

LOW-LEVEL ALPHA AND GAMMA RADIOACTIVITY

IN SOME NATURALLY OCCURRING SAMPLES.

by

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SUMMARY

This thesis discusses low-level alpha and gamma-detection techniques and their application to the determination of small quantities of radioactivity in some naturally-occurring samples. The main emphasis is placed on alpha-radioactivity, and the techniques of low-level alpha-particle detection and alpha-spectroscopy are reviewed. Certain aspects of gamma-spectroscopy are then discussed briefly.

The specific contributions of the candidate are listed separately in Appendices. They cover

- (a) the principles of alpha-counting plus "thorium-pairs" detection as a means of determining thorium and uranium in geological samples which are in radioactive equilibrium, a simple technique for reducing photomultiplier noise, and the theory of alpha-emission from sources containing inhomogeneously distributed radioactivity
- (b) the results of "total" alpha counting techniques applied to australites and to plankton
- (c) the results of two alpha-spectroscopic methods applied to whole rock granites and to granite minerals respectively

and, finally

(d) the results of uranium, thorium and potassium determinations in tektites using non-destructive gamma-spectrometry.

CERTIFICATION BY SUPERVISORS

In terms of regulation 7 of the "Regulations for the Degree of Ph.D." we, as supervisors of the candidate R. D. Cherry, certify that we approve of the inclusion in this thesis of material which has either been published or submitted for publication.

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INTRODUCTION

In the present work we shall be concerned with certain of the techniques and results of low-level radioactivity measurements as applied to naturally occurring samples. The fact that minute quantities of radioactive substances are found in most materials which form part of Man's "environment" has been known for a considerable time. Thus the well-known text of Rutherford, Chadwick and Ellis¹ contains a section (paragraph 114 in the 1930 edition) entitled "The apparent radioactivity of ordinary matter". In this they discuss various results obtained between 1900 and 1927, and comment that "since the radioactive elements are widely disseminated throughout the surface of the earth, it is to be expected that traces of active matter would be separated with all metals". They go further, and quote in footnotes values for the radium content of the earth's crust and of sea-water. In the period 1930 to 1945 this information was put on a firm footing, particularly as a result of the efforts of Evans and his co-workers (see, for example, Evans et al.² and Evans and Goodman³) in the geological, oceanographic and radiological fields.

It is, however, since 1945 - and more particularly since 1955 - that the subject has really developed. This has been

due partly to the increasing sensitivity of the available detection techniques, but it has in the main resulted from an increasing awareness of the possible hazards associated with the inhalation or ingestion of relatively small quantities of radioactivity and of the genetic defects which can be associated with low levels of radiation exposure. The addition of artificial radioactive contaminants to the already existing "natural radiation environment" has highlighted the serious lack of detailed knowledge of the latter, and has stimulated governmental and international organisations to support further research. Review articles such as those of Anderson and ⁴ Hayes and Anderson and Libby ⁵ began to appear about eight years ago. The field is now a lively one, and the past eighteen months alone have witnessed the publication of a book on ⁶ "Environmental Radioactivity", another one on "High Sensitivity Counting Techniques" ⁷ and the holding of an "International Natural Radiation Environment Symposium" ⁸.

A particularly pleasing feature of this activity is that it has attracted the interest of research workers in diverse fields. Since naturally-occurring radioactivity is so widespread, it is a subject of either direct or potential interest to biological, medical and earth scientists as well as to the physicists and/or chemists who are, in the first place, concerned

with the detection and measurement techniques. Thus the techniques described in the present work can be and have been applied to samples and problems from all of the above fields. More specifically, it is hoped that the particular results presented here will be of interest to geochemists, geophysicists and oceanographers as well as to radiation-detection physicists.

In this field it is convenient to classify radiation measurements according to whether they are applied to the categories of alpha, beta or gamma activity. Low-level radioactivity is associated in the minds of many scientists with low-level beta counting. This probably results from the general importance of the low-energy beta emitters tritium and carbon-14, and it is understandable but unjustified. To the physicist alpha- and gamma- radioactivity measurements are in fact usually more appealing, for the simple reason that the alpha- particles and gamma-rays emitted by radioactive nuclei possess definite energies whereas the beta-particles do not. Identification of a nucleus by means of energy measurements is in consequence much more clear-cut for alpha and/or gamma-emitters, and it is in fact usually impossible for very weakly radioactive beta sources to be identified in this way unless prior chemical treatment is undertaken.

This dissertation is concerned largely with low-level alpha-particle detection techniques and some results obtained by the use thereof. Although the pioneer work of Evans and others mentioned above concerned alpha-particles, this field appears to have been surprisingly neglected until the recent resurgence in which the activities of Mayneord and his group at the Royal Cancer Hospital, London have played a large part. (See for example, references 9, 10, 11, 12 and others.) Chapter 1 discusses "total" alpha-counting techniques, where no energy determinations are involved. The practice followed in this dissertation is to review the techniques in the main "Chapters", and to present the more specific contributions in the form of Appendices, most of which have either been published or submitted for publication in the standard journals. On this basis, Appendices 1, 2 and 3 comprise contributions to the general technique of "total" alpha-counting, while Appendices 4 and 5 deal with the application of this technique to tektites and plankton respectively. Chapter 2 reviews alpha-spectroscopic techniques, and Appendices 6 and 7 present the results of the applications of such techniques to a whole-rock sample of granite and to a mineral from a granite sample respectively. Chapters 1 and 2 are in fact a slightly revised version of a review paper (at present in press) delivered by the candidate to the International Natural Radiation Environment Symposium

in Houston in 1963 . Gamma-spectrometric techniques are well-known, and form a minor portion of this work. They are very briefly discussed in Chapter 3, where some emphasis is placed on the relative advantages of alpha-counting and gamma-spectrometric techniques as applied to low-level samples. Appendix 8 describes the results of gamma-spectrometric measurements applied to the non-destructive determination of uranium, thorium, and potassium in tektites. In the conclusion some suggestions are made for possible future experiments.

References to the Introduction, to Chapters 1, 2, and 3, and to the Conclusion are given after the Conclusion and before the Appendices. Each Appendix contains its own references, and the frontispiece to each Appendix acknowledges contributions made by other workers. It is perhaps worth stating that the actual writing of the basic manuscript was undertaken by the present candidate for each and every one of the Appendices included.

CHAPTER 1"TOTAL" ALPHA-COUNTING TECHNIQUES.

The use of alpha-particle detection techniques in studies of the natural radiation environment has tended to be a relatively neglected field. In the last five years, however, as a result of the refinement of these techniques and their application by a small number of research groups, attention has been focused on the following simple facts:

(a) Most naturally occurring radioactive elements are alpha-emitters.

(b) Although the short range of naturally occurring alpha-particles results in their being of small consequence as external radiation sources, the presence of alpha-emitters inside the human body is a feature of considerable importance.

(c) Alpha-emitting nuclei are frequently gamma-emitters also. Thus identification and measurement of the concentration of a particular alpha-emitter in a sample from the natural environment often enables information concerning the concentration of associated gamma-emitting nuclei to be deduced.

(d) Alpha-particle detection techniques possess certain definite advantages compared with comparable beta and gamma measurements. In particular, low background counting rates

(and hence increased sensitivity) are a feature of alpha-detectors while alpha-spectroscopic techniques are characterized by the lack of ambiguity in and the ease of the interpretation. Even the main disadvantage of alpha-detectors -- viz. the inherent limitation of sample volume due to the short range of the alpha particles -- falls away in cases where only a small amount of sample is available.

"TOTAL" ALPHA COUNTING.

(a) Theory.

The basic theory of alpha-particle emission from samples is well-known for the case where the alpha-emitters are homogeneously distributed throughout the sample. This case has been discussed by a number of authors; probably the best reference is still the early paper of Finney and Evans ¹³.

Other useful treatments have been given by Evans and Goodman, ¹⁴ Nogami and Hurley, ¹⁵ Kulp et al., ¹⁶ Turner et al., ⁹ and Keevil ¹⁷ and Grasham. The theory can be subdivided into two classes, viz. "thick" and "thin" sources, "thick" sources being those whose thickness is greater than the maximum range of the alpha particles emitted by the sample. This range is typically about 25 to 30 microns in solid materials, and is seldom greater than 90 microns; the volume of the sample which contributes

to the alpha-particle emission from the front face is thus very definitely limited.

The basic equation of thick-source alpha counting is

$$N_0 = \frac{NRA}{4} \quad (1)$$

where N_0 is the number of alpha particles emerging from an area A of the sample in unit time, N is the number of alpha-disintegrations per unit volume of sample per unit time and R is the range in the sample of the alpha particles concerned. N_0 is of course a measure of the counting rate; for 100 per cent efficient detection N_0 is the counting rate. N and R are usually variables beyond the control of the experimenter (although N can sometimes be artificially enhanced by concentration techniques), and one must therefore use a sample and detector of large area if maximum count rates are to be obtained.

For thin sources, of thickness t , the basic equation is:

$$N_0 = \frac{NRA}{4} \left[\frac{2t}{R} - \left(\frac{t}{R} \right)^2 \right] \quad (2)$$

The counting rate from a thin source is thus lower (since t is by definition less than R), and it is moreover necessary that t be known. In addition, uniform thin sources are considerably

more difficult to prepare than thick sources. Thin-source counting does nonetheless possess one important advantage; inspection of (2) shows that, in the first order, N_0 is independent of the range R . A less precise knowledge of R is thus required for the determination of N than is the case with thick-source counting, and the discussion of the range problem which is given below shows that this is by no means a trivial point. The extra effort involved in thin-source preparation might be worthwhile on this account, particularly if the quantitative precision of the results is of importance.

Both equations (1) and (2) must be modified to allow for (i) absorbers between the sample and the detector, (ii) the fact that alpha-particles below a certain minimum residual range might not give rise to a response in the detector and (iii) the fact that natural samples usually contain mixtures of alpha-emitters, thus necessitating summations over different N and R . With modern experimental techniques (see below) modifications (i) and (ii) are usually negligible; (iii) is, on the other hand, often necessary, and is a complicating feature. Since most of the naturally-occurring alpha-emitters are members of one of the three well-known natural radioactive series (see, e.g. Evans¹⁸, Chap. 16) questions of radioactive

equilibrium arise, and some assumption concerning the degree of secular equilibrium attained by the sample is necessary.

The favorite assumption is that secular equilibrium is complete, and the references quoted above (Finney and Evans¹³

1935; Evans and Goodman¹⁴; Nogami and Hurley¹⁵; Kulp et al.¹⁶

and Turner et al.⁹ all discuss this case in more or less detail.)

(b) Experimental Techniques.

In the early work (Finney and Evans; Evans and Goodman; Keevil et al.¹⁹) ion-chambers were used. Subsequently the proportional counter became popular, and analyses of natural

samples utilizing commercial proportional counting apparatus have been described by Adams et al.²⁰ and others. A flow type proportional counter designed specifically for measuring low-level alpha activity in biological materials has been described

by McDaniel et al.²¹ This utilizes rectangular, screen-wall counters accommodating sources up to 141 cm.² in area, with

background counting rates of 3.8 counts/hour. More recently

Kiefer and Maushart²² have discussed proportional flow counters of area up to 700 cm.² with backgrounds in the alpha pulse-height region of about .5 counts per hour per cm.² Mention should also

be made of the high quality proportional counters developed by the Glasgow group (Curran²³); although these have been applied

primarily to problems of low-energy beta-spectroscopy, they

could no doubt be utilized as alpha-detectors to good effect.

Proportional counters are still in use in a number of laboratories, and do possess certain advantages -- these have been enumerated by Kiefer and Maushart.²² The scintillation counter with an activated zinc sulphide phosphor would, however, appear to be the best general purpose low-level alpha detection instrument available today. Early examples of such apparatus were those of Reed²⁴ and Kulp et al.,¹⁶ but the most effective system is undoubtedly that devised by the group at the Royal Cancer Hospital (Turner et al.;⁹ Mayneord et al.¹⁰) This system is discussed in the references cited and will not be described in detail here. It will suffice to say that it provides a simple, economical, sealed sample-phosphor system of great sensitivity and convenience. No emanation problems (such as are encountered with flow-type proportional counters) arise; in fact, measurement of the counting rate of the sealed system as a function of time allows sample disequilibria to be studied effectively. Sample areas are limited by the size of the photomultiplier tube; areas of just under 100 cm.² (a 4½" photocathode) are commonplace. With reasonable care (good quality zinc sulphide, selected photomultiplier tubes and low cathode-to-first dynode voltages (Appendix 2 of this thesis and

Pagano et al.²⁵) background count rates of less than .01 counts per cm.² per hour are obtainable. For a phosphor area of about 100 cm.², these rates correspond to activities of a few hundredths of a micro-micro curie per gram in a typical thick source solid sample, or, in geochemical terms, to the activity of a typical rock sample containing twenty-five parts per thousand million of thorium and eight parts per thousand million of uranium. The sensitivity of the method is thus apparent although it must of course be borne in mind that extremely long counting times are necessary if the ultimate in sensitivity is to be attained. The associated electronics is, however, simple, and long-term stability is not a major problem.

(c) The Pairs Technique.

The parameter obtained from a "total" alpha counting experiment is essentially the specific alpha activity, N , of the sample. It is often desirable to obtain further information as to the alpha-emitting nuclides present, and it is possible to do this to a limited extent without recourse to alpha-spectroscopy by making use of the so-called "pairs" technique. This utilizes the fact that in two of the three natural radioactive series pairs of successive alpha particles are emitted within short intervals of time. These are due to the short-lived

alpha-emitters polonium-216 ($T_{1/2} = .158$ seconds) in the thorium series and polonium-215 ($T_{1/2} = .0018$ seconds) in the actinium series. Time analysis of the pulses from the alpha counter -- easily accomplished by simple paralysis circuits -- permits the separation of pulse-pairs due to these particular alpha-emitters; suitable equilibrium assumptions then enable the relative contributions of the three series to be assessed.

This method appears to have been suggested first by Hurley and Shorey²⁶, and later by Hirschberg^{27, 28}; it was the paper by Turner et al.⁹ which first described its successful application in any detail. Subsequently its application to the case of thorium and uranium determinations in geological samples has been discussed by the present writer (Appendix 1; Cherry²⁹). The pairs technique combined with the zinc sulphide scintillation counter previously discussed has already resulted in the accumulation of a vast amount of data concerning the alpha-activities of natural samples (Turner et al.^{9, 12, 30}; Turner³¹ and Radley³²; Mayneord³³; Mayneord et al.^{34, 35}; Marsden³⁶ and Cherry (see Appendix 4)) and its use is to be commended to workers in this field.

(d) The Range Problem.

From equations (1) and (2) it is obvious that a knowledge of the range, R , of the alpha-particle in the sample, is essential if a quantitative result is required. It is customary

to use some empirical formula for calculating alpha-particle ranges. The geological workers (Finney and Evans¹³; Evans and Goodman¹⁴; Nogami and Hurley¹⁵; Kulp et al.¹⁶) tend to favour the Bragg-Kleeman relation, which gives:

$$R\rho = .32(10^{-3}) \frac{11}{W^{\frac{1}{2}} R_a} \text{ gm/cm}^2 \quad (3)$$

ρ is the sample density, $W^{\frac{1}{2}}$ is the square root of the atomic weight calculated on the "atomic fraction" basis (Nogami and Hurley¹⁵) and R_a is the range in cm. in air of an alpha particle of the same energy. Turner et al.⁹, on the other hand, replace $W^{\frac{1}{2}}$ by $Z^{2/3}$, where Z is the atomic number. For many common natural materials (both geological and biological) we have $W^{\frac{1}{2}} \sim Z^{2/3} \sim 4.6$, and the two expressions give very similar results.

The question of the accuracy of these expressions is of major importance. Nogami and Hurley¹⁵ claimed that the Bragg-Kleeman relation is accurate to within 5 per cent. Beharrel³⁶ disputes this, and claims that the Bragg-Kleeman law gives ranges which are about 10 per cent too low. Yagoda³⁷ finds the reverse, and says that the computed ranges are 10 per cent too high. A recent review article by Whaling³⁸ presents the ranges of alpha-particles of various energies in twelve gaseous

and seven solid materials (all metallic). The ranges in gases agree fairly well with the Bragg-Kleeman law, but those in solids are definitely higher than those given by equation (3) in the low atomic weight range ($W^{\frac{1}{2}} = 5.0$ and less) which is applicable to most naturally-occurring samples. Thus if one draws smooth curves through Whaling's points, one finds that for $W^{\frac{1}{2}} = 4.6$ (which is generally equivalent to $Z^{2/3} = 4.6$) equation (3) gives ranges which are approximately 6 per cent, 13 per cent and 25 per cent too low for alpha-particles of energies 8, 6 and 4 M.E.V. respectively. Whaling's values were based on experimental data available to him at the time (1958), and it is instructive to consider experimental data (unfortunately very meagre) which has been published since the. Thus Garin and Faraggi³⁹ determined the ranges of 4.5 M.E.V. alphas in uranium, gold, zirconium and silicon. For these four elements they obtained ranges that were, respectively, 32 per cent, 28 per cent, 22 per cent, and 4 per cent higher than those given by the Bragg-Kleeman equation. Replacement of $W^{\frac{1}{2}}$ by $Z^{2/3}$ results in a considerable improvement; there is agreement with the Garin-Faraggi data to within 5 per cent for all four elements.

⁴⁰ Kamke and Kramer have determined alpha-ranges in boron; in the region of 4.5 M.E.V. their results are about 13 per cent higher than given by the Bragg-Kleeman equation and 23 per cent

higher than the same equation with $Z^{2/3}$ substituted for $W^{1/2}$. Finally, calibrations using the thorium series in equilibrium in thorium oxide (See Appendix 1) indicate that equation (3) gives results which are 25 per cent low; $Z^{2/3}$ instead of $W^{1/2}$ gives results which are only 5 per cent low.

The whole subject of alpha-particle ranges in solids is thus obviously in a state of some confusion, and is in need of serious attention. A systematic study of alpha ranges as a function of particle energy and atomic weight would be most valuable, and would help establish total alpha-counting as a reliable absolute method of measurement. Meanwhile, it would appear that the following very tentative conclusions can be drawn: (i) The Bragg-Kleeman equation (3) would appear to give ranges which are somewhere between 5 per cent and 30 per cent too low. (ii) Replacement of $W^{1/2}$ in equation (3) by $Z^{2/3}$ results in considerable improvement in the upper half of the periodic table, but makes matters worse for the lightest elements. (Unpublished data by Osborne⁴¹, would appear to substantiate this latter conclusion).

(e) The Homogeneity Problem.

Derivation of equations (1) and (2) is based essentially on the assumption that the alpha-activity is distributed homo-

geneously throughout the sample. For many natural samples this is not the case, and homogenization is necessary -- this is a problem of which the geologists are particularly aware (Kulp¹⁶ et al.⁴²; Hurley .) Grinding of the sample down to grain sizes very much less than the smallest alpha-range encountered (in practice this requires grinding to micron size or less) and following this by thorough homogenization will of course take care of this problem, but it seemed desirable that the theoretical aspects be systematically investigated. This problem is investigated in Appendix 3. Three different types of inhomogeneity have been assumed, viz., surface coatings, core concentrations and "hot-spot" activity, and it is concluded that:

(i) That grinding down to at least one-tenth of the alpha-particle range is necessary to ensure the accuracy of formula (1) and

(ii) The "pairs" count rate (see (c) above) is generally more sensitive to inhomogeneities in the radioactivity distribution than is the "total" alpha count rate.

(f) Concentration of the Activity.

As has been mentioned above, alpha-counting techniques are so sensitive that they can frequently be used without any

previous treatment of the sample concerned. Some environmental samples are, however, so low in radioactivity that some form of concentration is essential. Thus Turner ⁹et al. ashed food-stuffs prior to counting, and boiled drinking water (Turner ⁴³et al.) to dryness before counting the residue. Chemical extraction is of course also feasible in most cases, although it does introduce an additional element of uncertainty and should be avoided where possible. In this connection it is perhaps worthwhile to emphasize the utility of modern ion-exchange techniques; two useful references which discuss the methods for extracting the trans-lead alpha-emitters are those of Korkisch and Janauer ⁴⁴ and Choppin and Sikkeland ⁴⁵.

An intriguing and simple method of extracting the heavy ⁴⁶elements from aqueous solution has been mentioned by Rosholt and Morken ⁴⁷. Zinc sulphide scintillation phosphor powder is simply added to vials containing the solution to be investigated, the vial is shaken vigorously and the powder allowed to settle. The zinc sulphide apparently adsorbs some (or all) of the heavy-element alpha-emitters, and the scintillations emitted by the powder can be counted directly with a photomultiplier tube. Morken obtained over 95 per cent extraction for both polonium and plutonium under the right condi-

tions of pH, and considered that "An adsorption mechanism is indicated, in which case the extent of removal is probably independent of the element used". Turner et al.⁴³ have used this technique effectively to determine radon in water, and further investigations would be of great interest.

(g) Gaseous samples.

The above treatment has tacitly assumed that the sample materials are solids or liquids. Gaseous samples will of course require special techniques of counter design, but the basic detection principles remain the same. Two selected references to zinc sulphide type scintillation detectors for gaseous samples will serve as examples. Lucas⁴⁸ has described a radon counter, while Giffin et al.⁴⁹ have applied the pairs technique to the case where a gas is used in the detector chamber.

(h) Autoradiographic techniques.

These have been discussed by Yagoda³⁷ and their application to naturally occurring materials has been discussed by Ragland, (in reference 8). They are listed here merely for the sake of completeness. As total alpha counters they compare unfavourably with the techniques discussed above; as a tool

for the identification and study of microsites of radioactivity they are valuable and powerful.

In conclusion, two matters of general importance in low-level alpha-counting techniques (both "total" and alpha-spectroscopic) should be mentioned. These are

(1) The Natural Alpha-Activity of Materials:

In the construction of alpha-detectors it is important to ensure that the surfaces exposed inside the detector possess a low natural alpha-emission rate and a low emanating power (Hill, Osborne and Mayneord, in ref. 8). Data for alpha emission rates from various materials have been published by several authors (McDaniel ²¹ et al. ; Bearden ⁵⁰ ; Adams and Richardson ⁵¹ .) Features worth noting are the high levels of emission from solder (Bearden ⁵⁰) (2800 alphas per 100 sq. cm. per hour) and the extremely low level of emission from aluminized cellulose acetate (Hill ⁵²) (about .3 alphas per 100 sq. cm. per hour). In general, materials should be checked on a total alpha-counter before they are built into a low-level alpha detector.

(11) Counting Statistics:

Counting at low levels of radioactivity requires that particular attention be paid to problems of counting statistics.

A simple matter, not often discussed, is the fact that for a low number of total counts the usual assumption that the Poisson distribution is equivalent to the normal distribution is invalid. Confidence limits based on the Poisson distribution itself must be used, and these have been given by Garwood⁵³. The question of optimization of source-background ratios has been discussed by several authors (e.g. Jaffey⁵⁴, Freedman and Anderson⁵⁵) and this leads to the generally accepted (source count rate)²/background figure of merit mentioned in the next chapter.

A final problem which arises when counting members of the naturally occurring radioactive series is the question of the statistical distribution of counts from a sample containing both parent and daughter activities. The pioneer work concerning this complex question appears to have been that of Adams⁵⁶; more recent and more complete treatments are given by Huybrechts⁵⁷, who applies his results to specific cases (the uranium and thorium families in equilibrium) for a specific time interval (thirty days), and by Lucas and Woodward⁵⁸, who consider particularly problems associated with radium-224 and radon-222.

CHAPTER 2

ALPHA SPECTROSCOPIC TECHNIQUES.

The amount of information obtainable from "total" alpha counting, even when the "pairs" technique is used, is strictly limited, and it is very often desirable to obtain information concerning the relative contributions of the specific nuclides responsible for alpha-particle emission. In these cases recourse must be made to alpha-spectroscopic techniques -- these measure the energy of the alpha-particles and thus provide a means of identification of nuclear species. The power of the technique is of course matched by increased complexity, particularly insofar as the associated electronics is concerned -- a pulse height analyzer (preferably of the multi-channel variety) is an essential tool. The book by Chase¹⁰⁴ is an excellent introduction to the electronic problems of nuclear spectroscopy. Source preparation too is a considerably more critical matter -- sources must not only be "thin", they must be "spectroscopically thin", which is one or two orders of magnitude thinner (100 micrograms/cm² is a frequently quoted upper limit for an acceptable alpha-spectroscopic source). Source preparation, often a somewhat empirical art, has recently been reviewed by Yaffe⁵⁹, and special methods for the preparation of the large area sources

frequently needed in the alpha-spectroscopy of natural environmental samples have been given by Hill⁵² and Korolev and Kocharov^{60,61}. A recently described (Bjornholm and Lederer⁶²) cation-exchange foil technique is also worthy of special mention. We shall pass on to a brief survey of the detectors which can be used for low-level alpha spectroscopy.

(a) Ion-Chambers.

The ion-chamber is by far the most commonly used and most widely suitable tool for alpha-spectroscopic studies. The parallel plate, gridded pulse ionization chamber (Wilkinson⁶³; Rossi and Staub⁶⁴; Herwig et al.⁶⁵; Cranshaw and Harvey⁶⁶; Bunemann et al.⁶⁷ and Harvey et al.⁶⁸) is in turn the most popular type of chamber, and is commercially available. A typical chamber of this sort possesses a sample area of about 10 cm.² and a detection efficiency of about 45 per cent of 4π , and yields resolutions of about 60 K.E.V. for alphas of about 5 M.E.V. energy. Ray and Hammond⁶⁹ applied an instrument of this type to natural environmental samples without previous chemistry, and the work of Goldberg and Koide⁷⁰ on thorium isotopes in ocean sediments provides a good example of high class results obtained after chemical extraction. The big disadvantage of this type of chamber lies in its limited source area, and the quest for

greater sensitivity has led, in recent years, to the design of ion chambers capable of handling much larger sources. The properties of several of these are summarized in Table I. The resolution R is the usual full-width at half-maximum count rate; the background B is taken over this same spectral line width; an alpha energy of about 5 M.E.V. has been assumed. In general, the optimum figures quoted by the respective authors have been used; where no figures are quoted, the relevant parameters have been estimated from data given in the papers.

A study of Table I reveals the following essentials:

(1) Sensitivity: A suitable "figure of merit" for comparing the sensitivity of the ion-chambers listed would appear to be the quantity $\frac{(SE)^2}{B}$ where E is the (geometrical) counting efficiency expressed as a percentage of 4π . This figure takes into account the desirability of making the ratio (source count rate)²/background as high as possible in low-activity experiments (see Freedman and Anderson)⁵⁵, and seems to be more suitable than the figure $\frac{SE}{B}$ ⁷¹ used by Duke. Values of E are unfortunately not always quoted by the authors and thus the figure of merit cannot be calculated exactly. However the variation in E is not great (from about 20 to 50 per cent for all the chambers quoted) and useful comparisons can be made on

TABLE I

Comparison of various large area ion chambers.

Numbers quoted are approximate in many cases.

Author	Configura- tion	Grid	R(K.E.V.)	B(counts/ hr.)	$S(\text{cm})^2$	$\frac{S}{B} (10^{-6})$
Hill ⁵²	Cylindrical	No	110	4	15000	56
Hill and Osborne ⁸	Cylindrical	Yes	40	.3	1500	7.5
Kocharov & Korolev ⁶¹	Parallel plate	Yes	25	.03	200	1.3
Burmia ⁷⁴	Parallel plate	Yes	100	.03	300	3.0
Doke ⁷¹	Parallel plate	Yes (two)	70	.01	150	2.3
Macfarlane & Kohman ⁷⁵	Cylindrical	No	60*	.3*	1200	4.8
Lonati ⁷² <u>et al.</u> (I)	Parallel plate	Yes	300	1	110	.01
Lonati ⁷² <u>et al.</u> (II)	Cylindrical	Yes	300	35	2800	.2
Lonati and Tonolini ⁷³	Parallel plate	Yes	300	.18	110	.07

* Denotes an estimate at an alpha-energy of 2 M.E.V. instead of 5 M.E.V.

an approximate basis. It is easily seen that the ion-chamber⁵² of Hill⁵², which has an efficiency close to 50 per cent, possesses by far the largest figure of merit, a fact due almost entirely to its very large surface area. This chamber and the results obtained from it are discussed in the literature (Hill⁵²; Hill^{76, 77}; Mayneord and Hill⁷⁸; and Hill and Jaworowski⁷⁹).

It is, however, worth pointing out that its high sensitivity is obtained without recourse to electric background reduction techniques (e.g. anticoincidence shielding as used by Macfarlane⁷⁵ and Kohman⁷⁵ or utilization of the grid pulses as used by Kocharov and Korolev⁶¹ and Duke⁷¹).

In appendix 6 granite spectra obtained with this chamber are presented; it is worth emphasizing that the high sensitivity of the chamber enabled these samples to be analyzed in toto and without any prior chemical treatment.

(ii) Resolution: A study of the energies of the alpha-particles emitted by the naturally occurring alpha-emitters⁸⁹ (see, for example, the article by Hanna⁸⁹ or the isotope table of Strominger et al.⁸¹) shows that in many cases two or more alpha "lines" will lie very close together. Thus the alpha-particles from the common isotopes uranium-238 and thorium-232 are separated in energy by about 200 K.E.V.; these alpha-groups

are just separated by a chamber of the Hill type, and sources containing both the species can accordingly be counted with fair accuracy without prior chemical treatment. Other cases are, however, not so favorable; a particularly important clash is between thorium-230, uranium-234 and radium-226, which have their main alpha groups at 4.68, 4.77 and 4.78 M.E.V. respectively. To separate these requires either prior chemical extraction or better resolution, and attention is drawn to the excellent resolving power of the instrument of Kocharov and Kerolev⁶⁰. Subject to the availability of sufficiently thin sources (a useful figure to remember is that a $100 \mu\text{g}/\text{cm}^2$ source contributes about 80 K.E.V. to the resolution), this chamber should be able to separate thorium-230 from uranium-234 and radium-226, although it will not be able to distinguish between the latter two isotopes. Optimum resolution with this chamber is however only attainable at the cost of a reduction in the efficiency E (down to about 10 per cent).

Whether one selects a chamber of maximum sensitivity or one with maximum resolving power depends of course on the problem on hand. The chambers of Hill and Osborne (in reference 8), Nurmia⁷⁴;
⁷¹ Doke⁷⁵, and Macfarlane and Kohman⁷⁵ are all useful compromises
⁸² between the two extremes. Those of the Italian group (Lonati⁸²);

Lonati and Tonolini⁷³ and Lonati et al.⁷²) appear to have been superceded, but they can claim the honor of having been the pioneers of the large source ion chamber technique as applied to naturally occurring alpha-active samples (Lonati⁸² ; Lonati et al.⁷² ; Facchini et al.⁸³)

(b) Magnetic Spectrometers.

These provide the ultimate in resolution (down to about 3 K.E.V.), but possess such poor geometries (several orders of magnitude below the ion-chamber) that their use in studying natural environment samples is likely to be minimal. A good discussion of this type of instrument is given in the review of Baranov and Zalenkov⁸⁴.

(c) Scintillation Spectrometers.

Scintillation counters are in many respects more convenient to operate than ion-chambers. As an alpha-spectroscopic tool, however, they suffer from a major intrinsic defect -- poor resolution. Thus typical resolutions obtained with scintillation alpha-spectrometers have been 13 per cent (gaseous phosphor⁸⁵ (Forte) and 17 per cent (organic liquid phosphor (Seliger⁸⁶)). Gaseous phosphors can do better than this if operated at high pressures: thus Sayres and Wu⁸⁷ report about 4 per cent for xenon

at 40 to 60 p.s.i. Inorganic crystals are, in general, more promising. Thus the early work of Broser and Kallman⁸⁸ gave resolution better than 5 per cent for cadmium sulfide (CdS), while resolutions of 1.8 per cent (Martinez and Senftle⁸⁹) and 2.6 per cent (Fleury et al.⁹⁰) have been reported under optimum conditions for alphas in CsI(Tl). More typical of the sort of resolution likely to be obtained in practical applications (where one has larger area sources and no collimation) are the results of Gale⁹¹. Gale describes a simple CsI(Tl) alpha-spectrometric system capable of measuring activities as low as ⁻¹² 10 curies, and obtains a resolution of about 14 per cent using a .005 inch thick crystal of 1.5-inch diameter and source diameters up to one cm. Belyaev et al.⁹² reported similar results for CsI(Tl); resolutions from 11 to 22 per cent with 3 to 5½ cm. diameter sources, but resolution as low as 4 per cent with 3 mm. diameter sources. Since the emission spectrum of CsI(Tl) extends from the blue to the red⁹³, it is likely that use of the new red-sensitive tri-alkali photomultiplier tubes might improve matters. The present writer has attempted this with an E.M.I. 9558C tube, and resolutions of better than 3 per cent for a 5 mm. diameter plutonium-239 source have been obtained without difficulty. The potentialities of the CsI(Tl) (and possibly

also the CdS) alpha-spectrometer would appear to be worthy of further investigation, even though they cannot hope to compete seriously resolution-wise with the ion-chamber. In this connection, the useful reference of Aniansson⁹⁴ concerning the preparation of thin CsI(Tl) layers by vacuum deposition should be mentioned.

(d) Semi-Conductor Detectors.

The recently developed semi-conductor detectors possess many advantages for charged-particle spectroscopy: excellent resolution (e.g. 17 K.E.V. for a 1 cm.² detector (Blankenship and Borkowski⁹⁵)), good linearity, good stability and low background rates are the chief of these. They do, however, suffer from one major disadvantage as far as low-level detection is concerned, viz. their small area. Detectors with areas of several cm.² and resolutions approaching 50 K.E.V. are now available commercially. If areas can be increased to above 10 cm.² without sacrificing resolution, such detectors will provide a serious alternative to the "conventional" (i.e. small area) Frisch grid type ion chamber, and even now they are superior in resolution to the ion chamber if very small (millimetric dimension) sources are involved. Alpha particle spectroscopy with 1/4 cm.² silicon surface barrier type detectors has been

discussed by Chetham-Strode ⁹⁶ et al. , who emphasize the need for avoiding contamination of the detector by recoil nuclei if the excellent low background characteristics of the detector are to be maintained. A general review of semi-conductor detector devices has been given by Miller ⁹⁷ et al. . In appendix 7 the use of a semi-conductor detector to investigate the alpha-spectra from certain radioactive minerals is described. The results are interesting in that an unidentified alpha-line has been found; its possible origin is discussed.

(e) Nuclear Emulsions ³⁷ (Yagoda).

These suffer from the disadvantages of long exposure times, extremely tedious measurement and poor resolution (about five times worse than a good ion chamber ⁷⁵ (Macfarlane and Kohman)). They are, however, very sensitive, and have been employed in several experiments. Notable amongst these have been the searches for alpha-radioactivity in the medium-heavy elements (e.g. Porschen and Riezler ⁹⁸ ; Macfarlane and Kohman ⁷⁵ give a list of references to this sort of work) and the important experiments of Picciotto and Wilgain ⁹⁹ (1954) on thorium isotopes in deep sea sediments. The technique used by the latter authors is so sensitive that it permits the measurement of as little as ⁻⁹ 10 gm. of thorium provided it is sufficiently highly concentra-

ted. Another emulsion technique which also possesses a degree of sensitivity of this order has been described recently by Geiger ¹⁰⁰ et al.

(f) "Thick-Source" Spectrometry.

In an effort to avoid the necessity for the preparation of spectroscopically thin sources, and/or to increase the sensitivity by increasing the volume of sample material, several authors have investigated the nature of the alpha-spectrum from a "thick" source. Thus Graeffe and Nurmia ¹⁰¹ have applied thick-source spectrometry to determinations of the energies of alphas from the weakly-alpha-active medium heavy elements, while Stephenson ¹⁰² et al. have discussed the theoretical energy distribution of alphas emerging from a thick source. A final useful reference is that of Abrosimov and Kocharov ¹⁰³, who discuss the effects of source thickness on the shape of the energy and directional distributions of the alpha-particles.

CHAPTER 3

GAMMA-RAY SPECTROMETRY.

Gamma-ray spectrometric measurements comprise only a minor portion of this dissertation, and it is not proposed that the subject be discussed thoroughly here. The technique is by now well established, and several reviews have appeared. Of these, the article by Bell¹⁰⁵ was one of the early "standards"; more recently, there have been portions of the articles by Nott and Sutton¹⁰⁶ and by Murray⁹³, while the book "Applied Gamma-Ray Spectrometry" by Crouthamel¹⁰⁷ provides a comprehensive discussion of the whole subject. Finally we have the application of this technique to low-level counting discussed in Chapter 9 of the book by Watt and Ramsden⁷, and reviewed with biomedical emphasis by Marinelli et al.¹¹¹.

The basic principle of the method is of course to select a particular gamma-ray emitted by the nuclide to be measured and to count the number of photoelectric effect interactions undergone by gamma-rays of the specified energy in the scintillation crystal. Photoelectric effect interactions produce output pulses which are equivalent to (or very slightly less than) the total energy of the gamma-ray, and electronic analysis of the

scintillation counter output pulses then provides information about the energy and quantity of gamma-rays present in the sample. Pair production interactions can also be used, although they only occur for the higher energy gamma-rays and give rise to minor ambiguities in interpretation; Compton effect interactions give rise to a pulse continuum and are disadvantageous in that they compete with the photoelectric effect and also interfere with photoelectric peaks from lower energy gamma rays in the same sample. These points are discussed in the references listed above, and the fundamentals of the interaction of gamma-rays with matter are fully dealt with by Evans¹⁸. What concerns us here is the question of which gamma-ray energies to select. Sometimes there is no choice. Thus many measurements (e.g. Schroeder and Cherry¹⁰⁹) of the fall-out nuclide caesium-137 have been reported. Caesium-137 emits beta-particles, followed in the majority of disintegrations by a 662 K.E.V. gamma ray. No other gamma-ray is involved (if the low energy barium X-ray accompanying the internal conversion process is ignored) and the obvious procedure is to analyze the 662 K.E.V. photopeak. For naturally-occurring samples containing the gamma-emitting isotope potassium-40 and gamma-emitters from the uranium, thorium and actinium series as well the situation is more complicated, and some degree

of selection is required.

The pioneer application of gamma-spectrometric methods to samples from the natural radiation environment appears to have been that of Hurley¹⁰⁸. He used a 1-3/4" by 2" NaI (Tl) well-type crystal as detector, and selected energy bands centred at 180 K.E.V. and 238 K.E.V. for thorium and uranium detection. The 238 K.E.V. band is dominated by the photopeak of a gamma-ray from lead-212 in the thorium series, while the 180 K.E.V. band contains approximately equivalent contributions from both series. (This assumes equal parent disintegrations - see Fig. 4 of Hurley¹⁰⁸). For potassium measurements there was no choice; the solitary gamma-ray at 1.46 M.E.V. was used. With the development of larger crystals it became feasible to use higher gamma-ray energies for uranium and thorium determinations, and in 1958 Adams et al.²⁰ reported results from a 3" by 3 1/2" NaI(Tl) crystal. They used the 1.46 M.E.V. energy for potassium as before, but then selected the 1.76 M.E.V. gamma-ray from bismuth-214 for the uranium series and the 2.16 M.E.V. gamma-ray from thallium-208 for the thorium series. Appendix 8 utilized the 3" by 3" NaI(Tl) crystal facility in the iron shield at the Geology Department, Rice University. Multichannel pulse height analysis was available, and the determinations of

potassium, uranium and thorium in tektites were made using the 1.46, 1.76 and 2.62 M.E.V. gamma-rays listed above.

A nagging doubt remains as to whether the large-crystal cum high-energy gamma-ray combination now in common use is in fact always superior to a low-energy, smaller crystal set-up. The advantages of the former are obvious: the potassium gamma-ray does not interfere with the uranium and thorium-series gammas since it is of a lower energy; furthermore, the backgrounds are lower than they are at low energies. On the other hand, the detection efficiencies and hence the count rates are lower than they are at lower energies, and sufficient attention does not appear to have been given to the question of optimizing the desired (source count rate)² / background ratio (see Chapter 1) as a function of gamma-ray energy and crystal and sample size. Studies such as those conducted by Marinelli et al.¹¹¹ into the optimum crystal size for "whole-body" gamma-spectrometric measurements, and by May and Marinelli¹¹² into factors determining the ultimate detection sensitivity of gamma scintillation spectrometry are envisaged, and the problem would appear to be ripe for a thorough and systematic investigation. The encouraging results obtained by Parker¹¹⁰ with a small ($1\frac{1}{2}$ " by 1") NaI(Tl) crystal in investigating low-energy gamma-rays (up to 250 K.E.V.)

from naturally-occurring samples would appear to substantiate this opinion. It is perhaps unnecessary to add that small crystals possess considerable economic advantages!

In conclusion, it is of importance to compare the gamma-spectrometric technique with the "total plus pairs" alpha counting technique. As far as thorium and uranium determinations are concerned, both methods suffer from the defect that the assumption of secular radioactive equilibrium is a prerequisite. If ion-chambers or gas flow proportional counters are used, then the alpha-technique can be subject to serious emanation difficulties; with the sealed source-phosphor system of Turner et al.⁹, however, these problems no longer arise. One can therefore state that the alpha-technique is advantageous in that (a) exceptionally low backgrounds which result in great sensitivity can be obtained and (b) only small quantities of sample are required. On the other hand, gamma-ray techniques offer greater ease in sample preparation, and, more importantly, present negligible inhomogeneity problems. Both techniques currently require calibration samples for optimum accuracy; should the problems of computational detail in gamma-ray spectroscopy, or the range problem in alpha-particle counting, be solved, then either or both methods ..

could claim to be absolute techniques. If, however, alpha-spectroscopy as opposed to "total" alpha-counting is resorted to, then one becomes involved in (a) the inherent limitation of counting rate imposed by spectroscopically thin alpha-sources on the one hand, and, on the other (b) the inherently more specific information obtainable from alpha-spectrometric than from gamma-spectrometric techniques insofar as the upper members of the natural radioactive series are concerned. It is likely that both alpha- and gamma-counting techniques will continue to play a significant part in the investigation of samples from the natural radiation environment.

CONCLUSION.

The techniques described and the results obtained would appear to be of some utility and interest to research workers in various fields who are concerned with problems associated with the radioactivity in naturally occurring samples. Various projects for future research have been suggested in the preceding chapters and in the appendices. Those which seem to the author to be of particular interest can be summarized thus:

Techniques:

(a) It would appear to be highly desirable that the problem of alpha-particle ranges in solids be systematically investigated with alpha-particles of energies between 3 and 9 M.E.V. and absorbers of various compositions. The successful conclusion of such an investigation could result in the alpha-counting technique being established as an absolute standard for determinations of uranium and thorium in geochemical studies.

(b) The use of CsI(Tl) and CsS phosphors coupled to red-sensitive tri-alkali photomultiplier tubes should be looked into more thoroughly. Although they cannot, intrinsically, hope to compete resolution-wise with ion-chambers (and still less with

semi-conductor detectors) they might provide a convenient, economical alpha-spectrometric set-up of considerable utility in natural radiation environment investigations.

(c) The development of large-area semi-conductor detectors will be watched with interest.

(d) A theoretical study of the optimum crystal size and the optimum gamma-ray energy to be used in gamma-spectrometric studies of weakly radioactive natural samples of various shapes (e.g. point or disc sources) and sizes would be most welcome.

Results:

(a) Suggestions are made at the end of Appendix 5 for further investigations into the plankton problem. It is considered that these could yield results of substantial oceanographic (and perhaps even biological) importance.

(b) Further alpha-spectrometric studies of a variety of geological samples would appear to offer exciting possibilities. The origin of the alpha-particle of 4.4 M.E.V. energy in Appendix 7 remains indefinite, and this problem must be solved. An investigation into the alpha-spectra of materials such as thorium-rich granites and ocean sediments should be given high priority.

REFERENCES.

1. Rutherford, E., Chadwick, J. and Ellis, C.D., in "Radiations from Radioactive Substances", Cambridge University Press (1930).
2. Evans, R.D., Kip, A.F. and Moberg, E.G., American J. of Science, (5) 36, 241 (1938)
3. Evans, R.D. and Goodman, C., Geol. Soc. Amer. Bull., 52, 459, (1941).
4. Anderson, E.C., and Hayes, F.N., Ann. Rev. Nuclear Sci., 6, 303 (1956).
5. Anderson, E.C., and Libby, W.F., Advances in Biol. and Med. Phys. 5, 385 (1957).
6. Eisenbud, M. "Environmental Radioactivity", McGraw-Hill (1963).
7. Watt, D.E. and Ramsden, D., "High Sensitivity Counting Techniques", Pergamon Press (1964).
8. Proceedings of the International Symposium on Natural Radiation Environment, Houston, Texas, 1963. (In press, University of Chicago Press.)
9. Turner, R.C., Radley, J.M. and Mayneord, W.V., Brit. J. of Radiology, XXXI, 397 (1958).
10. Mayneord, W.V., Radley, J.M. and Turner, R.C., Second U.N. Conference on the Peaceful Uses of Atomic Energy, Paper 15/P/41 (1958).

11. Turner, R.C., Radley, J.M. and Mayneord, W.V., *Health Physics*, 1, 268 (1958).
12. Turner, R.C., Radley, J.M. and Mayneord, W.V., *Nature*, 189, 348 (1961).
13. Finney, G.D. and Evans, R.D., *Phys. Rev.* 48, 503 (1935).
14. Evans, R.D. and Goodman, C., *Phys. Rev.* 65, 216 (1944).
15. Nogami, N.H. and Hurley, P.M., *Trans. Amer. Geophys. Union* 29, 335 (1948).
16. Kulp, J.L., Holland, H.D. and Volchok, H.L., *Trans. Amer. Geophys. Union* 33, 101 (1952).
17. Keevil, N.B. and Grasham, W.E., *Canadian J. of Research*, 21A, 21 (1943).
18. Evans, R.D., "The Atomic Nucleus", McGraw-Hill, (1955).
19. Keevil, N.B., Keevil, A.R., Ingham, W.N. and Crombie, G.P., *Am. J. of Sci.*, 241, 345 (1943).
20. Adams, J.A.S., Richardson, J.E. and Templeton, C.C., *Geochim. et Cosmochim. Acta*, 13, 270 (1958).
21. McDaniel, E.W., Schaefer, H.G. and Colehow, J.K., *Rev. Sci. Instr.* 27, 864 (1956).
22. Kiefer, H. and Maushart, R., *Nucleonics*, 19, 12, 51 (1961).
23. Curran, S.C., in *Beta and Gamma-Ray Spectroscopy*, ed. K. Siegbahn, North Holland (1955).

24. Reed, C.W., *Nucleonics*, 7, 6, 56 (1950).
25. Pagano, R., Damerelli, C.J.S. and Cherry, R.D., *Rev. Sci. Instr.*, 33, 955 (1962).
26. Hurley, P.M. and Shorey, R.R., *Trans. Amer. Geophys. Union*, 33, 722 (1952).
27. Hirschberg, D., *Nuovo Cimento* (9) 12, 733 (1954).
28. Hirschberg, D., *Nuovo Cimento* (10) 1, 341 (1955).
29. Cherry, R.D., *Geochim. et Cosmochim. Acta*, 27, 183 (1963).
30. Turner, R.C., Radley, J.M. and Mayneord, W.V., *Nature*, 181, 518 (1958).
31. Turner, R.C. and Radley, J.M., *The Lancet*, May 28, 1197 (1960).
32. Mayneord, W.V., *Clinical Radiology* XI, (1) 2 (1960).
33. Mayneord, W.V., Turner, R.C. and Radley, J.M., *Nature*, 187, 208 (1960).
34. Marsden, E., *Nature*, 187, 192 (1960).
35. Marsden, E., in reference 8.
36. Beharrel, J., *Trans. Amer. Geophys. Union* 30, 333 (1949).
37. Yagoda, H., *Radioactive Measurements with Nuclear Emulsions*, John Wiley and Sons (1949).
38. Whaling, W., *The Energy Loss of Charged Particles in Matter*, Handbuch der Physik, Volume XXXIV, Springer Verlag. (1957).
39. Garin, A. and Faraggi, H., *Le Journal de Physique et le Radium*, 19, 76 (1958).

40. Kamke, D. and Kramer, P., Zeit. Physik, 168, 465 (1962).
41. Osborne, R.V., Ph.D. Thesis, London University (1962).
42. Hurley, P.M., Geol. Soc. Am. Bulletin, 61, 1 (1950).
43. Turner, R.C., Radley, J.M. and Mayneord, W.V., Nature, 189, 348 (1961).
44. Korkisch, J. and Janauer, G.E., Talanta, 9, 957, (1962).
45. Choppin, G.R. and Sikkeland, T., Procedure 19 in NAS- NS 3004, "The Radiochemistry of Thorium".
46. Rosholt, J.N., Anal. Chem. 29, 1398 (1957).
47. Morken, D.A., Health Physics, 2, 77 (1959).
48. Lucas, H.F., Rev. Sci. Instr., 28, 680 (1957).
49. Giffin, C., Kaufman, A. and Broecker, W., J. Geophysical Research, 68 (6), 1749, (1963).
50. Bearden, J.A., Rev. Sci. Instr., 4, 271, (1933).
51. Adams, J.A.S. and Richardson, K.A., Economic Geology, 55, 1060 (1960).
52. Hill, C.R., Nuclear Instruments and Methods, 12, 299 (1961).
53. Garwood, F., Biometrika, 28, 437 (1936).
54. Jaffey, A.H., Nucleonics, 18, No. 11, 180 (1960).
55. Freedman, A.J. and Anderson, E.C., Nucleonics, 10, No. 8, 57 (1952).
56. Adams, N.J., Phys. Rev., 44, 651 (1933).

57. Huybrechts, M., *Nuovo Cimento* (10) 6, 811 (1957).
58. Lucas, H.F. and Woodward, D.A., Argonne National Laboratory Report ANL-6646, page 78 (1962).
59. Yaffe, L., *Ann. Rev. of Nuc. Science*, Vol. 12, 153 (1962).
60. Korolev, G.A. and Kocharov, G.E., *Instruments and Experimental Techniques*, No. 5, 702 (1958).
61. Kocharov, G.E. and Korolev, G.A., English Translation of the Bulletin of the Academy of Sciences of the U.S.S.R., Physical Series, 25, 227 (1961).
62. Bjornholm, S. and Lederer, C.M., *Nucl. Instr. and Methods*, 15, 233 (1962).
63. Wilkinson, D.H., "Ionization Chambers and Counters", Cambridge U.P. (1950).
64. Rossi, B.B. and Staub, H.H., *Ionization Chambers and Counters*, McGraw-Hill, (1949).
65. Herwig, L., Miller, G. and Utterbach, N., *Rev. Sci. Instr.*, 26, 929 (1955).
66. Cranshaw, T.E. and Harvey, J.A., *Canad. J. of Research*, 26A, 243 (1948).
67. Buneman, O., Cranshaw, T.E. and Harvey, J.A., *Canad. J. of Research*, 27A, 191 (1949).
68. Harvey, B.G., Jackson, H.G., Eastwood, T.A. and Hanna, G.C., *Canad. J. of Physics*, 35, 258 (1957).

69. Ray, E.L. and Hammond, S.E., *Health Physics*, 5, 50 (1961).
70. Goldberg, E.D. and Kolde, H., *Geochim. et Cosmochim. Acta*, 26, 417 (1962).
71. Doke, T., *Canad. J. of Physics*, 40, 607 (1962).
72. Lonati, R.D., Facchini, U., Iori, I., Houtermans, F.G. and Tongiorgi, E., *Nuovo Cimento* (10) 7, 133 (1958).
73. Lonati, R.D. and Tonolini, F., *Energia Nucleare*, 7, 107 (1960).
74. Nurmi, M., *Nuclear Electronics*, I. 297 (I.A.E.A., Vienna, 1962).
75. Macfarlane, R.D. and Kohman, T.P., *Phys. Rev.*, 121, 1758 (1961).
76. Hill, C.R., *Nature*, 187, 211 (1960).
77. Hill, C.R., *Health Physics*, 8, 17 (1962).
78. Mayneord, W.V. and Hill, C.R., *Nature*, 184, 667 (1959).
79. Hill, C.R. and Jaworowski, Z.S., *Nature*, 190, 353 (1961).
80. Hanna, G.C., in *Experimental Nuclear Physics*, Vol. 3, ed. E. Segre, John Wiley and Sons (1959).
81. Strominger, D., Hollander, J.M. and Seaborg, G.T., *Rev. Mod. Phys.*, 30, 585 (1958).
82. Lonati, R.D., *Energia Nucleare*, 8, 217 (1961).
83. Facchini, U., Forte, M., Malvicini, A. and Rossini, T., *Nucleonics* 14, No. 9, 126 (1956).
84. Baranov, S.A. and Zalenkov, A.G., *Instruments and Experimental Techniques*, No. 5, 695 (1959).

85. Forte, M., *Nuovo Cimento* (10) 3, 1443 (1956).
86. Seliger, H.H., *Intern. J. Appl. Radiation and Isotopes*, 8, 29 (1960).
87. Sayres, A. and Wu, C.S., *Rev. Sci. Instr.*, 28, 758 (1957).
88. Broser, I. and Kaliman, H., *Nature*, 163, 20 (1949).
89. Martinez, P. and Senftle, P.E., *Rev. Sci. Instr.*, 31, 974 (1960).
90. Fleury, J., Perin, P., Boge, M. and Laugier, J., *Le Journal de Physique et le Radium*, 21, 480 (1960).
91. Gale, H.J., *Physics in Medicine and Biology*, 6, 577 (1962).
92. Belyaev, L.M., Gil'varg, A.B. and Panova, V.P., *Soviet Physics - Crystallography*, 6, 108 (1961).
93. Murray, R.B., in "Nuclear Instruments and Their Uses" Vol. I. p. 102, ed. A.H. Snell, John Wiley and Sons (1962).
94. Aronsson, G., *Trans. Royal Inst. of Techn., Stockholm*, No. 176 (1961).
95. Blankenship, J.L. and Borkowski, C.J., *I.R.E. Trans. on Nuclear Science*, NS-8, 17 (1961).
96. Chetham-Strode, A., Tarrant, J.R. and Silva, R.J., *I.R.E. Trans. on Nuclear Science*, NS-8, 59 (1961).
97. Miller, G.L., Gibson, W.M. and Donovan, P.F., *Ann. Rev. of Nuclear Science*, 12, 189 (1962).
98. Porschen, W. and Riezler, W., *Z. Naturforsch*, 11A, 143 (1956).

99. Picciotto, E. and Wilgain, S., *Nature*, 173, 632 (1954)
100. Geiger, E.L., Tschaeche, A.H. and Whittaker, E.L., *Health Physics*, 4, 302 (1961).
101. Graeffe, G. and Nurmi, M., *Annales Acad. Scient. Fennicae, A*, VI, No. 77 (1961).
102. Stephenson, G.J., Evans, R.D. and Kraner, H.W., in M.I.T. Radioactivity Center Progress Report, p.55, May 1962.
103. Abrosimov, N.K. and Kocharov, G.E., *Bull. Acad. Sci. U.S.S.R., Physical Series*, 26, 235 (1962).
104. Chase, R.L., "Nuclear Pulse Spectrometry", McGraw-Hill (1961).
105. Bell, P.R., in "Beta- and Gamma-Ray Spectroscopy", ed. K. Siegbahn, North Holland (1953).
106. Mott, W.E. and Sutton, R.B., in "Handbuch der Physik, Band XLV," Springer Verlag (1958).
107. Crouthamel, C.E., "Applied Gamma-Ray Spectrometry", Pergamon Press (1960).
108. Hurley, P.M., *Bull. Geol. Soc. Amer.*, 67, pp. 395 and 405 (1956).
109. Schroeder, B.W. and Cherry, R.D., *Nature*, 194, 669 (1962).
110. Parker, R.P., *Physics in Medicine and Biology*, 7, 301, (1962).
111. Marinelli, L.D., Miller, C.E., May, H.A. and Rose, J.E., *Advances in Biol. and Med. Phys.*, 8, 81, (1962).

112. May, H.A. and Marinelli, L.D., Paper 25 in "Proceedings of the Total Absorption Gamma-Ray Spectrometry Symposium". United States Atomic Energy Commission TID-7594 (1960).

APPENDIX 1: THE DETERMINATION OF THORIUM AND
URANIUM IN GEOLOGICAL SAMPLES BY AN
ALPHA-COUNTING TECHNIQUE.

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LOW-LEVEL ALPHA AND GAMMA RADIOACTIVITY

IN SOME NATURALLY OCCURRING SAMPLES.

by

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the University of Cape Town, April 1964.

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SUMMARY

This thesis discusses low-level alpha and gamma-detection techniques and their application to the determination of small quantities of radioactivity in some naturally-occurring samples. The main emphasis is placed on alpha-radioactivity, and the techniques of low-level alpha-particle detection and alpha-spectroscopy are reviewed. Certain aspects of gamma-spectroscopy are then discussed briefly.

The specific contributions of the candidate are listed separately in Appendices. They cover

- (a) the principles of alpha-counting plus "thorium-pairs" detection as a means of determining thorium and uranium in geological samples which are in radioactive equilibrium, a simple technique for reducing photomultiplier noise, and the theory of alpha-emission from sources containing inhomogeneously distributed radioactivity
- (b) the results of "total" alpha counting techniques applied to australites and to plankton
- (c) the results of two alpha-spectroscopic methods applied to whole rock granites and to granite minerals respectively

and, finally

(d) the results of uranium, thorium and potassium determinations in tektites using non-destructive gamma-spectrometry.

CERTIFICATION BY SUPERVISORS

In terms of regulation 7 of the "Regulations for the Degree of Ph.D." we, as supervisors of the candidate R. D. Cherry, certify that we approve of the inclusion in this thesis of material which has either been published or submitted for publication.

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INTRODUCTION

In the present work we shall be concerned with certain of the techniques and results of low-level radioactivity measurements as applied to naturally occurring samples. The fact that minute quantities of radioactive substances are found in most materials which form part of Man's "environment" has been known for a considerable time. Thus the well-known text of Rutherford, Chadwick and Ellis¹ contains a section (paragraph 114 in the 1930 edition) entitled "The apparent radioactivity of ordinary matter". In this they discuss various results obtained between 1900 and 1927, and comment that "since the radioactive elements are widely disseminated throughout the surface of the earth, it is to be expected that traces of active matter would be separated with all metals". They go further, and quote in footnotes values for the radium content of the earth's crust and of sea-water. In the period 1930 to 1945 this information was put on a firm footing, particularly as a result of the efforts of Evans and his co-workers (see, for example, Evans et al.² and Evans and Goodman³) in the geological, oceanographic and radiological fields.

It is, however, since 1945 - and more particularly since 1955 - that the subject has really developed. This has been

due partly to the increasing sensitivity of the available detection techniques, but it has in the main resulted from an increasing awareness of the possible hazards associated with the inhalation or ingestion of relatively small quantities of radioactivity and of the genetic defects which can be associated with low levels of radiation exposure. The addition of artificial radioactive contaminants to the already existing "natural radiation environment" has highlighted the serious lack of detailed knowledge of the latter, and has stimulated governmental and international organisations to support further research. Review articles such as those of Anderson and ⁴ Hayes and Anderson and Libby ⁵ began to appear about eight years ago. The field is now a lively one, and the past eighteen months alone have witnessed the publication of a book on ⁶ "Environmental Radioactivity", another one on "High Sensitivity Counting Techniques" ⁷ and the holding of an "International Natural Radiation Environment Symposium" ⁸.

A particularly pleasing feature of this activity is that it has attracted the interest of research workers in diverse fields. Since naturally-occurring radioactivity is so widespread, it is a subject of either direct or potential interest to biological, medical and earth scientists as well as to the physicists and/or chemists who are, in the first place, concerned

with the detection and measurement techniques. Thus the techniques described in the present work can be and have been applied to samples and problems from all of the above fields. More specifically, it is hoped that the particular results presented here will be of interest to geochemists, geophysicists and oceanographers as well as to radiation-detection physicists.

In this field it is convenient to classify radiation measurements according to whether they are applied to the categories of alpha, beta or gamma activity. Low-level radioactivity is associated in the minds of many scientists with low-level beta counting. This probably results from the general importance of the low-energy beta emitters tritium and carbon-14, and it is understandable but unjustified. To the physicist alpha- and gamma- radioactivity measurements are in fact usually more appealing, for the simple reason that the alpha- particles and gamma-rays emitted by radioactive nuclei possess definite energies whereas the beta-particles do not. Identification of a nucleus by means of energy measurements is in consequence much more clear-cut for alpha and/or gamma-emitters, and it is in fact usually impossible for very weakly radioactive beta sources to be identified in this way unless prior chemical treatment is undertaken.

This dissertation is concerned largely with low-level alpha-particle detection techniques and some results obtained by the use thereof. Although the pioneer work of Evans and others mentioned above concerned alpha-particles, this field appears to have been surprisingly neglected until the recent resurgence in which the activities of Mayneord and his group at the Royal Cancer Hospital, London have played a large part. (See for example, references 9, 10, 11, 12 and others.) Chapter 1 discusses "total" alpha-counting techniques, where no energy determinations are involved. The practice followed in this dissertation is to review the techniques in the main "Chapters", and to present the more specific contributions in the form of Appendices, most of which have either been published or submitted for publication in the standard journals. On this basis, Appendices 1, 2 and 3 comprise contributions to the general technique of "total" alpha-counting, while Appendices 4 and 5 deal with the application of this technique to tektites and plankton respectively. Chapter 2 reviews alpha-spectroscopic techniques, and Appendices 6 and 7 present the results of the applications of such techniques to a whole-rock sample of granite and to a mineral from a granite sample respectively. Chapters 1 and 2 are in fact a slightly revised version of a review paper (at present in press) delivered by the candidate to the International Natural Radiation Environment Symposium

in Houston in 1963 . Gamma-spectrometric techniques are well-known, and form a minor portion of this work. They are very briefly discussed in Chapter 3, where some emphasis is placed on the relative advantages of alpha-counting and gamma-spectrometric techniques as applied to low-level samples. Appendix 8 describes the results of gamma-spectrometric measurements applied to the non-destructive determination of uranium, thorium, and potassium in tektites. In the conclusion some suggestions are made for possible future experiments.

References to the Introduction, to Chapters 1, 2, and 3, and to the Conclusion are given after the Conclusion and before the Appendices. Each Appendix contains its own references, and the frontispiece to each Appendix acknowledges contributions made by other workers. It is perhaps worth stating that the actual writing of the basic manuscript was undertaken by the present candidate for each and every one of the Appendices included.

CHAPTER 1"TOTAL" ALPHA-COUNTING TECHNIQUES.

The use of alpha-particle detection techniques in studies of the natural radiation environment has tended to be a relatively neglected field. In the last five years, however, as a result of the refinement of these techniques and their application by a small number of research groups, attention has been focused on the following simple facts:

(a) Most naturally occurring radioactive elements are alpha-emitters.

(b) Although the short range of naturally occurring alpha-particles results in their being of small consequence as external radiation sources, the presence of alpha-emitters inside the human body is a feature of considerable importance.

(c) Alpha-emitting nuclei are frequently gamma-emitters also. Thus identification and measurement of the concentration of a particular alpha-emitter in a sample from the natural environment often enables information concerning the concentration of associated gamma-emitting nuclei to be deduced.

(d) Alpha-particle detection techniques possess certain definite advantages compared with comparable beta and gamma measurements. In particular, low background counting rates

(and hence increased sensitivity) are a feature of alpha-detectors while alpha-spectroscopic techniques are characterized by the lack of ambiguity in and the ease of the interpretation. Even the main disadvantage of alpha-detectors -- viz. the inherent limitation of sample volume due to the short range of the alpha particles -- falls away in cases where only a small amount of sample is available.

"TOTAL" ALPHA COUNTING.

(a) Theory.

The basic theory of alpha-particle emission from samples is well-known for the case where the alpha-emitters are homogeneously distributed throughout the sample. This case has been discussed by a number of authors; probably the best reference is still the early paper of Finney and Evans ¹³.

Other useful treatments have been given by Evans and Goodman, ¹⁴ Nogami and Hurley, ¹⁵ Kulp et al., ¹⁶ Turner et al., ⁹ and Keevil ¹⁷ and Grasham. The theory can be subdivided into two classes, viz. "thick" and "thin" sources, "thick" sources being those whose thickness is greater than the maximum range of the alpha particles emitted by the sample. This range is typically about 25 to 30 microns in solid materials, and is seldom greater than 90 microns; the volume of the sample which contributes

to the alpha-particle emission from the front face is thus very definitely limited.

The basic equation of thick-source alpha counting is

$$N_0 = \frac{NRA}{4} \quad (1)$$

where N_0 is the number of alpha particles emerging from an area A of the sample in unit time, N is the number of alpha-disintegrations per unit volume of sample per unit time and R is the range in the sample of the alpha particles concerned. N_0 is of course a measure of the counting rate; for 100 per cent efficient detection N_0 is the counting rate. N and R are usually variables beyond the control of the experimenter (although N can sometimes be artificially enhanced by concentration techniques), and one must therefore use a sample and detector of large area if maximum count rates are to be obtained.

For thin sources, of thickness t , the basic equation is:

$$N_0 = \frac{NRA}{4} \left[\frac{2t}{R} - \left(\frac{t}{R} \right)^2 \right] \quad (2)$$

The counting rate from a thin source is thus lower (since t is by definition less than R), and it is moreover necessary that t be known. In addition, uniform thin sources are considerably

more difficult to prepare than thick sources. Thin-source counting does nonetheless possess one important advantage; inspection of (2) shows that, in the first order, N_0 is independent of the range R . A less precise knowledge of R is thus required for the determination of N than is the case with thick-source counting, and the discussion of the range problem which is given below shows that this is by no means a trivial point. The extra effort involved in thin-source preparation might be worthwhile on this account, particularly if the quantitative precision of the results is of importance.

Both equations (1) and (2) must be modified to allow for (i) absorbers between the sample and the detector, (ii) the fact that alpha-particles below a certain minimum residual range might not give rise to a response in the detector and (iii) the fact that natural samples usually contain mixtures of alpha-emitters, thus necessitating summations over different N and R . With modern experimental techniques (see below) modifications (i) and (ii) are usually negligible; (iii) is, on the other hand, often necessary, and is a complicating feature. Since most of the naturally-occurring alpha-emitters are members of one of the three well-known natural radioactive series (see, e.g. Evans¹⁸, Chap. 16) questions of radioactive

equilibrium arise, and some assumption concerning the degree of secular equilibrium attained by the sample is necessary.

The favorite assumption is that secular equilibrium is complete, and the references quoted above (Finney and Evans¹³

1935; Evans and Goodman¹⁴; Nogami and Hurley¹⁵; Kulp et al.¹⁶

and Turner et al.⁹ all discuss this case in more or less detail.)

(b) Experimental Techniques.

In the early work (Finney and Evans; Evans and Goodman; Keevil et al.¹⁹) ion-chambers were used. Subsequently the proportional counter became popular, and analyses of natural

samples utilizing commercial proportional counting apparatus have been described by Adams et al.²⁰ and others. A flow type proportional counter designed specifically for measuring low-level alpha activity in biological materials has been described

by McDaniel et al.²¹ This utilizes rectangular, screen-wall counters accommodating sources up to 141 cm.² in area, with

background counting rates of 3.8 counts/hour. More recently

Kiefer and Maushart²² have discussed proportional flow counters of area up to 700 cm.² with backgrounds in the alpha pulse-height region of about .5 counts per hour per cm.² Mention should also

be made of the high quality proportional counters developed by the Glasgow group (Curran²³); although these have been applied

primarily to problems of low-energy beta-spectroscopy, they

could no doubt be utilized as alpha-detectors to good effect.

Proportional counters are still in use in a number of laboratories, and do possess certain advantages -- these have been enumerated by Kiefer and Maushart.²² The scintillation counter with an activated zinc sulphide phosphor would, however, appear to be the best general purpose low-level alpha detection instrument available today. Early examples of such apparatus were those of Reed²⁴ and Kulp et al.,¹⁶ but the most effective system is undoubtedly that devised by the group at the Royal Cancer Hospital (Turner et al.;⁹ Mayneord et al.¹⁰) This system is discussed in the references cited and will not be described in detail here. It will suffice to say that it provides a simple, economical, sealed sample-phosphor system of great sensitivity and convenience. No emanation problems (such as are encountered with flow-type proportional counters) arise; in fact, measurement of the counting rate of the sealed system as a function of time allows sample disequilibria to be studied effectively. Sample areas are limited by the size of the photomultiplier tube; areas of just under 100 cm.² (a 4½" photocathode) are commonplace. With reasonable care (good quality zinc sulphide, selected photomultiplier tubes and low cathode-to-first dynode voltages (Appendix 2 of this thesis and

Pagano et al.²⁵) background count rates of less than .01 counts per cm.² per hour are obtainable. For a phosphor area of about 100 cm.², these rates correspond to activities of a few hundredths of a micro-micro curie per gram in a typical thick source solid sample, or, in geochemical terms, to the activity of a typical rock sample containing twenty-five parts per thousand million of thorium and eight parts per thousand million of uranium. The sensitivity of the method is thus apparent although it must of course be borne in mind that extremely long counting times are necessary if the ultimate in sensitivity is to be attained. The associated electronics is, however, simple, and long-term stability is not a major problem.

(c) The Pairs Technique.

The parameter obtained from a "total" alpha counting experiment is essentially the specific alpha activity, N , of the sample. It is often desirable to obtain further information as to the alpha-emitting nuclides present, and it is possible to do this to a limited extent without recourse to alpha-spectroscopy by making use of the so-called "pairs" technique. This utilizes the fact that in two of the three natural radioactive series pairs of successive alpha particles are emitted within short intervals of time. These are due to the short-lived

alpha-emitters polonium-216 ($T_{1/2} = .158$ seconds) in the thorium series and polonium-215 ($T_{1/2} = .0018$ seconds) in the actinium series. Time analysis of the pulses from the alpha counter -- easily accomplished by simple paralysis circuits -- permits the separation of pulse-pairs due to these particular alpha-emitters; suitable equilibrium assumptions then enable the relative contributions of the three series to be assessed.

This method appears to have been suggested first by Hurley and Shorey²⁶, and later by Hirschberg^{27, 28}; it was the paper by Turner et al.⁹ which first described its successful application in any detail. Subsequently its application to the case of thorium and uranium determinations in geological samples has been discussed by the present writer (Appendix 1; Cherry²⁹). The pairs technique combined with the zinc sulphide scintillation counter previously discussed has already resulted in the accumulation of a vast amount of data concerning the alpha-activities of natural samples (Turner et al.^{9, 12, 30}; Turner³¹ and Radley³²; Mayneord³³; Mayneord et al.^{34, 35}; Marsden³⁶ and Cherry (see Appendix 4)) and its use is to be commended to workers in this field.

(d) The Range Problem.

From equations (1) and (2) it is obvious that a knowledge of the range, R , of the alpha-particle in the sample, is essential if a quantitative result is required. It is customary

to use some empirical formula for calculating alpha-particle ranges. The geological workers (Finney and Evans¹³; Evans and Goodman¹⁴; Nogami and Hurley¹⁵; Kulp et al.¹⁶) tend to favour the Bragg-Kleeman relation, which gives:

$$R\rho = .32(10^{-3}) \frac{11}{W^{\frac{1}{2}} R_a} \text{ gm/cm}^2 \quad (3)$$

ρ is the sample density, $W^{\frac{1}{2}}$ is the square root of the atomic weight calculated on the "atomic fraction" basis (Nogami and Hurley¹⁵) and R_a is the range in cm. in air of an alpha particle of the same energy. Turner et al.⁹, on the other hand, replace $W^{\frac{1}{2}}$ by $Z^{2/3}$, where Z is the atomic number. For many common natural materials (both geological and biological) we have $W^{\frac{1}{2}} \sim Z^{2/3} \sim 4.6$, and the two expressions give very similar results.

The question of the accuracy of these expressions is of major importance. Nogami and Hurley¹⁵ claimed that the Bragg-Kleeman relation is accurate to within 5 per cent. Beharrel³⁶ disputes this, and claims that the Bragg-Kleeman law gives ranges which are about 10 per cent too low. Yagoda³⁷ finds the reverse, and says that the computed ranges are 10 per cent too high. A recent review article by Whaling³⁸ presents the ranges of alpha-particles of various energies in twelve gaseous

and seven solid materials (all metallic). The ranges in gases agree fairly well with the Bragg-Kleeman law, but those in solids are definitely higher than those given by equation (3) in the low atomic weight range ($W^{\frac{1}{2}} = 5.0$ and less) which is applicable to most naturally-occurring samples. Thus if one draws smooth curves through Whaling's points, one finds that for $W^{\frac{1}{2}} = 4.6$ (which is generally equivalent to $Z^{2/3} = 4.6$) equation (3) gives ranges which are approximately 6 per cent, 13 per cent and 25 per cent too low for alpha-particles of energies 8, 6 and 4 M.E.V. respectively. Whaling's values were based on experimental data available to him at the time (1958), and it is instructive to consider experimental data (unfortunately very meagre) which has been published since the. Thus Garin and Faraggi³⁹ determined the ranges of 4.5 M.E.V. alphas in uranium, gold, zirconium and silicon. For these four elements they obtained ranges that were, respectively, 32 per cent, 28 per cent, 22 per cent, and 4 per cent higher than those given by the Bragg-Kleeman equation. Replacement of $W^{\frac{1}{2}}$ by $Z^{2/3}$ results in a considerable improvement; there is agreement with the Garin-Faraggi data to within 5 per cent for all four elements.

⁴⁰ Kamke and Kramer have determined alpha-ranges in boron; in the region of 4.5 M.E.V. their results are about 13 per cent higher than given by the Bragg-Kleeman equation and 23 per cent

higher than the same equation with $Z^{2/3}$ substituted for $W^{1/2}$. Finally, calibrations using the thorium series in equilibrium in thorium oxide (See Appendix 1) indicate that equation (3) gives results which are 25 per cent low; $Z^{2/3}$ instead of $W^{1/2}$ gives results which are only 5 per cent low.

The whole subject of alpha-particle ranges in solids is thus obviously in a state of some confusion, and is in need of serious attention. A systematic study of alpha ranges as a function of particle energy and atomic weight would be most valuable, and would help establish total alpha-counting as a reliable absolute method of measurement. Meanwhile, it would appear that the following very tentative conclusions can be drawn: (i) The Bragg-Kleeman equation (3) would appear to give ranges which are somewhere between 5 per cent and 30 per cent too low. (ii) Replacement of $W^{1/2}$ in equation (3) by $Z^{2/3}$ results in considerable improvement in the upper half of the periodic table, but makes matters worse for the lightest elements. (Unpublished data by Osborne⁴¹, would appear to substantiate this latter conclusion).

(e) The Homogeneity Problem.

Derivation of equations (1) and (2) is based essentially on the assumption that the alpha-activity is distributed homo-

geneously throughout the sample. For many natural samples this is not the case, and homogenization is necessary -- this is a problem of which the geologists are particularly aware (Kulp¹⁶ et al.⁴²; Hurley .) Grinding of the sample down to grain sizes very much less than the smallest alpha-range encountered (in practice this requires grinding to micron size or less) and following this by thorough homogenization will of course take care of this problem, but it seemed desirable that the theoretical aspects be systematically investigated. This problem is investigated in Appendix 3. Three different types of inhomogeneity have been assumed, viz., surface coatings, core concentrations and "hot-spot" activity, and it is concluded that:

(i) That grinding down to at least one-tenth of the alpha-particle range is necessary to ensure the accuracy of formula (1) and

(ii) The "pairs" count rate (see (c) above) is generally more sensitive to inhomogeneities in the radioactivity distribution than is the "total" alpha count rate.

(f) Concentration of the Activity.

As has been mentioned above, alpha-counting techniques are so sensitive that they can frequently be used without any

previous treatment of the sample concerned. Some environmental samples are, however, so low in radioactivity that some form of concentration is essential. Thus Turner ⁹et al. ashed food-stuffs prior to counting, and boiled drinking water (Turner ⁴³et al.) to dryness before counting the residue. Chemical extraction is of course also feasible in most cases, although it does introduce an additional element of uncertainty and should be avoided where possible. In this connection it is perhaps worthwhile to emphasize the utility of modern ion-exchange techniques; two useful references which discuss the methods for extracting the trans-lead alpha-emitters are those of Korkisch and Janauer ⁴⁴ and Choppin and Sikkeland ⁴⁵.

An intriguing and simple method of extracting the heavy ⁴⁶elements from aqueous solution has been mentioned by Rosholt and Morken ⁴⁷. Zinc sulphide scintillation phosphor powder is simply added to vials containing the solution to be investigated, the vial is shaken vigorously and the powder allowed to settle. The zinc sulphide apparently adsorbs some (or all) of the heavy-element alpha-emitters, and the scintillations emitted by the powder can be counted directly with a photomultiplier tube. Morken obtained over 95 per cent extraction for both polonium and plutonium under the right condi-

tions of pH, and considered that "An adsorption mechanism is indicated, in which case the extent of removal is probably independent of the element used". Turner et al.⁴³ have used this technique effectively to determine radon in water, and further investigations would be of great interest.

(g) Gaseous samples.

The above treatment has tacitly assumed that the sample materials are solids or liquids. Gaseous samples will of course require special techniques of counter design, but the basic detection principles remain the same. Two selected references to zinc sulphide type scintillation detectors for gaseous samples will serve as examples. Lucas⁴⁸ has described a radon counter, while Giffin et al.⁴⁹ have applied the pairs technique to the case where a gas is used in the detector chamber.

(h) Autoradiographic techniques.

These have been discussed by Yagoda³⁷ and their application to naturally occurring materials has been discussed by Ragland, (in reference 8). They are listed here merely for the sake of completeness. As total alpha counters they compare unfavourably with the techniques discussed above; as a tool

for the identification and study of microsites of radioactivity they are valuable and powerful.

In conclusion, two matters of general importance in low-level alpha-counting techniques (both "total" and alpha-spectroscopic) should be mentioned. These are

(1) The Natural Alpha-Activity of Materials:

In the construction of alpha-detectors it is important to ensure that the surfaces exposed inside the detector possess a low natural alpha-emission rate and a low emanating power (Hill, Osborne and Mayneord, in ref. 8). Data for alpha emission rates from various materials have been published by several authors (McDaniel ²¹ et al. ; Bearden ⁵⁰ ; Adams and Richardson ⁵¹ .) Features worth noting are the high levels of emission from solder (Bearden ⁵⁰) (2800 alphas per 100 sq. cm. per hour) and the extremely low level of emission from aluminized cellulose acetate (Hill ⁵²) (about .3 alphas per 100 sq. cm. per hour). In general, materials should be checked on a total alpha-counter before they are built into a low-level alpha detector.

(11) Counting Statistics:

Counting at low levels of radioactivity requires that particular attention be paid to problems of counting statistics.

A simple matter, not often discussed, is the fact that for a low number of total counts the usual assumption that the Poisson distribution is equivalent to the normal distribution is invalid. Confidence limits based on the Poisson distribution itself must be used, and these have been given by Garwood⁵³. The question of optimization of source-background ratios has been discussed by several authors (e.g. Jaffey⁵⁴, Freedman and Anderson⁵⁵) and this leads to the generally accepted (source count rate)²/background figure of merit mentioned in the next chapter.

A final problem which arises when counting members of the naturally occurring radioactive series is the question of the statistical distribution of counts from a sample containing both parent and daughter activities. The pioneer work concerning this complex question appears to have been that of Adams⁵⁶; more recent and more complete treatments are given by Huybrechts⁵⁷, who applies his results to specific cases (the uranium and thorium families in equilibrium) for a specific time interval (thirty days), and by Lucas and Woodward⁵⁸, who consider particularly problems associated with radium-224 and radon-222.

CHAPTER 2

ALPHA SPECTROSCOPIC TECHNIQUES.

The amount of information obtainable from "total" alpha counting, even when the "pairs" technique is used, is strictly limited, and it is very often desirable to obtain information concerning the relative contributions of the specific nuclides responsible for alpha-particle emission. In these cases recourse must be made to alpha-spectroscopic techniques -- these measure the energy of the alpha-particles and thus provide a means of identification of nuclear species. The power of the technique is of course matched by increased complexity, particularly insofar as the associated electronics is concerned -- a pulse height analyzer (preferably of the multi-channel variety) is an essential tool. The book by Chase¹⁰⁴ is an excellent introduction to the electronic problems of nuclear spectroscopy. Source preparation too is a considerably more critical matter -- sources must not only be "thin", they must be "spectroscopically thin", which is one or two orders of magnitude thinner (100 micrograms/cm² is a frequently quoted upper limit for an acceptable alpha-spectroscopic source). Source preparation, often a somewhat empirical art, has recently been reviewed by Yaffe⁵⁹, and special methods for the preparation of the large area sources

frequently needed in the alpha-spectroscopy of natural environmental samples have been given by Hill⁵² and Korolev and Kocharov^{60,61}. A recently described (Bjornholm and Lederer⁶²) cation-exchange foil technique is also worthy of special mention. We shall pass on to a brief survey of the detectors which can be used for low-level alpha spectroscopy.

(a) Ion-Chambers.

The ion-chamber is by far the most commonly used and most widely suitable tool for alpha-spectroscopic studies. The parallel plate, gridded pulse ionization chamber (Wilkinson⁶³; Rossi and Staub⁶⁴; Herwig et al.⁶⁵; Cranshaw and Harvey⁶⁶; Bunemann et al.⁶⁷ and Harvey et al.⁶⁸) is in turn the most popular type of chamber, and is commercially available. A typical chamber of this sort possesses a sample area of about 10 cm.² and a detection efficiency of about 45 per cent of 4π , and yields resolutions of about 60 K.E.V. for alphas of about 5 M.E.V. energy. Ray and Hammond⁶⁹ applied an instrument of this type to natural environmental samples without previous chemistry, and the work of Goldberg and Koide⁷⁰ on thorium isotopes in ocean sediments provides a good example of high class results obtained after chemical extraction. The big disadvantage of this type of chamber lies in its limited source area, and the quest for

greater sensitivity has led, in recent years, to the design of ion chambers capable of handling much larger sources. The properties of several of these are summarized in Table I. The resolution R is the usual full-width at half-maximum count rate; the background B is taken over this same spectral line width; an alpha energy of about 5 M.E.V. has been assumed. In general, the optimum figures quoted by the respective authors have been used; where no figures are quoted, the relevant parameters have been estimated from data given in the papers.

A study of Table I reveals the following essentials:

(1) Sensitivity: A suitable "figure of merit" for comparing the sensitivity of the ion-chambers listed would appear to be the quantity $\frac{(SE)^2}{B}$ where E is the (geometrical) counting efficiency expressed as a percentage of 4π . This figure takes into account the desirability of making the ratio (source count rate)²/background as high as possible in low-activity experiments (see Freedman and Anderson)⁵⁵, and seems to be more suitable than the figure $\frac{SE}{B}$ ⁷¹ used by Duke. Values of E are unfortunately not always quoted by the authors and thus the figure of merit cannot be calculated exactly. However the variation in E is not great (from about 20 to 50 per cent for all the chambers quoted) and useful comparisons can be made on

TABLE I

Comparison of various large area ion chambers.

Numbers quoted are approximate in many cases.

Author	Configura- tion	Grid	R(K.E.V.)	B(counts/ hr.)	$S(\text{cm})^2$	$\frac{S}{B} (10^{-6})$
Hill ⁵²	Cylindrical	No	110	4	15000	56
Hill and Osborne ⁸	Cylindrical	Yes	40	.3	1500	7.5
Kocharov & Korolev ⁶¹	Parallel plate	Yes	25	.03	200	1.3
Burmia ⁷⁴	Parallel plate	Yes	100	.03	300	3.0
Doke ⁷¹	Parallel plate	Yes (two)	70	.01	150	2.3
Macfarlane & Kohman ⁷⁵	Cylindrical	No	60*	.3*	1200	4.8
Lonati ⁷² <u>et al.</u> (I)	Parallel plate	Yes	300	1	110	.01
Lonati ⁷² <u>et al.</u> (II)	Cylindrical	Yes	300	35	2800	.2
Lonati and Tonolini ⁷³	Parallel plate	Yes	300	.18	110	.07

* Denotes an estimate at an alpha-energy of 2 M.E.V. instead of 5 M.E.V.

an approximate basis. It is easily seen that the ion-chamber⁵² of Hill⁵², which has an efficiency close to 50 per cent, possesses by far the largest figure of merit, a fact due almost entirely to its very large surface area. This chamber and the results obtained from it are discussed in the literature (Hill⁵² ; Hill^{76, 77} ; Mayneord and Hill⁷⁸ ; and Hill and Jaworowski⁷⁹). It is, however, worth pointing out that its high sensitivity is obtained without recourse to electric background reduction techniques (e.g. anticoincidence shielding as used by Macfarlane⁷⁵ and Kohman⁷⁵ or utilization of the grid pulses as used by Kocharov and Korolev⁶¹ and Duke⁷¹).

In appendix 6 granite spectra obtained with this chamber are presented; it is worth emphasizing that the high sensitivity of the chamber enabled these samples to be analyzed in toto and without any prior chemical treatment.

(ii) Resolution: A study of the energies of the alpha-particles emitted by the naturally occurring alpha-emitters⁸⁹ (see, for example, the article by Hanna⁸⁹ or the isotope table of Strominger et al.⁸¹) shows that in many cases two or more alpha "lines" will lie very close together. Thus the alpha-particles from the common isotopes uranium-238 and thorium-232 are separated in energy by about 200 K.E.V.; these alpha-groups

are just separated by a chamber of the Hill type, and sources containing both the species can accordingly be counted with fair accuracy without prior chemical treatment. Other cases are, however, not so favorable; a particularly important clash is between thorium-230, uranium-234 and radium-226, which have their main alpha groups at 4.68, 4.77 and 4.78 M.E.V. respectively. To separate these requires either prior chemical extraction or better resolution, and attention is drawn to the excellent resolving power of the instrument of Kocharov and Kerolev⁶⁰. Subject to the availability of sufficiently thin sources (a useful figure to remember is that a $100 \mu\text{g}/\text{cm}^2$ source contributes about 80 K.E.V. to the resolution), this chamber should be able to separate thorium-230 from uranium-234 and radium-226, although it will not be able to distinguish between the latter two isotopes. Optimum resolution with this chamber is however only attainable at the cost of a reduction in the efficiency E (down to about 10 per cent).

Whether one selects a chamber of maximum sensitivity or one with maximum resolving power depends of course on the problem on hand. The chambers of Hill and Osborne (in reference 8), Nurmia⁷⁴;
⁷¹ Doke⁷⁵, and Macfarlane and Kohman⁷⁵ are all useful compromises
⁸² between the two extremes. Those of the Italian group (Lonati⁸²);

Lonati and Tonolini⁷³ and Lonati et al.⁷²) appear to have been superceded, but they can claim the honor of having been the pioneers of the large source ion chamber technique as applied to naturally occurring alpha-active samples (Lonati⁸² ; Lonati et al.⁷² ; Facchini et al.⁸³)

(b) Magnetic Spectrometers.

These provide the ultimate in resolution (down to about 3 K.E.V.), but possess such poor geometries (several orders of magnitude below the ion-chamber) that their use in studying natural environment samples is likely to be minimal. A good discussion of this type of instrument is given in the review of Baranov and Zalenkov⁸⁴.

(c) Scintillation Spectrometers.

Scintillation counters are in many respects more convenient to operate than ion-chambers. As an alpha-spectroscopic tool, however, they suffer from a major intrinsic defect -- poor resolution. Thus typical resolutions obtained with scintillation alpha-spectrometers have been 13 per cent (gaseous phosphor⁸⁵ (Forte) and 17 per cent (organic liquid phosphor (Seliger⁸⁶)). Gaseous phosphors can do better than this if operated at high pressures: thus Sayres and Wu⁸⁷ report about 4 per cent for xenon

at 40 to 60 p.s.i. Inorganic crystals are, in general, more promising. Thus the early work of Broser and Kallman⁸⁸ gave resolution better than 5 per cent for cadmium sulfide (CdS), while resolutions of 1.8 per cent (Martinez and Senftle⁸⁹) and 2.6 per cent (Fleury et al.⁹⁰) have been reported under optimum conditions for alphas in CsI(Tl). More typical of the sort of resolution likely to be obtained in practical applications (where one has larger area sources and no collimation) are the results of Gale⁹¹. Gale describes a simple CsI(Tl) alpha-spectrometric system capable of measuring activities as low as ⁻¹² 10 curies, and obtains a resolution of about 14 per cent using a .005 inch thick crystal of 1.5-inch diameter and source diameters up to one cm. Belyaev et al.⁹² reported similar results for CsI(Tl); resolutions from 11 to 22 per cent with 3 to 5½ cm. diameter sources, but resolution as low as 4 per cent with 3 mm. diameter sources. Since the emission spectrum of CsI(Tl) extends from the blue to the red⁹³, it is likely that use of the new red-sensitive tri-alkali photomultiplier tubes might improve matters. The present writer has attempted this with an E.M.I. 9558C tube, and resolutions of better than 3 per cent for a 5 mm. diameter plutonium-239 source have been obtained without difficulty. The potentialities of the CsI(Tl) (and possibly

also the CdS) alpha-spectrometer would appear to be worthy of further investigation, even though they cannot hope to compete seriously resolution-wise with the ion-chamber. In this connection, the useful reference of Aniansson⁹⁴ concerning the preparation of thin CsI(Tl) layers by vacuum deposition should be mentioned.

(d) Semi-Conductor Detectors.

The recently developed semi-conductor detectors possess many advantages for charged-particle spectroscopy: excellent resolution (e.g. 17 K.E.V. for a 1 cm.² detector (Blankenship and Borkowski⁹⁵)), good linearity, good stability and low background rates are the chief of these. They do, however, suffer from one major disadvantage as far as low-level detection is concerned, viz. their small area. Detectors with areas of several cm.² and resolutions approaching 50 K.E.V. are now available commercially. If areas can be increased to above 10 cm.² without sacrificing resolution, such detectors will provide a serious alternative to the "conventional" (i.e. small area) Frisch grid type ion chamber, and even now they are superior in resolution to the ion chamber if very small (millimetric dimension) sources are involved. Alpha particle spectroscopy with 1/4 cm.² silicon surface barrier type detectors has been

discussed by Chetham-Strode ⁹⁶ et al. , who emphasize the need for avoiding contamination of the detector by recoil nuclei if the excellent low background characteristics of the detector are to be maintained. A general review of semi-conductor detector devices has been given by Miller ⁹⁷ et al. . In appendix 7 the use of a semi-conductor detector to investigate the alpha-spectra from certain radioactive minerals is described. The results are interesting in that an unidentified alpha-line has been found; its possible origin is discussed.

(e) Nuclear Emulsions ³⁷ (Yagoda).

These suffer from the disadvantages of long exposure times, extremely tedious measurement and poor resolution (about five times worse than a good ion chamber ⁷⁵ (Macfarlane and Kohman)). They are, however, very sensitive, and have been employed in several experiments. Notable amongst these have been the searches for alpha-radioactivity in the medium-heavy elements (e.g. Porschen and Riezler ⁹⁸ ; Macfarlane and Kohman ⁷⁵ give a list of references to this sort of work) and the important experiments of Picciotto and Wilgain ⁹⁹ (1954) on thorium isotopes in deep sea sediments. The technique used by the latter authors is so sensitive that it permits the measurement of as little as ⁻⁹ 10 gm. of thorium provided it is sufficiently highly concentra-

ted. Another emulsion technique which also possesses a degree of sensitivity of this order has been described recently by Geiger ¹⁰⁰ et al.

(f) "Thick-Source" Spectrometry.

In an effort to avoid the necessity for the preparation of spectroscopically thin sources, and/or to increase the sensitivity by increasing the volume of sample material, several authors have investigated the nature of the alpha-spectrum from a "thick" source. Thus Graeffe and Nurmia ¹⁰¹ have applied thick-source spectrometry to determinations of the energies of alphas from the weakly-alpha-active medium heavy elements, while Stephenson ¹⁰² et al. have discussed the theoretical energy distribution of alphas emerging from a thick source. A final useful reference is that of Abrosimov and Kocharov ¹⁰³, who discuss the effects of source thickness on the shape of the energy and directional distributions of the alpha-particles.

CHAPTER 3

GAMMA-RAY SPECTROMETRY.

Gamma-ray spectrometric measurements comprise only a minor portion of this dissertation, and it is not proposed that the subject be discussed thoroughly here. The technique is by now well established, and several reviews have appeared. Of these, the article by Bell¹⁰⁵ was one of the early "standards"; more recently, there have been portions of the articles by Nott and Sutton¹⁰⁶ and by Murray⁹³, while the book "Applied Gamma-Ray Spectrometry" by Crouthamel¹⁰⁷ provides a comprehensive discussion of the whole subject. Finally we have the application of this technique to low-level counting discussed in Chapter 9 of the book by Watt and Ramsden⁷, and reviewed with biomedical emphasis by Marinelli et al.¹¹¹.

The basic principle of the method is of course to select a particular gamma-ray emitted by the nuclide to be measured and to count the number of photoelectric effect interactions undergone by gamma-rays of the specified energy in the scintillation crystal. Photoelectric effect interactions produce output pulses which are equivalent to (or very slightly less than) the total energy of the gamma-ray, and electronic analysis of the

scintillation counter output pulses then provides information about the energy and quantity of gamma-rays present in the sample. Pair production interactions can also be used, although they only occur for the higher energy gamma-rays and give rise to minor ambiguities in interpretation; Compton effect interactions give rise to a pulse continuum and are disadvantageous in that they compete with the photoelectric effect and also interfere with photoelectric peaks from lower energy gamma rays in the same sample. These points are discussed in the references listed above, and the fundamentals of the interaction of gamma-rays with matter are fully dealt with by Evans¹⁸. What concerns us here is the question of which gamma-ray energies to select. Sometimes there is no choice. Thus many measurements (e.g. Schroeder and Cherry¹⁰⁹) of the fall-out nuclide caesium-137 have been reported. Caesium-137 emits beta-particles, followed in the majority of disintegrations by a 662 K.E.V. gamma ray. No other gamma-ray is involved (if the low energy barium X-ray accompanying the internal conversion process is ignored) and the obvious procedure is to analyze the 662 K.E.V. photopeak. For naturally-occurring samples containing the gamma-emitting isotope potassium-40 and gamma-emitters from the uranium, thorium and actinium series as well the situation is more complicated, and some degree

of selection is required.

The pioneer application of gamma-spectrometric methods to samples from the natural radiation environment appears to have been that of Hurley¹⁰⁸. He used a 1-3/4" by 2" NaI (Tl) well-type crystal as detector, and selected energy bands centred at 180 K.E.V. and 238 K.E.V. for thorium and uranium detection. The 238 K.E.V. band is dominated by the photopeak of a gamma-ray from lead-212 in the thorium series, while the 180 K.E.V. band contains approximately equivalent contributions from both series. (This assumes equal parent disintegrations - see Fig. 4 of Hurley¹⁰⁸). For potassium measurements there was no choice; the solitary gamma-ray at 1.46 M.E.V. was used. With the development of larger crystals it became feasible to use higher gamma-ray energies for uranium and thorium determinations, and in 1958 Adams et al.²⁰ reported results from a 3" by 3 1/2" NaI(Tl) crystal. They used the 1.46 M.E.V. energy for potassium as before, but then selected the 1.76 M.E.V. gamma-ray from bismuth-214 for the uranium series and the 2.16 M.E.V. gamma-ray from thallium-208 for the thorium series. Appendix 8 utilized the 3" by 3" NaI(Tl) crystal facility in the iron shield at the Geology Department, Rice University. Multichannel pulse height analysis was available, and the determinations of

potassium, uranium and thorium in tektites were made using the 1.46, 1.76 and 2.62 M.E.V. gamma-rays listed above.

A nagging doubt remains as to whether the large-crystal cum high-energy gamma-ray combination now in common use is in fact always superior to a low-energy, smaller crystal set-up. The advantages of the former are obvious: the potassium gamma-ray does not interfere with the uranium and thorium-series gammas since it is of a lower energy; furthermore, the backgrounds are lower than they are at low energies. On the other hand, the detection efficiencies and hence the count rates are lower than they are at lower energies, and sufficient attention does not appear to have been given to the question of optimizing the desired (source count rate)² / background ratio (see Chapter 1) as a function of gamma-ray energy and crystal and sample size. Studies such as those conducted by Marinelli et al.¹¹¹ into the optimum crystal size for "whole-body" gamma-spectrometric measurements, and by May and Marinelli¹¹² into factors determining the ultimate detection sensitivity of gamma scintillation spectrometry are envisaged, and the problem would appear to be ripe for a thorough and systematic investigation. The encouraging results obtained by Parker¹¹⁰ with a small ($1\frac{1}{2}$ " by 1") NaI(Tl) crystal in investigating low-energy gamma-rays (up to 250 K.E.V.)

from naturally-occurring samples would appear to substantiate this opinion. It is perhaps unnecessary to add that small crystals possess considerable economic advantages!

In conclusion, it is of importance to compare the gamma-spectrometric technique with the "total plus pairs" alpha counting technique. As far as thorium and uranium determinations are concerned, both methods suffer from the defect that the assumption of secular radioactive equilibrium is a prerequisite. If ion-chambers or gas flow proportional counters are used, then the alpha-technique can be subject to serious emanation difficulties; with the sealed source-phosphor system of Turner et al.⁹, however, these problems no longer arise. One can therefore state that the alpha-technique is advantageous in that (a) exceptionally low backgrounds which result in great sensitivity can be obtained and (b) only small quantities of sample are required. On the other hand, gamma-ray techniques offer greater ease in sample preparation, and, more importantly, present negligible inhomogeneity problems. Both techniques currently require calibration samples for optimum accuracy; should the problems of computational detail in gamma-ray spectroscopy, or the range problem in alpha-particle counting, be solved, then either or both methods ..

could claim to be absolute techniques. If, however, alpha-spectroscopy as opposed to "total" alpha-counting is resorted to, then one becomes involved in (a) the inherent limitation of counting rate imposed by spectroscopically thin alpha-sources on the one hand, and, on the other (b) the inherently more specific information obtainable from alpha-spectrometric than from gamma-spectrometric techniques insofar as the upper members of the natural radioactive series are concerned. It is likely that both alpha- and gamma-counting techniques will continue to play a significant part in the investigation of samples from the natural radiation environment.

CONCLUSION.

The techniques described and the results obtained would appear to be of some utility and interest to research workers in various fields who are concerned with problems associated with the radioactivity in naturally occurring samples. Various projects for future research have been suggested in the preceding chapters and in the appendices. Those which seem to the author to be of particular interest can be summarized thus:

Techniques:

(a) It would appear to be highly desirable that the problem of alpha-particle ranges in solids be systematically investigated with alpha-particles of energies between 3 and 9 M.E.V. and absorbers of various compositions. The successful conclusion of such an investigation could result in the alpha-counting technique being established as an absolute standard for determinations of uranium and thorium in geochemical studies.

(b) The use of CsI(Tl) and CsS phosphors coupled to red-sensitive tri-alkali photomultiplier tubes should be looked into more thoroughly. Although they cannot, intrinsically, hope to compete resolution-wise with ion-chambers (and still less with

semi-conductor detectors) they might provide a convenient, economical alpha-spectrometric set-up of considerable utility in natural radiation environment investigations.

(c) The development of large-area semi-conductor detectors will be watched with interest.

(d) A theoretical study of the optimum crystal size and the optimum gamma-ray energy to be used in gamma-spectrometric studies of weakly radioactive natural samples of various shapes (e.g. point or disc sources) and sizes would be most welcome.

Results:

(a) Suggestions are made at the end of Appendix 5 for further investigations into the plankton problem. It is considered that these could yield results of substantial oceanographic (and perhaps even biological) importance.

(b) Further alpha-spectrometric studies of a variety of geological samples would appear to offer exciting possibilities. The origin of the alpha-particle of 4.4 M.E.V. energy in Appendix 7 remains indefinite, and this problem must be solved. An investigation into the alpha-spectra of materials such as thorium-rich granites and ocean sediments should be given high priority.

REFERENCES.

1. Rutherford, E., Chadwick, J. and Ellis, C.D., in "Radiations from Radioactive Substances", Cambridge University Press (1930).
2. Evans, R.D., Kip, A.F. and Moberg, E.G., American J. of Science, (5) 36, 241 (1938)
3. Evans, R.D. and Goodman, C., Geol. Soc. Amer. Bull., 52, 459, (1941).
4. Anderson, E.C., and Hayes, F.N., Ann. Rev. Nuclear Sci., 6, 303 (1956).
5. Anderson, E.C., and Libby, W.F., Advances in Biol. and Med. Phys. 5, 385 (1957).
6. Eisenbud, M. "Environmental Radioactivity", McGraw-Hill (1963).
7. Watt, D.E. and Ramsden, D., "High Sensitivity Counting Techniques", Pergamon Press (1964).
8. Proceedings of the International Symposium on Natural Radiation Environment, Houston, Texas, 1963. (In press, University of Chicago Press.)
9. Turner, R.C., Radley, J.M. and Mayneord, W.V., Brit. J. of Radiology, XXXI, 397 (1958).
10. Mayneord, W.V., Radley, J.M. and Turner, R.C., Second U.N. Conference on the Peaceful Uses of Atomic Energy, Paper 15/P/41 (1958).

11. Turner, R.C., Radley, J.M. and Mayneord, W.V., *Health Physics*, 1, 268 (1958).
12. Turner, R.C., Radley, J.M. and Mayneord, W.V., *Nature*, 189, 348 (1961).
13. Finney, G.D. and Evans, R.D., *Phys. Rev.* 48, 503 (1935).
14. Evans, R.D. and Goodman, C., *Phys. Rev.* 65, 216 (1944).
15. Nogami, N.H. and Hurley, P.M., *Trans. Amer. Geophys. Union* 29, 335 (1948).
16. Kulp, J.L., Holland, H.D. and Volchok, H.L., *Trans. Amer. Geophys. Union* 33, 101 (1952).
17. Keevil, N.B. and Grasham, W.E., *Canadian J. of Research*, 21A, 21 (1943).
18. Evans, R.D., "The Atomic Nucleus", McGraw-Hill, (1955).
19. Keevil, N.B., Keevil, A.R., Ingham, W.N. and Crombie, G.P., *Am. J. of Sci.*, 241, 345 (1943).
20. Adams, J.A.S., Richardson, J.E. and Templeton, C.C., *Geochim. et Cosmochim. Acta*, 13, 270 (1958).
21. McDaniel, E.W., Schaefer, H.G. and Colehow, J.K., *Rev. Sci. Instr.* 27, 864 (1956).
22. Kiefer, H. and Maushart, R., *Nucleonics*, 19, 12, 51 (1961).
23. Curran, S.C., in *Beta and Gamma-Ray Spectroscopy*, ed. K. Siegbahn, North Holland (1955).

24. Reed, C.W., *Nucleonics*, 7, 6, 56 (1950).
25. Pagano, R., Damerelli, C.J.S. and Cherry, R.D., *Rev. Sci. Instr.*, 33, 955 (1962).
26. Hurley, P.M. and Shorey, R.R., *Trans. Amer. Geophys. Union*, 33, 722 (1952).
27. Hirschberg, D., *Nuovo Cimento* (9) 12, 733 (1954).
28. Hirschberg, D., *Nuovo Cimento* (10) 1, 341 (1955).
29. Cherry, R.D., *Geochim. et Cosmochim. Acta*, 27, 183 (1963).
30. Turner, R.C., Radley, J.M. and Mayneord, W.V., *Nature*, 181, 518 (1958).
31. Turner, R.C. and Radley, J.M., *The Lancet*, May 28, 1197 (1960).
32. Mayneord, W.V., *Clinical Radiology* XI, (1) 2 (1960).
33. Mayneord, W.V., Turner, R.C. and Radley, J.M., *Nature*, 187, 208 (1960).
34. Marsden, E., *Nature*, 187, 192 (1960).
35. Marsden, E., in reference 8.
36. Beharrel, J., *Trans. Amer. Geophys. Union* 30, 333 (1949).
37. Yagoda, H., *Radioactive Measurements with Nuclear Emulsions*, John Wiley and Sons (1949).
38. Whaling, W., *The Energy Loss of Charged Particles in Matter*, Handbuch der Physik, Volume XXXIV, Springer Verlag. (1957).
39. Garin, A. and Faraggi, H., *Le Journal de Physique et le Radium*, 19, 76 (1958).

40. Kamke, D. and Kramer, P., Zeit. Physik, 168, 465 (1962).
41. Osborne, R.V., Ph.D. Thesis, London University (1962).
42. Hurley, P.M., Geol. Soc. Am. Bulletin, 61, 1 (1950).
43. Turner, R.C., Radley, J.M. and Mayneord, W.V., Nature, 189, 348 (1961).
44. Korkisch, J. and Janauer, G.E., Talanta, 9, 957, (1962).
45. Choppin, G.R. and Sikkeland, T., Procedure 19 in NAS- NS 3004, "The Radiochemistry of Thorium".
46. Rosholt, J.N., Anal. Chem. 29, 1398 (1957).
47. Morken, D.A., Health Physics, 2, 77 (1959).
48. Lucas, H.F., Rev. Sci. Instr., 28, 680 (1957).
49. Giffin, C., Kaufman, A. and Broecker, W., J. Geophysical Research, 68 (6), 1749, (1963).
50. Bearden, J.A., Rev. Sci. Instr., 4, 271, (1933).
51. Adams, J.A.S. and Richardson, K.A., Economic Geology, 55, 1060 (1960).
52. Hill, C.R., Nuclear Instruments and Methods, 12, 299 (1961).
53. Garwood, F., Biometrika, 28, 437 (1936).
54. Jaffey, A.H., Nucleonics, 18, No. 11, 180 (1960).
55. Freedman, A.J. and Anderson, E.C., Nucleonics, 10, No. 8, 57 (1952).
56. Adams, N.J., Phys. Rev., 44, 651 (1933).

57. Huybrechts, M., *Nuovo Cimento* (10) 6, 811 (1957).
58. Lucas, H.F. and Woodward, D.A., Argonne National Laboratory Report ANL-6646, page 78 (1962).
59. Yaffe, L., *Ann. Rev. of Nuc. Science*, Vol. 12, 153 (1962).
60. Korolev, G.A. and Kocharov, G.E., *Instruments and Experimental Techniques*, No. 5, 702 (1958).
61. Kocharov, G.E. and Korolev, G.A., English Translation of the Bulletin of the Academy of Sciences of the U.S.S.R., Physical Series, 25, 227 (1961).
62. Bjornholm, S. and Lederer, C.M., *Nucl. Instr. and Methods*, 15, 233 (1962).
63. Wilkinson, D.H., "Ionization Chambers and Counters", Cambridge U.P. (1950).
64. Rossi, B.B. and Staub, H.H., *Ionization Chambers and Counters*, McGraw-Hill, (1949).
65. Herwig, L., Miller, G. and Utterbach, N., *Rev. Sci. Instr.*, 26, 929 (1955).
66. Cranshaw, T.E. and Harvey, J.A., *Canad. J. of Research*, 26A, 243 (1948).
67. Buneman, O., Cranshaw, T.E. and Harvey, J.A., *Canad. J. of Research*, 27A, 191 (1949).
68. Harvey, B.G., Jackson, H.G., Eastwood, T.A. and Hanna, G.C., *Canad. J. of Physics*, 35, 258 (1957).

69. Ray, E.L. and Hammond, S.E., *Health Physics*, 5, 50 (1961).
70. Goldberg, E.D. and Kolde, H., *Geochim. et Cosmochim. Acta*, 26, 417 (1962).
71. Doke, T., *Canad. J. of Physics*, 40, 607 (1962).
72. Lonati, R.D., Facchini, U., Iori, I., Houtermans, F.G. and Tongiorgi, E., *Nuovo Cimento* (10) 7, 133 (1958).
73. Lonati, R.D. and Tonolini, F., *Energia Nucleare*, 7, 107 (1960).
74. Nurmi, M., *Nuclear Electronics*, I. 297 (I.A.E.A., Vienna, 1962).
75. Macfarlane, R.D. and Kohman, T.P., *Phys. Rev.*, 121, 1758 (1961).
76. Hill, C.R., *Nature*, 187, 211 (1960).
77. Hill, C.R., *Health Physics*, 8, 17 (1962).
78. Mayneord, W.V. and Hill, C.R., *Nature*, 184, 667 (1959).
79. Hill, C.R. and Jaworowski, Z.S., *Nature*, 190, 353 (1961).
80. Hanna, G.C., in *Experimental Nuclear Physics*, Vol. 3, ed. E. Segre, John Wiley and Sons (1959).
81. Strominger, D., Hollander, J.M. and Seaborg, G.T., *Rev. Mod. Phys.*, 30, 585 (1958).
82. Lonati, R.D., *Energia Nucleare*, 8, 217 (1961).
83. Facchini, U., Forte, M., Malvicini, A. and Rossini, T., *Nucleonics* 14, No. 9, 126 (1956).
84. Baranov, S.A. and Zalenkov, A.G., *Instruments and Experimental Techniques*, No. 5, 695 (1959).

85. Forte, M., *Nuovo Cimento* (10) 3, 1443 (1956).
86. Seliger, H.H., *Intern. J. Appl. Radiation and Isotopes*, 8, 29 (1960).
87. Sayres, A. and Wu, C.S., *Rev. Sci. Instr.*, 28, 758 (1957).
88. Broser, I. and Kaliman, H., *Nature*, 163, 20 (1949).
89. Martinez, P. and Senftle, F.E., *Rev. Sci. Instr.*, 31, 974 (1960).
90. Fleury, J., Perin, P., Boge, M. and Laugier, J., *Le Journal de Physique et le Radium*, 21, 480 (1960).
91. Gale, H.J., *Physics in Medicine and Biology*, 6, 577 (1962).
92. Belyaev, L.M., Gil'varg, A.B. and Panova, V.P., *Soviet Physics - Crystallography*, 6, 108 (1961).
93. Murray, R.B., in "Nuclear Instruments and Their Uses" Vol. I. p. 102, ed. A.H. Snell, John Wiley and Sons (1962).
94. Arinsson, G., *Trans. Royal Inst. of Techn., Stockholm*, No. 176 (1961).
95. Blankenship, J.L. and Borkowski, C.J., *I.R.E. Trans. on Nuclear Science*, NS-8, 17 (1961).
96. Chetham-Strode, A., Tarrant, J.R. and Silva, R.J., *I.R.E. Trans. on Nuclear Science*, NS-8, 59 (1961).
97. Miller, G.L., Gibson, W.M. and Donovan, P.F., *Ann. Rev. of Nuclear Science*, 12, 189 (1962).
98. Porschen, W. and Riezler, W., *Z. Naturforsch*, 11A, 143 (1956).

99. Picciotto, E. and Wilgain, S., *Nature*, 173, 632 (1954)
100. Geiger, E.L., Tschaeche, A.H. and Whittaker, E.L., *Health Physics*, 4, 302 (1961).
101. Graeffe, G. and Nurmi, M., *Annales Acad. Scient. Fennicae, A*, VI, No. 77 (1961).
102. Stephenson, G.J., Evans, R.D. and Kraner, H.W., in M.I.T. Radioactivity Center Progress Report, p.55, May 1962.
103. Abrosimov, N.K. and Kocharov, G.E., *Bull. Acad. Sci. U.S.S.R., Physical Series*, 26, 235 (1962).
104. Chase, R.L., "Nuclear Pulse Spectrometry", McGraw-Hill (1961).
105. Bell, P.R., in "Beta- and Gamma-Ray Spectroscopy", ed. K. Siegbahn, North Holland (1953).
106. Mott, W.E. and Sutton, R.B., in "Handbuch der Physik, Band XLV," Springer Verlag (1958).
107. Crouthamel, C.E., "Applied Gamma-Ray Spectrometry", Pergamon Press (1960).
108. Hurley, P.M., *Bull. Geol. Soc. Amer.*, 67, pp. 395 and 405 (1956).
109. Schroeder, B.W. and Cherry, R.D., *Nature*, 194, 669 (1962).
110. Parker, R.P., *Physics in Medicine and Biology*, 7, 301, (1962).
111. Marinelli, L.D., Miller, C.E., May, H.A. and Rose, J.E., *Advances in Biol. and Med. Phys.*, 8, 81, (1962).

112. May, H.A. and Marinelli, L.D., Paper 25 in "Proceedings of the Total Absorption Gamma-Ray Spectrometry Symposium". United States Atomic Energy Commission TID-7594 (1960).

APPENDIX 1: THE DETERMINATION OF THORIUM AND
URANIUM IN GEOLOGICAL SAMPLES BY AN
ALPHA-COUNTING TECHNIQUE.

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The determination of thorium and uranium in geological samples by an alpha-counting technique

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Abstract—The use of a thick-source alpha-particle detection technique for the simultaneous determination of both thorium and uranium in geological samples is discussed. The technique depends on the presence of the “thorium pairs” resulting from the successive decays of thoron and the short-lived isotope thorium A, and has been extensively employed by Mayneord and others in biophysical problems. The absolute accuracy, the sensitivity and the limitations of the method are considered. Finally, thorium and uranium determinations for the granites G-1 and Tory Hill and the diabase W-1 are presented.

INTRODUCTION

THE determination of the alpha-radioactivity of geological samples is a well-known technique. The fundamentals thereof have been discussed by FINNEY and EVANS (1935) and NOGAMI and HURLEY (1948) while KULP *et al.* (1952) have considered the problem with special reference to the case where a scintillation counter is used as a detector. If we assume that (a) the sample is in radioactive equilibrium and (b) the U^{238} to U^{235} ratio is known, then we can write the absolute alpha count rate as

$$C = k_1 \text{Th} + k_2 \text{U} \quad (1)$$

where C is the count rate (usually in counts/hr) and Th and U are the thorium and uranium concentrations (usually in p.p.m. by wt.). The constants k_1 and k_2 depend on the decay constants and atomic weights of U^{238} , U^{235} and Th^{232} , the area of the sample and, finally, the ranges of the alpha-particles of the thorium, uranium and actinium series. If *either* Th or U is known for the sample, measurement of C will then provide the other. Thus ADAMS *et al.* (1958) determined U fluorometrically and used the alpha count rate to determine the Th/U ratio. Recently TURNER *et al.* (1958 a and b) have described a technique which enables the thorium content to be determined simultaneously with the total alpha count rate, and MAYNEORD, MARSDEN and others* have successfully applied this technique to several materials of largely biological interest. The purpose of the present paper is to discuss the applicability of the method to geological samples.

THE THORIUM PAIRS

The disintegration scheme of the thorium series includes two consecutive alpha transitions from thoron (Em^{220}) to ThA (Po^{216}), and from ThA to ThB (Pb^{212}). The

* Several papers, of which TURNER R. C., RADLEY J. M. and MAYNEORD W. V. (1961). Naturally occurring alpha-activity of drinking waters, *Nature Lond.*, **189**, 348 and MARSDEN E. (1960) The radioactivity of soils, plants and bones, *Nature Lond.*, **187**, 192, are among the more recent.

half-life of ThA is only 0.158 sec (WARD, 1942); thus the alpha counts from a sample containing members of the thorium series will include counts occurring as pairs with a spacing of about 0.2 sec. The number of pairs per unit time will be proportional to the thoron concentration and, if radioactive equilibrium exists, to the concentration of the head member of the thorium series, viz. Th²³². Following the argument of TURNER *et al.* (1958 a and b) (with minor modification to allow for the different ranges of the two alpha-particles involved) it can be shown that the "pairs" count rate P (in pairs/hr) is given by

$$P = 1.847A \text{ Th } R_1 \rho \left[1 - \frac{R_1}{3R_2} \right] \quad (2)$$

where A is the area of the sample, ρ is the density of the sample, Th is the thorium content in p.p.m. and R_1 and R_2 are the ranges in the sample of the alpha-rays from thoron and ThA respectively. Combining eqns. (1) and (2) shows that measurement of the count-rate C and the pairs rate P will yield values of both the thorium and the uranium concentrations. It should at this stage be pointed out that the underlying principle of this method was suggested several years ago by HURLEY and SHOREY (1952) as a means of discriminating between thoron and radon alpha activity.

EXPERIMENTAL TECHNIQUE

A scintillation counter is used as an alpha-particle detector and the experimental procedure follows closely that described by TURNER *et al.* (1958 a and b). Details of the extremely simple method of sample preparation are given by TURNER *et al.* (1958 a and b). Here it will suffice to mention that no chemistry is necessary; the sample is simply finely ground and then packed. The method is one of "thick-source" alpha counting.

All electronic apparatus is operated from a stabilized mains supply. Pulses from the photomultiplier are fed into a conventional pulse amplifier with a gain of 50, and thence into a discriminator circuit with a variable bias. The E.H.T. supply to the photomultiplier and the discriminator bias voltage must be set so that, ideally, *all* the alpha counts from the sample are recorded and *all* the other pulses (beta and gamma rays and tube noise) are rejected. This is done by the usual method of plotting the count rate from a suitable source ("old" thorium oxide was used in the present work) as a function of the E.H.T. for a fixed discriminator bias. With a suitable choice of bias it is possible to obtain a satisfactory long "plateau" and to determine the true alpha counting rate to within a few per cent. The chosen operating point must of course give rise to a count rate as close to the true alpha rate as possible.

From the discriminator pulses are fed into (a) a conventional electronic scaler with a resolving time of about 200 μ sec or less and, simultaneously, into (b) an electro-mechanical register circuit with a dead-time of about 0.3 or 0.4 sec. The counts in (a) yield the total count-rate, while those in (a) *minus* those in (b) give the "pairs" rate. Both these rates must be corrected for background. If the operating point has been chosen correctly this is extremely low. Background total count rates of about 0.1 counts/cm²/hr are readily obtainable with the E.M.I. photomultiplier tubes in use in this laboratory and use of selected low noise tubes and low value cathode-to-first dynode resistors (PAGANO *et al.*, 1962) enables this figure to be reduced by a

factor of three or more. Background "pairs", due presumably to spurious electronic effects, are seldom as much as one pair per day, and can frequently be neglected. In addition to this background correction, the observed pairs rate must be corrected for (i) spurious pairs arising from chance coincidence in time of alpha counts as opposed to the "genuine" thorium A pairs and (ii) the fact that only a certain fraction of the ThA decays occur within the dead-time of the electromechanical register. The problem of the spurious pairs correction is a difficult one, and one which is likely to be controversial. TURNER *et al.* (1958 a and b) calculated the spurious pairs rate by calculating the probability that two pulses will occur within a time τ equal to the dead-time of the register circuit. The present writer feels that it is more correct to state that the spurious pairs rate is equal to the observed count rate multiplied by the probability of a *single* pulse occurring within a time τ . This seems to be more in accord with the experimental situation, where the spurious pairs are due to a single pulse arriving in an interval τ *after* the arrival of a registered pulse rather than to two pulses arriving in an *arbitrary* interval τ which is not initiated by some other pulse. Assuming a Poisson distribution then gives the spurious pairs rate S by the formula:

$$S = N^2\tau \exp(-N\tau) \quad (3)$$

where N is the observed total count rate and τ is the dead-time of the register circuit. Eqn. (3) gives a spurious pairs rate twice as high as that calculated by TURNER *et al.* (1958 a and b). Fortunately the correction involved is small except at very large N and any uncertainty in the basic theory will in consequence not usually be serious.* The half-life correction (ii) (which is to be applied after correcting for the spurious pairs) is of course straightforward and depends only on the ratio of the dead-time τ to the ThA half-life of 0.158 sec. Use of $\tau = 0.43$ sec, for example, means that a correction factor of 1.18 must be applied.

THE ALPHA RANGE PROBLEM

Once the corrected total and pairs count rates, C and P , have been obtained, eqn. (1) and (2) can be used to determine U and Th. Unfortunately, however, both (1) and (2) require knowledge of the range, *in the sample*, of α -particles of various energies and it is lack of certainty in this connection which is currently hindering the development of the alpha-counting method as an accurate *absolute* method of U and Th determination. It is customary to use some empirical formula for calculating the alpha-ray ranges. Thus NOGAMI and HURLEY (1948) used the Bragg-Kleeman relation in the form:

$$R\rho = 0.32(10^{-3})W^{1/2}R_a \text{ g/cm}^2 \quad (4)$$

where R is the required range in the sample, R_a is the range in cm of an alpha-particle of the same energy in standard air, ρ is the density of the sample and $W^{1/2}$ is the square root of the at. wt. of the sample calculated on the usual "atomic fraction" basis (NOGAMI and HURLEY, 1948). NOGAMI and HURLEY (1948) have claimed that

* Both eqn. (3) and the expression given by TURNER *et al.* (1958a and b) should be strictly modified by the introduction of extra terms which allow for 2, 3, 4, etc. pulses occurring in the time interval τ after the initiating pulse. This modification can easily be made, but is nearly always completely negligible.

the Bragg-Kleeman expression is accurate to within 5 per cent; this has, however, subsequently been disputed by BEHARREL (1949), who claims that the Bragg-Kleeman law gives ranges which are about 10 per cent too low. YAGODA (1949), on the other hand, finds that the computed ranges are in general about 10 per cent too high. A recent review article by WHALING (1958) is of some use in clarifying the situation. Using a variety of experimental data, old and new, WHALING has calculated the ranges of alpha-particles of various energies in 12 gaseous and 7 solid materials (all metallic). The ranges in gases seem to agree fairly well with the Bragg-Kleeman law, but those in the solids are distinctly higher in the low atomic weight range ($W^{1/2} = 5.0$ and less) which is applicable to most geological materials. Thus smooth curves through WHALING's points indicate that for $W^{1/2} = 4.60$, the Bragg-Kleeman formula gives ranges which are approximately 6, 13 and 25 per cent too low for alpha-particles of energies 8, 6 and 4 MeV respectively.

It is evident from the above that the whole topic of alpha-particle ranges in non-gaseous media is in a complicated and not very satisfactory condition. The degree of deviation from the Bragg-Kleeman formula is a function of both the atomic weight (or the atomic number) of the medium and the energy of the alpha-particle. The resolution of this uncertainty will require a thorough and systematic experimental determination of the ranges of alpha-particles of various energies in a large number of solid elements and compounds. Pending the availability of such data, we have found that the following method of evaluating the parameters in eqn. (1) and (2) yields results which are satisfactory in practice:

(i) The ratios of the parameters k_2 , R_1 and R_2 to the parameter k_1 are calculated using the WHALING (1958) data and alpha-particle energies from the compilation of HANNA (1959).

(ii) The absolute value of the parameter k_1 is determined experimentally by counting old (≥ 30 years) thorium oxide, which can be assumed to be in radioactive equilibrium and for which the alpha emission rate can accordingly be calculated.

These procedures have been carried out in this laboratory and the final eqn. obtained for the count rate C and the pairs rate P were:

$$C = W^{1/2}A[0.155 U + 0.0434 \text{ Th}] \quad (5)$$

and
$$P = W^{1/2}A \left[\frac{\text{Th}}{378} \right] \quad (6)$$

Both C and P are counts/hr, U and Th in p.p.m. and the phosphor area A in cm^2 .

Eqn. (5) and (6) are of course subject to revision as and when more information concerning alpha-particle ranges becomes available. Meanwhile it would appear to be reasonable to claim that it is unlikely that either eqn. is in error by more than 10 per cent.

THE ACCURACY OF THE METHOD

The errors in the results obtained will depend on

(a) The accuracy of eqn. (5) and (6). This has been discussed above. If the maximum possible accuracy is vital, internal standardization as discussed by FINNEY and EVANS (1935) can presumably be used to determine the parameters in eqn. (1) and (2) directly. This possibility has not been investigated in the current work.

(b) Errors in sampling. This is a problem common to all geochemical experimental techniques.

(c) Errors due to lack of homogeneity in the sample counted. The basic theory assumes that the alpha-emitting nuclei are distributed uniformly throughout the sample. This condition can be fulfilled provided the sample is sufficiently finely ground and thoroughly mixed. Ball-mill grinding down to micron size (i.e. less than the ranges of the alphas) is necessary for complete safety.

(d) Uncertainty in the value of $W^{1/2}$. If a major element chemical analysis of the sample is available, then $W^{1/2}$ can be calculated to a sufficiently high degree of accuracy. If no analysis is available then $W^{1/2}$ must be estimated from knowledge of the rock type. Although unsatisfactory, this is often adequate since $W^{1/2}$ is fortunately not very sensitive to small changes in sample composition (BIRCH, 1961). Internal standardization, as mentioned in (a), would of course eliminate the necessity of determining $W^{1/2}$.

(e) Errors due to the statistical nature of the counting process. These errors, unlike those enumerated above, are inherent to the technique and can only be reduced by counting for an adequate length of time. They are of course most serious in the determination of the pairs rate P , since the ratio C/P is of the order of 30 for the Th/U ratios encountered in practice. Accuracy of about 10 per cent is nonetheless usually easily obtainable.

The thorium content is of course calculated directly from eqn. (6) and the percentage error in Th is the same as that in P . The uranium content, however, has to be calculated from a combination of eqn. (5) and (6) and we have:

$$\frac{U}{Th} = \left[\frac{C}{P} - 16.4 \right] (0.0171) \quad (7)$$

As U/Th tends to zero, we see that C/P tends to 16.4 and that the percentage error in U tends to infinity. This exposes an inherent defect in the technique, viz., the fact that for abnormally high Th/U ratios the accuracy with which the uranium content can be determined is far inferior to the accuracy of the experimental values P and C .

THE ULTIMATE SENSITIVITY OF THE TECHNIQUE

If unlimited time and satisfactory long-term electronic stability are assumed, the limits of sensitivity will be set by the background counting rates of the apparatus. Suppose we assume $W^{1/2}A$ to be 500 cm² (a 5 in. phosphor with a typical geological material), a background pairs rate of one count in 30 hr (attainable fairly easily with sound electronics) and a background total count rate of one count/hr (attainable with some difficulty). A thorium content of 25 parts per thousand million will then give a source pairs rate of one pair per 30 hr and this, together with a uranium concentration of 8 parts per thousand million, would give a total count rate of one count/hr. These levels are in principle detectable; counting time would, however, be of the order of months!

RESULTS

To illustrate the possibilities and limitations of the technique and to confirm the reliability of eqn. (5) and (6), measurements have been made on 3 samples of geological interest. The first of these is the granite "Tory Hill". This has been extensively

studied by TILTON *et al.* (1955) and the uranium and thorium contents have been determined by isotope dilution to an accuracy of 5 per cent or better. A complete chemical analysis of the granite is also available (TILTON, 1955) and from this $W^{1/2}$ has been calculated to be 4.49. The known thorium and uranium contents are 41.9 p.p.m. and 2.7 p.p.m. respectively; alpha counting experiments yielded values of 42 ± 4 p.p.m. and 2.0 ± 1.2 p.p.m. respectively. The agreement is therefore excellent, although the error in the uranium determination is very high since this granite has the high Th/U ratio of 15.5.

The other two samples tested were the granite G-1 and the diabase W-1. The composition of these is well-known and the available data has been summarized by AHRENS and FLEISCHER (1960). $W^{1/2}$ for G-1 is calculated to be 4.49, while for W-1 it is 4.59. For G-1 AHRENS and FLEISCHER (1960) quote Th values ranging from 45 to 61 p.p.m.; alpha-counting gives 58 ± 5 p.p.m. Previously determined U values range from 3.2 to 3.9 p.p.m.; alpha-counting gives 2.5 ± 1.3 p.p.m. Agreement is again satisfactory, although again the error in the uranium determination is high. Finally, with W-1 alpha-counting gave 2.6 ± 0.5 p.p.m. Th (quoted values (AHRENS and FLEISCHER, 1960) from 1.9 to 3.6 p.p.m.) and 0.9 ± 0.6 p.p.m. U (quoted values (AHRENS and FLEISCHER, 1960) from 0.50 to 0.53 p.p.m.). The errors quoted in this section are errors due to counting statistics alone and represent the usual standard deviation limits.

CONCLUSION

Thick source alpha-counting plus the thorium pairs technique of MAYNEORD and his co-workers can be successfully applied to geological materials. The method is simple and sensitive, the apparatus inexpensive and only small amounts of sample material are required. It appears to yield accurate thorium values and as a method of thorium determination it should be useful in several geochemical and geophysical problems. Useful uranium values are also provided by the method, although their accuracy is limited unless the Th/U ratio in the sample is relatively low. Programmes involving thorium and uranium determinations in (a) tektites and (b) selected Southern African granites are currently nearing completion in this laboratory.

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REFERENCES

- ADAMS J. A. S., RICHARDSON J. E. and TEMPLETON C. C. (1958) Determination of Th and U in sedimentary rocks by two independent methods. *Geochim. et Cosmochim. Acta* **13**, 270.
 AHRENS L. H. and FLEISCHER M. (1960) IV—2nd report on a co-operative investigation of the composition of two silicate rocks. *U.S. Geol. Surv. Bull.*, 1113.
 BEHARREL J. (1949) Absorption of alpha-rays in thick-sources. *Trans. Amer. geophys. Un.* **30**, 333.
 BIRCH F. (1961) Composition of the earth's mantle. *Geophys. J.* **4**, 295.
 FINNEY G. D. and EVANS R. D. (1935) The radioactivity of solids determined by alpha-ray counting. *Phys. Rev.* **48**, 503.
 HANNA G. C. (1959) Alpha-radioactivity. *Experimental Nuclear Physics—III*, John Wiley, New York.

- HURLEY P. M. and SHOREY R. R. (1952) Discrimination of thoron alpha activity in presence of radon. *Trans. Amer. geophys. Un.* **33**, 722.
- KULP J. L., HOLLAND H. D. and VOLCHOK H. L. (1952) Scintillation alpha counting of rocks and minerals. *Trans. Amer. geophys. Un.* **33**, 101.
- NOGAMI N. H. and HURLEY P. M. (1948) The absorption factor in counting alpha rays from thick mineral sources. *Trans. Amer. geophys. Un.* **29**, 335.
- PAGANO R., DAMERELL C. J. S. and CHERRY R. D. (1962) The effect of photocathode to first dynode voltage on photomultiplier noise. *Rev. Sci. Instrum.* **33**, 955.
- TILTON G. R., PATTERSON C., BROWN H., INGRAM M., HAYDEN R., HESS D. and LARSEN E. Jr. (1955) Isotopic composition and distribution of lead, uranium and thorium in a pre-Cambrian granite. *Bull. Geol. Soc. Amer.* **66**, 1131.
- TURNER R. C., RADLEY J. M. and MAYNEORD W. V. (1958a) The alpha-ray activity of human tissues. *Brit. J. Radiol.* **XXXI**, 397.
- TURNER R. C., RADLEY J. M. and MAYNEORD W. V. (1958b) Alpha-ray activities of humans and their environment. *Nature, Lond.* **181**, 518.
- WARD A. G. (1942) A new method of determining half-value periods from observations with a single geiger counter. *Proc. Roy. Soc. (Lond.)* **181A**, 183.
- WHALING W. (1958) The energy loss of charged particles in matter. *Handbuch der Physik*—XXXIV, Springer-Verlag, Berlin.
- YAGODA H. (1949) *Radioactive Measurements with Nuclear Emulsions*. John Wiley, New York.

APPENDIX 2: EFFECT OF PHOTOCATHODE-TO-FIRST DYNODE
VOLTAGE ON PHOTOMULTIPLIER NOISE PULSES.

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that given in Figure 1) was taken by myself. I was
responsible for suggesting the project and for the supervision
thereof.

R. D. Cherry

R. D. Cherry.

Effect of Photocathode-to-First Dynode Voltage on Photomultiplier Noise Pulses

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Attention is drawn to a simple method of improving the signal-to-noise performance ratio of photomultiplier tubes used in scintillation counting. Representative results are presented and the underlying physical principles are discussed briefly.

THE problem of reducing the counting rate due to photomultiplier noise in scintillation counters is of major importance, and techniques such as refrigeration, the use of photomultipliers in coincidence, and dark adaptation have been extensively discussed. The purpose of this brief note is to draw attention to a simple method of noise reduction which does not appear to be generally appreciated, viz., that of 'tuning' the voltage between the photocathode and first dynode of the photomultiplier tube so as to obtain a minimum noise count rate for a given signal output voltage. Manufacturers of photomultiplier tubes generally recommend the use of a resistor between the photocathode and the first dynode which is at least twice the value of the subsequent interdynode resistors, and many workers appear to follow this custom slavishly. Our experience with six photomultipliers of different types from three different manufacturers indicates that this is distinctly bad policy if minimum noise is required. By way of illustration, we show in Fig. 1. the results obtained for an EMI 9530B photomultiplier tube, a tube with a $4\frac{1}{2}$ -in. photocathode and one for which the manufacturers recom-

mend a cathode to first dynode voltage, V_c , of three or four times the succeeding interdynode voltage. The noise counting rate is plotted as a function of V_c/V_d , where V_d is the

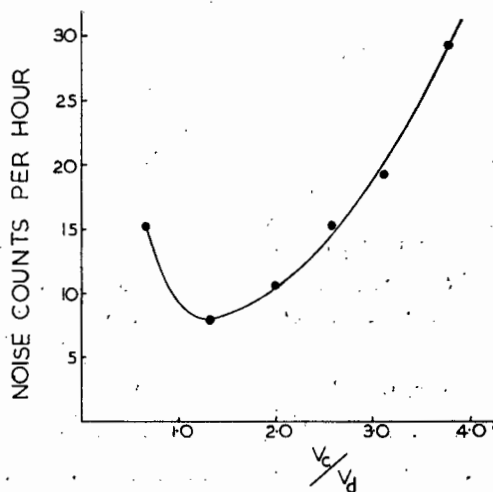


FIG. 1. Noise count rate as a function of V_c/V_d for an EMI 9530B photomultiplier tube. Values are integral count rates above a convenient bias voltage, and for all points the over-all voltage on the tube has been adjusted so as to produce an arbitrary fixed pulse height for α particles from a Pu^{239} source.

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succeeding interdynode voltage. For each experimental point the over-all E.H.T. on the photomultiplier was adjusted so as to produce some arbitrary fixed signal pulse-height output from a convenient source ($\text{Pu}^{239}\alpha$'s on ZnS were used). The source and phosphor were then removed (the lights in the room being switched off so as to avoid the necessity for dark adaptation) and the noise count rate above some fixed bias voltage was determined over a period of a day. It is seen that for this particular tube the optimum setting from the noise point of view is that for which V_c/V_d is about 1.3. For higher values of V_c/V_d the noise rate increases.

A legitimate query which might be raised at this stage is whether or not the reduction in noise at low V_c/V_d values is due to a reduction in the sensitive area of the photocathode. The points in Fig. 1 were obtained with the ZnS phosphor centrally situated, and to test the above query the measurements were repeated with the phosphor at the extreme edge of the photocathode. The same effect of an optimum setting at a low V_c/V_d value was observed, indicating that the effect does represent a real reduction in noise. The question of the discriminator bias voltages used is also of interest. We have found that the effect occurs over a wide range of noise count rates, from those of a few counts per hour (such as are applicable in low-level alpha-detection experiments with ZnS phosphors) up to several tens of counts per minute.

This feature of increasing noise rate at higher V_c values seems to be generally true for the tubes tested by us, and it is interesting to speculate on its origin. The following two factors are possible contributory causes:

(a) *Positive ion feedback.* Primary electrons starting from the cathode may ionize the atoms of the residual gas in the tube. The gas ions, on reaching the cathode, may release further electrons by secondary emission to give one or more 'after pulses.' Two previous workers^{1,2} have observed 'humps' in the high energy end of the pulse-height spectrum at high V_c values, and these humps have been attributed² to positive ion feedback.

Ion feedback could cause large noise pulses equivalent to the emission of several electrons from the photocathode by either (i) releasing several electrons on striking the cathode or (ii) if the afterpulses are produced in a time which is short compared with the output RC time constant of the photomultiplier, by 'pile-up' of successive small pulses.³

¹ F. Boeschoten, J. M. W. Milatz, and C. Smit, *Physica* XX, 139 (1954).

² Brat Pal Singh, H. S. Hans, and P. S. Gill, *Indian J. Phys.* 32, 183 (1958).

³ It is perhaps worthwhile to emphasize that experiments performed

If mechanism (ii) operates, the situation can be improved by using a smaller RC time constant, a dodge which we found convenient in one particular case, viz., a Du Mont 6292 which showed a great deal of afterpulsing operated with an organic scintillator (diphenyl anthracene). Reducing the RC time constant from 5 to 0.2 μsec resulted in an improvement in the signal-to-noise ratio by a factor of about 50 for signal pulses lying in the upper region of noise pulse heights. The improvement would naturally not have been as great for inorganic scintillators, since reducing the RC time constant here would have reduced the signal pulse heights also. In general, however, mechanism (i) might operate as well, and in this case, a lower V_c (which implies fewer and lower-energy positive ions) must be used to alleviate the situation.

(b) *The Schottky effect.* It can be shown⁴ that the application of an electric field to a thermionically emitting surface will result in a lowering of the work function of the surface and a consequent increase in thermionic emission. Approximate calculations performed by one of us⁵ indicate that, for a typical "venetian blind" type of tube geometry this increase could be of the order of 20% as V_c is increased from 0 to 400 V. That this order of magnitude is roughly correct appears to be borne out by our results for an EMI 9502S photomultiplier. This is a low-noise type tube which shows no signs whatsoever of afterpulsing, and for which mechanism (a) is accordingly inoperable. For this tube the noise count rate (again taken under conditions of fixed signal output) increased by 25% as V_c was increased from 70 to 350 V.

In conclusion we should perhaps emphasize that the use of a low cathode to first dynode voltage, while desirable from the noise point of view, might have deleterious effects on such properties as resolution and uniformity of photocathode response. Such effects are, however, often of secondary importance in low-noise applications where it is common to take integral count rates above a fixed bias. In any event the procedure which we suggest of tuning the first stage voltage with a variable resistor does enable a reasonable compromise value of V_c to be selected for any particular application.

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with a view to studying the underlying fundamentals of noise pulses from photomultipliers should utilize an RC time constant smaller than the average spacing between afterpulses. In this way the effects of "pile-up" pulses will be eliminated, and a true representation of the noise pulse-height distribution obtained.

⁴ F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. 5.

⁵ R. Pagano, M. Sc. thesis, University of Cape Town, 1959.

**APPENDIX 3: THE ROLE OF SAMPLE INHOMOGENEITIES IN THE THEORY
OF ALPHA-COUNTING.**

Submitted to "The Journal of Geophysical Research".

ABSTRACT

In the measurement of the alpha radioactivity of "thick" sources, errors may arise as a result of inhomogeneities in the distribution of radioactivity in the sample. The magnitude of this effect has been calculated for three simple cases, viz. surface coatings, core concentrations and "hot-spot" activity. It is shown that these inhomogeneities can lead to considerable anomalies in the total count rate and to an even greater effect in the pairs rate; it is suggested that for complete safety samples should be ground down to sub-micron size.

INTRODUCTION:

Measurements of the alpha radioactivity of solid samples have been made by numerous workers since the first comprehensive discussion of the theory by Finney and Evans (1935). Such measurements have involved total alpha counting (eg. Evans and Goodman, (1941), Kulp et al. (1952)) or, more recently, (Turner et al. (1958), Cherry (1963)) total alpha counting plus determination of the number of alpha particle "pairs" due to the successive decays of the isotopes Em^{220} and Po^{216} in the thorium series, or Em^{219} and Po^{215} in the actinium series. The basic theory assumes a homogeneous distribution of radioactivity throughout the sample - a condition which is frequently untrue for geological samples, and which has been the cause of some concern. Hurley (1950) in particular has directed attention to the very high results obtained when measuring the alpha particle emission from crushed granite samples, and has produced convincing evidence to support his theory that these anomalously high values are due to the fact that much of the radioactivity is distributed in extremely thin layers on the surface of mineral grains rather than homogeneously throughout the sample. During the course of a series of measurements involving the "pairs" technique, the present writer found that certain samples gave anomalous count rate/pairs rate ratios, and it seemed likely that these anomalies

might also be due to the effects of inhomogeneity. It thus appeared worthwhile to investigate theoretically the effects on alpha count and pairs rates of simple types of inhomogeneities in the distribution of alpha radioactivity in samples, and the present work is a brief discussion of the results of these calculations.

II. BASIC THEORY:

We shall use the notation of Turner et al. (1958) and briefly recapitulate the essentials of the basic theory. Under suitable experimental conditions (eg., Turner et al. 1958) essentially all the alpha particles emerging from the front surface of the sample are counted. Consider an element of volume $dAdh$ situated a perpendicular distance h from the plane front surface of the sample. Then, if R is the range of the alpha particles in the sample, the fraction of alpha disintegrations in the element $dAdh$ which are counted is equal to $\frac{R-h}{2R}$. To obtain the total count rate integration is performed over all the elements $dAdh$ for which $h < R$. Provided the linear dimensions of the front surface are very much greater than R (nearly always true in practice) edge effects can be ignored. If we assume that the radioactivity is homogeneously distributed throughout the sample and that the concentration is N alpha disintegrations per unit volume per second, then we obtain the count rate C from a "thick" source (i.e. thickness $> R$):

$$C = \frac{NRA}{4} \quad (1)$$

Alpha particle "pairs" are emitted when two successive alpha disintegrations are separated by an isotope of short half-life (e.g. .158 seconds in the case of the nuclide Po^{216}). It is assumed that the two decays take place from the same spatial position, i.e. that recoil displacement effects are negligible. The fraction of alpha pairs from the element $dAdh$ which are detected as pairs will, of course, be equal to $\left(\frac{R-h}{2R}\right)^2$. Integration then yields the pairs rate P from a thick source:

$$P = \frac{mRA}{12} \quad (2)$$

where m is the number of alpha pairs disintegrations per unit volume per second. (This assumes that the ranges of the two alpha particles constituting the "pair" are both equal to R . The fact that this is not exactly true introduces a minor modification to equation (2) (Cherry, 1963) which will be ignored in the present treatment).

III. INHOMOGENEITIES:

It is of course possible to devise any number of types of inhomogeneity, and any general discussion would be extremely tedious and probably unrewarding. In practice alpha counting is usually performed on crushed samples, and the present discussion will be confined to three rather extreme types of inhomogeneity in the

distribution of radioactivity throughout the sample grains. For mathematical convenience cubical grains will be assumed; the fact that this is an obviously invalid assumption is unlikely to affect the semi-quantitative conclusions drawn from the calculations. Usually one is interested in obtaining values of the average activity throughout the whole volume of the sample. In what follows the quantities N and n of section (2) will therefore retain their definitions as "disintegrations per unit volume per second", although it must now be borne in mind that these are obtained by averaging out over the inhomogeneities involved. It should also be borne in mind that we shall continue to assume that alpha-recoil effects are negligible; this is usually still valid, but it is not true for all possible types of inhomogeneities.

(1) Surface Coatings: This is the type of inhomogeneity envisaged by Hurley (1950). We assume sample grains to be cubes of side d , and we assume further that all the radioactivity in a grain is contained in an arbitrarily thin surface coating. The case when the coating is of finite thickness will give a result intermediate between the homogeneous and the arbitrarily thin surface coating cases. The calculations are simple and will not be reproduced in detail. If the count rate is now C' and the pairs rate is P' ,

the following results are obtained:

$$(a) \quad d > R \quad \frac{C'}{C} = \frac{1}{3} \left[2 + \frac{d}{R} \right] \quad (3)$$

$$\frac{P'}{P} = \frac{2}{3} \left[1 + \frac{3}{4} \frac{d}{R} \right] \quad (4)$$

C and P are as given in equations (1) and (2). We see that the effect of the inhomogeneity is to give count and pairs rates which are anomalously high if interpreted on the basis of the homogeneous theory equations (1) and (2). If, for example, one takes $R = 25$ microns (true for an average alpha particle in an average geological material) and assumes $d = 150$ microns (probably typical of material which has been ground to an average but not especially high degree of fineness) then it is seen that the count rate obtained would be too high by a factor of 2.7 and the pairs rate by 3.7. It is to be noted that the pairs rate is more sensitive to the inhomogeneity than is the simple count rate.

$$(b) \quad R = nd \quad \text{where } n = 1, 2, 3, \dots,$$

Then we get

$$\frac{C'}{C} = 1 \quad (5)$$

and

$$\frac{P'}{P} = 1 + \frac{1}{6n^2} \quad (6)$$

In this case no anomalies arise in the count rate, while those in the pairs rate are much smaller than in case (a). Thus $\frac{P'}{P} = 1.04$ for $n = 2$, and $\frac{P'}{P} \rightarrow 1.00$ as $n \rightarrow \infty$. The case where n is non-integral does not yield quite such neat mathematical expressions and is not reproduced here. The deviations from formulae (5) and (6) are in this case small (of the order of 4% at most).

(2) Core concentrations: This is the inverse of case (1).

Here we assume that all the radioactivity is concentrated in point sources at the centre of cubical grains of side d . If $d \gg 2R$, we will, of course, obtain zero counts and pairs. The two non-trivial sub-cases are: (a) $R < d < 2R$. This gives

$$\frac{C'}{C} = \frac{2d}{R} - \frac{d^2}{R^2} \quad (7)$$

and

$$\frac{P'}{P} = \frac{3d}{R} - \frac{3d^2}{R^2} + \frac{3d^3}{4R^3} \quad (8)$$

(b) $R = nd \quad (n = 1, 2, 3, \dots)$

$$\frac{C'}{C} = 1 \quad (9)$$

$$\frac{P'}{P} = 1 - \frac{1}{4n^2} \quad (10)$$

We see from equations (7), (8), and (10) that this type of inhomogeneity generally results in anomalously low counts and pairs rates as opposed to the high rates which result from a surface coating of activity. Once again it is the pairs rates which are more sensitive to the departure from homogeneity.

(3) "Hot-spot" Activity: In this case we assume that the material is non-alpha active apart from the presence of "hot spots" consisting of cubical grains of side d . We assume that the alpha activity is homogeneously distributed within such a grain, and, further, that these grains are randomly distributed throughout the sample. The remainder of the sample is assumed to consist not of non-active grains of size d , but to be completely structureless; thus one can obtain a "hot spot" grain at an arbitrary distance from the sample face and not merely at distances which are integral multiples of d . The case when the whole sample consists of grains of cube d , some radioactive, some not, can of course easily be considered, but it would appear to be less interesting and less realistic than the situation dealt with here. The calculations give :

$$(a) \quad d < R \quad \frac{C'}{C} = 1 - \frac{d}{R} + \frac{1}{3} \frac{d^2}{R^2} \quad (11)$$

$$\frac{P'}{P} = 1 - \frac{3}{2} \frac{d}{R} + \frac{d^2}{R^2} - \frac{1}{4} \frac{d^3}{R^3} \quad (12)$$

$$(b) \quad d > R \quad \frac{C'}{C} = \frac{R}{3d} \quad (13)$$

$$\frac{P'}{P} = \frac{R}{4d} \quad (14)$$

As in case 2 the observed counts and pairs rates are lower than in the homogeneous case, and once again the pairs rate is more sensitive to the inhomogeneity. In terms of deviation from the "normal" counting rate, this inhomogeneity is the most serious of the three types considered; thus, in order to obtain C' agreeing with C to within 10% one would require d to be as low as about $.10R$ and 10% agreement between P and P' would require an even smaller d of about $.07R$. R is typically about 25 microns, and is even lower (down to about 10 microns) for the lower energy alphas. Avoidance of the effects of this "hot-spot" inhomogeneity would thus require grinding of the sample down to micron sizes.

IV. EXPERIMENTAL EVIDENCE:

A limited amount of experimental evidence is available concerning inhomogeneities in geological samples which have been alpha counted. All the instances which have been brought to our attention are indicative of surface coating effects, but it would be very surprising if the core and hot-spot types did not exist as well. The

first example is the paper by Hurley (1950) already referred to. He quotes alpha count rates as being "several times" (~ 3 or 4) too high for crushed granite samples, and from an excess of large pulses in the alpha spectrum and from leaching experiments he deduces that the anomalies are due to a thin surface coating. In an experiment involving Southern African granites (Cherry, unpublished) regrinding from 120 mesh down to about 10 micron size resulted in an average (30 samples) drop of 19% in the count rate and of 26% in the pairs rate. Finally, Gottfried et al. (1959) in their discussion of the lead-alpha age method state that "acid leaching of zircon may produce a 5 to 10 per cent loss in alpha activity in some samples of metamict zircon". Since this loss in alpha activity is not accompanied by an equivalent loss of lead it seems likely that an inhomogeneity effect is operating in the counting of the unleached metamict zircons. The above examples are all consistent in a semiquantitative way with the results of III (1).

V. THIN SOURCES:

If the source thickness is less than the alpha range equations (1) and (2) are no longer valid; the necessary modifications are discussed in the standard references (eg. Finney and Evans, 1935). The effects of inhomogeneities have been calculated for cases 1 and 2 (case 3 is somewhat unrealistic for thin sources). The count

rates do not differ from the homogeneous case, and the pairs rates only to a small extent (generally $< 5\%$). The results are consequently not of much interest and are not reproduced here; it is nevertheless worthwhile to draw attention to this advantage of thin-source counting.

VI. SUMMARY:

Inhomogeneities will in practice be more complicated than the simple types considered here. The types considered are, however, representative of fairly extreme conditions, and enable certain semiquantitative conclusions to be drawn:

- (a) Inhomogeneities can affect alpha count rates to a considerable extent.
- (b) The pairs count rate is generally more sensitive to a departure from homogeneity than is the simple total count rate.
- (c) For complete safety samples should be ground down to below micron size (i.e. $<$ one-tenth of the range of a low-energy alpha particle in normal geological material) and then homogenized. If this is done the standard equations (1) and (2) can be used for the determination of N and m .

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REFERENCES:

Cherry, R. D. (1963). The determination of thorium and uranium in geological samples. Geochim et Cosmochim. Acta, 27, 183.

Evans, R. D. and Goodman (1941). Radioactivity of Rocks. Geol. Soc. Amer. Bull., 52, 459.

Finney, G. D., and Evans R. D., (1935). The radioactivity of solids determined by alpha-ray counting. Phys. Rev., 48, 503.

Gottfried, D., Jaffe, H. W., and Senftle, P. E., (1959). Evaluation of the lead-alpha (Larsen) Method for Determining Ages of Igneous Rocks, U.S. Geol. Survey Bull., 1097-A. p.60.

Hurley, P. M., (1950) Distribution of Radioactivity in Granites and Possible Relation to Helium Age Measurements, Bull. Geol. Soc. of Amer., 61, 1.

Kulp, J. L., Holland, H. D., and Volchok, H. L. (1952) Scintillation alpha counting of rocks and minerals. Trans. Amer. Geophys. Un., 33, 101.

Turner, R. C., Radley, J. M., and Mayneord, W. V., (1958). The alpha-ray activity of human tissues. Brit. J. Radiol., XXXI, 397.

APPENDIX 4: THORIUM AND URANIUM CONTENTS
OF AUSTRALITES.

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THORIUM AND URANIUM CONTENTS OF AUSTRALITES

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THE thorium and uranium contents of six australites have been measured in this laboratory. The technique used was that of 'thick-source' alpha counting¹⁻³ combined with the thorium-*A* pairs method of Mayneord *et al.*⁴. A scintillation counter was used as a detector, and the experimental apparatus was similar to that described by Turner *et al.*⁵. A total alpha count-rate, *C*, and a 'pairs' rate, *P*, are measured. If one assumes radioactive equilibrium and a known uranium-238 to uranium-235 ratio, then *C* and *P* are related to the uranium and thorium concentrations *U* and *Th* by equations of the type:

$$C = k_1 \text{Th} + k_2 \text{U} \quad (1)$$

and

$$P = k_3 \text{Th} \quad (2)$$

The constants *k*₁, *k*₂ and *k*₃ depend on the decay constants and atomic weights of uranium-238, uranium-235 and thorium-232, the area of the sample and, finally, the ranges of the alpha-particles of the thorium, uranium and actinium series. The evaluation of these constants has been discussed in detail by me⁶; here it will suffice to point out that in practice *C* is about thirty times larger than *P*, and is accordingly subject to a much smaller percentage error in the counting statistics.

The australites used included two from Victoria (Nos. 1 and 4), two from South Australia (Nos. 355 and 475) and two from Western Australia (Nos. 379 and 1176). The samples were supplied by Dr. S. R. Taylor and Mrs. M. Kaye. They had all been ground to 120 mesh and had previously been analysed for alkali metals^{7,8}, trace elements^{9,10} and major elements¹⁰. No chemistry was necessary; the samples were merely packed and sealed on 'Perspex' rings in the manner described by Turner *et al.*⁵, allowed to stand for a month or more and then counted.

APPENDIX 5: THE ALPHA-RADIOACTIVITY OF PLANKTON.

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THE ALPHA-RADIOACTIVITY OF PLANKTON

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In recent years considerable attention has been paid to the problem of radioactive contamination of the marine environment, and several measurements of artificially produced radioactive isotopes in plankton have been reported (see, for example, Osterberg et al.¹). By comparison, the naturally occurring radioactivity of plankton has received scant attention. The activity due to the mixed beta-gamma emitter Potassium-40 has been the subject of some discussion and Rama et al.⁴ have made brief mention of Lead-210. The alpha-activity appears to have been almost totally neglected since the early work of Evans et al.² and Pryn et al.³ on the radium contents. A recent report by Marsden⁵, which indicated high alpha-activities and interesting problems associated with possible disequilibria in the radioactive series has revived interest in this problem, and as a result of this report a programme for investigating the alpha radioactivity of plankton has been started at the University of Cape Town.

EXPERIMENTAL PROCEDURE

So far only "total" alpha-counting plus thorium-series "pairs" measurements have been made. The experimental set-up is based on that of Turner et al.⁶. This consists of a sealed phosphor-sample system of high sensitivity and simplicity.

This type of system has been used with success in several investigations⁷ of samples from the natural radiation environment, and it provides (a) a measurement of the total alpha-activity and (b) an estimate of the percentage of this activity which is due to the thorium series. The particular set-up used in these experiments employed Levy-West G86 ZnS(Ag) as phosphor, E.M.I. 9530 B photomultiplier tubes and low cathode - to-first dynode resistor values⁸. This combination resulted in the low background value of less than 1 count per hour for a $4\frac{1}{2}$ inch diameter phosphor. It is perhaps worth mentioning that, on such a phosphor, one sample count per hour above background will correspond to less than .1 picocuries per gram of alpha-activity in the sample, or to a thorium content of less than .1 ppm in a hypothetical sample containing only the thorium series in equilibrium.

Sample preparation is very simple. The plankton is dried at 105°C, finely ground and then packed on the Scotch tape-perspex ring-ZnS phosphor system as described by Turner et al.⁶. The sample is sealed on top with additional tape. No emanation problems arise provided that the sample is left for two to three weeks after preparation in order to allow radon to regain equilibrium. Ashing of the sample was avoided in order to prevent loss of the volatile element polonium; in any event the extra concen-

tration provided by ashing was not required.

Results have been calculated using the usual "thick-source" alpha-counting formula (e.g. Finney and Evans⁹, Turner et al.⁶, Cherry¹⁰). This requires a knowledge of the range of the alpha-particle in the sample material, and the formula which assumes proportionality to $Z^{2/3}$ has been used in the present work. The range problem has been discussed previously¹¹ by the present writer; here it will suffice to mention that lack of consistent experimental knowledge concerning alpha-particle ranges in solids results in an inherent uncertainty in the absolute values of results obtained by thick-source alpha counting techniques. Thus the recent data of Kamke and Kramer¹² for alpha-ranges in boron (which has $Z^{2/3} = 2.9$, the same order as for plankton) indicate that the $Z^{2/3}$ formula gives ranges which are 23% too low for 4.5 M.E.V. alphas. Should these results be substantiated, then all the activity values in the present paper might have to be lowered by about 25%. $Z^{2/3}$ has of course to be calculated on the usual "atomic fraction" basis. For dry zooplankton a composition of major elements with an atomic ratio of 212: 176: 106: 16: 1 for O: H: C: N: P has been assumed. These values give $Z^{2/3} = 2.81$. The phytoplankton samples measured

are mostly diatomaceous, and atomic ratios of 191: 158: 95: 38: 15: 4: 2: 1 for O: H: C: Si: N: Ca: Fe: P have been used to calculate $Z^{2/3} = 3.11$. The compositions used are based on data given in Sverdrup et al.¹³, pages 230, 234, 236 and 237, and might be subject to some error. Fortunately, however, $Z^{2/3}$ is a slowly varying function, and the resulting error in $Z^{2/3}$ is likely to be unimportant at this stage; the 10% difference between the zoo- and phyto-plankton values of $Z^{2/3}$ is probably indicative of the order of magnitude of the most serious discrepancy which is likely to arise from this source.

SAMPLES AND RESULTS

The five sections of Table I represent different groups of samples. Section I comprises samples consisting predominantly of zooplankton which were collected at various dates from 1899 until early in 1962. With the exception of the last sample listed (No. 6) all these specimens were obtained from the collections of the South African Museum, Cape Town, and were supplied by Mr. J. G. Grindley of that institution. Sample No. 6 and those in Sections II and III were collected by the University of Cape Town research vessel "John D. Gilchrist". The Section II samples are also zooplankton; they are being collected at approximately monthly

intervals from the "Slangkop Station". Section III comprises phytoplankton data; these samples are collected at the same time as the zooplankton specimens of Section II, but with a different net. Finally, Section IV gives data for phytoplankton collected either during the 1958 I.G.Y. cruises of the S.A.S. "Natal" or during the 1962 International Indian Ocean Expedition cruises of the same vessel. The "John D. Gilchrist" and the S.A.S. "Natal" samples were provided by Messrs. J. Stone, F.J.R. Taylor and P. Zoutendyk of the C.S.I.R. Oceanographic Research Unit, University of Cape Town. The solitary sample in Section V represents the only pre-war phytoplankton specimen so far obtainable. It came from the same source as the samples of Section I.

Results are also given in Table I. Total alpha-activities are quoted in picocuries per gram (i.e. $\mu\mu$ curies/gm.). Relative standard deviations due to counting statistics are in all cases 5% or less, and are generally of the order of 3%. The most serious errors will probably arise from the alpha range problem discussed above; as previously indicated, it is possible that this could result in all the values quoted being too high by as much as 25%. Percentage contributions to the total alpha-activity by the activity due to the thorium series alone are also quoted. These are obtained by counting

the "pairs"^{6, 10} due to the successive alpha-decays of the isotopes Emanation-220 and Polonium-216. Since these "pairs" rates are, typically, lower by a factor of about 40 or 50 than the total count-rates, the errors due to counting statistics are appreciably larger than for the total alpha-activities. A standard deviation of about 20% would be average. A further uncertainty is caused by the fact that it is not known for certain whether the thorium series activity is in complete equilibrium from the isotope Thorium-232 downwards. This has been assumed to be the case in calculating the percentages quoted; should either Radium-228 or Thorium-228 prove to be the true parent of the "pairs" activity, the quoted values would have to be lowered by a factor of about 0.9.

The data in Table I requires to be supplemented by some comments about the time dependence of the counting rates of samples. All the data quoted in the table were obtained from counts during the period December 1963 to March 1964. Samples in Sections II and III were, if possible, counted about one month after collection (and about three weeks after drying and mounting); in some cases, however, the interval between collection and counting was as great as ten weeks. In addition to the results quoted, additional counts, separated in time by

varying intervals, have been made on several of the samples listed. The project has not been under way for a sufficiently long time for definite conclusions to be drawn, but the results so far obtained can be summarized thus:

- (i) None of the phytoplankton samples has exhibited any time dependence in the alpha-activity within the limits of statistical error.
- (ii) Several of the zooplankton samples in Section II, which are all recent samples, have shown slight decreases (of up to 25%) when recounted two to three months after the original count.
- (iii) With the exception of sample No. 6, which will be discussed separately, none of the zooplankton samples in Section I has exhibited any time dependence over a period of about six months.
- (iv) None of the samples has exhibited a rise in alpha-activity with time apart, of course, from the small rise sometimes observed due to radon build-up if the samples are counted too soon (within two or three weeks of drying).
- (v) The pairs rates statistics are at present too poor to permit of any serious conclusions re variations with time. It is nonetheless worth

mentioning that, within the wide limits of statistical error, no time dependence in the pairs rate has been observed for any of the samples.

- (vi) Sample 6 (zooplankton) is worthy of special mention since its alpha-activity has been followed intermittently over a period of two years. A month after preparation its alpha-activity was as high as 19 pc/gm. This declined steadily until eighteen months later (in September, 1963) the level was down to 2.1 pc/gm. In January, 1964, the value was as given in Table I (2.1 pc/gm.) indicating no significant change during the intervening four-month period. The rate of fall-off between March 1962 and September 1963, as measured by a set of six readings, fitted an exponential decay with a half-life of about 140 days. It is difficult to see how this can be ascribed to anything other than the presence of the well-known alpha-emitter Polonium-210, which has a half-life of 138 days. The experimental facts support the hypothesis that the sample initially contained about 17 pc/gm. of unsupported Polonium-210 plus a "long-lived"

($T_{1/2} > 2$ years) alpha-activity of about 2 pc/gm.

No statistically significant variation in the pairs rate was observed between March 1962 and January 1964; the percentage contribution of the thorium-series activity has thus risen from about 2% to the present value of 22% .

DISCUSSION.

(a) The total alpha-activity of plankton.

The data presented indicate that fresh plankton contains in general (if the samples tested are typical) upwards of 4 picocuries of alpha-activity per gram of dried sample. The means for the "routine" samples of Sections II and III are in fact 6.7 pc/gm. for zooplankton and 5.1 pc/gm for phytoplankton. It is clear, moreover, that for the zooplankton some of the initial activity is often of "short-lived" (< 2 years) duration, and that this short-lived activity can, as in the case of sample 6 and possibly GIL 526 as well, contribute an activity considerably in excess of the "basic" 4 pc/gm. No such short-lived activity has been observed in phytoplankton samples, but this may merely be a reflection on the relatively small number of samples thus far tested. Some phytoplankton samples, on the other hand, do show almost sensationally high values of alpha-activity, and this high level seems to persist for a time of five years or more -

see the I.G.Y. samples in Section IX.

It is of interest to consider the above comments in relation to the radiation dosage received by the living planktonic organism. The range of a typical alpha-particle in living plankton will be about 10 to 15 microns. If we consider a plankton specimen with dimensions very much larger than this figure (true for most zooplankton), then to a good approximation all the alpha-particles emitted by the specimen will be absorbed in the specimen itself. This will of course not be true if the alpha-particles are distributed on the surface alone, but even in this case only a small correction factor of the order of 2 or 3 will be involved. Suppose that the plankton contains 4 pc of alpha-activity per gm. of dried material. The concentration factor between "wet" and dry plankton will be about 16 (Sverdrup et al.¹³ p. 929), thus giving us a concentration of about .25 pc alpha-activity per gm. of living plankton. If we next assume that the average alpha-particle energy is 5 M.E.V., then we find that the radiation dosage to the organism from its own inherent alpha-activity is about $(2.6)(10^{-3})$ millirads per hour or about 23 millirads per year. Furthermore, alpha-radiation is generally considered to have a relatively high biological efficiency; if we use the usually quoted relative biological efficiency (R.B.E.)

of 10 for naturally occurring alphas, then we end up with a dosage of about 230 millirem per year. In an interesting paper, Folsom and Harley¹⁴ quote radiation doses in millirads per year in "eleven radiological domains". They estimate the radiation doses to a micro-organism near the sea-surface to be about 39 millirad per year from external sources; since most of this is due to minimum ionization radiation, this can be considered to be equivalent to about 39 millirem per year. It is thus apparent that the radiation dose to our plankton specimens will be derived very largely (80% or more) from internal alpha radio-activity. Contrast this with the situation in human body tissue:
¹⁵
 Eisenbud quotes tissue dose rates of between 120 and 140 millirem per year to various body tissues, and the contribution of internal alpha-activity to these figures varies between 4 and 15%. Furthermore, it should be emphasized that the "basic" figure of 4 pc/gm. is definitely at the lower limits of the alpha-activity concentration in fresh plankton as far as the present samples are concerned. Consider the phytoplankton sample NGY 16, with about 96 pc alpha-activity per gm. dried plankton. This sample has been identified by Mr. F.J.R. Taylor as a mixed bloom with

the relatively large diatom Rhizosolenia hyalina Ostenfeld predominating. The diatoms in this sample have typical dimensions of about 300 microns length and 35 microns diameter, and with typical alpha-ranges of about 10 to 15 microns it is reasonable to assume that something like half of the alpha energy is internally absorbed. A simple calculation then shows that the alpha-radiation will deliver a dose of about 2.8 rem per year to the diatom. This is exceptionally high, and bears comparison with the large external radiation doses received by the human population living on the thorium-bearing sands in Kerala, India (see Eisenbud¹⁵.) Most phytoplankton are of course smaller, and will thus tend to "lose" more of their alpha-particle energy to the surrounding sea. What has been said will nonetheless suffice to indicate that at least some plankton must carry an abnormally high internal radiation burden of natural origin. It is perhaps also relevant to compare the dried plankton figure of 4 pc./gm. with the reported alpha-activities of foodstuffs. Thus Turner et al²⁴ quote up to .005 pc./gm. for meats, .04 pc./gm. for fish and .6 pc./gm. for cereals. Only in exceptional cases (eg. Brazil nuts, 1.7 pc./gm.) do the activities rise above the dried plankton figure.

(b) Alpha-emitting elements in plankton.

The results presented above involve no chemistry or alpha-spectrometry, and do not therefore permit definite identification of the nuclei responsible for the alpha-particle emission. However, the use of the "pairs" technique, the measurements of time dependence of the alpha-activity and the fact that a few measurements have been made on relatively old samples do allow of a few reasonable deductions. We shall consider the figure of 4 pc/gm dried material to be "basic" for fresh plankton, as in the previous section. It must, however, be borne in mind that this figure is probably on the low side and is certainly subject to very wide variation. We shall discuss elemental abundances as follows:

- (i) Polonium: As suggested above, there is strong evidence that the 138-day isotope Polonium-210 can in some cases be responsible for a substantial portion of the initial activity of plankton specimens. This is not surprising; Polonium-210 is, after all, a "natural fall-out" product, and Hill^{16,17} and others have measured this nuclide in grass, various tissues and other environmental samples. What is surprising is that the measurements on sample 6 and on some of those in Section II seem to indicate that the polonium is, in part at

least, unsupported by its parent Lead-210. Lead-210 has a 22 year half-life, and is generally considered to be an important contributor to natural fall-out. Since the residence time of Lead-210 in the atmosphere is estimated to be of the order of a few weeks,^{18,25} it is unlikely that Polonium-210 will accompany fall-out Lead-210 in amounts approaching equilibrium activity. In fact, Burton and Stewart¹⁸ found an average Lead-210 to Polonium-210 activity ratio of 10 in rain-water samples. After fall-out Lead-210 will of course decay to Polonium-210, and one would therefore expect an exponential increase of alpha-activity with the 138-day Polonium-210 time constant if the plankton samples at the time of collection contained appreciable amounts of fresh, unsupported, Lead-210 fall-out nuclei. No such increase has been observed in any of our samples, although increases in activity with time have been reported by Marsden⁵. The results quoted above might even be construed as indicating preferential intake of Polonium-210 by planktonic organisms, although obviously much more data is required before the situation can be clarified. It is perhaps worth drawing attention to the fact that Polonium-210 radioactivity appears to be assuming increasing biological

importance; thus Hill¹⁷ states that "in bone and many of the soft tissues of normal unexposed human subjects, Polonium-210 appears to be responsible for a large part of the total natural activity". He quotes Polonium-210 concentrations in various human tissues which are typically of the order of 4×10^{-3} pc/gm. of wet tissue. If we assume (see Sections I and II of the table) that about half of the "basic" 4 pc/gm. in dry zooplankton is due to Polonium-210, then a typical value would appear to be of the order of 125×10^{-3} pc/gm. "wet" plankton - considerably larger than for human tissue. The "concentration factor" for Polonium-210 from sea-⁴ water to zooplankton is also of interest. Rama et al. quote a Lead-210 concentration in surface waters of about .1 disintegrations per minute per litre, or about 5×10^{-5} pc/gm.¹⁹ Picciotto quotes a Radium-226 concentration in sea-water of about 9×10^{-5} pc/gm.⁵ Both of these nuclei are parents of Polonium-210, and it seems reasonable to assume that the Polonium-210 content of sea-water will not be more than 10^{-4} pc/gm.⁴ Comparing this with our figure of 250×10^{-3} pc/gm.³ in wet plankton implies a concentration factor of more

than 2500; even this figure is likely to be a conservative estimate.

(ii) Thorium series isotopes: The thorium series comes into equilibrium rapidly after the 1.9 year nuclide Thorium-228, and it is plain that the thorium series activity in the plankton must be supported by either Thorium-228 or its precursors, 6.7 year Radium-228 and/or 1.4×10^{10} year Thorium-232. The fact that the 1899 and 1904 samples still show considerable thorium-series activity indicates that the long-lived Thorium-232 is probably at least partially responsible. For the purposes of the present discussion it seems safe to assume that the thorium series will contribute, typically, upwards of .4 pc/gm. of dried plankton to the alpha activity. This is equivalent to about .025 pc/gm. of wet plankton. Calculations based on Picciotto's data (which gives 1.2×10^{-7} dis/sec/ml. for Thorium-228 in sea-water) give a thorium series contribution to the sea-water alpha-activity of about 2×10^{-5} pc/gm. This gives a concentration factor of about 1250, and again this is likely to be a conservative estimate.

⁴
Rama et al. have suggested in their paper on Lead-210

in the ocean that "the marine biosphere is responsible for the conveyance of lead from surface to deeper waters". The results just discussed indicate that the same may be true for the nuclides at the head of the thorium series, although of course the ferric hydroxide precipitation mechanism suggested by Pettersson²⁰ to account for the deficiency in sea-water of ionium (i.e. Thorium-230, a uranium series nuclide) might also operate.

(iii) Uranium and radium: After allowing for short-lived activity and for the thorium series contributions of (i) and (ii) we are left with upwards of 1 to 2 pc/gm. of alpha-activity unaccounted for. This must presumably be due to the uranium-series, and is probably supported by 1620-year Radium-226 and/or one or both of its uranium parents. 1.6 pc/gm. dry plankton would give about .1 pc/gm. wet plankton; Picciotto's sea-water data gives us a concentration of just under .002 pc/gm. sea-water for the uranium series contributions, implying a concentration factor of the order of 50. It is interesting to note that the pre-war measurements of Evans et al.² on a single zooplankton sample gave a concentration factor of about 100 for radium, while

those of Føyn et al.³ on a phytoplankton sample gave a factor of 1000 for the same element. The data we have quoted do not enable us to distinguish between the uranium and the radium contributions, but the approximate agreement with the sample of Evans et al. is interesting. It would, of course, be easy to match the Føyn et al. sample with one of the more active phytoplankton samples from Section 3 of the table. It is perhaps worth stating that Evans et al.² quoted a content of $.04 \times 10^{-12}$ gm. radium per gm. dry zooplankton, while Føyn et al.³ obtained 2×10^{-12} gm. radium per gm. dry phytoplankton. If we assume Radium-226 to be the head of the uranium series contribution, and assume radioactive equilibrium from there downwards, then 1 pc/gm. of radium-supported alpha-activity corresponds to $.2 \times 10^{-12}$ gm. radium per gm. dry plankton.

(c) Locality of Sample Collection.

Since relatively few samples have been measured in this preliminary survey, very little emphasis has been placed on the question of sample locality. For record purposes, we can

divide up the collection sites as follows:

- (a) All the samples in Sections II and III of the table were obtained at the "Slangkop Station", situated about 7 miles offshore west of the Cape Peninsula.
- (b) Samples No. 3, 4, 6 and "Robben Island" were also obtained in the vicinity of the Cape Peninsula.
- (c) Sample No. 5 was obtained from Lambert's Bay, about 120 miles north of Cape Town.
- (d) Sample No. 1 was from Mossel Bay, about 250 miles east of Cape Town.
- (e) Sample No. 2 and the I.G.Y. and Indian Ocean Expedition samples in Section IV were obtained off the South-East coast of South Africa between Port Elizabeth and Durban. NGY 16 and NIOE 7 are the only two of these samples which were obtained at points clearly off the continental shelf. The IGY samples in Section IV have²¹ been described in detail by Zoutendyk.

It is tempting to associate the higher activities of the Section IV samples with the warmer waters of the Eastern side of the sub-continent, but this is not justified on the basis of the data presented here. Additional information is obviously required.

SUMMARY

The situation can be summarized as follows:

(a) Plankton samples exhibit relatively high and easily detectable levels of alpha-activity. A value of about 4 pc/gm. dried plankton would appear to be a conservative estimate for a typical sample but wide variations are observed.

(b) Some phytoplankton samples exhibit exceptionally high levels of activity of up to nearly 100 pc/gm. dried material. Such samples must, if the organisms are large enough compared with the alpha-particle range, be subjected to abnormally high radiation doses of the order of 20 times the dose to "normal" human tissue. The genetic and evolutionary implications of such doses might be worth considering

(c) Some zooplankton samples exhibit a relatively short-lived activity which is probably identifiable with the 138-day nuclide Polonium-210. This presumably arises from "natural fall-out", although the actual mechanism of incorporation into the organism is not clear.

(d) It is clear that plankton samples must concentrate the heavy alpha-emitting elements from sea-water. Crude

estimates of the concentration factor would appear to be between 1000 and 10,000 for thorium series nuclides and for polonium, and between 100 and 1000 for radium and/or uranium. Biological transport of at least some of these elements from surface to deeper waters must be a mechanism of some importance.

Further investigations should be interesting, and the following projects are suggested:

- (i) A world-wide survey of plankton alpha-activities in an attempt to establish a "global" average.
- (ii) A detailed survey of large numbers of samples from limited areas in order to establish the magnitude of local variations in alpha-activity.
- (iii) An investigation into samples collected at depth; virtually all the data reported here concerns 0 to 100 metre surface samples.
- (iv) Long term (of the order of years) study of time variations in the alpha-activity. It would be particularly interesting to know whether Polonium-210 decay is exhibited in samples collected at sites remote from land masses and therefore presumably less subject to "natural fall-out".
- (v) Attempts should be made to ascertain whether

particularly high alpha-activities are associated with particular planktonic species; see, for example, Osterberg's ²² work on the accumulation of artificial radionuclides by the organism Euphausia pacifica. It might well be that some phytoplankton species are ²³ "accumulator" plants of the type described by Schütte .

(vi) Lastly, and perhaps most important of all, alpha-spectroscopic investigations should be undertaken in order to identify conclusively the individual alpha-emitting nuclides present in plankton.

ACKNOWLEDGMENTS.

It is a pleasure to thank Sir Ernest Marsden for drawing my attention to this problem, and Professor J. H. Day and Messrs. J. G. Grindley, J. Stone, F. J. R. Taylor and P. Zoutendyk for the provision of samples and for much useful discussion. Mr. L. A. Pasvol and Mr. L. V. Shannon are to be thanked for preparing some of the samples for counting and financial assistance from the C.S.I.R. Oceanographic Research Unit at the University of Cape Town is gratefully acknowledged.

TABLE I

ALPHA-ACTIVITIES OF DRIED PLANKTON SAMPLES

Section and type	Sample No.	Date of collection	Total alpha activity in pc/gm. dried material	Thorium series contribution in per cent.
SECTION I ZOOPLANKTON	1	1899	1.8	29
	2	1904	3.6	28
	3	1947	2.5	32
	4	1950	2.0	46
	5	1957	2.5	14
	6	1962	2.1	22
SECTION II ZOOPLANKTON	GIL 526	2/10/63	12.0	17
	GIL 527	29/10/63	3.9	13
	GIL 528	26/11/63	6.7	22
	GIL 537	18/12/63	5.3	31
	GIL 536	29/ 1/64	5.7	14
SECTION III PHYTOPLANKTON	GIL 526	2/10/63	7.7	20
	GIL 527	29/10/63	3.4	34
	GIL 528	26/11/63	3.6	17
	GIL 537	18/12/63	4.4	16
	GIL 536	29/ 1/64	6.3	29
SECTION IV PHYTOPLANKTON	NGY 8	2/ 3/58	18.3	35
	NGY 16	3/ 3/58	95.5	8
	NGY 25	18/ 5/58	16.5	14
	NGY 29	19/ 5/58	28.6	8
	NGY 33	21/ 5/58	31.4	13
	NGY 38	22/ 5/58	5.5	29
	NGY 42	24/ 5/58	6.3	26
	NIOE 7	8/ 4/62	4.0	33
	NIOE 18	12/ 4/62	6.5	36
SECTION V PHYTOPLANKTON	ROBBEN ISLAND	7/ 7/35	3.8	24

REFERENCES.

1. Osterberg, C., Small, L. and Hubbard, L., Nature, 197, 883 (1962).
2. Evans, R. D., Kip, A. F. and Moberg, E. G. American Journal of Science, (5) 36, 241 (1938).
3. Föyn, E., Karlik, B., Pettersson, H. and Rona, E. Göteborgs Kgl. Vetenskaps-Vitterkrets Samhäll. Ser. B. 6, No. 12 (1939).
4. Rama, Koide M. and Goldberg, E.D., Science, 134, 98 (1961).
5. Marsden, E., Proc. of the International Symposium on Natural Radiation Environment, Houston, 1963. (In press, University of Chicago Press).
6. Turner, R. C., Radley, J. M. and Mayneord, W.V., Brit. J. of Radiology, XXXI, 397 (1958).
7. For example, Turner, R. C., Radley, J. M. and Mayneord, W. V., Nature, 189, 348 (1961).
8. Pagano, R., Damerell, C. J. S. and Cherry, R. D., Rev. Sci. Instr. 33, 955 (1962).
9. Finney, G. D. and Evans, R. D., Phys. Rev. 48, 503 (1935).
10. Cherry, R. D., Geochim. et Cosmochim. Acta, 27, 183 (1963).
11. Cherry, R. D., Proceedings of the International Symposium on Natural Radiation Environment, Houston, 1963. (In press, University of Chicago Press).

12. Kamke, D. and Kramer, P., Zeitschrift für Physik, 163, 465 (1962).
13. Sverdrup, H. V., Johnson, M. W. and Fleming, R. H., "The Oceans", Prentice Hall, New York (1942).
14. Folsom, T. R. and Harley, J. N., "Comparison of Some Natural Radiations Received by Selected Organisms", in "The Effects of Atomic Radiation on Oceanography and Fisheries", Publication No. 551, N.A. of Sciences - N.R.C., Washington, D.C. (1957).
15. Eisenbud, M. "Environmental Radioactivity", McGraw-Hill, New York (1963), p. 170.
16. Hill, C. R., Nature, 187, 211 (1960).
17. Hill, C. R., Health Physics, 8, 17 (1962).
18. Burton, W. M. and Stewart, N. G., Nature, 186, 584 (1960).
19. Picciotto, E. E. in "Oceanography", American Assn. for the Advancement of Science, p. 367 (1961).
20. See H. Pettersson in "Nuclear Geology", ed. H. Paul, p.115, John Wiley, New York, (1954).
21. Zoutendyk, P., University of Cape Town Oceanography Department, Publication No. 1, (1960).
22. Osterberg, C., Science, 134, 98 (1961).
23. Schütte, K. H., in "The Biology of Trace Elements", Crosby Lockwood, London (1964), p. 156.

24. Turner, R. C., Radley, J. M. and Mayneord, W. V.,
Health Physics, 1, 268 (1958).
25. Reference 15, but p. 158.

APPENDIX 6: TOTAL GRANITE ALPHA SPECTRA FROM A LARGE AREA ION
CHAMBER.

UNPUBLISHED MATERIAL.

Acknowledgements: The granite samples and information pertaining thereto were supplied by Dr. L. O. Nicolaysen of the Bernard Price Institute for Geophysics, Johannesburg. The preparation of the samples for counting and the measurements were made by myself with assistance and guidance from Dr. C. R. Hill, of the Physics Department of the Royal Cancer Hospital, London. The large area ion-chamber used was the instrument designed and developed by Dr. Hill.

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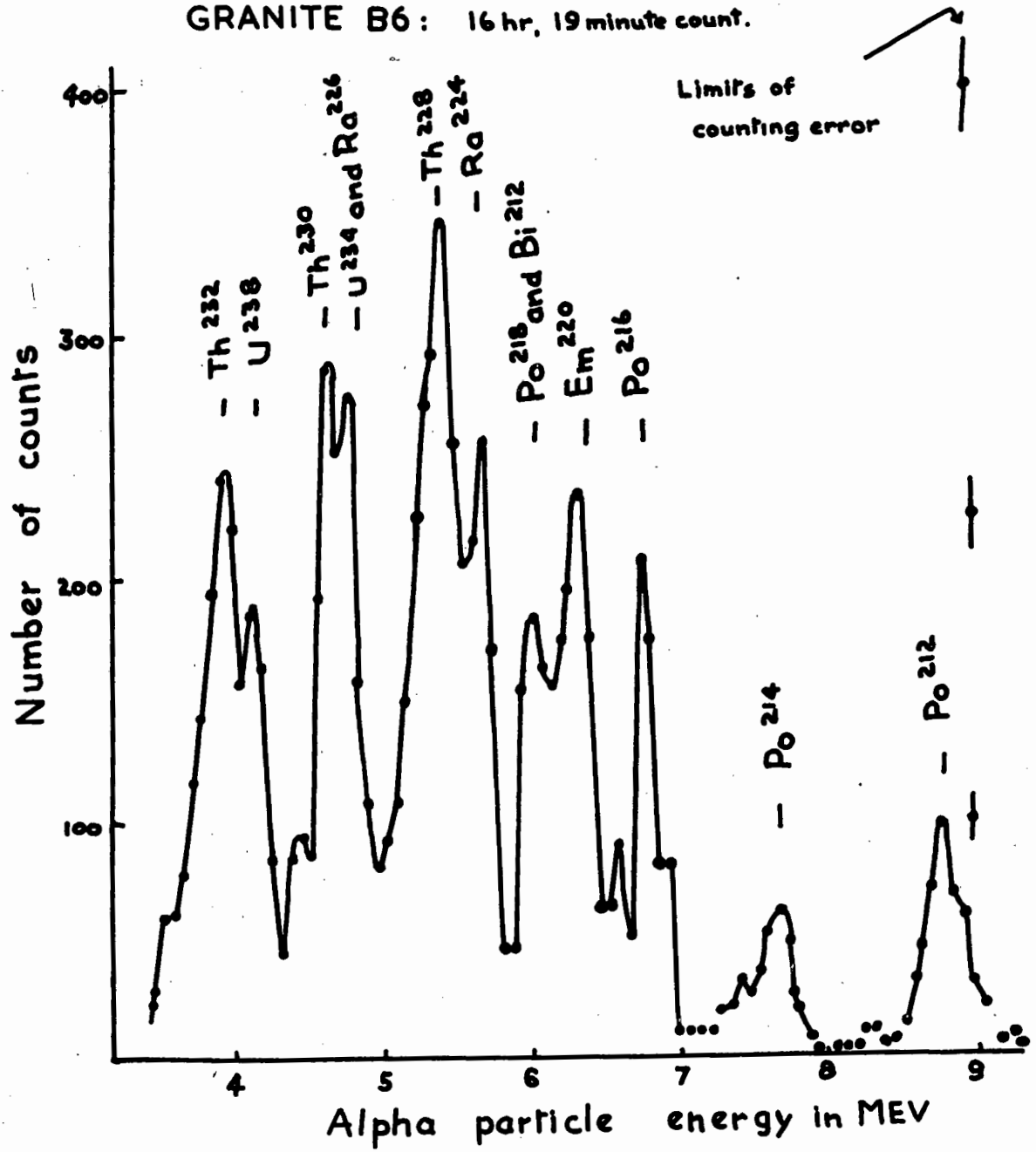
Two alpha spectra illustrated on the following pages are included in order to illustrate the potentialities of the large area (15,000 sq.cm.) ion-chamber developed by Dr. C. R. Hill. (See Hill, C. R., Nuclear Instruments and Methods, 12, 299 (1961).) Crushed granite samples B6 and OG 10 were finely ground under teepol in a mechanical mortar and pestle and then sprayed onto an aluminized cellulose acetate sheet (See Hill, op.cit.). The sheet then formed the cylindrical cathode of the ion-chamber, and the alpha-spectra were obtained by conventional multichannel pulse height analysis of the ion chamber pulses. The great sensitivity of the technique (despite the complete absence of any chemistry) is immediately obvious. It is interesting to compare this method with the semi-conductor detector technique used in Appendix 7. In the latter microgram quantities of a "hotter" sample (viz. a radioactive mineral from a granite) are used, and fewer counts result in a longer counting time. The area of the sample is, however, over 15,000 times smaller than for the Hill ion chamber.

The results show an interesting feature. Both samples are considered to be geologically "fresh" granites, and indeed, B6 gives a completely normal "thorium-series" type spectrum with a minor uranium-series admixture. The OG 10 spectrum is predominantly thorium-series, but it shows a clear peak at about 4.68 MEV. This is almost certainly due to a combination of some

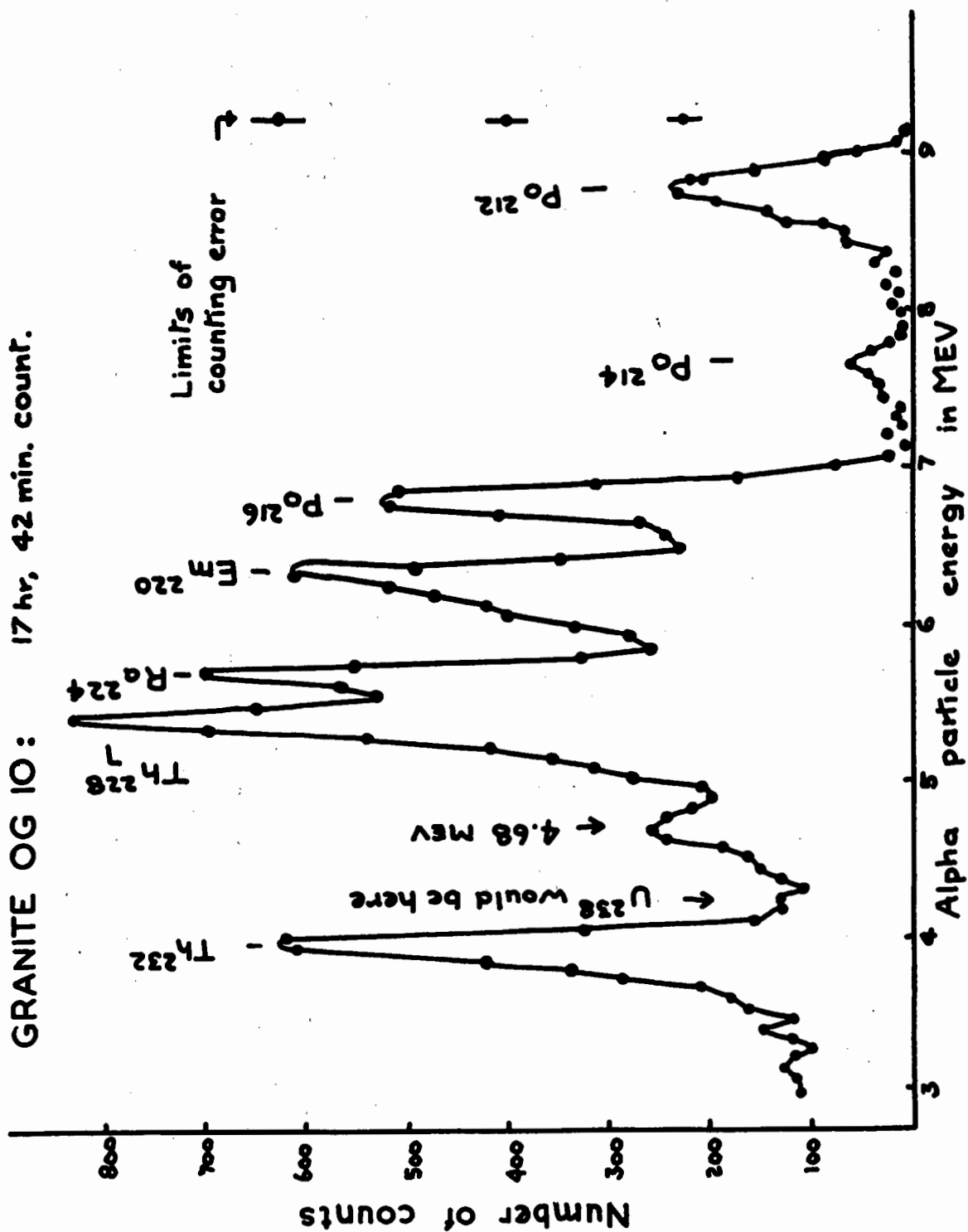
or all of the three alpha-emitters thorium-230, uranium-234 and radium-226, which have their main alpha groups at 4.68, 4.77 and 4.78 MEV respectively. These are, however, all uranium-series nuclides, and the surprising fact is that there is almost no sign of the parent nuclide uranium-238 in the spectrum. The most plausible explanation is that uranium has been leached out of the sample, and that the 4.68 MEV peak represents the less mobile nuclide thorium-230 plus, probably, some radium-226. It is worth stating that the OG 10 spectrum result has been checked by repeated runs on the ion chamber and also by repeating the measurement with a fresh sample from the same locality.

The Hill chamber has not previously been used for measurements on geological samples. The brief results presented here suggest that this type of instrument might be a useful accessory in geological age laboratories where it is desired to check on the equilibrium or otherwise of dubious samples.

GRANITE B6: 16 hr, 19 minute count.



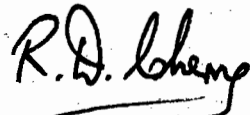
GRANITE OG 10: 17 hr, 42 min. count.



APPENDIX 7: UNIDENTIFIED EXCESS ALPHA ACTIVITY IN THE 4.4 MEV
REGION IN NATURAL THORIUM SAMPLES.

(NATURE, in press, by R. D. Cherry, K. A. Richardson and
J. A. S. Adams).

Acknowledgements: These results were obtained while I was on leave
at Rice University, working in the laboratory of Dr. J. A. S. Adams,
Professor of Geology. The original Conway granite sample was
supplied by my co-authors, and they were responsible for the
mineral separations, the sample preparations and the plutonium
fraction separation. The calibration of the semi-conductor
set-up and the actual measurements were performed jointly by
Dr. Richardson and myself, and I was responsible for the initial
draft of the paper.



R. D. CHERRY.

**UNIDENTIFIED EXCESS ALPHA ACTIVITY IN THE 4.4 MEV REGION
IN NATURAL THORIUM SAMPLES.**

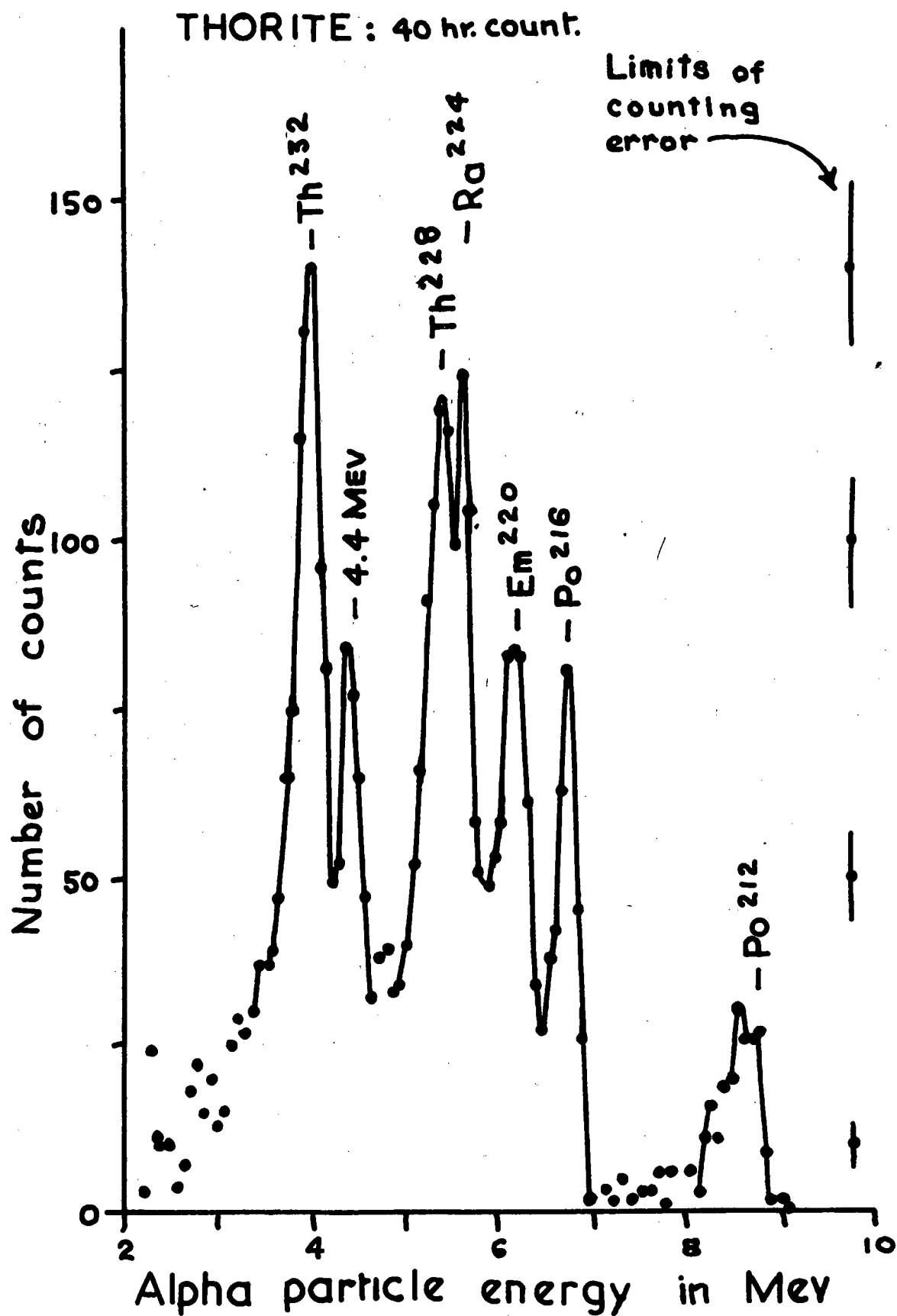
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***on leave from Department of Physics, University of
Cape Town, South Africa.**

Cherdyntsev and Mikailov¹ recently reported the presence in geologically young samples of an alpha-particle emitter with a complex spectrum in the 4.2 to 4.6 MEV region. They detected this alpha emitter in preparations of "thorium" and "uranium", separated from samples of molybdenite and fossil bone; these preparations contained subordinate amounts of other elements and exhibited excess activity in the above energy band. Additional experimentation involving alpha-gamma coincidence measurements and ion-exchange chemistry was employed to substantiate their claim that the radioactive element causing the activity was Curium-247. This identification was considered to be in accord with previous work^{2,3} which indicated the presence in some natural minerals of an excess activity of a daughter of Curium-247, viz. the well-known nuclide Uranium-235.

The main purpose of the present communication is to report that we too have observed an unidentified alpha activity with an energy of about 4.4 MEV in certain samples. The figure on the next page shows the alpha-spectrum obtained from the mineral thorite separated from a sample of Conway granite from New Hampshire, U.S.A. (Thorite and other radioactive minerals in the Conway granite were identified by Richardson⁴, and alpha particle spectrometric studies of these minerals have been



described by Richardson⁴, and Adams⁵). A few micrograms of thorite were dissolved in acid, and the solution was evaporated on a stainless steel planchet. The planchet was then placed in a vacuum chamber, a millimetre or two away from a 1-cm²-area semi-conductor detector. The resulting spectrum was measured on a multichannel pulse height analyzer in a counting period of 40 hours.

The detector used in this experiment had a resolution of less than 1% for alpha particles in the energy range shown in Figure 1. However, the overall resolution in this spectrum, limited by the source thickness, is between 5% and 10%. Shortly after the spectrum in Figure 1 was obtained, background in the counting chamber was measured over a four day period. No background alpha activity was found except a negligible amount in the 5.48 MEV region, attributed to Emanation-222. Errors in the number of counts in each channel, due to counting statistics, are indicated on Figure 1. The 4.4 MEV line has been resolved in spectra from replicate counts of the source represented in Figure 1.

It can be seen that the resulting spectrum is a typical "thorium series" spectrum with two exceptions, viz. (i) a line at about 4.38 MEV and (ii) a minor peak at about 4.77 MEV. The latter is almost certainly representative of a minor contribution from the uranium series nuclides Uranium-234 (4.77 MEV), Radium-226 (4.78 MEV) and Thorium-230 (4.68 MEV) and need cause no comment.

Other members of the uranium series are probably also present but their activity is obscured by the heavy thorium series predomination. Thus the bulge on the upper side of the 3.98 MEV Thorium-232 peak can be explained plausibly as the result of a contribution from Uranium-238 (4.18 MEV). The line at 4.38 MEV is more intriguing, and forms the basis of this communication. Before discussing it further, it is perhaps worthwhile to mention that a similar (although not so pronounced) line has been observed at about 4.4 MEV in the alpha-spectrum from some grains of the mineral huttonite from the same granite. Once again this is a spectrum dominated by the thorium series alpha activity.

Our results, unlike those of Cherdyntsev and Mikhailov, were obtained without any substantial prior chemical treatment - dissolution in acid is all that was involved. Reservations about chemical uncertainties and contamination possibilities are thus considerably reduced, and we feel that our results provide substantial support for the above authors' claim that there is excess alpha-activity present in certain natural samples in the 4.2 to 4.6 MEV region. Positive and definite identification of the source of this activity is, we feel, still an unresolved problem. A search through tables of known alpha-particle energies (Table I of Perlman and Rasmussen⁶ and Table 26 of Hanna⁷) reveals that the only nuclei which are known to emit alpha-particles of energy between 4.25

and 4.55 MEV in any quantity (1% of the total alpha-activity being taken as a criterion) are Uranium-235, with a major group at 4.40 MEV, and Uranium-236 with groups at 4.45 and 4.50 MEV. Uranium-236 has a half-life of 2.4×10^7 years⁶, and it is accordingly highly unlikely that it will still continue to exist unsupported in present-day specimens. The Uranium-235 alpha-energy is almost exactly right. However, examination of Figure I shows that if the unidentified activity is assigned to Uranium-235 then we require a staggering $U^{235}: U^{238}$ activity ratio, one to two orders of magnitude greater than the usual value encountered in nature. This is improbable to say the least; even the relatively minor Uranium-235 "excesses" of up to 1.45 times normal which have been reported by Cherdyntsev and others are not yet fully substantiated (See, for example, the negative results of Wetherill et al.⁸). It thus appears unlikely that the 4.4 MEV activity can be ascribed to an alpha-emitter whose energy spectrum has already been measured experimentally.

Future experimental work on alpha-radioactivity might well provide the answer. Meanwhile, we are left with the task of speculating as to which "unknown" alpha-emitter is responsible. Alpha-decay energetics and systematics are of some help in providing a lead. Thus Figure I of Perlman and Rasmussen⁶ shows that an alpha-emitter giving the required energy and possessing a sufficiently long life is most likely to be found either in the region between

A-230 and A-250 or else in a rather narrow band around or just below A-208. A more detailed study has suggested to us only two possibilities, viz. Curium-247 (as suggested by Cherdyntsev and Mikhailov¹) and Plutonium-244. Our own work, since it has thus far involved no chemistry and no attempts at refinements such as alpha-gamma coincidences, can shed no further light on the situation, and if Cherdyntsev and Mikhailov's extra information in these spheres is substantiated, then Plutonium-244 would appear to be ruled out. We are, however, unconvinced by their identification of Curium-247 for the following reasons:

(i) They state that "the decay period of Curium-247 is estimated at about $(2.5 \pm 0.5) \times 10^8$ years." A recent careful redetermination by Fields et al.⁹ has, however, given a half-life of $(1.64 \pm 0.24) \times 10^7$ years. If this is so, then we must reject Curium-247 on the same grounds that we have rejected Uranium-236, i.e. it is highly unlikely that there is still sufficient Curium-247 around to make a substantial contribution to an alpha spectrum.

(ii) Agreement with the predicted decay-energy of Curium-247 is not very good. Thus Foreman and Seaborg¹⁰ estimate the Q-value for the Curium-247 decay to be 5.29 MEV. This implies a ground-state alpha-particle energy of about 5.18 MEV. From this we can subtract an amount of up to .25 MEV to allow for decays to excited states (Cherdyntsev and Mikhailov detected alpha-gamma

coincidences with gammas of up to .25 MEV). The predicted alpha-particle energy could then be as low as 4.93 MEV. This is far above the median observed energy of about 4.4 MEV, and close examination of Figure 6 of Foreman and Seaborg shows that it is highly unlikely that their prediction is in error by more than .2 MEV.

What then, about Plutonium-244? This, too, has a half-life which is rather too low to be feasible, viz. $(7.6 \pm 2) \times 10^7$ years as determined by Diamond and Barnes¹¹ seven years ago. Its possible existence in nature has been considered previously¹², but it has generally been disregarded since the half-life was determined experimentally. A plutonium fraction from our sample with Plutonium-236 tracer showed no excess activity at 4.4 MEV.

In conclusion, we would suggest that great interest would attach to

- (a) Attempts to find excess alpha-activity in the 4.4 MEV region in other naturally occurring samples
- (b) The application of chemical and coincidence techniques to such excess activity in order to check on the results of Cherdymtsev and Mikhailov

and

- (c) A redetermination of the Plutonium-244 half-life, and, if feasible, a determination of the energies of the

7.

Plutonium-244 alpha-particles in order either to
eliminate finally or to substantiate the claims of
Plutonium-244.

Acknowledgement:

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REFERENCES:

1. Cherdyntsev, V. V. and Mikhailov, V. P. Geochemistry (English Translation), no.1, p. 1, (1963).
2. Cherdyntsev, V. V., Isabayev, A. A., Syrkov, Yu. A., Orlov, D.P. and Usatov, E. S. Geokhimiya, No. 4, 373 (1960).
3. Cherdyntsev, V. V., Orlov, D. P., Isabayev, E. A. and Ivanov, V.I., Geokhimiya, No. 10, 840 (1961).
4. Richardson, K. A., Radioactivity, sites of alpha emitters, and radioactive disequilibrium in the Conway granite, Ph.D. thesis, Rice University, (1963).
5. Adams, J. A. S. , Geologic aspects of thorium recovery from common rocks, Oak Ridge Technical Information Extension Service, Paper No. TID-18456, February, 1963.
6. Perlman, I. and Rasmussen, J. O., "Alpha Radioactivity" in Handbuch der Physik, Vol XLII, ed. S. Flugge, Springer-Verlag, (1957).
7. Hanna, G. C. "Alpha-Radioactivity" in Experimental Nuclear Physics, Vol III, ed. E. Segre, John Wiley and Sons (1959).
8. Wetherill, G. and Libby, W. F., J. Geophys. Res., 67, 3609, (1962).
9. Fields, P., Friedman, A. M., Iemer, J., Metts, D. and Sjoblom, R. Physical Review, 131, 1249 (1963).
10. Foreman, B. M. and Seaborg, G.T., Journal of Inorganic and Nuclear Chemistry, 7, 305, (1958).

11. Diamond, H. and Barnes, R. F., Physical Review, 101, 1064, (1956).
12. Rankama, K., Progress in Isotope Geology, p.565, Pergamon Press (1963).

APPENDIX 8: GAMMA-SPECTROMETRIC DETERMINATIONS OF
THORIUM, URANIUM AND POTASSIUM IN
TEKTITES.

Acknowledgment: This work was performed in the laboratory of Dr. John A. S. Adams at Rice University. The tektite samples were obtained via Dr. Adams, and the measurements were made on the gamma-spectrometer set-up designed and calibrated by him. Dr. Adams was also responsible for the suggestion that "Silastic" be used as moulding material. The preparation of samples, the actual measurement, the calculations and the writing of the paper were undertaken by myself.

R. D. Cherry

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Gamma-spectrometric determinations of thorium, uranium and potassium in tektites

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Abstract—Thorium, uranium and potassium have been determined in nine tektites and two Peruvian glasses by a non-destructive gamma-spectrometric technique. The nine tektites include three indochinites from Thailand, one indochinite from China, two bediasites, one philippinite, one moldavite and one australite, and the average thorium, uranium and potassium contents of these samples are 11.9 ppm, 2.0 ppm and 1.9 per cent respectively. Attention is drawn to the rather high (average, 6.0) Th/U ratio observed for these tektites. Previous thorium and uranium data on tektites are tabulated, and compared with the present work.

INTRODUCTION

MEASUREMENTS of the thorium and/or uranium contents of tektites have been reported by several workers (DUBEY, 1933; TILTON, 1958; ADAMS, 1956 and 1959; FRIEDMAN, 1958; HEIDE, 1961 and CHERRY, 1962). Over forty uranium determinations exist, and provide a fairly representative coverage of the various tektite groups. Disagreements exist; thus the earlier measurements tend on the whole to give higher U contents than the later work. Thorium values are meagre, and subject to a great deal of uncertainty. Moreover, measurements of thorium in the important Asian groups of tektites (philippinites, indochinites, etc.) are almost completely lacking.

Further work on this topic appeared to be desirable, and the present paper reports the results of gamma-spectrometric determinations of thorium, uranium and potassium in nine tektites, two Peruvian glasses and three soil samples obtained from tektite localities.

EXPERIMENTAL PROCEDURE

Gamma spectrometry utilizing NaI(Tl) phosphors is by now a well-known technique. It was first applied geologically by HURLEY (1956), who used a small ($1\frac{3}{4}$ in. $\times$ 2 in.) crystal and low-energy gamma rays. ADAMS *et al.* (1958) described the geological application of the technique in the case when a larger (3 in. $\times$ 3 in.) crystal and higher energy gamma rays are used, and it is this method which has been employed in the present work.

The spectrum analysis is based on the photopeaks due to the gamma-rays from Th^{232} (2.62 MeV), Bi^{214} (1.76 MeV) and K^{40} (1.48 MeV). With the usual assumption of radioactive equilibrium, the counts in these peaks enable the thorium, uranium and potassium contents of the sample to be determined. The counting rates obtained depend of course on sample size and sample geometry, and calibration is necessary. Customarily the measurements are made on crushed samples which are

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packed into containers of standard size and geometry; in the present work, however, a non-destructive technique was obviously highly desirable, and the following procedure was adopted: Each individual tektite was set in a mould made from "Silastic" RTU 881. After counting the tektite was removed unaltered from the mould and successive counts were then taken with the mould filled with reagent grade sodium chloride (to provide a background measurement), reagent grade potassium carbonate, a zircon sand of known thorium and uranium content and, finally, a uranium in dunite standard. These counts enabled the parameters in the usual calibration equations to be worked out. These equations are of the form:

$$\text{Th} = k_1 C_3$$

$$\text{U} = k_2 [C_2 - r_1 C_3]$$

$$\text{K} = k_3 [C_1 - r_2 \{C_2 - r_1 C_3\} - r_3 C_3]$$

Th, U and K are the thorium, uranium and potassium contents (in ppm for Th and U and in per cent for K) and the constants k_1 , k_2 , k_3 , r_1 , r_2 and r_3 are dependent primarily upon sample size and geometry. C_1 , C_2 and C_3 are the counting rates (in counts/gram sample/min) in the potassium, uranium and thorium photopeaks listed above. It is perhaps worth noting that, although the tektites measured were of varying shapes and sizes, the constants k_1 , k_2 and k_3 were found to depend on the sample mass in a fairly regular manner. The ratios r_1 , r_2 and r_3 (which are all of the order of unity) are relatively independent of sample mass. The values obtained for these parameters for the nine tektites and the two Peruvian glasses are shown in Table 1.

Table 1. Values of the parameters in the calibration equations for the nine tektites and the two Peruvian glasses measured

Specimen	Mass (g)	k_1	k_2	k_3	r_1	r_2	r_3
Indochinite K30	187	937	231	21.1	0.82	1.11	0.83
Philippinite	152	813	218	19.4	0.86	1.08	0.93
Indochinite K28	136	935	238	21.7	0.83	1.04	0.95
Indochinite B19	108	730	211	18.4	0.91	1.05	0.99
Bediasite	87	854	205	18.6	1.00	1.05	1.02
Indochinite (China)	84	685	197	16.9	1.00	1.05	1.08
Peruvian Glass	49	628	166	15.3	0.92	1.05	1.03
Peruvian Glass	32	669	154	13.9	0.95	1.06	0.85
Bediasite	28	599	166	14.6	1.01	1.08	1.02
Australite	26	571	162	14.1	0.97	1.03	1.04
Moldavite	14	579	134	12.3	0.89	1.03	0.89

It should be mentioned that a similar non-destructive method of gamma-spectrometric measurement involving a rather more complicated system of mould preparation has been described by VAN DILLA *et al.* (1960).

RESULTS

These are given in Table 2. The errors quoted are those due to counting statistics alone. Imperfections in packing during the calibration process could give rise to additional errors of about 5 per cent, and the *absolute* accuracy is of course limited by the accuracy of the standards used in calibration. It is immediately

obvious that the counting errors for the smaller samples are rather large; this is due, of course, to the long counting times required to obtain statistics of high confidence level, and exposes a limitation of the technique. The small moldavite was counted for five days to obtain an accuracy of only 19 per cent in the thorium value; the

Table 2. Thorium, uranium and potassium contents for the nine tektites and the two Peruvian glasses measured. Errors are those due to counting statistics alone

Specimen	Mass (g)	Th(ppm)	U(ppm)	$\frac{\text{Th}}{\text{U}}$	K%
Philippinite	152	15.7 ± 0.4	1.85 ± 0.19	8.5	1.90 ± 0.03
Indochinite (China)	84	12.5 ± 0.5	1.54 ± 0.17	8.1	1.61 ± 0.04
Indochinite K30	187	14.6 ± 0.3	2.56 ± 0.12	5.7	1.91 ± 0.02
Indochinite K28	136	14.9 ± 0.5	2.78 ± 0.21	5.4	1.87 ± 0.04
Indochinite B19	108	9.9 ± 0.4	1.6 ± 0.2	6.2	1.81 ± 0.05
Australite	26	12.9 ± 1.0	2.7 ± 0.5	4.8	1.90 ± 0.09
Moldavite	14	9.8 ± 1.8	2.1 ± 0.5	4.7	2.9 ± 0.1
Bediasite	87	8.7 ± 0.4	1.66 ± 0.14	5.2	1.34 ± 0.04
Bediasite	28	8.4 ± 1.3	1.3 ± 0.6	6.5	2.00 ± 0.09
Peruvian Glass	49	3.4 ± 0.8	17.9 ± 0.7	0.19	2.87 ± 0.12
Peruvian Glass	32	3.7 ± 0.7	18.8 ± 0.3	0.20	2.73 ± 0.05

large philippinite, on the other hand, gave 3 per cent accuracy after only fifteen hours counting.

The following features of the results are worthy of note:

(a) Average values for the nine tektites measured are:

Thorium, 11.9 ppm; uranium, 2.0 ppm potassium, 1.92 per cent. These values are similar to those obtained by previous workers, and are easily matched by values for samples of terrestrial origin, e.g. common shales, silicic igneous rocks, (see ADAMS *et al.*, 1959). They are orders of magnitude higher than the values for known extra-terrestrial material.

(b) The Th/U ratio is distinctly higher than the crustal "average" of about 3.5 (ADAMS *et al.*, 1959). The values in Table 2 range from 4.7 to 8.5, with a mean of 6.1. This high value is likely to be of some significance, although, once again, it is possible to match it with specific terrestrial samples. Whether it can be matched by random, widespread crustal material is another question, and one which deserves some consideration when discussing theories of tektite origin.

(c) Certain regional differences (based admittedly on few samples) seem to be real. Thus both the philippinite and the indochinite from China show higher than average thorium contents and Th/U ratios of about 8. The two indochinites classified by Dr. VIRGIL E. BARNES as "Muong Nong" tektites (Nos. K28 and K30) are rather high in both thorium and uranium; the bediasites, on the other hand, have lower than average thorium and uranium contents.

(d) The Peruvian glasses are of a completely different character to the tektites. They are very high in uranium and low in thorium, and have a Th/U ratio of about 0.2.

(e) The australite measured is probably not typical of australites as a whole. It comes from the same area as a sample (TAYLOR, 1960, sample No. 541) which possesses a potassium content of 2.11 per cent, i.e. 12 per cent higher than the

average potassium content of 14 australites measured by TAYLOR (1960). The potassium value obtained by gamma-spectrometry is lower (1.90 per cent), but it nonetheless seems likely that the sample is somewhat extreme chemically as far as australites are concerned. In view of the positive correlation between the total alpha count rate and the potassium content noted by CHERRY (1962), we should expect higher than normal thorium and uranium contents as well, and this is indeed borne out by the values obtained. Thorium and uranium in another sample of similar high potassium content (2.12 per cent TAYLOR (1960), sample 1176) have been determined by CHERRY (1962); values of 11.7 ± 1.3 ppm and 1.8 ± 4 ppm respectively were obtained by alpha-pairs counting, and these overlap the results of the present gamma-spectrometric determinations. Because of poor counting statistics the results in both cases are, however, somewhat inaccurate.

PREVIOUSLY REPORTED RESULTS

(1) *Uranium*. Table 3 gives the uranium contents of tektites as reported in the literature to date. Apart from the pre-war values of DUBEY and the first batch of results by FRIEDMAN (which were obtained two years earlier than those in the column labelled "FRIEDMAN 2"), the agreement is fairly good. DUBEY and "FRIEDMAN 1" give values which are generally higher than the later work, and are probably

Table 3. Uranium contents (in ppm) for tektites and Peruvian glasses as reported in the literature to date

Location	DUBEY (1933)	TILTON (1958)	ADAMS (1959)	FRIEDMAN 1 (1958)	FRIEDMAN 2 (1958)	HEIDE (1961)	CHERRY (1962)	CHERRY and ADAMS (this paper)
Java and Billiton tektites	2.7				1.5, 1.4			
Philippinites			1.6*	2.7, 2.7 2.6	1.7, 1.8			1.9
Indochinites			1.6*, 1.7*	1.1, 2.4 2.5	3.0	2.24		2.8, 2.6 1.6, 1.5
Australites	2.7, 2.4	1.74	1.7*, 1.7*, 1.5*, 1.5*	2.4	1.6		2.0†	2.7
Moldavites	2.2, 2.8, 2.9, 3.0		1.8*		1.6, 1.5	1.89, 1.97		2.1
Bediasites			1.2, 1.2, 1.2, 1.5	2.4	1.1			1.3, 1.7
Ivory Coast tektites					0.91			
Peruvian glass				18.0				18.8, 17.9

* Denotes a composite sample,

† Denotes the mean of five samples.

less accurate on this account. When comparing the data of the present paper with the earlier values the probable atypicality of the australite and the two Muong Nong types indochinites should be kept in mind.

(2) *Thorium*. The only previously reported determinations of thorium have been those of DUBEY (1933), ADAMS (1956 and 1959), CHERRY (1962) and the single value of TILTON (1958). As with uranium, DUBEY's thorium values are probably to be rejected; they show great variation, and are generally high. The values of ADAMS, on the other hand, are generally low. These were obtained by using total alpha-counting and subtracting empirically the contribution from the fluorometrically determined uranium content. Using the raw data (ADAMS, 1956), the experimental parameters (OCKERMAN and DANIELS, 1954) and a recently published absolute equation for the total alpha count-rate from a thick source in terms of its uranium and thorium contents (CHERRY, 1963), the thorium values have been recalculated. These new values are shown in Table 4, along with the other thorium

Table 4. Thorium contents (in ppm) for tektites and Peruvian glasses reported in the literature to date

Location	DUBEY (1933)	TILTON (1958)	ADAMS (1956 and 1959)	ADAMS (recalculated)	CHERRY (1962)	CHERRY and ADAMS (this paper)
Billitonite	9.6					
Philippinites			7.5	15*		15.7
Indochinites			5.6, 5.9	11*, 10*		14.6, 14.9 9.9, 12.5
Australites	5.0, 18.4	9.19	3.6, 5.1 6.5, 5.3	6*, 8* 11*, 10*	9.4†	12.9
Moldavites	10.8, 16.0 16.0, 18.6		6.5	11*		9.8
Bediasites			3.3, 3.9 4.7 (7.0)‡	5, 6, 8		8.7, 8.4
Peruvian glass						3.7, 3.4

* Denotes composite samples.

† Denotes the mean of five samples.

‡ Denotes an alternative value obtained by a different method.

data. Although they are subject to errors of up to 20 per cent (because of uncertainties in the experimental parameters), it is seen that these recalculated values are in reasonable agreement with the data of the present paper and with the alpha-pairs counting results of CHERRY (1962).

(3) *Potassium*. This element is of secondary interest in the present work, as it has been extensively studied by other methods. For comparison purposes the mean potassium contents of seven groups of tektites calculated from the data of BARNES (1940) are given in Table 5. Nothing noteworthy emerges from the present study, except perhaps the fact that the high value for the Moldavite is in accord with the unexpectedly high average for this group shown by the Barnes data.

THE MUONG-NONG TEKTITES

BARNES and PITAKPAIVAN (1962) recently described work on the Muong-Nong type tektites from Thailand. These are found associated with lateritic soil, and Barnes and Pitakpaivan produced evidence to support their suggestion that these

Table 5. Mean potassium content (in per cent) of seven groups of tektites as calculated from the data of BARNES (1940)

Location	No. of Analyses	K content (%)
Billitonites	7	1.89
Philippinites	4	1.60
Indochinites	24	1.99
Moldavites	10	2.41
Australites	9	1.70
Bediasites	2	1.53
Ivory Coast tektites	3	1.27

tektites are chemically similar to the laterite if the changes that take place during laterization are considered. Indochinites K28 and K30, from Phang Daeng, Thailand, were provided by Dr. BARNES, as was a third sample (B19, from Kam Luang Dong, Thailand) which was not associated with laterite. The thorium and uranium contents (Table 2) of K30 and K28 are both distinctly higher than those of B19, suggesting the possibility of some significant difference in the formation process. Samples of laterite soils associated with K30 and K28 and of fines associated with B19 were also measured gamma-spectrometrically (this time by counting in a standard bottle) and the results are given in Table 6. Comparison with the K28 and K30

Table 6. Thorium, uranium and potassium contents for three soil samples found associated with Indochinites. Errors are those due to counting statistics alone

Specimen	Th(ppm)	U(ppm)	Th/U	K%
Phang Daeng laterite 9-11 in. Depth	17.2 $\pm$ 0.8	7.4 $\pm$ 0.3	2.3	0.89 $\pm$ 0.07
Phang Daeng laterite 30 in. depth	15.5 $\pm$ 0.8	4.9 $\pm$ 0.3	3.2	1.10 $\pm$ 0.06
Fines with tektites, Kam Luang Dong	7.1 $\pm$ 0.8	1.8 $\pm$ 0.3	3.9	0.39 $\pm$ 0.07

values in Table 2 shows immediately that both uranium and thorium are enhanced in the laterite—uranium by a factor of as much as two or three. Multiplication of the tektite values by 1.34 (BARNES and PITAKPAIVAN, 1962) to give the original amount present on the basis of no change in Al_2O_3 in the soil implies a slight decrease in the thorium content from original to laterized soil, but still shows a considerable enhancement of uranium. One would in general expect uranium to be lost in a laterization process, and the present results would therefore appear to be in disagreement with the suggestion of BARNES and PITAKPAIVAN. K. A. RICHARDSON (private communication) has, however, suggested that if the uranium in the soil is located in resistate minerals then laterization could in fact result in an apparent increase in the uranium content (see ADAMS and RICHARDSON, 1960; FLILER and

ADAMS, 1962). The present work has not investigated the location of the uranium in the laterized soil; the problem is thus open, and requires further study.

CONCLUSION

The uranium and thorium contents of tektites appear to be well established at levels centering around 2 and 12 ppm respectively. A high Th/U ratio of about 6 is characteristic of these objects—a fact which must be of some significance to theories of tektite origin. Differences in the uranium and thorium contents between the different tektite groups appear to be real, and further work with a view to establishing valid regional averages would be valuable.

Note added in proof

In a recent number of this journal, Vol. 27, p. 983 ff. Rowe *et al.* write "On the Radioactivity of Stone Meteorites" and report the following gamma spectrometric determinations of thorium in tektites:

Bediasites	8.6 ± 0.4	ppm Th
	9.4 ± 0.4	ppm Th
Australite	12.2 ± 0.4	ppm Th
Indochinite	11.9 ± 0.4	ppm Th
Philippinites		
Santiago	13.9 ± 0.4	ppm Th
Coco Grove	14.4 ± 0.4	ppm Th
Santa Mesa	15.1 ± 0.4	ppm Th
Pugad Babuy	15.4 ± 0.4	ppm Th
Libyan Glass	3.3 ± 0.2	ppm Th

These data of Rowe *et al.* and the data reported in this paper are in excellent agreement as regards the absolute thorium concentrations found in tektites and the generally lower thorium contents of bediasites.

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REFERENCES

- ADAMS J. A. S. (1956) The uranium contents and alpha particle activities of tektites. *Proc. 20th Int. Geol. Cong.*, Mexico City.
- ADAMS J. A. S., RICHARDSON G. E. and TEMPLETON C. C. (1958) Determination of thorium and uranium in sedimentary rocks by two independent methods. *Geochim. et Cosmochim. Acta* **13**, 270.
- ADAMS J. A. S. and RICHARDSON K. A. (1960) Thorium, uranium and zirconium concentrations in bauxites. *Econ. Geol.* **55**, 1653–1675.
- ADAMS J. A. S., OSMOND J. K. and ROGERS J. J. W. (1959) The Geochemistry of thorium and uranium. *Physics and Chemistry of the Earth*, Vol. III.
- BARNES V. E. (1940) *North American Tektites*. University of Texas Publication No. 3945, pp. 477–656.
- BARNES V. E. and PITAKPAIVAN K. (1962) Origin of indochinite tektites. *Proc. Nat. Acad. Sci. Wash.* **48**, 947–955.

- CHERRY R. D. (1962) Thorium and uranium contents of australites. *Nature, Lond.* **195**, 1184-1186.
- CHERRY R. D. (1963) The determination of thorium and uranium in geological samples by an alpha-counting technique. *Geochim. et Cosmochim. Acta* **27**, 183-189.
- DUBEY V. S. (1933) The origin of tektites. *Nature, Lond.* **132**, 678.
- FRIEDMAN J. (1958) The water, deuterium, gas and uranium content of tektites. *Geochim. et Cosmochim. Acta* **14**, 316-322.
- HEIDE F. (1961) Über der Urangehalt der Tektite. *Acta Geol.* **VII**, 105.
- HURLEY P. M. (1956) Direct radiometric measurement by gamma-ray scintillation spectrometry. *Geol. Soc. Amer. Bull.* **67**, 395-404.
- OCKERMAN J. B. and DANIELS F. (1954) Alpha radioactivity of some rocks and common materials. *J. Phys. Chem.* **58**, 926-927.
- PLILLER R. and ADAMS J. A. S. (1962) The distribution of thorium and uranium in a Pennsylvanian weathering profile. *Geochim. et Cosmochim. Acta* **26**, 1137-1146.
- TAYLOR S. R. (1960) Abundance and distribution of alkali elements in australites. *Geochim. et Cosmochim. Acta* **20**, 85-100.
- TILTON G. R. (1958) Isotopic composition of lead from tektites. *Geochim. et Cosmochim. Acta* **14**, 323-330.
- VAN DILLA M. A., ARNOLD J. R. and ANDERSON E. C. (1960) Spectrometric measurement of natural and cosmic ray induced radioactivity in meteorites. *Geochim. et Cosmochim. Acta* **20**, 115-121.