group, making radium oxalate the most soluble.

3. A precipitate of manganese dioxide is also known as efficient carrier for radium. Under alkaline conditions Nakai (32) found this precipitate 100% efficient as a radium carrier. However, these conditions could not be obtained for meteorite solutions without first complexing the iron present. Tests of this carrier were made from slightly acid and neutral radium solutions. The precipitate was produced on the 30 mgm scale by adding $KMnO_4$ solution to the radium solution containing the necessary amount of manganous chloride.

$$2KMnO_4 + 3MnCl_2 + 2H_2O = 5MnO_2 + 2KCl + 4HCl$$

From a radium solution slightly acid with HCl, MnO_2 carried down 28% of the radium present. From a similar solution kept neutral 45% of the radium was found on the precipitate of MnO_2. Using Nakai's method of precipitation in alkaline conditions 100% recovery of the radium was found. R.B. Jacobi(25) used MnO_2 as carrier for the radium analysis of some natural waters. After adding a few drops of HCl to take up any lime of temporary hardness, the water sample was extracted with MnO_2 produced by the permanganate reaction, and 100% extraction was obtained. This does not agree with the results obtained above. The differences in technique employed for the natural water analyses were (i) 300 mgm MnO_2 were used (ii) the precipitate was left to digest in the hot mother liquor for an hour or so.

This type of adsorption carrier might be expected to be sensitive to variations in conditions. To be reliable for meteorite solutions where large amounts of holdback carrier would be present, precipitation of MnO_2 would have to be carried out in alkaline conditions. A complexing agent for iron would be necessary and with this proviso there are several carriers which could be used.

4. The investigation was enlarged to find a suitable precipitation which would give a permanent thorium source as well as bringing down radium isotopes. If this could be achieved then the thorium analysis would not merely depend on thorium X (3.64 days) allowing only one thorium figure to be obtained, but would depend on radiothorium (1.9 years) so allowing repeated thoron runs.

B.S. Hopkins describes the following reaction (33). A neutral solution of cerium in cerous condition is heated to boiling and potassium permanganate solution added till a permanent pink colour is obtained. Then a solution containing potassium permanganate and sodium carbonate in the proportion of 1 : 4 is added slowly as long as precipitation takes place and carbon dioxide is evolved.

$$3Ce(NO_3)_3 + KMnO_4 + 4Na_2CO_3 + 8H_2O$$

$$= 3Ce(OH)_4 + MnO_2 \cdot 2H_2O + 8NaNO_3 + 4CO_2 + KNO_3$$

The solution should show a faint pink colour during this precipitation. The precipitate is separated and washed with hot water. It was thought that this precipitate might serve as a joint carrier for thorium (carried by cerium hydroxide) and radium (carried by manganese dioxide). A chemical test of the reaction using 60 mgms of cerium as starting material gave the stoichiometric amount of precipitate, which only contained 6 mgm of iron out of a total of 400 mgm present in the solution.

A preliminary radiochemical test of the cerium-manganese carrier idea was carried out. In this test, no iron was present. Known amounts of thorium and radium were added to a solution containing 60 mgms of cerium as chloride and 60 mgms of manganese as chloride, sodium hydroxide solution was added and the resulting precipitate centrifuged off, washed, and dissolved in dilute HCl.. The thorium and radium recovered by this precipitate were estimated by means of their emanations in the usual way. The precipitate was found to contain 91 ± 4% of the radium, and 100 ± 5% of the thorium, added to the solution. The thoron run was performed 19 days after precipitation and so gave a figure representative of the efficiency of mixed cerium and manganese hydroxides as a carrier for thorium rather than for thorium X. This time

(19 days) allowed the thorium X known to be carried by manganese dioxide to decay.

This test showed that an emanating source giving more than one estimation of the two main radioactive families concerned was perhaps possible. However, further tests of the procedure under the conditions to be met in meteorite work gave disappointing results. The reaction producing cerium precipitates from a neutral solution was tested with known amounts of thorium and radium present. Iron was also present in amount comparable to meteorite solutions but did not interfere with the reaction. No radium was found on the precipitate and only 10 ± 3% of the thorium present had been extracted. It is interesting to note that the doubts expressed in the previous section on the use of MnO_2 as a radium carrier for neutral or acid meteorite solutions are confirmed by these results on the joint $Ce(OH)_4 - MnO_2$ precipitate. From an alkaline medium good efficiencies are obtained but from neutral or acid media the extraction efficiencies have been found to be poor. That no radium was found on a precipitate of $Ce(OH)_4$ and MnO_2 which had been formed in a neutral medium in the presence of iron, supports the idea that holdback is taking place since with no iron present MnO_2 had been shown to bring down 45% of the radium from a neutral solution.

5. Barium sulphite is another possible radium carrier

when precipitated from a radium containing solution. Its solubility at lab. temperature is 22 mgm/litre and decreases with increasing temperature. It is practically insoluble at 100°C. This looked promising but it proved difficult to prevent oxidisation of the precipitate to $BaSO_4$. If SO_2 is used as the reducing agent for the Fe^{+++} present then H_2SO_4 is produced. If a source of nascent hydrogen was used to keep the iron present in the ferrous state then when SO_2 was bubbled through the solution, a lot of sulphur came down. On the 1 litre scale, with a hundred grams of iron as chloride, the manipulation necessary would seem to make no improvement on the $BaSO_4$ method.

6. Complexing agents to keep the iron in solution during an alkaline precipitation were then tried. A solution of 1 gm of nickel-steel in HCl was made and 5 gm of citric acid was added. Ammonium hydroxide was added dropwise and the 'light green in acid' to 'orange red in alkaline' change was noted, but no precipitate was observed. It was shown by B.D.H. wide-range test paper that the solution was at pH 9 or more. This was repeated with cerium added to the acid solution. On rendering the solution alkaline with ammonia no precipitate was observed. If the alkaline reagent used was NaOH there was still no precipitate until such a quantity of NaOH had been added that the complex had been destroyed and everything came down. In the case of $BaCO_3$ both ammonium carbonate and

sodium carbonate proved incapable of bringing barium out of solution in the presence of Fe/citrate complex. Similarly MnO_2 could not be brought down from an alkaline solution of Fe/citrate complex. Further it was shown that the cerous nitrate-alkaline $KMnO_4$ reaction discussed above did not work either in the presence of this complex. The whole procedure of tests was repeated, using tartaric acid instead of citric acid. Exactly similar results were obtained. The only positive results obtained was that cerium came down as oxalate in the presence of Fe/citrate using ammonium oxalate as reagent. Calcium was also precipitated from such a medium but it had already been shown that radium was not brought down by such a procedure. This meant that cerium and calcium when precipitated together as oxalates would not yield a 'permanent' radon-thoron source.

Finally, salicylic acid was tried as a complexing agent. Fe and Ni were found to remain in solution in the presence of salicylate when the solution was rendered alkaline. Also Ba as carbonate and Ce and Mn as hydroxides were precipitated in the normal way from an Fe/salicylate solution. The Fe/salicylate complex proved unstable on heating the solution, unlike the tartrate and citrate complexes. Tests showed that a ratio of salicylic/Fe of 6/1 gave a solution which was stable for more than one hour at lab. temperature when rendered alkaline. Extraction using $BaCO_3$ precipitation was tested. To compensate for not being able to boil the solution during the $BaCO_3$ extraction a test was made where more weight of carrier than usual was used. Carried out at lab. temperature an extraction test showed that 300 mgms of Ba as $BaCO_3$ carried down 103 ± 5% of the radium contained in 300 mls of alkaline solution containing Fe/salicylate complex. It is most probable that the $BaCO_3$ precipitate would carry down thorium from a solution as well as radium (see page 139). In any case it can be seen from the various procedures discussed in this chapter that suitable precipitates could be easily arranged to carry down thorium and radium quantitatively from an alkaline medium. The thoron analysis would then no longer depend on thorium X (3.64 days half-life) but on radiothorium (1.9 years), and a sustained thoron source would be available for repeated analysis.

The behaviour of the various precipitates with respect to the method of complexing the iron present, is interesting. The behaviour of cerium in the presence of Fe/citrate or Fe/tartrate complex as described in section 6 would be expected from the complexing properties of cerium. Manganese would also be expected to behave as a complex forming element with these hydroxy-acids, but the experimental findings with $BaCO_3$ seem to be surprising. That some strong complex is being formed is evinced by the fact that $BaCo_3$ which was found not to precipitate, has a low solubility, 2 mgm/100 mls at 20°C.

Ferric ion does form a fairly stable complex with carbonate ion (34 page 1364), when $K_4[Fe(CN)_6]$ gives no reaction for the ferric ion. However, a subsidiary experiment with Fe absent showed that Ba was not precipitated by ammonium carbonate from an alkaline solution of ammonium citrate. It would appear, therefore, that Ba is forming a complex with the hydroxy acid. Sidgwick (34 page 260) points out the behaviour of calcium derivatives of hydroxy acids (citric, lactic etc.) in giving solutions of low Ca^{++} content which behaviour is important physiologically. Since a complexing property such as this would be expected to change as one passes down the group useful differences in complexing behaviour towards various hydroxy acids might occur between barium and radium. The $BaSo_4$ extraction method had been successfully modified as described but another idea to shorten the $BaSo_4$ procedure was not connected with new carrier procedures and so is described in conclusion. This was to dry the $BaSo_4$ precipitate (after separation and washing etc.) and then to dissolve it in conc. H_2So_4. The resulting solution could then be transferred to a bubbler and a thoron or radon run performed in the normal way. That the bubblers contents are conc. H_2So_4 and not dilute HCl should not affect the form of the thoron radon apparatus. Any acid spray etc. would be stopped by the vessels of KOH pellets. In fact with the thoron apparatus it might be an advantage to have no water vapour considerations which possibility might conceivably lead to a prolongation of the thoron counting time, and correspondingly greater accuracy.

Tests were carried out using known amounts of radium co-precipitated with $BaSO_4$, and after drying the precipitate, it was dissolved in conc. H_2SO_4 and transferred to a bubbler. Radon runs were performed in the normal way. The results obtained are expressed as percentages of the usual radon calibration

(a) 63 ± 4% (b) 58 ± 4%

Thus the emanating power of such a viscous solution is not sufficiently high to permit the use of the technique. Heating the solution to increase the emanating power would have been the next step but the radon thoron method was being superseded by other methods and no further tests were made.

The ionisation chamber method of counting radon and thoron is not as sensitive a means of determining the amounts of the two radioactive series present as are the new techniques of scintillation counting and fluorimetry (see pages 2+3.). The scintillation counter as developed is suitable for any α active nuclide prepared in a thin solid source. The instrument is described in the next chapter. The fluorimeter (35) can only be used for the determination of uranium but is easily the best method for the estimation of sub-micro gram quantities of this element. Radiochemical methods were needed to make use of both these instruments. These were developed and are described in Chapter VI.

Chapter V The Scintillation Counter

The radon-thoron method was limited to its sensitivity by the background of the ionisation chamber. This could never be reduced below 20 cph and was more usually 30-40 cph. The accuracy with which any low α activity could be determined was seriously reduced by this background level. Correspondingly the lowest detectable limit of activity was of the order of 4.10^{-7} g thorium which for meteorite work is rather high. A counting method was sought with as low a natural background as possible. The scintillation counter combines this advantage with great stability. The background is of the order of 1 cph. The lowest detectable limit of activity becomes 1×10^{-7} g Th, which means that meteorites can be tackled more surely and sometimes with less starting material than by the radon-thoron method.

If a radioactive material emitting α particles is placed near a zinc sulphide screen small flashes of light appear as a result of the bombardment. This phenomenon is the basis of the spinthariscope which appeared early in the history of radioactivity.(36)

The scintillation counter to be described uses the same basic principle but instead of visually counting the flashes as was attempted earlier, they are registered by means of electronic equipment. The detection of the flashes is performed by a photomultiplier tube which transmits the pulses produced via an amplifier to a discriminator and scaling unit. (37)

The apparatus necessary is shown in Figure 13. The photomultiplier tube assembly is shown in some detail but the standard pieces of equipment such as the potentiometer are merely indicated. The power supply unit and the potentiometer are type 1007. The scaling unit is type 200, the C.R.O. monitor is type 1000, and the discriminator unit is type 1028. These type numbers refer to M.O.S. instruments.

The potentiometer taps off the potential required (usually - 1450 volts) from the volts supplied and after passing through a smoothing circuit A the H.T. is led to two parts of the phototube, one the light-sensitive photocathode B and the other the dynode pins at the valve base (via C).

Resting underneath the glass face of the phototube is a perspex disc whose underside is coated with a "phosphor" Lumifax 686 Blue. This is a commercial product and is zinc sulphide, activated with silver.

When an α active source is held close to this "phosphor" small flashes of light are produced which are picked up by the photocathode. The ensuing electrons are multiplied at each of the dynodes and the final pulse is passed out to the amplifier which completes the magnification.

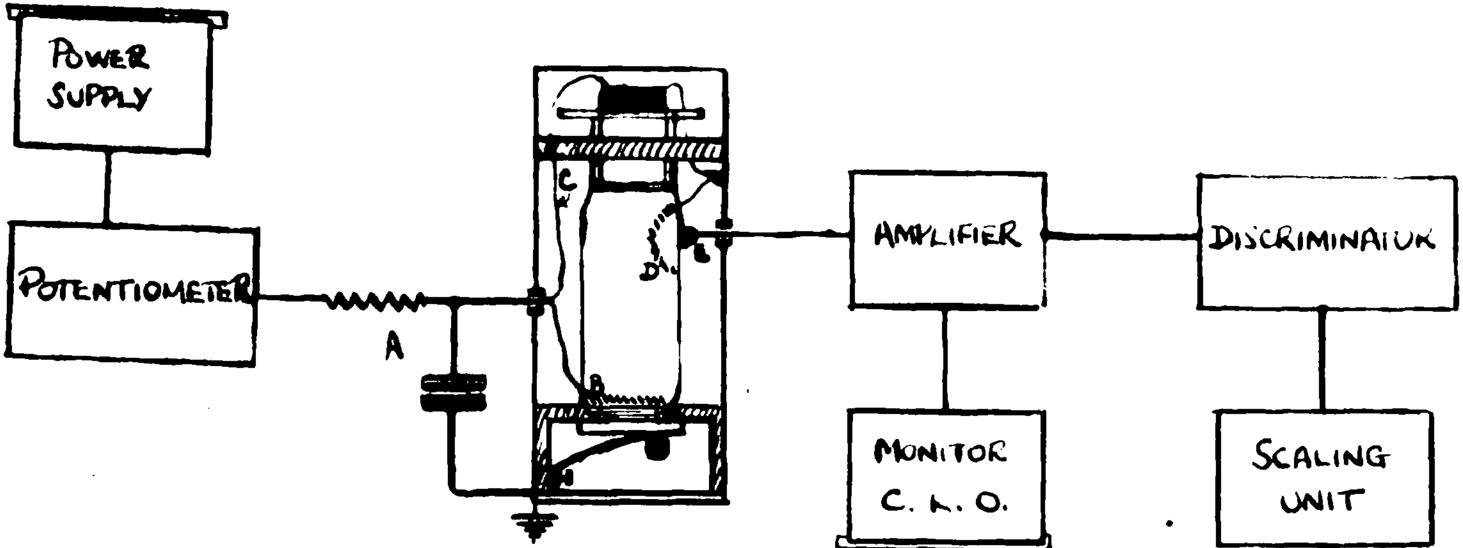

POWER SUPPLY
POTENTIOMETER
A
C
D
E
B
AMPLIFIER
MONITOR C. R. O.
DISCRIMINATOR
SCALING UNIT
PEN RECORDER

FIGURE 13.

The C.R.O. gives a picture of the pulse and its background. The pulse is passed to a discriminator and thence to a scaling unit which incorporates a counting meter. The instrument was designed for low counting rates (< 100 per hour) but the scaling unit is useful for counting efficiency tests etc. A pen recorder is included to check the validity of counts.

The details of the photomultiplier tube assembly are shown in Figure 14. The photomultiplier tube was obtained from E.M.I. Ltd., and was type V 5032 (26 μamps/lumen, 1.3×10^6 gain). Between the photocathode and the collecting electrode there are 11 dynodes. The tube housing is copper sheet screwed and soldered on to a frame of angular brass.

Supports P and M for the tube (J) and the counting tray support F were all made of perspex which has a very low natural activity. After passing through the smoothing circuit A the H.T. is led to the door switch B. In this way the door (I) cannot be opened without the potential being taken off the photocathode. The door and any removable panels are edged with velvet to ensure light tightness and all inside surfaces of the box were painted dull black. Held by H, beneath the photocathode C, is the perspex disc D, whose underside is coated with phosphor. The counting disc support F so fits that the

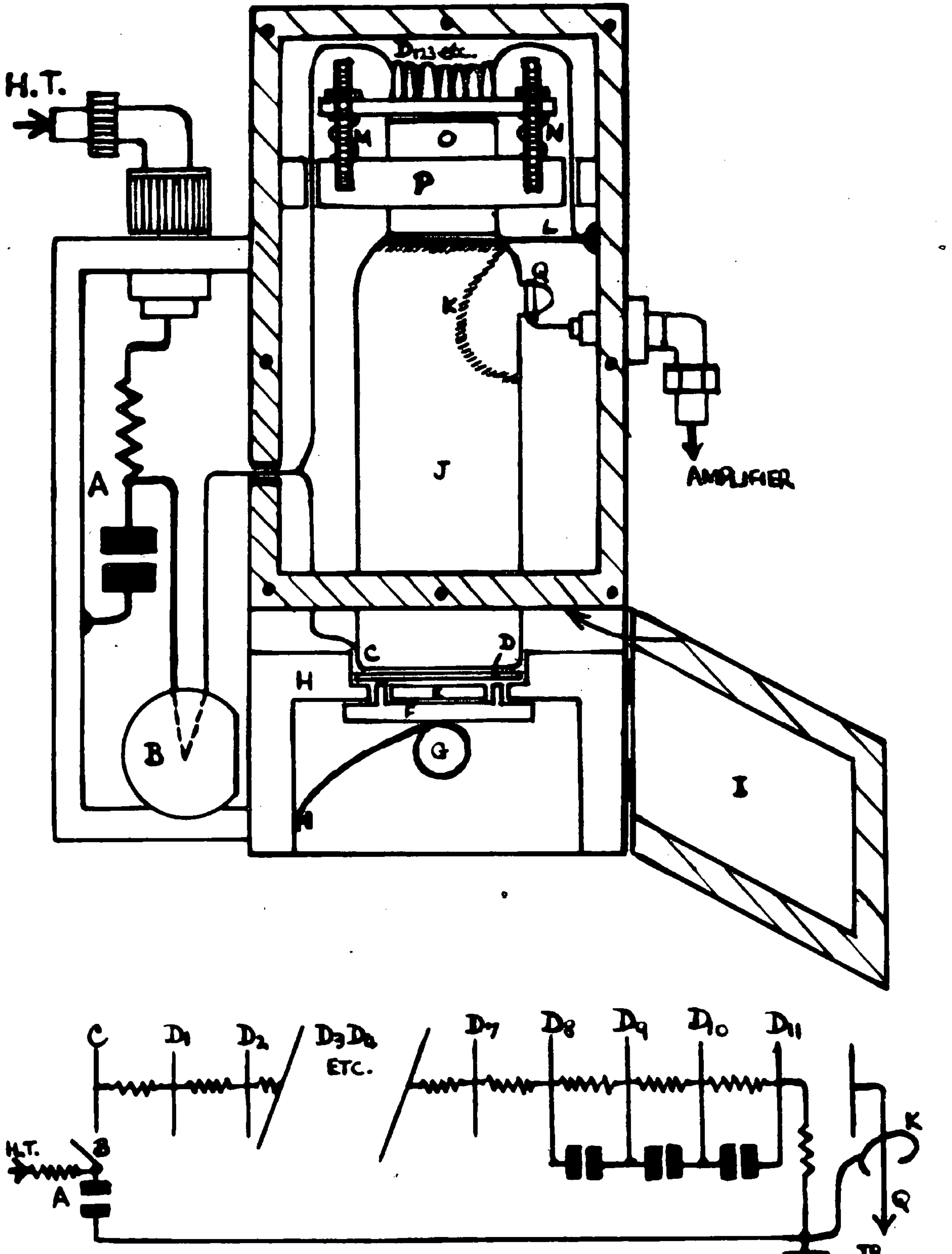

H.T.
D1 2 3 etc.
M
O
N
P
L
Q
K
J
A
B
C
D
H
F
G
I
AMPLIFIER
C
D1
D2
D3 D4
ETC.
D7
D8
D9
D10
D11
H.T.
B
A
K
Q
TO AMPLIFIER

FIGURE 14.

surface of the counting disc E having upon it the α active source, is within a mm. or two of the phosphor. F is held by means of a spring G. The phosphor disc D is prepared in the following way. The perspex disc of 5 cm. diameter is cleaned and several drops of a 5% solution of phosphoric acid in acetone are placed on it. These spread and merge into a film and the phosphor, which is a fine powder, is shaken through a mesh evenly on to the disc, until it is coated. The disc is then inverted and tapped leaving a thin semi-transparent layer of material. If this layer is too thick then it will be opaque to the minute light-flashes, and on the other hand if too thin some α particles will not give rise to flashes. The optimum is approximately 15 mgms/cm^2.

The dynode D pins D1, 2, 3 etc. on the valve base O are connected as shown in the lower circuit diagram. All the resistances shown except that in the smoothing circuit A are 250 K ± 1%. The decoupling condensers are all 200 pf. The collecting electrode Q is connected to the amplifier. The glass envelope J has to be kept clean since it insulates C (at -1500 volts) from Q. A guard ring of graphite (K) and a similar deposit where O joins J are connected to earth. The tube is kept rigid by springs M and N.

The disc E of polystyrene has a diameter of 3cm. The active material, kept at 3 mgm to prevent subsequent internal absorption of α particles, is placed on the disc either as a slurry or solution and dried to an even deposit by an infra-red lamp. As an aid to achieving this, a device described by Wright (38) was employed. In this small jets of air are blown through holes pierced in a brass tube in the form of a ring. The disc is placed inside the ring and the jets of air impinging on the liquid to be dried, cause it to rotate and to leave an even deposit.

An aliquot of a known-strength uranium solution was dried on a platinum foil of 3 cm diameter. The residue was moistened with pyridine, redried and ignited to produce a durable source of practically no weight, hence negligible self-absorption. This source of α particles was used to estimate the efficiency of the instrument, and acted as primary standard. Too frequent use of such a source would risk contaminating the apparatus and so a polonium source was prepared. This was placed on an aluminium tray. The centre of this, where the polonium was located, was covered with mica.

The counting efficiency of a typical phosphor disc of approximately 15 mgms/cm^2 was 35%. This efficiency refers only to the α particles from UI and UII. The efficiency should be higher for the more energetic ThC α particles (6 Mev.). The count of the polonium secondary standard could be noted for a particular phosphor and any deviations from the efficiency could be easily detected.

Counting discs made of platinum which enabled a fast drying rate to be employed had been used but were found to have too high a natural background. Polystyrene discs contributed no count but the source had to be dried more slowly. (Deformation of the source disc through overheating might result in the phosphor being damaged.)

It is worth noting that it is essential for the source tray support (F) and a source tray (E) to be in position when background counts are taken. If not, then a much higher background than usual will be obtained. The α particles formed by the radon in the air enclosed in the base of the instrument will give rise to counts. Expressed as the corresponding amount of radium the average radon content of air is approximately equivalent to 80.10^{-18} gm Ra/cc of air. (39). This can be expressed as $1.07 .10^{-2}$ α's/hr/cc of air.

The base volume of the scintillation counter is approximately 930 ccs, hence approximately 9 α's/hr will result in the total volume. Only some of these will be counted but the relevant considerations are not the geometrical ones (i.e. the dimensions of the box and the range of the α particles). The phosphor surface is charged up to the voltage at which the photocathode operates (-1450 or -1500 volts). Consequently it will pick up some fraction of the active deposit produced in the volume considered. A background was counted over a period of several weeks with E and F removed. As far as the ± 5% to ± 10% error would allow such an inference, the 'background' remained steady at approximately 8 cph. This would seem to suggest that radon was being emanated from the materials (brass, paint, etc.) inside the instrument box.

After a long spell of usage, the instrument, which was frequently tested by means of the polonium substandard was found to have decreased in efficiency. The phosphor was still in perfect condition and it was presumed that the photomultiplier tube was at fault.

The count obtained from a given source is very dependent on the voltage used for the photomultiplier tube. Results are given in the following table for the polonium substandard.

Volts on Tube.	Cpm.	Background cpm.
1400	273 ± 6	-
1450	614 ± 8	0.6 ± 0.16
1500	1171 ± 20	1.4 ± 0.3
1550	1560 ± 22	

Before the falling off of efficiency the Po source with the tube at -1450 volts gave approximately 1070 cpm. To restore the status quo as nearly as possible counts were taken with the tube at -1500 volts. A gain control on the amplifier used after the tube, was a further possibility of restoring the efficiency. The following table shows the c.p.m. given by the Po source at the values of the gain obtainable.

Gain	2	3	4
Cpm.	23 ± 4	614 ± 8	1586 ± 20

A possible cause of the decreased efficiency at a given voltage on the tube was the formation of moisture droplets on the glass face of the envelope enclosing the photocathode. Then light flashes would be diminished by reflection. In an attempt to overcome this possible defect a small vessel of dry silica gel was placed in the base of the instrument box. However, no significant increase in efficiency was noted.

Chapter VI Radiochemical Methods

The scintillation counter needed a method of separation for a member of the thorium series resulting in an α-active source of only a few milligrams weight, containing all of that particular nuclide from fifty or more grams of an iron meteorite. A method for a member of the uranium series (other than uranium itself which would be best analysed by the fluorimeter) resulting in a similar source would be useful as a check on the fluorimeter result. It was along these lines that the radiochemical methods were evolved bearing in mind that the separations would be best performed from the same sample.

However, before designing any extraction procedures, it was thought worthwhile to obtain an analysis of a typical iron meteorite for its trace constituents. Then the methods to be developed could be tested rigorously before being applied to meteorite samples. Savik, an iron meteorite of the Om class, was chosen.

(i) Spectrographic Analysis of Savik

The apparatus used was the same as in the case of Beddgelert (see page 56), but since more time was available a full quantitative analysis was performed. The method employed was to weigh off a sample of Savik as Fe_2O_3 and "dilute" this with a known weight of ammonium sulphate. The total weight of

Savik used for this analysis was less than 2 grams. This mixture was pressed into pellets and burned in the D.C. arc under standard conditions. Then ammonium sulphate acts as a flux and steadies the arc. The light from the arc was focussed on to the slit of the spectrograph and a photographic record of the spectrum was obtained.

Further "dilutions" were effected with a flux consisting of 50% ammonium sulphate/ 50% ferric sulphate so that elements present in large amounts could have their spectral intensities reduced to convenient levels for measurement. Series of pellets of these dilutions were spectrographed. The basis of the method is to use the iron spectrum as an internal standard.(40). One has to obtain an ordinary chemical figure for the iron present in the unknown substance and then the spectrum lines of the element looked for are compared with standard iron lines and density ratios are worked out. On standard plates photographs of known amounts of the given elements are listed together with the percentage with respect to iron. These standard mixtures are spectrographed under the same conditions as the sample. When a given element line density equals a certain iron line density, it is known that the element is present as a certain percentage with respect to iron. Using a Judd-Lewis comparator these densities can be matched visually since the iron spectrum abounds in lines of varying intensity, so that matched lines (or homologous pairs (41) as they are called) for a wide range of element content can be found. This visual method has an error generally thought to be within ± 10% of the figure stated. This estimate of the error has been arrived at after regular comparison of the method with the corresponding chemical method for the elements concerned. Comparison between these line densities can also be made with a microphotometer. The microphotometer method has an error thought to be within ± 5% of the figure stated. (42)

The Savik sample was assessed by the visual method. This method is much quicker than the microphotometric one, and the error involved was low enough to enable a sufficiently accurate survey to be made. The iron figure obtained by chemical analysis was 91%. The spectrographic analysis is shown in the following table, where the figures given are percentages. Copper electrodes were used in the analysis, and so copper could not be estimated on those spectra. However, the sample was spectrographed, using graphite electrodes and the spectra were recorded on a separate photographic plate for qualitative reading only. Copper was detected.

Spectrographic Analysis of Savik

Element	Ni	Co	Si	Cr	Sn	Al	Mg
Percentage	7.5	0.4	0.2	0.15	0.11	0.06	0.04

Element	Zn	Ca	Mn	Be	Sb	Pb
Percentage	0.02	0.015	0.015	0.012	0.012	0.008

The following elements were not detected; the figures given are the upper limits for their presence.

Element	W	Bi	Zr	Cb	As
Percentage	0.12	0.08	0.08	0.08	0.05

Element	Ta	B	Mo	Ag	Sr
Percentage	0.05	0.03	0.018	0.018	0.018

Element	Ti	V	Cd	Rh	Ru
Percentage	0.018	0.018	0.015	0.015	0.015

(ii) Methods already tested

Two ideas for the estimation of thorium by separating ThB which would generate ThC, had been tested (using standard thorium solutions) by previous workers. (E.R. Mercer and R. Aeschbacher).

The first of these methods was to electrolyse the 15% nitric acid solution containing a few milligrams of lead as carrier.

Using a potential difference of 3 volts, a current of 0.5 amp and a Pt anode of 1 cm^2 area the lead was deposited on the anode as PbO_2 together with ThB and ThC.

The following table (due to Aeschbacher) shows the variation in extraction of ThB with the time spent on electrolysis, 2 mgm of lead being used throughout.

Time in hours of electrolysis	ThB found %	Mean %
1	2.5, 2.2, 2.1, 2.3	2.3
2	8.3, 7.9, 8.0, 8.2	8.1
3	12.5, 12.5, 12.5, 12.4	12.5
4	26.8, 26.1, 27.7	26.9
5	41.2, 40.9, 40.8	41.0
6	50.5, 49.7, 50.3, 50.4	50.2

The results on increasing the amount of Pb present for 6-hour electrolyses gave no improvement. In the work for these results sufficient ThB was used to permit its direct assay by Geiger counter. It can be seen that the electrolysis method is not an ideal one since the preparation of the 50% source is lengthy and is fairly complicated. A special anode incorporating a platinum counting disc had to be designed so as to arrange all the deposit on only one side of the disc. This and the obtaining of low-background-count Pt discs proved troublesome.

The second idea already tested was the dithizone method. In this the lead complexed with citrate was extracted from a slightly ammoniacal solution by means of a 0.1% solution of dithizone in chloroform. The combined extracts were evaporated in a Pt dish and the residue decomposed with HNO_3 and finally evaporated on to a counting disc. The following table of results (due to Aeschbacher) shows the effects of increased amount of Pb on the % of ThB obtained.

Mgms Pb used	% ThB found	Mean %
2	78.0, 80.9, 76.8	78.5
3	84.1, 82.7, 85.3	84.0
4	88.1, 91.8, 88.6	89.5
5	85.2, 88.5, 88.7	87.5
6	72.3, 73.4, 79.6	75.1

With both these above methods only standard thorium solutions were tested. The task of working directly with a solution of 50 or more grams of iron meteorite to obtain from it a few milligrams of added Pb seemed likely to be difficult and intermediate stages would then have to be interpolated. Further the problem was to obtain a count relevant only to one of the radioactive series. In the electrolysis method, however, polonium which would interfere with the determination of ThB could be taken out of solution in a preliminary electrolysis.

(iii) Proposed two stage method

Figures 2 and 3 may be of some use to the reader. Work was begun on the idea of a two stage method, i.e. a concentration of the relevant nuclides from the 50 gm. sample scale to the 100 mgm scale followed by a concentration to the 2 mgm scale. If these two stages could be arranged then the main difficulty of using a necessarily small weight of the final precipitate (to avoid self absorption of α particles in the prepared source) would be overcome. It would be difficult to design an efficient method of extraction for a member of a radioactive series from a litre of concentrated ferric chloride solution using only 2 mgms of carrier.

For the two stage method various procedures were tested but for the estimation of the thorium series the second stage (concentration to 2 mgm) was common to them all. This was the extraction of ThB (10.6 h. half life) by precipitating 2 mgm of lead as lead sulphide from the solution. ThB is β active but its daughter ThC (60.5 min. half life) is α active, and so an α-active source dependent on the half life of ThB would be obtained. It became obvious later that ThC, a bismuth isotope, was also quantitatively extracted by means of lead sulphide (see page 110), and so the ThB - ThC α-active source decayed simply with the half life of ThB and no initial growth to equilibrium of ThC' occurred.

Some preliminary tests had been carried out with lead iodide. These showed that from a manipulative point of view a precipitate of 2 mgm of lead iodide could easily be separated and deposited on a counting tray. However, the extraction of thorium B using this precipitate was only 70% efficient using excess iodide ion, and carrying out the precipitation at a low temperature (4°C). It was presumed that the solubility of lead iodide (40 mgm/100 ml at 0°C) was too great.

Lead sulphide is practically insoluble (8.6×10^{-5} gm/100 ml at 18°C) but unlike lead iodide, it can give rise to colloidal types of precipitate which can prove difficult to separate.

Care had to be taken with the acidity of the solution from which precipitation was made, and a fixed centrifuging time had to be followed. If the solution was centrifuged too long (approximately 15 m) the PbS deposit on counting showed an activity which decayed much more slowly than a ThB source, the decay curve showing that ThX and RdTh had been brought. down as well. With 5 minutes centrifuging time only ThB and

ThC were brought down, from a solution of thorium in equilibrium with the rest of the series. Simply precipitating lead sulphide on the 2 mgm scale had advantages over the more complicated electrolysis and dithizone methods. It is simply performed and with due care extraction efficiencies close to 100% are obtained.

The PbS separation is useful, since as well as not interfering with the rest of the series (the members which are important in this context being thorium and radium isotopes) it permits a fair number of carrier-techniques to be considered for the first stage (the concentration of thorium to the 100 mgm scale). Further, since the PbS technique interrupts the series at a member with a half life of 10.6 hours, it permits the repeated extraction of this member (ThB) from the parent matrix, where after a few days the ThB will have grown to equilibrium again. Hence from a given sample many estimations of the amount of thorium series present should be possible. The limitation imposed by the PbS technique is that the PbS precipitate would carry down any radium active deposit members present in solution notably RaF (polonium, α active, half life 140 days). The count obtained would no longer be relevant to the thorium series alone. In effect, this means that Ra must be absent from the solution to be extracted with PbS. This led to the idea of separating thorium from the meteorite solution by a suitable procedure on the 100 mgm scale which would leave behind radium isotopes. The members of the thorium series separated would be thorium itself and RdTh, with ThX left behind. The member of the uranium series relevant to the problem, which would be separated, would be ionium (thorium isotope), and radium would be left behind. ThX would grow to equilibrium with the separated radiothorium with a half-period of growth of 3.64 days. On the other hand, radium would grow to equilibrium with the separated ionium with a half-period of growth of 1590 years and so would not interfere. The members between ThX and ThB are short lived enough to follow the growth of ThX very closely and we can consider RdTh, ThX and ThB as being three generations. Using the Bateman solution for three generations of a radioactive family it is found that the grand-daughter (ThB) lags behind the daughter (ThX) in growth by approximately 1 mean life of the grand-daughter (ThB), i.e. 15.3 hours. If a period of growth of several weeks is allowed then both ThX and ThB activities will be approaching equilibrium, and the known large fraction of the equilibrium amount of ThB can be separated using PbS, and a count obtained. The following figures show the growth of ThX and ThB expressed as percentages of the equilibrium amount.

Days	3.64	7.28	10.92
ThX	50%	75%	87.5%
ThB	43.4%	72%	87.5%

Thus after 11 days the lag of 15.3 hours makes no sensible difference, and the fraction of the equilibrium amount of ThB present can be taken to be the same as that of ThX. The method appeared feasible provided the above mentioned radium-free thorium separation could be performed, and it was shown later that this could be effected. Another reason for establishing a radium-thorium separation was the possibility of developing a separation of radium from the meteorite solution followed by its estimation.

However, it is interesting to note the procedure which could be used if radium was present in the RdTh/ThX solution. The solution could be rid of the Ra active deposit members by a preliminary PbS precipitate which could be discarded. The ThB and ThC would be extracted by this procedure but would grow to equilibrium again in a few days and the long lived members of the radium active deposit would no longer interfere. Of the rest, RaB (27 m, giving rise to RaC) would grow to equilibrium and be extracted by the PbS precipitate to be counted. If the source could be counted 1 - 1½ hours after precipitation then RaB - RaC would no longer interfere and a count purely relevant to the thorium series would be obtained.

It was now necessary to test the efficiency of extraction of ThB by the PbS technique. At first the scintillation counter was used with low activities of ThB and encouraging results were obtained which are described below. Highly active RdTh solutions (from which ThB could be separated) were used later in a separate laboratory and more precise information was obtained (see page 103).

The theoretically expected count from a microgram of Th is approximately 15 α's/hr. With a phosphor of efficiency 35% the best practical count obtainable would be 5.25 α's/hr. The time for source preparation was usually 40 minutes during which 4.3% of the ThB decays. Calibration results obtained are given below with the duration of the count. Known thorium solutions had 2 mgm Pb added to them and were saturated with H_2S for several minutes. The PbS was separated, dissolved and transferred to a counting disc. The results obtained were:-

	Cph. per 10^{-6} gm Th.		
4 hour calibrations	4.4 ± 0.3	4.4 ± 0.3	4.8 ± 0.3
16 hour calibrations	2.8 ± 0.1	2.8 ± 0.1	3.1 ± 0.1

The mean of the 4 hour calibrations is 4.53 ± 0.2 cph/μg. Th. The error in accepting this count as the one representative of the end of the first 2 hours of the count, is negligible. Hence this count is 87.8% of the count obtaining at the beginning of the count and 84% of the count obtaining at precipitation. We thus obtain a corrected calibration of 5.4 ± 0.35. This agrees with the expected calibration assuming the counting efficiency.

Two opposing factors operate here. One is the difference in energy between the α particles of the uranium standard source (4.21 and 4.75 MeV.) and the α particles from ThC (6.0 MeV). This factor makes the theoretically expected count (5.25) a minimum. The other factor is the shape of the source on the counting disc. The standard source, weighing less than a tenth of a milligram, is practically all concentrated in the centre of the disc. The technique employing 2 mgm of Pb as PbS carrier results in a thin disc of material spread out to within 3 or 4 mm. of the edge of the 3 cm. diameter counting disc. (This is to avoid losses due to self-absorption of particles). Hence one would expect the uranium standard in this respect to be more efficiently counted, making the theoretically expected count a maximum.

This means of estimating the efficiency of the ThB-C source can, therefore, be considered accurate enough since the counting error is ± 6.5%.

It seemed from the above data that the second stage of a method for thorium could be established. A complementary first stage was needed. This would have to concentrate thorium free of radium from the meteorite solution to the 100 mgm scale.

It had already been shown that iron could be held up in alkaline solution while extraction precipitations were carried out, if salicylate ion was present in sufficient quantity. (See page 12).

If 100 mgms. of cerium hydroxide were precipitated in such a medium, thorium isotopes would be carried down (see page 68) and radium isotopes would be expected to be mainly left behind in solution. ThX would grow in the precipitate, and ThB and ThC could be extracted later, by means of a precipitate of PbS and the ThC α's counted. Whether or not $Ce(OH)_4$ precipitated at lab. temperature carried down radium isotopes was tested, and the precipitate was found to contain 4% of the radium originally present in solution. By repeating this precipitation the radium carried down could be reduced to negligible proportions.

It seemed from the above data that a complementary first stage of a method for thorium could be established. However, it was probable that any uranium present would also be carried down on the precipitate of $Ce(OH)_4$. In order to allow for a separation of uranium to take place another first stage for thorium was tested. This was to use a precipitate of cerium or zirconium iodate to carry down any thorium from a 2N HNO_3 solution of a meteorite. It was most probable that neither radium nor uranium would be carried down under these conditions, and further techniques for their separation could be applied to the mother liquor. A precipitate of zirconium iodate dissolved easily in HCl and after boiling, the solution was stable when 0.29N with respect to HCl and 2 mgms of PbS could be precipitated from it. This appeared promising for the thorium procedure. Tests were then made in an attempt to establish a two m stage separation of uranium. As with thorium a concentration to the 100 mgm scale was envisaged followed by a final concentration to the 2 mgm scale for scintillation counting or fluorimetric analysis which proved more sensitive. Uranyl oxalate is slightly soluble (80 mgm/100 ml at 14°C) but it might be expected that with excess oxalate ion present a precipitate of lanthanum oxalate might carry down any uranium present. However, under these conditions lanthanum oxalate carried down $< 1\%$ of the uranium present in a solution. Uranyl ferrocyanide is insoluble in neutral solutions but is soluble in dilute acids, whereas molybdenum ferrocyanide is insoluble in both. To a solution containing uranyl nitrate and ammonium molybdate a solution of potassium ferrocyanide was added. The precipitate of molybdenum ferrocyanide was separated and extracted with dilute nitric acid and a counting source prepared from this extract. However, only 2% of the uranium initially present was recovered. Noyes and Bray (43) point out that uranyl ferrocyanide at low concentrations tends to form a coloration rather than a deposit. Here it seems that the molybdenum carrier precipitate does not overcome this tendency.

Precipitates of aluminium hydroxide proved disappointing as carriers for uranium until carbonate-free ammonia, prepared by distillation over KOH, was used. Then recoveries of 100% were obtained. A proved method for the separation of uranium is to ether-extract the solution to which nitric acid and ammonium nitrate have been added. Hence for uranium also a two stage separation was feasible, since $Al(OH)_3$ precipitation could be used for the first stage and ether-extraction for the second.

Detailed tests of the conditions for the zirconium iodate precipitation were made. The elements present for the iodate separation would be mainly iron and nickel in a solution 2N with HNO_3. Barium would be present as a holdback carrier for radium and zirconium as the carrier for thorium. It was shown that at 2N HNO_3 no metal present in a typical meteorite gave an iodate precipitate, nor did barium. It was also shown that zirconium came down completely, provided that the solution was 0.15N with KIO_3. Arranging these conditions and using a solution with similar concentrations to those expected in a meteorite solution with added barium and zirconium no precipitate could be obtained. Taking the components one by one, it was shown that without iron present (or with its concentration greatly reduced) the zirconium iodate precipitation proceeded in the normal way.

To make the method work most of the iron which seems to form a complex with iodate ion, would have to be removed in a preliminary step. A proved method for this task is to ether extract a 6.5 N HCl solution of iron when it passes as $HFeCl_4$ into the ether layer. (44 page 212). Three such extractions would reduce the iron to negligible proportions.

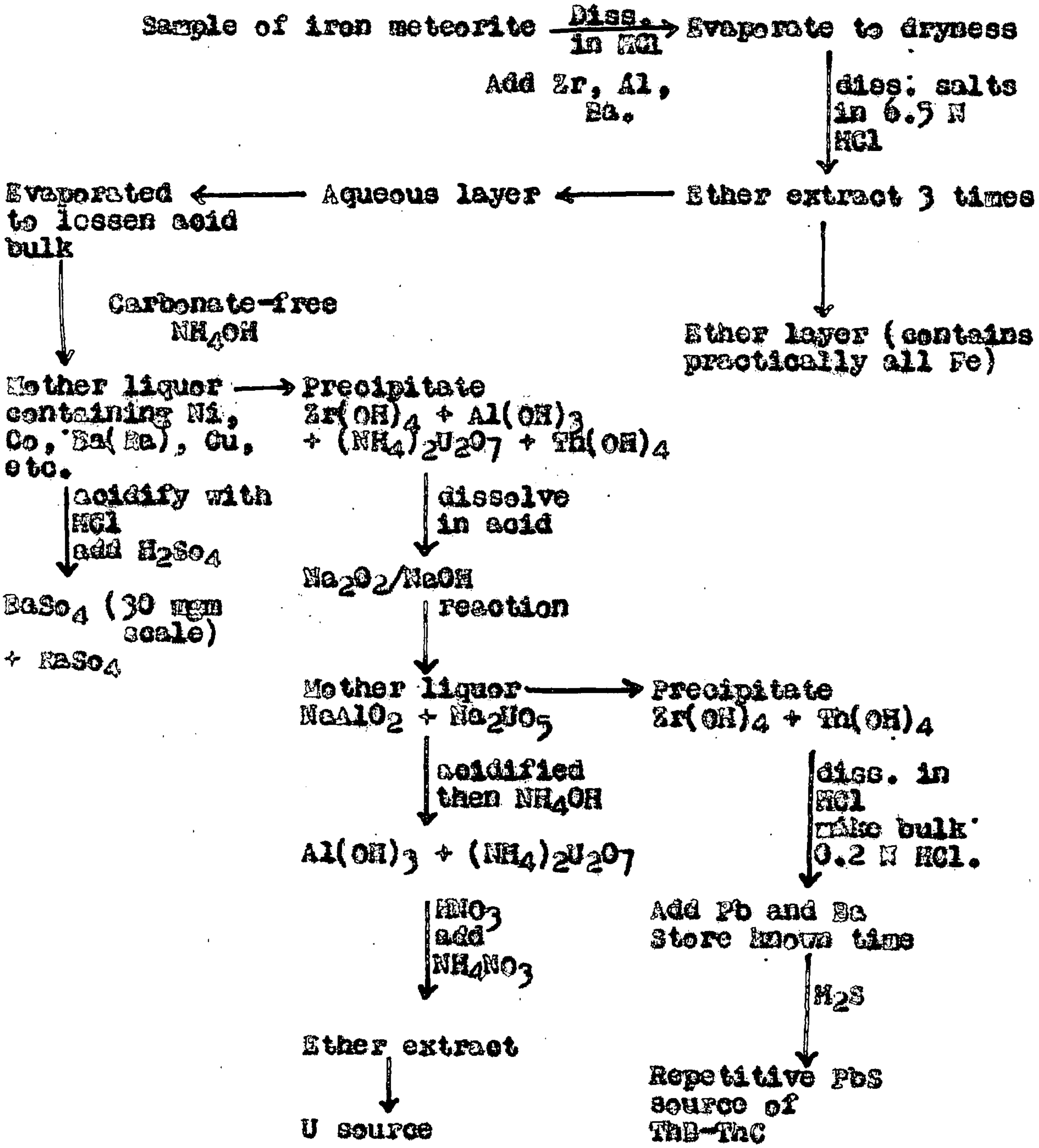
Having made this step further ideas were possible. If zirconium and aluminium were added to the aqueous layer of such an extraction and carbonate free ammonia added, any thorium and uranium would be expected to follow the combined precipitate. Thus in two fairly simple stages the uranium and thorium from a meteorite solution could be concentrated on a 100 mgm or less of mixed hydroxides. It would seem that radium would be left behind in solution. These hydroxides and their carried radioactivities could then be separated by the classical group procedure using Na_2O_2 and NaOH as reagents.

The zirconium precipitate plus thorium could be dissolved, stored and later extracted with PbS to provide a ThB-C source. The sodium aluminate mother liquor could be acidified and aluminium plus uranium precipitated by carbonate free ammonia prior to ether-nitric extraction.

There are obvious advantages to a method involving group procedures. These procedures have been proved reliable and there is much less risk than with the iodate method for example, of interference from the many elements, present in trace quantity in iron meteorites. (See page 87). It had been hoped when those ideas were arrived at, to include a separation of radium in a form suitable for the scintillation counter. The mother liquor from the first hydroxide-precipitation would probably contain most of the radium and a second precipitation would ensure complete removal. However, more than a few mgms of barium proved to be necessary as holdback carrier in such precipitations (see page 116). Moreover, there was the fundamental difficulty of preparing a non-emanating source of low self-absorption. These qualities appear incompatible, since large crystals are necessary for non-emanating properties (21). A further idea was to extract the polonium (RaF) in equilibrium with the series by means of PbS but the adequate covering of such a source to prevent it contaminating the instrument, again posed a self-absorption problem. The straightforward $BaSO_4$ extraction (30 mgm scale) or a modification of it (see Chapter IV) is feasible, of course, if an ionisation-chamber radon estimation can be considered.

The scheme which was chosen to investigate in detail is given below in the form of a flowsheet.

Scheme of Analysis



(iv) Detailed testing of the selected procedures.

The testing of the above procedures would have proved long and perhaps indecisive if it had been carried out on the scintillation counter. Using strong sources on this instrument would have run the risk of seriously contaminating the photomultiplier tube and its accessories. Yet without large counting rates much time would have had to be spent to achieve decisive results. Moreover, the testing methods using strongly active materials would jeopardise later work in the laboratory which would have to be used for the manipulation of meteorite extractions containing very small traces of the radio elements sought. It was, therefore, decided to use a completely separate laboratory for high activity testing work. Careful precautions were taken to ensure that no contaminating activity reached the low activity laboratory.

The main development work envisaged was the testing of the outlined procedures at each step to find the directions taken by thorium, uranium and radium during such an analysis.

Thorium Investigations.

Uranium X_1 was used as a tracer for thorium since as well as being a thorium isotope and hence chemically identical, it has a convenient half life (24.5 days). The β radiation of UX_1 is very weak, i.e. 0.2 Mev but its daughter UX_2 (half life

1.14 minutes) has β radiation of 2.3 Mev. After 10 to 15 minutes it can be assumed that the UX_2 is in equilibrium with its parent. In any extraction test the UX_2 was in equilibrium before the finish of the source preparation. A preliminary investigation was carried out to ascertain whether the end-window of the Geiger counter used would allow the weak radiation of UX_1 to penetrate and register counts. If this happened then the counts obtained on a given run might depend too critically on source thickness and so introduce anomalies. To find out if this was so an absorption curve was plotted using a UX_1 source and aluminium absorbers of known thicknesses. The curve so obtained showed that there was no large decrease of count for a small increase of thickness at the beginning of the curve.

Another advantage of using UX_1 is the ease of its preparation. It was prepared from uranyl nitrate hexahydrate in the following way (45). Some of this salt was dissolved in water and acid ferric chloride solution was added. The pH of the solution was adjusted to approximately 3 with ammonium hydroxide solution when the iron was precipitated as ferric hydroxide. This precipitate, containing most of the thorium present as $Th(OH)_4$ and some of the uranium was digested with ammonium carbonate which removed all the uranium as the complex carbonate but did not affect the thorium (UX_1). If, however, the basic carbonate of iron had been brought down with ammonium carbonate in the first place, then thorium carbonate would have been complexed and held up in solution, and the resulting $Fe(OH)_3$-UX_1 extract would have had only weak activity.

Thorium hydroxide on the other hand does not form a complex on being digested with ammonium carbonate. The ferric hydroxide was centrifuged off, and dissolved in HCl.

(a) Source preparation

Sources were prepared from a standard UX_1 solution by drying aliquots on small nickel trays suitable for support in the Geiger assembly. Using a grade A pipette 0.5 ml. portions of the UX_1 solution were transferred to trays and evaporated to dryness under an infra-red heater. The counts obtained were:-

(a) 663 ± 9 cpm. (b) 654 ± 8 cpm. Mean 659 ± 6 cpm.

(b) Zirconium as a carrier for thorium

Aliquots of the UX_1 solution were added to solutions of dil. HCl containing 2 mgm. of Zr as $ZrCl_4$. The Zr was precipitated as $Zr(OH)_4$ by the addition of NH_4OH solution. The precipitate was centrifuged off, washed, and transferred to a counting tray. It was found best not to dry the gel-like $Zr(OH)_4$ so far that a light powder was obtained. Counting trays treated in this way gave varied results. If the drying was stopped when the residue was still gel-like, concordant results were obtained. Any radiation stopped within the solid was negligible since only 2 mgms. were employed covering a tray approximately 3 cm^2 in area. The following results were obtained:-

(a) 677 ± 9 cpm. (b) 638 ± 8 cpm.

Mean: 658 ± 6 cpm. corresponding to 100 ± 1%

From these results the conclusion was drawn that within experimental error zirconium carries out thorium completely from a solution when it is precipitated by ammonium hydroxide in the presence of ammonium chloride. Having proved this point $Zr(OH)_4$ could be used in this manner to extract the available thorium from a given medium under test.

(c) Testing the effect of ether/6.5 N HCl extractions on thorium

Aliquots of the UX_1 solution were dried and the residues dissolved in 6.5N HCl. These solutions were shaken with equal volumes of ether which had been previously equilibrated with 6.5 N HCl. The aqueous layers were evaporated to small bulk to remove most of the HCl. (2 mgm of Zr as $ZrCl_4$ were added to each solution). After dilution the resulting solutions were rendered alkaline with NH_4OH solution and the solutions centrifuged.

The $Zr(OH)_4$ precipitates were transferred to trays, dried and counted, giving the following results:-

(a) 97 ± 2% (b) 103 ± 2% Mean 100 ± 2%

Therefore, on shaking a solution which is 6.5 M with respect to HCl, with previously equilibrated ether any thorium present remains practically completely in the aqueous phase.

(d) Testing of the NaOH/Na_2O_2 treatment on thorium

Standard volumes of the UX_1 solution were added to solutions containing 2 mgm of Zr and were treated with 10% NaOH solution followed by 200-300 mgm of Na_2O_2. The solutions were warmed till all effervescence ceased and then centrifuged. The $Zr(OH)_4$ precipitates were washed, transferred to trays, dried and counted in the normal way and gave the following recoveries:-

(a) 95 ± 1% (b) 100 ± 1% Mean 97.5 ± 1%

Therefore, a precipitation of $Zr(OH)_4$ carries out practically all the thorium from a solution when it is precipitated by 10% NaOH in the presence of sodium peroxide.

(e) Testing of separation of ThB from its parents by PbS precipitation

Sections (a) and (d) show that any thorium and consequently any radiothorium present will follow Zr through the analysis. The radiothorium would then decay (half-life 1.9 y.) giving rise to its daughter, thorium X (half-life 3.64 d.). The thorium X decays in its turn to produce thoron, thorium A, and thorium B. The work described in this section was carried out to test the extraction of ThB on PbS from such a matrix.

A strong radiothorium solution of unknown strength was available. Obviously a PbS extraction of the unknown RdTh solution could not be used to find this strength for further tests using PbS. The method of drying an aliquot of the RdTh solution and counting the ThB betas was discarded because the dried source might emanate and possibly contaminate the Geiger and its accessories. (This would not have been a serious objection except that other experimenters were using the Geiger equipment. Any Th active deposit would decay quite quickly into inactive ThD.). The method chosen for standardisation was to count the ThC γ radiation. A small fixed wire frame was assembled alongside the Geiger counter which was arranged vertically, its end window facing down to the tray support. A loop in the wire frame was arranged to hold small uniform glass tubes. The wire frame kept the tubes close enough to the counter to pass an appreciable fraction of the γ rays through it. Tests were made with aliquots of the radiothorium solution in the small corked tubes and with the tube mounted in the wire chassis provided for it the following counts were registered. (1 ml of RdTh solution in each)

Tube 1	782 ± 12 cpm.	Tube 3	774 ± 12 cpm.
Tube 2	776 ± 4 cpm.	Tube 4	770 ± 12 cpm.

<u>Mean 776 ± 10 cpm.</u> (corresponding to 100%).

The method appears to be reproducible both with respect to tube dimensions (a series of ignition tubes were used) and with respect to position in the wire frame.

A solution was then made up containing 1 ml of RdTh solution, 1 mgm $BaCl_2$ and 2 mgm Pb as acetate. The solution was approximately 0.2 N acid. Hydrogen sulphide gas was bubbled through the solution for three minutes, and the solution was then centrifuged. The residue after washing was dissolved in a small amount of nitric acid and transferred to an ignition tube and made up to a standard level. Carried through in duplicate this test gave the following results:-

(a) 724 ± 12 (b) 738 ± 12

Mean: 731 ± 12 (corresponding to 96 ± 2%).

As a check on this method of extraction of ThB, counts were determined for these tubes at regular intervals. The decay curve is shown in figure 15, and shows that with only Ba present as a hold-back for ThX the PbS brings down RdTh. The curve first shows a decay approximately that of ThB until after a certain time when the radiothorium brought down has produced sufficient ThX and eventually ThB. However, if ThX had been brought down then the initial approximately 11 hour half-life decay would not have occurred.

A similar aliquot of RdTh solution was similarly extracted but with Zr present as a holdback for radiothorium. The PbS precipitate was washed once and the γ radiation counted as described. The counting was repeated at regular intervals and a decay curve plotted. Here it was evident (see figure 15) that practically all the RdTh and ThX were being held up in solution.

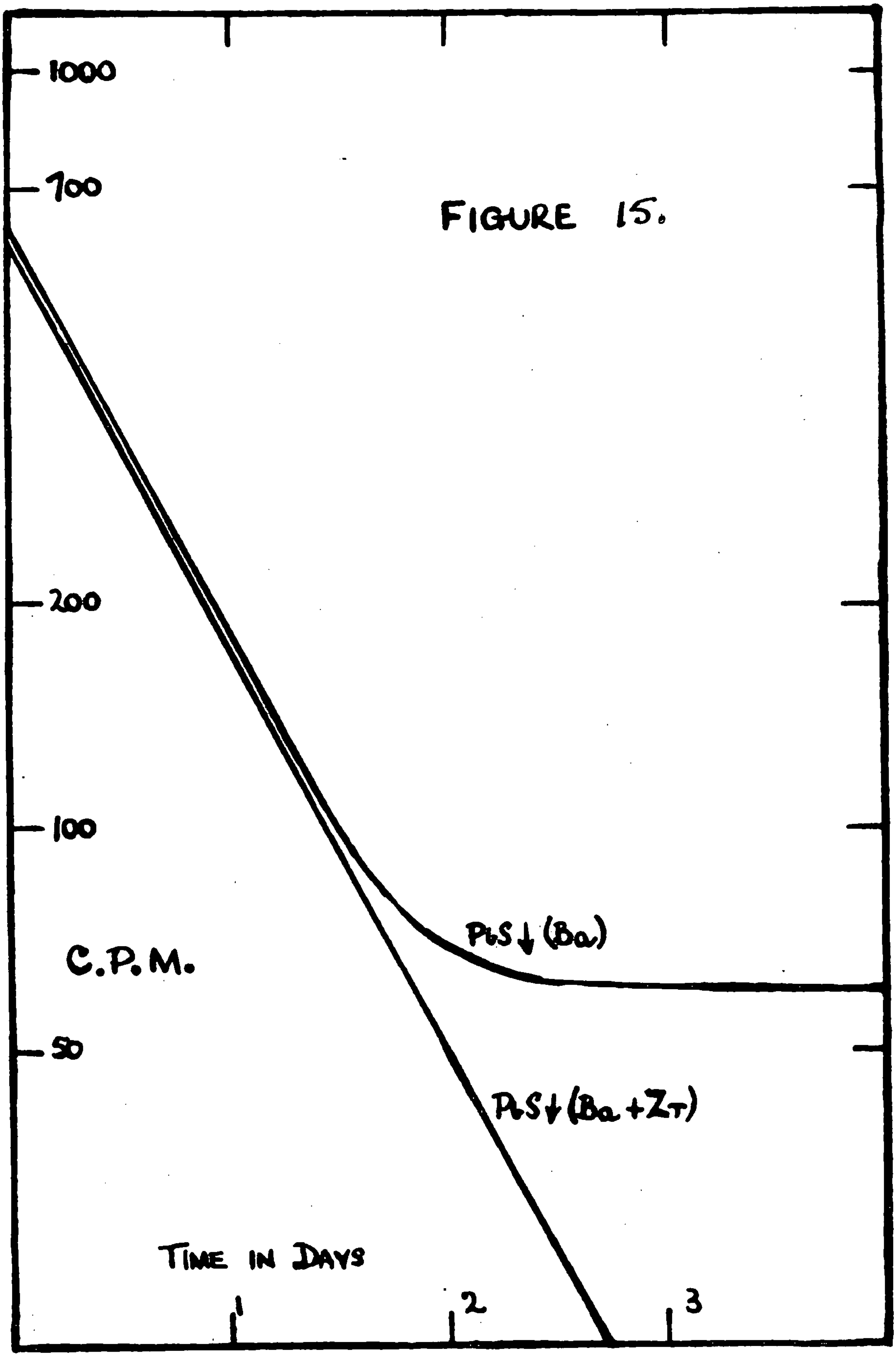


FIGURE 15.

Counting tests carried out at the beginning of the ThB decay did not show any increase in count with time. This would have occurred if ThC (bismuth isotope) had not been co-precipitated. Since I was counting the γ radiation of ThC (half life 60.5 m) there would have been a growth period in the count until ThC had grown to equilibrium with ThB. It is evident from the curves that, as is to be expected, ThC comes out of solution with ThB on PbS. Then the decay of the shorter lived daughter ThC closely follows that of its parent.

A sequence of ThB extractions on PbS was envisaged, and the corresponding curve shows that very little parent activity is lost in the PbS by this treatment. A second precipitation to make sure of this would make the source preparation time longer and hence the fraction of ThB decayed greater, without sensibly increasing the efficiency of further extractions.

However, difficulties were met in the establishing of a sequence of ThB extractions on PbS. Since ThB has a half-life of 10.6 hours, then 3 days after a PbS extraction a further similar extraction will be possible because an amount of ThB will have grown corresponding to 6.8 half-lives (72/10.6). This amount will be > 99% of the equilibrium amount. Provided no loss of the parent activity has occurred it is possible to perform a series of such extractions, but the results obtained were inconsistent. Preliminary runs had given 96 ± 2%, 92 ± 1%, 92 ± 1%, as recoveries on 3 separate tests. The slight discrepancies obtained must have arisen because no special care had been taken with the concentration of free acid except to ensure that it was approximately at 0.2 - 0.4 N HCl.

Controlling the acid normality precisely to 0.25N, close to 100% extractions were achieved. It was thought opportune here to investigate the dependence of the efficiency of PbS extraction on free acid concentration. Results were obtained and a curve plotted for acid normality values varying between 0 and 0.8. A standardised procedure was adopted. The length of time H_2S was passed through the solution (4 minutes), and the time of centrifuging (4 minutes) etc., were fixed. Also fixed were the concentrations of Zr and Ba.

At 0.025 and 0.05 N HCl the PbS was precipitated in a form which could not be centrifuged down in 4 minutes. At 0.8 N HCl no PbS was visible after 4 minutes of bubbling H_2S. The curve obtained is shown in figure 16. It is evident that the acid normality has to be carefully controlled at 0.2 N to obtain the best results. The dependence of the % extraction on the time of centrifuging is illustrated by comparing the dotted curve (centrifuged 2 minutes) with the main one (centrifuged 4 minutes) Too long a centrifuging time had been found to introduce errors when no 'holdback' carriers (Ba + Zr) were present, because radioelements appeared in the centrifuged residue which did not

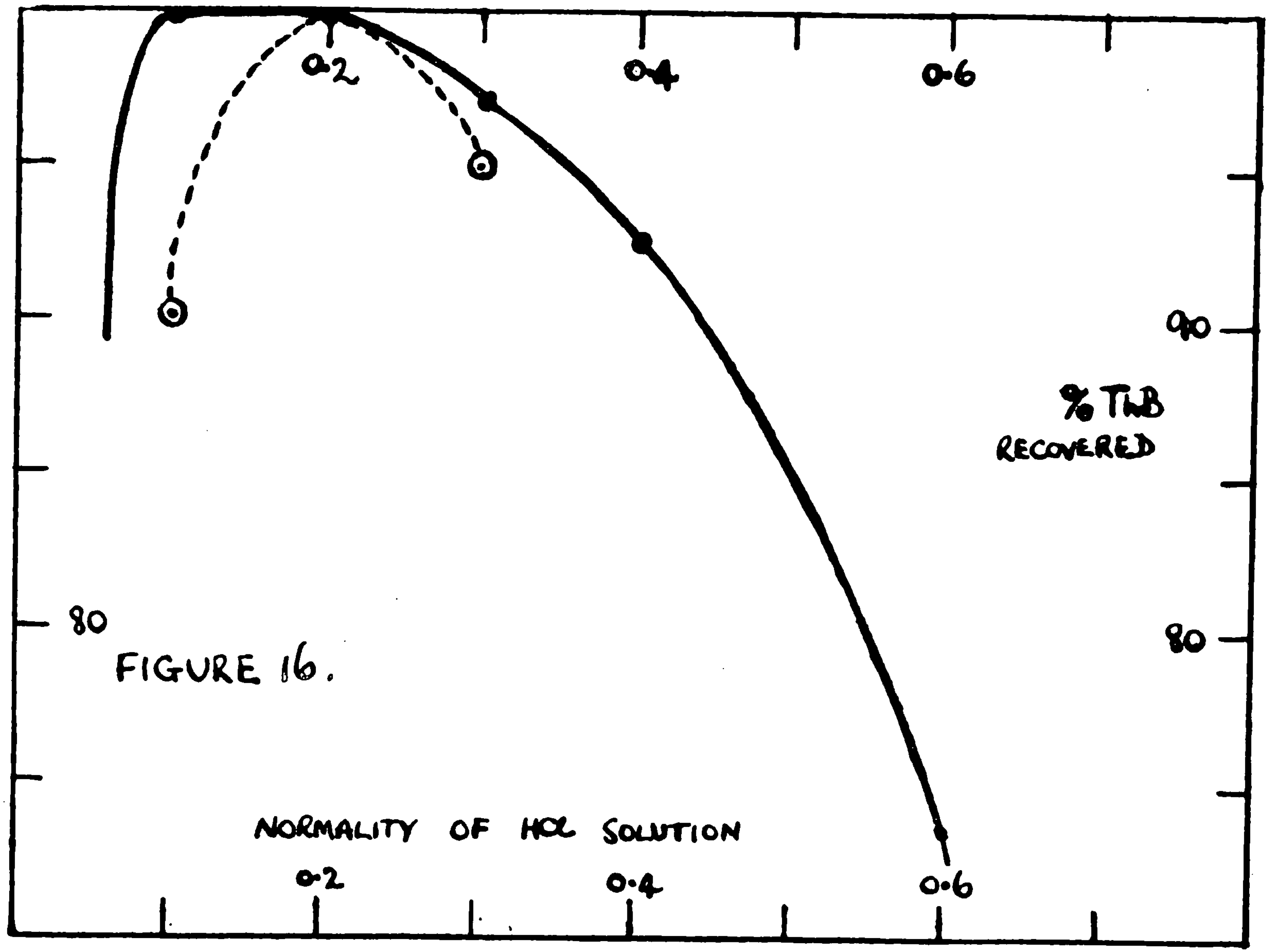

0·2
0·4
0·6
90
% ThB
RECOVERED
80
80
NORMALITY OF HCl SOLUTION
0·2
0·4
0·6

FIGURE 16.

normally do so.

All ThB extractions were corrected for the time elapsed between precipitation of the PbS and the beginning of the count. After this investigation the acid normality was carefully controlled at 0.2N. Sequence tests were performed without waiting the necessary number of three day intervals. A PbS extraction was performed and counted and after adjusting the acid normality after adding a washing etc., a further PbS extraction was carried out but this time not counted. However, this second extraction would cause its due share of interference with later extractions although not counted, and so the next extraction could be duly labelled the third. This was done for the third and fourth extractions but the fifth was allowed to grow a known time and after extraction it was counted. The following figures were obtained:

<u>5th extraction:</u> (a) 98 ± 1% (b) 99 ± 1%

The sixth was likewise allowed to grow and gave the following results:

<u>6th extraction:</u> (a) 99 ± 1% (b) 101 ± 1.5%

When the above solutions were stored so that the ThB could be regenerated from ThX it was found unnecessary to take any precautions against thoron escaping. Completely efficient growths of ThB were achieved in solutions held in open test tubes. This confirms the findings on page 23.

The thorium side of the proposed scheme of analysis had now been checked and proved to be practicable and six or more thorium results (sufficient for assessment of statistical errors) could be obtained from a given sample of meteorite.

Uranium investigations

For the measurement of the concentration of uranium in a given medium the fluorimeter (35) was used since it is much more sensitive and convenient than a counting method.

(a) Testing the effect of ether/6.5 N HCl extractions on uranium

This was carried out as described for thorium except that 5.10^{-5} g. U was employed, and that the ether layer, being the layer probably deficient in uranium, was tested. A series of sodium fluoride beads were prepared, their fluorescence measured and from two runs the ether layer was found to contain:

(a) 0.15 ± 0.01% of the available uranium
(b) 0.08 ± 0.01% " " " "

Hence any uranium present practically completely stays in the aqueous phase during this extraction.

(b) Zirconium hydroxide as a carrier for uranium

A solution containing $1.25 . 10^{-5}$ g. U, and 2 mgm. of Zr was treated with ammonium chloride followed by ammonium hydroxide. Having used a large amount of uranium it was again easy to obtain useful information from the uranium deficient phase. The mother liquor of the precipitation was analysed and was found to contain 0.1 ± 0.02% of the available uranium. Hence any uranium present is to be found practically completely in the precipitate.

(c) Testing of the $NaOH/Na_2O_2$ treatment on uranium.

This was performed as in the UX_1 tests described except that 1.25 10^{-5} g. U was used. The $Zr(OH)_4$ precipitate was analysed and was found to contain $<0.05\%$ of the available uranium. Hence any uranium present is held in the mother liquor.

(d) Testing of ether /HNO_3 extraction of uranium

1.25 10^{-5} g. U was added to a volume of conc. HNO_3 saturated with ammonium nitrate. An equal volume of ether was added and the mixture vigorously shaken. This was repeated twice more, and the aqueous layer analysed. It contained 0.3% of the available uranium. Hence uranium is completely extracted by this procedure into the ether layer.

Having completed these tests the proposed scheme is seen to separate conveniently uranium and thorium from the meteorite matrix and from each other. The problem left outstanding was to determine the path followed by radium during the analytical procedure.

Radium investigations

ThX was used as an indicator for radium. A strong source of RdTh in equilibrium with its daughters was available. Some of this solution had $Zr(OH)_4$ precipitated through it twice and then the RdTh solution had $BaCO_3$ precipitated from it. This was dissolved in HCl and made up to a known volume from which aliquots could be taken. After a test, a precipitate or solution was allowed to stand 3 days when the equilibrium amount of ThB had grown. Counts given by a precipitate etc. were compared with a similar aliquot which had decayed the same length of time. A source tray having been prepared, the β's of ThB were counted by the Geiger equipment. It had already been found unnecessary to take precautions against the escape of thoron during the growth of ThB from ThX.

(a) Testing the effect of ether/6.5N HCl extractions on radium

A known aliquot of ThX - $BaCl_2$ solution was added to a volume of 6.5 N HCl and the resulting solution extracted with ether. The ether phase was evaporated after water had been added and the aqueous solution obtained was stored for 3 days until ThB had grown to equilibrium with any ThX present. Then counts were compared with those from aliquots of the original ThX solution. It is to be noted that the 3 day growth period also allows any extraneous ThB, which may have passed into the ether, time to decay. Two runs were performed:

(a) 0.91 ± 0.1% and (b) 0.94 ± 0.1%

of the available ThX being found in the ether phase. Hence radium is left behind almost completely in the aqueous phase.

(b) Testing the effect of the $Zr(OH)_4$ precipitation on radium

Here aliquots of the ThX solution were extracted by a

$Zr(OH)_4$ precipitation brought down by NH_4Cl and NH_4OH reagents in the presence of Ba as a holdback carrier. In the case of a meteorite solution it had been hoped to keep back the radium from 30-40 mgm Zr as $Zr(OH)_4$ with 2 mgm Ba for a possible non-emanating α source for the scintillation counter. However, it was obvious that the successful preparation of a non-emanating lightweight source would take a fairly long time to develop and it is obvious from the results that follow that much more Ba is needed to hold back the radium, repeated precipitations being necessary in the presence of Ba.

The results are given in the following tables. Table 1 gives details of a series of $Zr(OH)_4$ precipitations carried out in the presence of varying amounts of Ba. The precipitate was brought down by NH_4Cl + NH_4OH reagents, at lab. temperature.

TABLE 1

Ratio Zr : Ba	Washings of Ppt.	% ThX carried out of solution by $Zr(OH)_4$
7 : 1	1	32 ± 2
1 : 1	1	28 ± 1.3
1 : 2	1	18 ± 1.3
1 : 5	1	16.7 ± 1.3

In Table 2 the details of a further series of precipitations of $Zr(OH)_4$ are shown. Here the ratio Zr : Ba is fixed at unity with the temperature and number of precipitations and washes varied.

Table 2

Number of Precipitations	Washings of Ppt.	% ThX carried out of solution by $Zr(OH)_4$	Temperature
1	3	16.0 ± 1.2	Lab. temp.
2	2	7.8 ± 1.2	" "
3	1	4.1 ± 0.1	" "
1	3	9.8 ± 0.3	100° C.
2	2	3.9 ± 0.3	100° C.
3	1	1.9 ± 0.2	100° C.

It was to be expected that the next step in the analytical procedure, the precipitation of $Zr(OH)_4$ by $NaOH/Na_2O_2$ reagents would show a behaviour similar to that of radium, if Ba was present. The following brief test confirmed this.

To a solution containing equal weights of Zr and Ba, NaOH and Na_2O_2 were added at laboratory temperature. The radium brought down by the zirconium precipitate was 27 ± 1.3% of that available. In one duplicated run the precipitate of zirconium was mistakenly left in contact with the mother liquor. Here (a) 68 ± 1% (b) 65 ± 1% of the ThX available was found on the $Zr(OH)_4$ precipitates. This seems to confirm that the carrying of the radium is a surface phenomenon.

From the results obtained it can be seen that two NH_4Cl - NH_4OH precipitations of $Zr(OH)_4$ followed by two NaOH - Na_2O_2 precipitations of zirconium will denude the Zr of any adsorbed radium if (i) the precipitations are carried out in boiling solutions and the precipitates well washed (ii) Ba is present preferably in excess of the Zr.

These conditions are easily arranged in the procedure. More than 90% of the radium will be contained in the mother liquor from the NH_4Cl - NH_4OH precipitations and only a little will pass into the NaOH - Na_2O_2 reaction mother liquors. These are analysed for uranium after an ether/HNO_3 extraction and so the radium cannot interfere.

It is possible to extract a nitric acid solution of a meteorite for uranium directly, but this interferes with any proposed thorium separation. Over 30% of any thorium present is extracted into the ether layer from an 8N HNO_3 solution (44). It was likely that this figure would be different under the conditions maintained for maximum uranium extraction, i.e. the solution saturated with NH_4NO_3. A test using UX_1 showed that 11.2 ± 2.0% of the UX_1 passed into the ether layer during such an extraction. Since three such extractions are needed to extrac all the uranium a substantial fraction of any thorium present would be lost. It is therefore better to follow out the suggested scheme where both the uranium and thorium from a given sample can be estimated.

The detailed testing of the procedures has not altered the basis of the scheme given on page 102. However, the carbonate-free NH_3 and NaOH - Na_2O_2 precipitations have to be performed twice to ensure complete holdback of radium.

Chapter VII Meteorite residues from the radon-thoron method

Many meteorite solutions were available which had been extracted with a precipitate of $BaSO_4$ for the radon-thoron method already described. Dependent upon what effect this precipitate had had on any thorium and uranium present it was thought possible to obtain more data from these solutions. It was already known (3) that $BaSO_4$ brought down approximately 50% of any thorium present. This was checked using UX_1 and concentrations and conditions closely resembling a typical $BaSO_4$ extraction of a meteorite solution. The figure obtained was 47.5 ± 0.5% for the amount of UX_1 carried down, which agrees with the results published by Berry (46) if the concentrations of Ba (0.08 mgm/ml) and H_2SO_4 (0.5%) obtaining in meteorite runs are considered. However, it was probable that a precipitate of $BaSO_4$ under these conditions would not affect the uranium present (9).

Since the meteorite solutions considered already have uranium figures obtained by the radon method it was thought interesting to try out the new procedures on them, when any practical difficulties might be expected to show up.

Firstly, the thorium position with regard to $BaSO_4$ was investigated. As already stated, 48% of any thorium is brought down on the $BaSO_4$ precipitate. This precipitate was fused with fusion mixture twice and the corresponding amount of $BaCl_2$ (which was also still available) stored in solution in a bubbler. If the thorium carried down remained with barium during these fusions etc. then a residue thorium determination was still possible. This possibility was investigated by precipitating $BaSO_4$ in a solution containing UX_1. The precipitate was fused with more than 10 times its weight of fusion mixture and after cooling this was leached and centrifuged. The $BaCO_3$ precipitate was then transferred to a tray and counted. The $BaCO_3$ was shown to contain (a) 35.8 ± 0.2% and (b) 34.5 ± 0.6% of the amount of UX_1 brought down by the $BaSO_4$, i.e. 65% of the UX_1 brought down had been leached off in the concentrated alkali carbonate solution, leaving 17% of the original UX_1 with the $BaCO_3$.

After a second carbonate fusion and leaching only 6% of the original UX_1 would be held on the $BaCO_3$ precipitate and hence only this percentage passes into the bubbler. It is clear, since the carbonate solution leachings were not stored, that no more thorium analyses can be obtained using these meteorite residues.

Secondly, the effect of a precipitation of $BaSO_4$ on a uranium solution was investigated. Three such $BaSO_4$ precipitates were found to contain (a) 0.22% (b) 0.23% (c) 0.23% of the uranium available, showing that uranium determinations on meteorite solution residues were possible.

A procedure was easily adapted from the tested procedure given in the previous section. This was to evaporate an aliquot of the meteorite solution to dryness, and to dissolve the residue in 6.5 N HCl. This solution could be shaken with an equal volume of ether which had previously been equilibrated with 6.5 N HCl. After repeating this extraction twice more practically all the iron would have been removed. Aluminium (20 mgm scale) could be added to the aqueous layer which, after suitable reduction in its acidity by boiling, could be rendered alkaline with carbonate-free ammonia. The precipitate of $Al(OH)_3$ after separation could be dissolved in concentrated HNO_3, the solution saturated with ammonium nitrate, and the uranium present extracted into ether. After evaporation of the ether a small aqueous extract would be obtained from which a sequence of sodium fluoride beads could be made, of which uranium content could be assayed by the fluorimeter.

This procedure had to be tested using known amounts of uranium. Some difficulties arose. The meteorite solution residues proved to contain mainly ferrous iron. This was overcome by introducing a preliminary step where chlorine gas was bubbled through the solution. Being all in the ferric state the iron was then removed quantitatively by ether but not otherwise.

The carbonate-free ammonia step was performed by passing NH_3 gas from a vessel containing ammonia liquor containing KOH.

The 'blank' contribution of this NH_3 was very small and 100% recoveries of uranium were obtained using it. An interesting result was obtained during an investigation into some low recovery test runs. After the ether-nitric-NH_4NO_3 extraction the ether layers containing uranium are combined, water is added and the ether evaporated. The aqueous solution left then has to be evaporated to small bulk (< 10 mls) so that fractions of it (1 ml or less) can be incorporated in 1 gm NaF beads prepared in 1 ml capacity Pt vessels. If this aqueous solution is taken down too far and dried, only 10% of the uranium present in the solution evaporated is recoverable, e.g. by boiling the beaker with concentrated HNO_3 etc. So long as the evaporated solution is not taken to dryness then the uranium is fully recoverable.

When the aqueous layer, after ether-HCl extraction of iron was boiled to decrease the bulk of acid a precipitate of silica was formed. Performing test runs, it was found that this carried down < 0.2% of the uranium available.

Finally, a duplicated test of the whole procedure gave the following recovery figures:

(a) 98.2 ± 2.5%   (b) 99.4 ± 1.6%

Pressure of other work confined residue determinations to two meteorites, Savik and Ahnighito. Runs were carried out on the residues from Savik 144 gm and 201 gm samples using the procedures described above, and employing the fluorimeter to to measure the quantities of uranium separated. The following results were obtained when the contributions from 'blank' runs had been subtracted.

144 gm. sample   0.25 ± 0.02 10^{-8} gm U/gm Savik
201 " "   0.23 ± 0.04   " " "

These agree with those obtained both by the radon method (see page 51) and directly by the fluorimeter (0.21 ± 0.05 by J.C. Dalton).

The uranium analysis of Ahnighito had not given such concordant results. The first analyses of this meteorite by both the radon method and the fluorimetric method were rather high giving

75 gm sample   3.3 ± 0.3 10^{-8} gm U/gm Ahnighito
and   2.4 ± 0.3   " " " " , respectively

However, further meteorite radon runs of this period were contaminated (see page 53) and this made the first figure suspect. Moreover, the fluorimetric run was later found to have been carried out in contaminating conditions. Fresh samples were analysed by both methods, and gave the following results:-

Radon run   111 gm sample   0.21 ± 0.08 10^{-8} gm U/gm Ahnighito
Fluorimetric run   0.56 ± 0.05   " " " "

No more of this meteorite was available and so determinations carried out on residue solutions were specially useful.

These determinations were carried out and gave the following results.

Ahnighito 111 gm sample

(a)	1.1 ± 0.2	10^{-8} gm U/gm	Ahnighito
(b)	1.9 ± 0.14	"	"
(c)	2.3 ± 0.14	"	"
Mean	1.8 ± 0.10		

Ahnighito 75 gm sample

(a)	0.63 ± 0.08	10^{-8} gm U/gm	Ahnighito
(b)	0.61 ± 0.06	"	"

From all the figures available it seems that

(i) the uranium content of Ahnighito is probably 0.60 ± 0.06. This agrees with the reliable fluorimetric run (0.56 ± 0.05).

(ii) the 111 gm sample was contaminated with uranium but not with radium.

(iii) the 75 gm sample was contaminated with radium but not with uranium.

Chapter VIII Investigation of the Caustic Soda-peroxide procedure

Detailed testing of individual procedures had already been performed and it remained to check the whole scheme for the recovery of uranium and thorium. To ensure thorough testing, meteorite solutions with added uranium and thorium were used. The uranium was finally estimated by the fluorimeter. Normally, after precipitation of $Zr(OH)_4$ and its dissolving for storage, a period of several weeks would have to be waited while ThX and its daughters grew sufficiently to make analysis by PbS and ThB-C counting worthwhile. To avoid this delay an aliquot of the freshly precipitated $Zr(OH)_4$ was prepared as a source and the α particles due to Th and RdTh counted. The risk here was that emanation from the source would contaminate the phosphor. With short tests using such sources no increase in background was found. If the phosphor had been contaminated with thoron active deposit this would be practically completely decayed in a few days. Using this counting method it was shown that the silica precipitate which comes down on boiling the aqueous layer after ether-HCl iron extraction, contains $< 1.8\%$ of the thorium available. This counting method could, of course, be used instead of obtaining a repetitive ThB-ThC source by modifying the procedure, but the variables in source-preparation would be averaged out in the repetitive method.

On performing complete tests of the scheme, recovery efficiencies for uranium of only (50 - 75)% were obtained while the thorium recoveries were practically 100%. The weak link in the method was found to be the NaOH-Na_2O_2 reaction which is the reaction effecting the separation of uranium and thorium. The conditions imposed were the same as those which had given complete separation in the early tests (see page 107). Excess 10% NaOH had been added followed by 2-300 mgms Na_2O_2. The mixture had been warmed only long enough to reduce the effervescense to a level allowing successful centrifuging of the precipitate.

Tests were then made using the technique recommended by Vogel (47). The zirconium hydroxide precipitate was dissolved in the minimum quantity of conc. HCl and the solution was poured into an equal volume of '20 volume' H_2O_2 rendered strongly alkaline with 10% NaOH solution. The mixture was boiled for 5 minutes, and precipitate centrifuged. Using UX_1 for thorium the following recovery percentages were found from such precipitates:

(a) 98.5 ± 1%   (b) 101.0 ± 0.8%

The uranium in such precipitates was found to be

(a) 8.0%   (b) 7.5% of the uranium available.

Since 2 precipitations were needed to clear the precipitate of carried radium this procedure was acceptable. Also H_2O_2 was an improvement on Na_2O_2 from the point of view of lowering the contribution due to reagents. Noyes and Bray (43 page 413) point out that boiling the peroxy-uranate solution with a hydroxide precipitate tends to destroy the peroxy-uranate complex. Hence the increase in the amount of uranium carried down in the '5 minute boiling' technique might be expected.

Since variations had been found with this key reaction, it was decided to investigate it thoroughly. The ether-nitric-NH_4NO_3 extraction which extracts the uranium in a suitable form after this reaction takes a fairly long time to perform. Accordingly, for the series of tests envisaged a quicker termination to the preparation for the fluorimeter was sought. The sodium aluminate mother liquors were acidified, boiled and the 10 mgms. of aluminium precipitated by means of carbonate-free NH_3 gas. This precipitate was dissolved and reprecipitated and redissolved to free the solution of sodium nitrate etc. Aliquots containing 1 mgm Al could then be dried on the Pt. trays used to prepare the NaF beads for the fluorimeter. When the beads were prepared it was shown that Al at this level did not interfere with the fluorescence due to the uranium content of the bead. This cut out the ether-nitric extraction altogether for many of the tests. Only when a trace of iron was present in the final aluminium solution and discoloured the NaF beads was the ether extraction method brought into use.

In all the tests to be described an alkaline peroxide reagent was used. This reagent was a mixture of equal volumes of '20 volume' H_2O_2 and 20% NaOH solution. Into 40 mls of this mixture was poured 10 mls of HCl solution containing 7 mgm zirconium, 10 mgm aluminium, and known amounts of uranium and thorium. The resulting mixture was boiled for 5 minutes and the precipitate centrifuged off. The alkaline mother liquor was acidified and boiled and rendered alkaline with NH_3 gas. The aluminium after a further precipitation was incorporated into NaF beads, and their uranium content assayed by the fluorimeter. Consistent recoveries of approximately 10% of the available uranium were obtained. Further similar tests were performed except that the reaction was carried out in the cold, and the mixture allowed to stand overnight until the precipitate could be centrifuged. Here again consistently low extraction efficiencies of approximately 10% of the available uranium were obtained.

Since it seemed that much testing would be needed a 'master solution' containing all the required elements was prepared. Aliquots of this could then be added to varying amounts of the alkaline peroxide reagent. A 100 ml solution was prepared containing 764 μg Th, 63 μg U, a 10 gm meteorite solution with most of the iron removed by ether extraction 250 mgm Zr, and 250 mgm Al.

It was found that whether or not the reaction was carried out in the cold, or just at the boil, or boiled for 5 minutes the recovery efficiency was 10-20% for the ratio of master solution : alkaline peroxide reagent of 1 : 4. When this ratio was changed to 1 : 6 recovery efficiencies of 70-80% were achieved. Yet when simplified tests were performed using this ratio of 1/6 but with only Zr, Al, U, and Th present (i.e. not using the master solution) low efficiencies were obtained. Thus for the 5 minute boil technique the efficiencies were approximately 30%. Increasing the volume of alkaline peroxide to make the ratio 1 : 10 made no difference to these results.

Fresh tests were begun using a solution containing a few grams of dissolved meteorite to which was added U + Th and Zr and Al. The full procedure was tested as outlined. On boiling the aqueous layers from the ether-HCl extractions, silica precipitates came down. These were analysed for uranium and thorium and gave the following figures:

U	(a) < 0.1%	Th	(a) 1.0%
	(b) < 0.1%		(b) 0.5%

When the alkaline peroxide reaction was reached the 5 minute boil technique was followed, with the ratio of acid solution to alkaline peroxide reagent of 1 : 6. The alkali mother liquors were analysed as before and gave

(a) 85 ± 2% (b) 86 ± 3%

recoveries of the uranium available.

On reverting to simpler tests with no meteorite solution present, poor recoveries were again obtained (approximately 30%). A series of these simple tests was performed with iron added. Thus an acid solution containing U and Th, 7 mgm Zra 10 mgm Al, and 4.5 mgm Fe as $FeCl_3$, was added to six times its volume of alkaline peroxide reagent. The technique of boiling for 5 minutes was used and the recoveries were 91 ± 8%, 88 ± 7%, and 83 ± 5%. In all previous tests where approximately 80% or more recovery of uranium had been achieved it was noted that iron had always been present. In the earlier testing of the procedure (see page 104) UX_1 was used and the UX_1 had been prepared on iron as a carrier. Whenever simplified tests were performed which contained no iron very low efficiencies resulted. On the other hand, working through the whole scheme of analysis but using meteorite solutions and hence with some iron passing through, much higher efficiencies were obtained. However, the data obtained using the master solution which contained iron show low efficiency if the ratio of acid solution to alkaline peroxide reagent is greater than 1:6. Observing this latter condition a duplicated test was performed with iron absent, zirconium present, and the 5 min. boiling technique. Recoveries of

(a) 26 ± 6% (b) 32 ± 7%

were found. This test was repeated except that iron was substituted for zirconium. The recoveries were

(a) 81 ± 5% and (b) 70%

Two variables (i) concentration of alkaline peroxide reagent, and (ii) presence of Fe, having been found it seemed from the figures that something else was still wrong. The last step before the fluorimetric determination was tested. This is the sweeping out of the uranium from approximately 200 mls of acidified mother liquor and washings by 10 mgm Al as $Al(OH)_3$. It was found to be only 70-80% efficient. This cleared up the problem since with increased amounts of Al carrier or by reverting to ether-extraction of the mother liquor acidified with nitric acid full recoveries were obtained.

Complete tests were carried out using (i) iron as the thorium carrier instead of zirconium, (ii) acid to alkaline peroxide reagent ratio of 1:6, and (iii) the mother liquor acidified with nitric acid and ether extracted.

The thorium recoveries as always in the tests were near 100%.

(a) 96 ± 2% (b) 98 ± 3%

The uranium recoveries were

(a) 96 ± 3% (b) 100 ± 3%

If the necessary conditions outlined above are imposed the reaction is capable of complete separation and recovery of uranium and thorium.

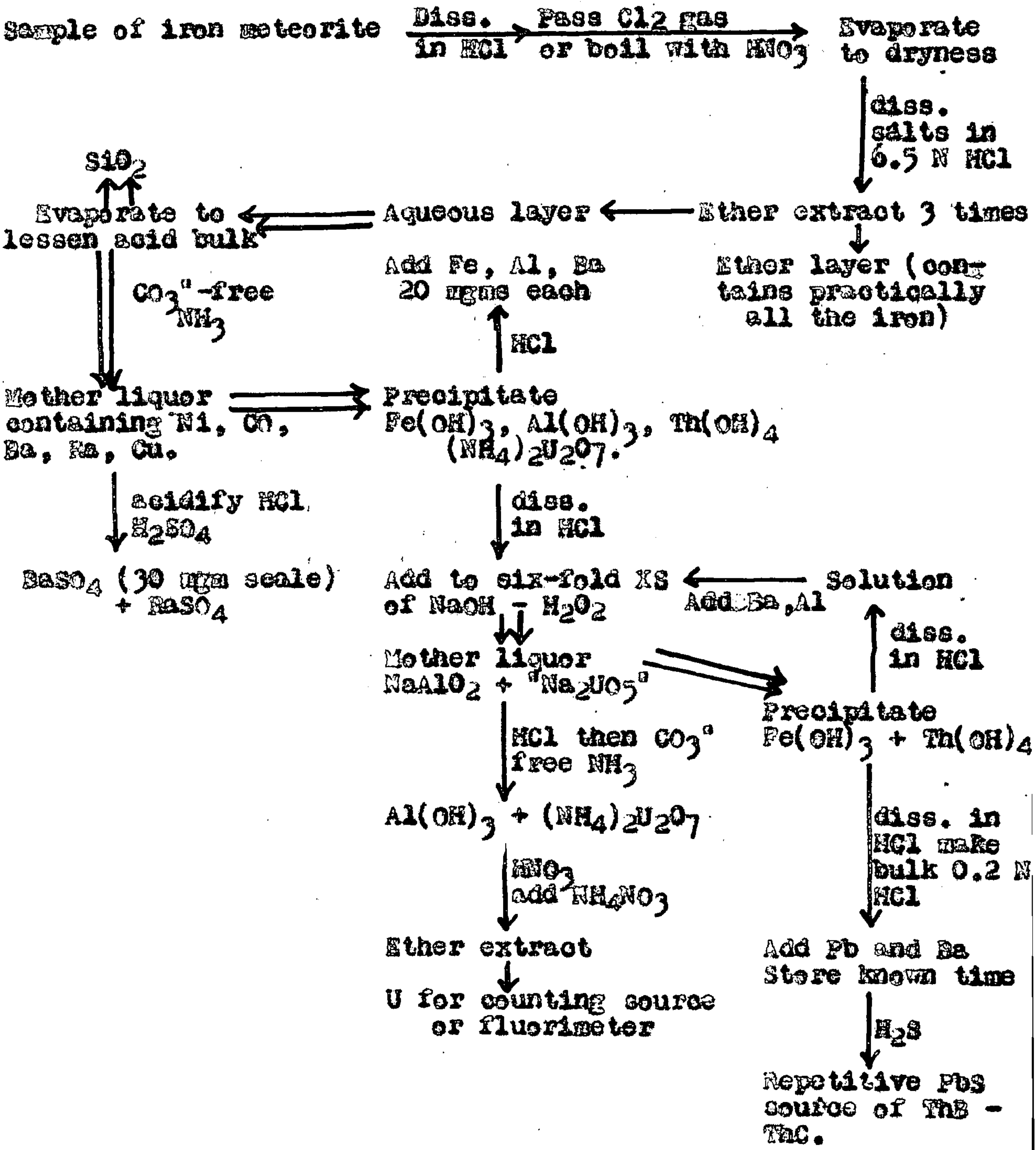
No difference was found between the 5 minute boil technique which gave the above figures, the technique where the mixture was just brought to the boil, and the carrying-out of the reaction in the cold, but one of the hot techniques is better since enough H_2O_2 is decomposed to allow successful centrifuging of the precipitate. Earlier (see page 128) a loss of uranium to the precipitate was plausible from the fact that a peroxy-uranate solution had been boiled with a hydroxide precipitate. Since both iron and zirconium were present then it is probably more complex than this. The above data show that with zirconium alone the loss of uranium to the precipitate is considerable, whereas with iron alone that loss is negligible. It was also demonstrated that with iron alone no loss of uranium to the precipitate could be found by using a technique involving boiling the solution. When zirconium alone is used it is found that after a few minutes heating the first formed precipitate of zirconium hydroxide seems to disappear completely. (It is difficult to be sure of this, since the liquid seethes with bubbles of oxygen gas provided by the decomposing H_2O_2). However, the solution which is almost clear, clouds and a whitish granular precipitate is thrown out. This is believed to be a peroxide of zirconium but its constitution does not seem to be known.

When iron alone is used no such changes occur and the red-brown particulate precipitate remains the same throughout. It seems likely that these facts are linked up with the properties of both elements with respect to the peroxy-uranate complex.

It might be expected that the precipitate which dissolves and precipitates again as a "peroxide" (zirconium) would interfere with the sodium peroxy-uranate solution, whereas the straightforward hydroxide precipitate (iron), apart from prolonged boiling, would not so interfere.

However, complete checking had been performed and there was no doubt that the scheme, after suitable modification, worked. Since the drawing-up of the scheme on page 102, several modifications had been introduced.

Modified Scheme



It can be seen that the modifications are (i) introduction of an oxidation stage for ferrous iron present, (ii) the deposition of SiO_2 which has been proved not to interfere, (iii) repeated precipitations by carbonate-free NH_3 and by $NaOH-H_2O_2$ to ensure that no radium reaches the thorium extract. These are shown by double arrows. (iv) iron used instead of zirconium as carrier for thorium. It is easier to extract for complete removal of iron by ether and then to add a known (20 mgm) amount than to arrange to leave behind such an amount for use as carrier.

Note on the failure to replace the ether-nitric extraction in the uranium procedure.

The inconvenience of the ether-nitric technique is that evaporation of the ether layers containing nitric acid often results in a violent reaction taking place. Consequently either material is lost or much time has to be spent in supervising the evaporation of ether and final boiling down of the resulting aqueous solution. Alternative procedures were tested. The direct use of the $Al(OH)_3$ precipitate which carries the uranium, to make NaF beads is described above. However, in the work described in the above section not enough $Al(OH)_3$ was used. When the amount of carrier was increased the procedure was successful for tests.

However, when dealing with meteorite solutions using this procedure it is very difficult to obtain a precipitate of $Al(OH)_3$ completely free of elements which interfere with the fluorescence of the NaF/U bead. A further idea was tested. This was to extract the $Al(OH)_3$ precipitate carrying the uranium with concentrated ammonium carbonate solution when it might be expected that uranium would pass into solution as the complex carbonate $(NH_4)_4\left[UO_2(CO_3)_3\right]$. This was found to be so if 4 N ammonium carbonate was used to extract 20 mgm of $Al(OH)_3$. Only 0.2 ± 0.1% of the available uranium stayed behind on the $Al(OH)_3$ precipitate. Approximately 1/3 of the Al was also found in the ammonium carbonate solution. This was not critical since Al can be incorporated into NaF beads on this scale without interfering, but coloured ions (Mn^{++}, Co^{++}, etc.) were also passing into the ammonium carbonate liquor. The NaF beads from such an extract were coloured and any U-NaF fluorescence was inhibited. The ether/nitric extraction is a proved barrier to such interferences and the method had to be resumed.

Chapter IX Reagent Purification

As already explained, the sensitivity of a method and the accuracy with which a given result can be stated depend on the contribution from the reagents. Accordingly the reagents were purified of uranium and thorium where necessary. Purification generally proved possible. The exception was conc. HCl which could not be purified. The uranium content is reasonably low but the thorium content cannot be regarded as satisfactory. It would not be expected that ether, or ether equilibrated with conc. HCl, would contribute any measurable amount of uranium or thorium to a run. This was found to be the case when blank runs were performed with or without this step.

It was intended to use lanthanum in the purification of some reagents so this had to be purified first. A solution of lanthanum nitrate was ether extracted 10 times and the tenth extract left a solution which contained 1.10^{-10} gm U per 10 mgms La. Zirconium solutions were purified and although not finally used the data on them is included. Purification methods specific to each reagent were used but before these are described, two general methods and their results are given, (a) the $BaSO_4$ method and (b) the $BaCO_3$ method.

(a) The $BaSO_4$ Method

The first of these was the shaking of reagents with $BaSO_4$.

This has already been described for the purification of reagents from radium isotopes (page 45). While the method cannot be expected to extract any uranium from a solution it might be expected to extract some thorium. (see page 120). Tests of the method were performed on H_2O, conc. HCl, $Zr(NO_3)_4$ solution, $Al(NO_3)_3$ solution, and $Ba(NO_3)_2$ solution. To 10 mls of each of these a known amount of UX_1 solution was added, and 2 gms of $BaSO_4$. These samples were shaken by the shaking machine for known times and ½ ml. aliquots of the mother liquors (after settling) were dried and β-counted. In all the solutions tested, 54 hours of shaking reduced the concentration of UX_1 by $<$ 10%. A further 64 hours shaking made no further difference.

(b) The $BaCO_3$ Method

In Mme. Joliot-Curie's textbook (45 page 62) it is stated that if solid $BaCO_3$ is mixed with a thorium solution where all the series is at equilibrium, all the members are carried down except $MsTh_2$. The value of this for the purification of reagents was tested. Again UX_1 was used as an indicator for thorium. $BaCO_3$ was prepared and washed with approximately 100 litres of distilled H_2O. This was to ensure that any effects noted would be due simply to $BaCO_3$ and not to adsorbed Ba^{++} or carbonate ions. Salt solutions were adjusted to "just acid" conditions with HCl. Forty mls of each of foll: were taken:- H_2O, Zr reagent, Al reagent, and Ba reagent. A known amount of UX_1 solution was added to each. A slurry of ½ gm of $BaCO_3$ was then added to each, and the vessels corked. The vessels were then upturned to mix the $BaCO_3$ with the solutions and then set down to allow the $BaCO_3$ to settle. The settling took place within several minutes and aliquots of the mother liquers were taken.

The results are set out below.

Solution	Cpm/½ ml before $BaCO_3$ Shaking	Cpm/½ ml after $BaCO_3$ Shaking	% UX_1 left*)	% (Fe free) UX_1 left
H_2O No $BaCO_3$	380 ± 8	389 ± 10	100 ± 2	-
H_2O + $BaCO_3$	333 ± 6	18 ± 1	0.9 ± 0.3	-
Al + $BaCO_3$	443 ± 7	18 ± 1	0.9 ± 0.3	< 1.0
Ba + $BaCO_3$	403 ± 7	14 ± 1	< 0.3	< 1.0
Zr + $BaCO_3$	370 ± 7	16 ± 1	< 1.0	< 1.0

Geiger background = 14.7 ± 0.1 cpm.

*) In all solutions except Zr the iron added with the UX_1 solution came down with the $BaCO_3$ rendering it buff coloured.

With the Zr test as an indication that the reduction in UX_1 was not due to precipitated iron, data were obtained using a UX_1 solution of which carrier iron had been removed by ether-HCl extraction.

It is obvious that the $BaCO_3$ method which is simple and quickly performed can be very useful. However, limitations showed up in the tests for the above table. The $BaCO_3$ addition was found to have precipitated all the Al present in that solution. The zirconium solution was still as before but the particular conditions obtained could not be repeated and future zirconium/$BaCO_3$ tests and iron/$BaCO_3$ tests always resulted in complete precipitation of the Group III element.

Treadwell (48) describes a method of precipitating Fe, Cr and Al as the hydroxides and U as $Ba_2[UO_2(CO_3)_3]$, using a slurry of $BaCO_3$ as the precipitating agent. Stieglitz (49) describes a separation of the Al and Zn groups by means of $BaCO_3$.

Bearing in mind the limitations of the $BaCO_3$ method in not being able to purify Group III metal solutions, tests of the method's ability to scavenge a solution of uranium were carried out. The same procedure as in the UX_1 tests already described was adopted, except that known amounts of U were present. After simple admixture with $BaCO_3$ and settling, the mother liquors of H_2O and Ba reagent samples were found to contain $<0.1\%$ of the U initially present.

Tests were extended to include 20 volume H_2O_2 and 20% NaOH. UX_1 tests showed that with both of these reagents $<1\%$ of any thorium present was left behind after a simple admixture with $BaCO_3$.

Uranium tests with these two reagents showed that simple $BaCO_3$ mixing reduced the uranium concentration in 20 volume

H_2O_2 to <1% but that 20% NaOH had to be shaken with $BaCO_3$ to achieve the desired reduction. Shaking for 2 minutes left 67% of the uranium behind, 16 hours on the shaking machine left 14% behind and 44 hours on the shaking machine left 5.9 ± 0.4% of the uranium behind. This percentage reduction of the natural uranium content of A.R. NaOH was later proved adequate.

Although 20 volume H_2O_2 could be easily purified the natural uranium content of the A.R. reagent was low enough to need no reduction.

Reagents which still needed purification techniques were Zr and Al solutions. Zr solution is easily purified either by the $BaCO_3$ method or by carbonate-free-NH_3 precipitation of $Zr(OH)_4$ both of which methods quantitatively remove uranium and thorium.

Zirconium Reagent

Treating the zirconium solution with excess NaOH and Na_2O_2 under various conditions of temperature and concentration made no difference to the uranium content of the reagent. (See chapter VIII). Uranyl ferrocyanide is insoluble in acetic acid and an attempt was made to remove uranium from a slightly acetic acid solution of zirconium acetate by precipitating lanthanum ferrocyanide from the solution. This resulted in a 40% reduction of the uranium present in the reagent.

The zirconium reagent which had not been precipitated on shaking with $BeCO_3$ (see page 140) contained 23×10^{-8} gm U per mgm of zirconium which figure was also obtained for the original zirconium nitrate. Uranium-free zirconium reagent was prepared by ether extraction of a solution of zirconium nitrate. Four grams of zirconium as nitrate were dissolved and conc. HNO_3 and NH_4NO_3 added. This solution was ether extracted seven times, the seventh extract being analysed for uranium. The Zr solution was found to contain $<0.02 \, .10^{-8}$ g U/mgm Zr.

The Zr content had been reduced also because approximately 8% Zr passes into the ether layer during such an extraction (26).

For the removal of thorium the following methods were tested. Thorium oxalate does not dissolve in excess ammonium oxalate unless the solution is boiled, and is insoluble in dilute acids. Cerium oxalate behaves similarly. Zirconium oxalate on the other hand dissolves in excess ammonium oxalate, but the right conditions were difficult to achieve to enable cerium oxalate to precipitate without zirconium and with any thorium present.

It is to be expected that thorium will be carried out of solution by a precipitate of lanthanum ferrocyanide. However, the more reliable precipitate of lanthanum fluoride was used. Thorium fluoride is extremely insoluble whereas zirconium fluoride is soluble. There seemed little doubt that the LaF_3

carrier from slightly acid solution would carry out any thorium, but the zirconium reagent would have to be cleaned of any fluoride ion present since this interferes with the ether nitric extraction of uranium which follows the use of zirconium as a carrier. This was done by adding lanthanum solution to the zirconium reagent after purification when LaF_3 settled out on standing. This left the zirconium reagent with a slight lanthanum content but a negligible F' content. Thorium (44) is extracted by ether from a nitric acid solution, but to a lesser extent than uranium. Some zirconium nitrate was ether extracted in this way 7 times which considerably reduced the thorium content. It can be seen from the thorium results of the reagents that the zirconium reagent purified by LaF_3 is much the better reagent.

Aluminium Reagent

Uranium was removed by ether-HNO_3 extraction and thorium by LaF_3 precipitation.

Uranium level of Reagents

In the analysis of HCl and H_2O_2 solutions known volumes were concentrated and aliquots of the concentrate dried on the small Pt trays used to prepare the NaF beads for the fluorimeter. For the $BaCl_2$ reagent and the 20% NaOH solution (after acidification) an extract of the uranium was obtained on $Al(OH)_3$ using carbonate-free NH_3. This precipitate contained no elements as impurities which could interfere with fluorescence measurements and so could be incorporated directly into fluorimeter beads on the 1 mgm scale. On this basis the aluminium reagent was the simplest to analyse.

The results for all the reagents are given in the table below except conc. HNO_3, ammonium nitrate, distilled H_2O, and ether which were known to give negligible contributions to a uranium run.

Reagent	10^{-8} g U found	Aliquot Taken
$AlCl_3$ (10 mgm/ml) purified	<1.0	10 mgms
$BaCl_2$ (20 mgm/ml) purified	0.7 ± 0.1	10 mgms
$Zr(NO_3)_4$ 10 mgm/ml purified	<0.2	10 mgms
AR 20 vol. H_2O_2 unpurified	0.16 ± 0.17	20 mls
20% NaOH solution (shaken $BaCO_3$)	<0.2	20 mls
Crude conc. HCl	0.48 ± 0.16	500 mls
Distilled HCl	0.30 ± 0.10	500 mls

The substitution of iron for zirconium as the carrier for thorium creates no reagent purification difficulties. A supply of Th and U-free $FeCl_3$ was available from the ether/HCl iron extractions of meteorites. It has already been shown that neither U nor Th pass into the ether layer. A $FeCl_3$ reagent prepared in this way was found to make a negligible contribution to either the uranium or thorium value of the blank.

Thorium level of Reagents

It was assumed that the whole thorium series after RdTh was in radioactive equilibrium in a reagent. After suitable preparation of a sample of the reagent, e.g. concentration of a bulk of distilled water or acidification of a sample of 20% NaOH, ThB was carried out of solution and a ThB-C source prepared and counted. The results for all the reagents except conc. HCl are given in the table below. The H_2S procedure using 2 mgm of Pb as lead acetate gave a negligible contribution. The lead acetate was obtained from Brady and Martin.

Reagent	10^{-8} g Th found	Aliquot Taken
$AlCl_3$ (10 mgm/ml) purified	0.7 ± 0.15	10 mgm
$BaCl_2$ (20 mgm/ml) purified	< 0.4	10 mgm
$ZrCl_4$ (10 mgm/ml) purified LaF_3	< 0.9	10 mgm
$Zr(NO_3)_4$ (10 mgm/ml) purified Et_2O/HNO_3	9.7 ± 1	10 mgm
H_2O dist.	35 ± 7	Litre
H_2O dist. (Shaken $BaCO_3$)	14 ± 3	Litre
AR 20 vol. H_2O_2 (unpurified)	1.0 ± 0.6	10 mls
20% NaOH solution (Shaken $BaCO_3$	5.0 ± 1.6	10 mls

Concentrated hydrochloric acid was found to be a special case. It was the only reagent with a large thorium contribution from the quantities used in a meteorite run and efforts were made to purify it. All figures given for HCl analyses are units of 10^{-8} g Th per litre of HCl.

Four litre of Towers' conc. HCl (10 N) were evaporated down to a few mls. This residue contained $FeCl_3$. It was made up to a suitable volume to adjust the HCl normality to 0.2 N, 2 mgms Pb were added and H_2S gas passed through the solution. The figure obtained after counting the ThB-ThC source was 90 ± 20. A repeat of this analysis gave:- 156 ± 20.

A further analysis was made similar to the above, but $Al(OH)_3$ was used to carry out the Th and ThB as hydroxides. This gave the following figure:- 85 ± 25.
The mean of these three results is:- 110 ± 14.

An attempt at purifying HCl by distillation of the azeotropic mixture (20% HCl) was begun. The distillation was carrie out as slowly as possible and the distillate was led directly into polythene reagent bottles. When enough had been distilled it was poured into a 5 litre beaker evaporated down and the thorium estimated. From two such runs the following results were obtained:-

(a) 114 ± 20 (b) 160 ± 50

<u>Mean: 137 ± 25</u>

Since distillation had proved disappointing, preparation of conc. HCl by means of HCl gas was tried. The method used was to fit a dropping funnel and a gas outlet lead through a stopper for the Winchester in which the acid is supplied. Concentrated H_2SO_4 could then be added to the Winchester dropwise and the HCl gas produced led through an inverted funnel into purified distilled water in a 5 litre beaker.

It is known that $BaSO_4$ precipitated through an HCl-acid medium carries down 48% of any thorium present. This cannot be applied directly to the purifying of concentrated HCl because SO_4'' cannot be tolerated by the procedure using the conc. HCl. However, several grams of $BaCl_2$ were added to the Winchester producing HCl gas. Then when conc. H_2SO_4 was added dropwise, $BaSO_4$ was formed locally where HCl gas was being evolved and would be expected to carry down some thorium. Two litres of 6 N HCl were produced by this method and contained:- 168 ± 20 per litre.

Variations of the method were tried. A Winchester filled with cotton wool to act as a spray trap was inserted into the HCl gas line. No definite difference was found in the thorium content. Finally a drikold-cooled U-tube was inserted in the HCl gas stream (HCl boiling point = -84°C.) to prevent any mechanical carry-over. This batch of HCl contained 100 ± 18 per litre. The water used to dissolve the HCl gas had been previously agitated with $BaCO_3$ and contained 14 ± 3 per litre.

Disappointing results had also been obtained from attempts to purify hydrochloric acid for the radon-thoron method. It would seem from the figures obtained that thorium is being picked up from the glass ware used, probably during the boiling down of the acid's bulk. This could be tested by varying the surface area of glass in contact with the acid for different runs. However, to perform a meteorite run without having a bulk of hot hydrochloric acid in contact with glass might prove difficult.

Purification of Sodium Fluoride

The $BaCO_3$ technique described in the purification methods for reagents had proved so simple and efficacious that it was applied to the purification of sodium fluoride. This is used as the basic material in fluorimetric analysis for uranium. After freeing the sample from elements which would interfere with the fluorescence, aliquots are dried in Pt dishes of 1 ml capacity. Then 1 gm NaF is added and the dish heated until the NaF fuses and forms a homogeneous mixture with the uranium from the sample. Ultraviolet light impinges on such a 'bead' and the characteristic U-NaF fluorescence produced, is measured and compared with standard 'beads'.

It has already been explained that a low background count is desirable in the assay of small amounts of activity. In an exactly analogous manner the amount of fluorescence caused by the NaF itself has to be as low as possible. The problem of purifying NaF of its uranium content is important from this and the economic point of view since good quality NaF has to be imported from the U.S.A.

It was proposed to purify NaF of its uranium by shaking a NaF solution with $BaCO_3$. The relevant solubilities are

NaF	4.22 gms/100 ml	at	20° C.
BaF_2	0.17 "	"	"	10° C.
$BaCO_3$	0.002 "	"	"	20° C.

These figures show that the method is chemically feasible. NaF was shaken with several grams of $BaCO_3$, for several minutes. After settling, the clear liquid was removed to a Pt dish and dried. The NaF obtained was finely ground in a mortar and a series of beads made and their fluorescence estimated. The NaF used (Hopkins and Williams) normally gave a reading of 1300 volts per bead. (The readings of the fluorimeter are expressed on a volts scale). The average bead of the NaF which had been shaken with $BaCO_3$ was 11.8 volts, $<1\%$ of the original reading.

This reduction was useful, but the purified NaF was found to have only approximately 60% of the normal sensitivity towards uranium the reason for which was not found. As well as this it was found that other manufacturers' NaF was not improved by the $BaCO_3$ technique to the same extent. Thus a batch of BDH NaF gave an average 'bead' of 15 volts. This was reduced to 5 volts by $BaCO_3$ treatment and again uranium standard beads were reduced to 60-70% of their normal value. The best NaF, produced by Merck, usually gave an average bead of 4-5 volts and gave the uranium standards which were taken as normal values.

It was shown that the small amount of dissolved $BaCO_3$ (2 mgm/100 ml) was not the cause of the reduced sensitivity by adding comparable amounts (and more) of $BaCO_3$ to standard uranium beads. Varying the state of fineness of the NaF obtained after the procedure made no difference. After shaking several times with $BaCO_3$ the NaF 'blank' value obtained after the first shaking was always obtained.

This residual value was not changed by precipitating NaF from its aqueous solution by ethyl alcohol which would be expected to dissolve any uranyl fluoride present. The $BaCO_3$ method of purifying NaF shows some improvement but brings in a loss of sensitivity. If the method proved useful a column of $BaCO_3$ could be employed, which would be more convenient. A column of $BaCO_3$ could probably be quite useful for uranium separation work in general.

Chapter X Uranium and Thorium analysis of San Martin

When the procedures had been proved reliable a meteorite analysis using them was begun. San Martin was chosen because, although an iron meteorite, it was known to possess the high thorium content of 8.10^{-8} g Th per gm of meteorite (2).

21.2 gms of San Martin were attacked with conc. HCl. The residue was treated with conc. HNO_3. The HCl solution was cautiously treated with HNO_3 until there was no possibility of a violent reaction and then the two solutions from the two attacks were combined and the mixture was boiled ensuring that no ferrous iron was present. It had been thought that the use of nitric acid for this task ($Fe^{++} \rightarrow Fe^{+++}$) might endanger the uranium present when the next step - ether-HCl extraction - was performed. (Chlorine gas had previously been used as the oxidising agent). However, test-runs showed that uranium completely remained in the aqueous phase. The meteorite solution now containing no ferrous iron was evaporated to dryness and the residue dissolved in 6.5 N HCl. After 4 extractions with equilibrated ether the aqueous phase, showing the typical green colour due to nickel was boiled to reduce its bulk. The aliquots of the carrier element solutions were then added; 10 mgm Fe, 20 mgm Al, and 20 mgm Ba. Ammonia gas prepared from ammonia liquor containing KOH, was passed into the solution until it smelled strongly of the gas. The heat of neutralisation was sufficient to raise the temperature of the solution close to the boiling point, and the solution was kept hot for 10 - 15 minutes. The mixed hydroxide precipitate coagulated in the mother liquor which was deep blue due to the presence of copper. After centrifuging off the precipitate it was dissolved in HCl and the solution boiled. A precipitate of SiO_2 came down here. It was centrifuged off, washed and discarded.

More barium carrier solution was added (20 mgm Ba) and the precipitation by ammonia repeated. The precipitate after centrifuging, washing etc., was dissolved in HCl and more barium carrier solution was added (20 mgm Ba). This acid solution of 10 mls bulk was added to a mixture of 30 mls 20% NaOH and 30 mls 20 volume H_2O_2. The mixture was then brought just to the boil when the precipitate could be centrifuged. The mother liquor was kept. The precipitate was dissolved in HCl, aliquots of barium solution, and aluminium solution (20 mgm Al) were added and the alkaline/peroxide reaction repeated with another 60 mls of alkaline/peroxide mixture. The mother liquor was combined with the previous one and the resulting solution acidified with conc. HNO_3, saturated with NH_4NO_3 and ether extracted four times. The ether extracts were combined and water added. The ether was evaporated and an aqueous extract obtained from which a series of NaF beads were made for the fluorimeter. The uranium figure obtained by J.C. Dalton in this way was

$$0.75 \pm 0.04 \cdot 10^{-8} \text{ gm U/gm San Martin}$$

after the uranium contributed by the reagents had been estimated (a 'blank' run) and subtracted. The uranium figure published by Arrol Jacobi and Paneth (2) was $0.6.10^{-8}$ gm U/gm San Martin.

Meanwhile the final $Fe(OH)_3$ precipitate was dissolved in the minimum amount of HCl and the solution evaporated almost to dryness. The $FeCl_3$ was then dissolved in 25 mls of 0.2 N HCl and the solution stored to allow ThX and ThB to grow. An aliquot of barium solution was added (20 mgm Ba) together with an aliquot of lead solution (2 mgm Pb). After 18 days 2 hours which is 4.98 half lives of ThX PbS extraction was begun. ThX was present as 96.8% of the equilibrium amount and ThB could be taken as being at the same value of the equilibrium amount. A_2S was passed for 4 minutes, and the black precipitate was separated by centrifuging the solution for 4 minutes. The mother liquor was preserved. The precipitate was dissolved in a little HCl, transferred to a counting disc, and the ThB-C source counted for 16 hours on the scintillation counter.

Count obtained	10.3 ± 0.8 cph
Background	1.3 ± 0.1 cph
Count due to run	9.0 ± 0.8 cph

The mother liquor which had been preserved was boiled until free of H_2S and the acid normality again adjusted to 0.2 N HCl. Aliquots of lead and barium solutions were added and 3 days after the previous extraction PbS was again precipitated through the solution. The source prepared was counted for 16 hours.

Count obtained 8.8 ± 0.8 cph
Background 1.4 ± 0.1 cph
7.4 ± 0.8 cph

The time needed for a series of 6 or more ThB-C sources was not available. With San Martin the amount of thorium present ensures a fairly small counting error in the determination, and the increase in accuracy due to such a series was not so necessary in this case. The mean count for the two sources is 8.2 ± 0.8 cph.

Corrected for ThX growth this is 8.45 ± 0.8 cph. A blank run was performed of the reagentsused in the analysis of the meteorite, but double the quantities were used to lessen the error of the determination. Two successive ThB-C sources gave a mean count of 5.4 ± 0.6 cph for 16 hour counts.
Background count was 1.3 ± 0.1 cph
Count due to 'Blank' 4.1 ± 0.6 cph

There is no ThX growth correction to apply to this figure.
Count due to 21.2 gm San Martin + Blank 8.45 ± 0.8 cph
Count due to single Blank 2.05 ± 0.3 cph
Count due to 21.2 gm San Martin 6.40 ± 0.85 cph

Known strength thorium solutions with the series in equilibrium were PbS extracted in the normal way. The mean calibration figure obtained was 2.9 ± 0.1 cph per microgram of thorium. Hence The content =

$$\frac{6.40 \pm 0.85}{2.90 \pm 0.10} \times \frac{100}{21.2} .10^{-8} \text{ gm Th/gm San Martin.}$$

$$= 10.4 \pm 1.4 .10^{-8} \text{ gm Th/gm San Martin.}$$

The corresponding figure published by Arrol Jacobi and Paneth (2) was 8 x 10^{-8} gm Th/gm San Martin.

Chapter XI Discussion

Previous workers (Arrol Jacobi and Paneth) (2) have reported the helium content of some fifty iron meteorites and have made measurements of the uranium and thorium contents of six of them. If one accepts the average uranium and thorium content of these six as representative of iron meteorites in general, it is possible to calculate ages for all those meteorites of which the helium content is known. In this way ages ranging from about 1×10^6 to 7×10^9 years were found. Two points implicit in this argument may be questioned: (i) the assumption that uranium and thorium contents of iron meteorites are constant and (ii) the assumption that all the helium is of radiogenic origin.

(i) The determination of uranium and thorium in meteoritic irons.

The assumption of an average figure for the uranium and thorium contents of meteorites by Arrol Jacobi and Paneth was, of course, nothing but a reasonable expedient, since circumstances prevented a more adequate survey of the materials at the time. The present work was directed towards obtaining more reliable analytical data. on a wider range of meteorites, and, in particular, towards obtaining data on a few meteorites which are crucial to any theory concerning their origin. Initially the method involving the counting of α particles from radon or thoron and their daughter products was further developed and improved. Modern counting equipment was used and improvements made in the manipulation of thoron and radon and in the carrier procedures used to extract the parent activities. Useful results were obtained in particular those for the meteorites of which the helium content had previously been shown to be very low. (Savik, Ahnighito, and Muonionalusta). The small but definite radioactivity content of these meteorites was demonstrated for the first time.

In addition to the meteoritic irons an examination was made of a black chondrite, Beddgelert. The metal and stone phases of this meteorite were separated and analysed by the radon-thoron method.

Although modified, this method still suffers from the disadvantage that it is impossible in practice to reduce below level the "background" of natural α particle contamination in an ionisation chamber. This irreducible background sets an effective lower limit to the quantity of uranium or thorium which can be measured, and hence in practice to the concentration of these elements in iron which can be handled. Efforts were, therefore, made to utilise more modern techniques by which it was hoped to lower the effective limit of estimation of both uranium and thorium. The scintillation counter lowered the effective limit of estimation of thorium to 1.10^{-7} g, whereas this limit had been 4.10^{7} g for the thoron method. The fluorimeter lowered the effective limit of estimation of uranium to 0.6×10^{-8} g, whereas this limit had been 4.8×10^{-8} g for the radon method. These were significant improvements but analytical procedures were needed to enable these instruments to be used. Successful procedures were developed which separated uranium and thorium from the meteorite sample and from each other, the separated uranium being estimated using the fluorimeter. After a suitable period of time the daughter activities ThB and ThC could be separated from the thorium concentrated from the meteorite sample. This method of measuring the α activity of ThC with the scintillation counter makes it possible to perform repeated estimations of the thorium content of a meteorite sample, so improving the accuracy of the result.

The reaction by which uranium and thorium are separated is the caustic soda-hydrogen peroxide reaction on ferric iron acting as the thorium carrier which precipitates, and aluminium as the uranium carrier which remains in solution. When correct conditions are observed this is a quantitative separation. Some interesting results were obtained when zirconium was used as the carrier for thorium instead of iron. In this case much uranium was found in the precipitate as well as the thorium. It would seem that this is connected with the formation of zirconium peroxide which might interfere with the complex peroxy-uranate otherwise held in solution with the aluminium.

The radiochemical procedures were applied to solutions remaining from the radon-thoron analysis of meteorites. Tests had shown that the uranium initially present in the meteorite samples was still present in these solutions and this element was separated using the relevant parts of the procedures. More results were obtained to confirm the low uranium content of Savik, and useful figures on the uranium content of Ahnighito were obtained. It might be argued that, since these residue solutions had been stored for a long time, six months or more, their uranium content will have changed. However, these solutions were strongly acid (HCl) and were stored in pyrex, so that it is not very probable that uranium would be removed from solution by the glass. The other alternative, dissolving of uranium from the glass by the acid solution, seems unlikely when the uranium content of crude conc. HCl supplied in Winchesters, is considered (see page 145).

The reagents needed for a meteorite analysis were successfully purified where necessary, except concentrated hydrochloric acid. This reagent has a thorium content rather high for meteorite work. Attempts at purification, e.g. distillation, proved unsuccessful, and the results obtained indicate that thorium was probably being introduced from glassware. In the purification of reagents from uranium and thorium a slurry of $BaCO_3$ proved very useful where it could be employed. (45) This method of purification was also used in an attempt to purify sodium fluoride but with only partial success.

The procedures were then used for the analysis of a sample of San Martin meteorite. Results were obtained which agreed fairly well with those of earlier workers (2) and which could be stated with greater accuracy.

(ii) Helium production by cosmic rays

The second point that could be questioned is the assumption that all the helium is of radiogenic origin. This is fundamental to the problem of the ages of meteorites, and arises from the suggestion made by Bauer (50) and by Huntley (51) that a part of the helium content of meteorites arises not from radioactive decay but rather from the interactions of high energy cosmic ray particles with iron nuclei. It is known that the 'evaporation particles' produced under these circumstances consist of nuclei of the lightest elements, including both helium 3 and helium 4. A recent investigation by Paneth, Reasbeck and Mayne (52) has shown that the helium isolated from a number of meteorites does contain, in fact, a substantial proportion of helium 3, thus proving the essential correctness of the hypothesis of the cosmic-ray origin of part of the helium. This implies, of course, that the ages previously calculated must be regarded as constituting upper limits to the ages of the meteorites; it is likely, in fact, that many of them are gross overestimates, and that none of the meteorites has an age approaching 7 x 10^9 years. This problem can be resolved in the case of those meteorites which contain a comparatively small proportion of helium 3, since the subtraction of a small correction to allow for the cosmic ray contribution will not introduce gross errors into the assessment of the amount which has resulted from the radioactive decay of the uranium and thorium. In one particular case, Paneth, Reasbeck and Mayne were able to do this, and for the Bethany Harvard meteorite they suggest an age of 75 x 10^6 years; calculations by Martin have shown that it is not implausible to suggest that this represents the age of the bulk of the meteorites so far examined, the varying helium contents arising, as suggested by Bauer, from the varying thicknesses of matter which originally surrounded the fragment of meteorite remaining after passage through the atmosphere. It seems likely, however, that age determinations by the helium-uranium-thorium method will have to be restricted in future to those meteorites which have a demonstrably small cosmic ray contribution (indicated by their low helium 3 percentage).

These arguments do not, however, invalidate discussion of an interesting group of three meteorites, which form the main part of the material investigated in the present work. For Savik, Ahnighito, and Muonionalusta, careful investigation has failed to reveal a measurable amount of helium, and the question arises whether this absence of helium is to be correlated with a very low age (1 x 10^6 years) or with a correspondingly small amount of radioactive 'contamination'. The present investigation has shown conclusively that the latter suggestion is not correct, and that the three meteorites in question all contain amounts of uranium and thorium which, even if somewhat smaller than the average, are still large enough to give a significant amount of radiogenic helium. One can thus say with some certainty that these three bodies last solidified not more than about one million years ago (53); any contribution from cosmic ray produced helium will, of course, only serve to reduce still further the already low limit which can thus be set. The reason why these three meteorites appear to be so different from their fellows can only be a matter for conjecture. It has been suggested that these meteorites have lost their helium through being heated while passing close to the sun (54). A process of melting and solidifying taking place in the parent body has also been postulated (55). Evidence that meteorites in general were formed under pressure (56) seems to confirm the idea of an exploding planet origin of meteorites, although Ramsey (57) suggests that change in the internal structure of Venus could cause sufficient disturbance of its surface to account for their origin. Any comprehensive theory on the origin of meteorites must account for the small group of very low age. It seems to be quite certain that they must be regarded as having an origin in some way different from the others. There seems to be little doubt of their meteoritic origin; all three show well-developed Widmanstätten figures, which appear to be quite characteristic of meteoritic irons, and they bear no resemblance whatever to the so-called terrestrial irons.

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