STUDIES ON THE ANALYTICAL GEOCHEMISTRY OF URANIUM AND ASSOCIATED ELEMENTS IN THE HAWKS CRAG BRECCIA OF NEW ZEALAND

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ABSTRACT

Part I

Studies were carried out on the optimum conditions for the successful use of a large quartz spectrograph for the determination of thorium, yttrium and the rare earths in silicate rocks. The best line-to-background ratios were achieved by arcing samples in a matrix of 4% sodium chloride in carbon powder. An atmosphere of 20% argon and 80% oxygen was used to reduce background and eliminate cyanogen band interference. An anion-exchange procedure was used to separate the rare earths from other elements. The resulting enrichment allowed use to be made of less sensitive rare earth lines in the ultraviolet end of the spectrum where the spectrographic dispersion is greater. Line interferences were studied and necessary corrections for these interferences were calculated. The technique was tested by analysing the standard rocks, G-1, W-1 and CAAS syenite. Depending on its concentration, uranium was analysed by either fluorometric or spectrographic techniques. Good agreement with the recommended values for the standard rocks was obtained.

Part II

An investigation of the known areas of uranium mineralization in the Lower Buller Gorge of New Zealand was carried out to investigate the suitability of stream-sediment analysis for geochemical prospecting for uranium. General analysis of the minerals revealed certain elemental associations. The distribution of these elements in the weathering sequence, minerals, soils, stream-sediments, was studied in an attempt to discover

suitable pathfinders for uranium. All results were treated statistically. Rare earth analysis of stream sediments provided new information concerning the possible origin of the Hawks Crag Breccia.

Part III

Use was made of a high-resolution gamma spectrometer to study the gamma radiation of uranium minerals in the low energy region of the spectrum, 30-360 KeV. Identification of the gamma radiation, in this region, was achieved by use of chemical separations and standard sources. This provided the basis for the development, and successful use, of a new method for the determination of "percentage equilibrium radium". The significance of the values for the "percentage equilibrium radium" of the minerals studied is discussed.

GENERAL INTRODUCTION

In 1956, two prospectors, Cassin and Jacobsen, discovered uranium in the Lower Buller Gorge region in the South Island of New Zealand. In the search for radioactive minerals this find was of great geological significance because it transferred geological thinking from the granites and associated rocks to a hitherto unsuspected arkosic bedded formation known as the Hawks Crag Breccia. This discovery by Cassin and Jacobsen stimulated the search for uranium in this area until the early 1960's, when the fall in price of uranium, combined with unpromising initial findings, made further prospecting unattractive. Recently, as a result of Government encouragement, the interest in uranium prospecting has been revived and many of the known areas of mineralization are being re-evaluated. The need for a source of uranium has been heightened because of the possible installation of a nuclear reactor in the late 1970's.

Previous investigations have been carried out almost entirely by field geologists and were mainly of a petrological nature. In view of the increasing success of geochemical methods of exploration in other parts of the world, there was clearly a need for such an investigation in this area. The benefits of such a study would not only be confined to aspects of economic geology but also provide information on the history and origin of the uranium deposits and on the Hawks Crag Breccia itself. Considering the advantages of geochemical observations, it is somewhat surprising that with the exception of work by WODZICKI (1959a, 1959b), little or none of this work has been carried out in this area. One possible reason for lack of work is that the analytical methods of analysing for uranium and associated elements, such as thorium and the rare earths, are often tedious or unreliable, and require specialised equipment not generally available in many geochemical laboratories.

Provided that these analytical problems could be solved and a suitable technique could be developed, a geochemical survey of the area would be facilitated. This thesis describes somewhat intensive investigations into the development of such techniques and their subsequent application to geochemical studies in the Hawks Crag Breccia.

WHITEHEAD and BROOKS (1969a) in reconnaissance work in the area have highlighted the deficiencies of many scintillometric and other radiometric methods for the analysis of uranium in minerals, soils and stream sediments. The use of radiometric methods for accurate quantitative analysis relies on the assumption that the uranium sample is in radioactive equilibrium. However, a comprehensive study of radioactive equilibrium in this area has never been satisfactorily attempted, largely because of the lack of suitable methods. This problem was therefore investigated as a part of the present study and has been solved by the application of a new technique in gamma spectrometry. This is reported in Part III of this thesis.

To summarize, the aims of this thesis were threefold:

(1) To develop a method for the analysis of low concentrations of yttrium, thorium and rare earths with the use of a large quartz-optics spectrograph.

(2) To investigate the possible association of the above elements,

and any other elements, with uranium in the minerals from the South Side of the Buller River and to study the distribution of these elements in the weathering sequence: minerals, soils, stream-sediments. From these results, to examine critically the relative merits of direct analysis of uranium and of associated elements in stream-sediments, as a geochemical prospecting method for uranium mineralization.

(3) To develop a method, using only gamma radiation from U^{235} and Ra^{226}, to determine the "percentage equilibrium radium" of uranium minerals.

PART I

DEVELOPMENT OF ANALYTICAL PROCEDURES

INTRODUCTION

The progress of geochemistry depends ultimately on how effectively the collected quantitative abundance data are utilised. The value of this information is very dependent on the precision of the determinations and although it is impossible to assess the quality of each published analysis, an examination of some of the figures provided by the various methods most widely applied, does give an indication of the reliability of much of the existing data. Furthermore, this also gives an idea of the progress in the analytical procedures which are applied.

The classical or conventional methods of rock analysis were fairly well established during the second half of last century (HILLEBRAND, 1900) and have remained essentially unchanged (WASHINGTON, 1950; GROVES, 1951; HILLEBRAND and LUNDELL, 1953). Those who developed the classical procedures, as well as those who used them, frequently attempted to indicate their accuracy, but no real insight into the quality of this immense collection of published information was gained until FAIRBAIRN ET AL (1951) organised a world-wide, inter-laboratory investigation on granite (G-1) and diabase (W-1). Numerous analyses of these rocks were carried out by a large number of workers using a wide variety of techniques. The wide variation in the analytical data for identical samples clearly demonstrated the shortcomings of many existing analytical techniques. AHRENS (1957) using published data for G-1 and W-1, showed that for classical procedures, the logarithm of the standard deviation of replicate analyses was inversely related to the logarithm of the concentration of the constituent analysed. The significance of this relationship becomes extremely important when analysing at the trace element (ppm) level. For this reason, the analysis of many geochemically-important elements such as thorium, uranium, the rare earths and yttrium presents considerable difficulty.

Several radiometric methods have been used for the determination of uranium and thorium (EICHHOLZ ET AL, 1953; CHERRY and ADAMS, 1963; CHERRY, 1963; HEIR and ROGERS, 1963; VASSILAKI ET AL, 1966) but these procedures suffer from the disadvantage that radioactive equilibrium must be assumed and this is not always so. Of the above workers, only EICHHOLZ ET AL (1953) allowed for this possibility. Fluorimetry (GRIMALDI ET AL, 1952; PRICE ET AL, 1953; ANDERSON and HERCULES, 1964) is undoubtably one of the most sensitive methods for uranium (limit of detection 10^{-10}g) but has the disadvantage that extensive dilution is needed for samples containing even moderate amounts of this element. Other methods such as emission spectrography are by contrast extremely insensitive for uranium. It is clear, therefore that a combination of methods is required if the concentration range of this element spans several orders of magnitude.

Yttrium, thorium and the rare earths have been analysed by X-ray spectrography (GAVRILOVA and TURANSKAYA, 1958; BALASHOV ET AL, 1964; ALEKSIEV and BOVADJIEVA, 1966), spark source mass spectrography (BROWN and WOLSTENHOLME, 1964; TAYLOR, 1965; NICHOLLS ET AL, 1967), activation analysis (TOWELL ET AL, 1965; BRUNFELT and STEINNES, 1966; COBB, 1967; GORDON ET AL, 1968) and emission spectrography (FARIS, 1958; RADWAN ET AL, 1963; MYKYTIUK ET AL, 1966; NELMS and VOGEL, 1967). The relative merit of these techniques will be briefly discussed for the sake of completeness although only emission spectrography was available for use at this institution. X-ray spectrography has a relatively poor detection limit making it generally unsuitable. Spark source mass spectrography has been shown to be an accurate and extremely sensitive technique and has the advantage that all elements may be determined simultaneously. Neutron activation is also extremely sensitive but requires considerable chemical treatment of the sample to eliminate interference when using the NaI(Tl) detector. Direct analysis of the sample can now be achieved using the recently developed Ge(Li) detector although "cooling" times of the order of months are necessary for some elements in order to eliminate interference problems.

Emission spectrography has been for many years one of the most satisfactory methods for the analysis of rare earths in silicates (AHRENS and TAYLOR 1961). Unfortunately this technique nevertheless suffers from certain inherent disadvantages. These are: production of high background due to the complex spectra of the rare earths; interference from other rare earths, titanium and iron; the necessity of high amperages (FASSEL, 1949; ROSE ET AL, 1954) and long arcing times because of the relative involatility of the rare earth oxides. This last factor also results in high background due to cyanogen emission in the range 3500-4200 Å where most of the best analysis lines of the rare earths are found.

Line interference may also be reduced by use of a high-dispersion grating instrument and cyanogen emission may be controlled by arcing in various nitrogen-free atmospheres such as carbon dioxide (STEADMAN, 1948), argon, helium or oxygen (VALLEE ET AL, 1950) and a mixture of argon and oxygen (RADWAN, 1963; TENNANT and SEWELL, 1967). Use of a noble gas atmosphere results in an enhancement of ion line intensities relative to those of atom lines and a reduction in background. This is a distinct advantage as the most sensitive rare earth analysis lines are ion lines. The main disadvantage is that arcing times of the order of minutes are required. Another approach to the problem of line interference is the carrier distillation method (SCRIBNER and MULLIN, 1946; MYKYTIUK ET AL, 1966) which allows arcing times to be reduced by increasing volatilisation rates. To obtain high-precision quantitative results, use of zirconium (McCARTY ET AL, 1938), palladium (YOUNG, PH.D. THESIS) and certain rare earths (FASSEL and WILHELM, 1948; KNISELY ET AL, 1958; AHRENS and TAYLOR, 1961) as internal standards has been recommended.

The relatively-high sensitivity of rare earth analyses referred to in the literature (MITCHELL, 1948; AHRENS and TAYLOR, 1961) was obtained via a high-dispersion instrument and cannot be duplicated with a quartz-optics spectrograph. There is clearly a need for a method which will permit the use of such an instrument in rare earth analysis, particularly as such spectrographs greatly outnumber grating instruments in general use.

The majority of the above techniques require preliminary chemical treatment of the sample either to reduce interference or to concentrate the elements being determined. Separation methods commonly used are: precipitation of rare earths as hydroxides (ROSE ET AL, 1954) or oxalates (STEADMAN, 1948), solvent extraction (McCARTY ET AL, 1938; SCRIBNER and MULLIN, 1946; VALLEE ET AL, 1950; RADWAN ET AL, 1963; MYKYTIUK ET AL, 1966) and ion exchange (CARSWELL, 1957; DANON, 1958; NIETZEL ET AL, 1958; FARIS and WARTON, 1962; FRITZ and GARRALDA, 1962; TAKETATSU, 1963; AHRENS ET AL, 1963; KORKISCH and ARRHENIUS, 1964; STRELOW, 1966).

It was clear that a separation-enrichment procedure would be required for the present work because of line interferences and sensitivity problems. Separation is particularly necessary where samples contain more than five percent uranium, because the presence of a very large number of uranium lines in the range 2500-5000 Å results in a high background in the emission spectra. This background prevents analysis of elements other than uranium in this range.

Preliminary investigations showed that precipitation and solvent extraction techniques were unsuitable because of incomplete recoveries. Cation exchange chromotography was unsatisfactory because large eluting volumes were involved, with a subsequent reduction in the concentration of the analysis elements. Anion exchange appeared to be the most promising and was investigated further.

The following section reports on the analytical procedures which were developed for the analysis of uranium, thorium, yttrium and the rare earths in minerals, soils and stream sediments, and involves:-

(i) The development of optimum spectrographic operating conditions for the analysis of yttrium, thorium and the rare earths, using a medium-dispersion instrument.

(ii) Suitable methods for analysing uranium over a concentration range of several orders of magnitude.

(iii) The development of a suitable ion-exchange separation scheme for yttrium, thorium, uranium and rare earths in silicates.

ANALYTICAL PROCEDURES FOR THORIUM, YTTRIUM AND THE RARE EARTH ELEMENTS

(a) Optimum Spectrographic Conditions

(i) Apparatus

The experiments were carried out with a Hilger E742 Large Automatic Spectrograph with quartz optics (reciprocal dispersion 12 Å/mm at 4000 Å.) A Hilger microdensitometer with Galvoscale calibrated in B-values (BOSWELL and BROOKS, 1965) was used for densitometry.

An image of the arc was focussed on the slit via a quartz spherical lens and the spectra were recorded on Ilford G-30 spectrographic plates developed for 4½ minutes in Kodak D 19b developer at 20°.

(ii) Sample Preparation

In all cases, solutions of thorium, yttrium and rare earths, whether as ion-exchange eluants or as pure solutions, were treated in the following standard manner.

A quantity of finely-divided carbon powder (50 mg) was added to not more than 50 ml of a solution of thorium, yttrium and rare earths contained in a 100 ml beaker. The carbon powder (120 mesh) contained an added internal standard. After addition of the required amount of carrier, the contents of the beaker were evaporated to dryness at 80° and the dry carbon powder was removed, ground in a motar and loaded into graphite electrodes (cavity 6mm deep and 1.5mm bore) which were dried at 130° for 2 hr.

(iii) Reduction of Background

I. Investigation of Carriers

Preliminary experiments in a carbon dioxide atmosphere were carried out on samples with and without various concentrations of each of the following halides: caesium chloride, silver chloride, sodium chloride and sodium fluoride. Lanthanum was added to each mixture to give a final concentration of 100 ppm and the samples were arced at 12A d.c. using anode excitation. Table I-1 shows the relative intensities of La 4333 to background for the various carriers. From this it is seen that for an atmosphere of carbon dioxide, 4% sodium chloride was the most efficient carrier for a maximum line-to-background ratio. Volatilisation for a maximum line-to-background ratio was complete in thirty seconds, but the cyanogen emission and background, although less than that without carrier, were still too high. An attempt was made to reduce these further by changing the arcing atmosphere.

II. Investigation of Gas Conditions

Samples containing a mixture of thorium, yttrium and rare earths in a carbon matrix, with and without addition of 4% sodium chloride, were arced at 12A (d.c. with anode excitation) successively in air, carbon dioxide and a mixture of argon and oxygen in varying proportions from 100% argon to 100% oxygen. This study showed (Fig. I-1) that a mixture of 20% argon and 80% oxygen was the most efficient for reducing cyanogen emission and background. The samples with sodium chloride in each case had a lower background than those without carrier but the most striking difference was the considerable reduction of cyanogen emission and background with the 20% argon and 80% oxygen mixture. This level of background was quite acceptable but it was necessary to know whether 4% sodium chloride as carrier and 12A arcing current were in fact

TABLE I - 1

Effect of Carriers on Line-to-Background Ratio of La 4333 in a Carbon Dioxide Atmosphere

	Carrier												
	NaCl			NaF			AgCl			CsCl			None
	2%	4%	6%	2%	4%	6%	2%	4%	6%	2%	4%	6%	
Intensity ratio	1.2	1.7	1.0	1.3	1.0	0.8	0.5	0.5	0.5	1.3	1.0	0.8	0.5

A air with 4% sodium chloride matrix

B air with carbon matrix

C carbon dioxide with 4% sodium chloride matrix

D carbon dioxide with carbon matrix

E 80 : 20, O_2 : Ar mixture with 4% sodium chloride matrix

F 80 : 20, O_2 : Ar mixture with carbon matrix

Fig. I-1 Spectrograms of rare earth mixtures (CN band region) arced at 10A in various atmospheres.

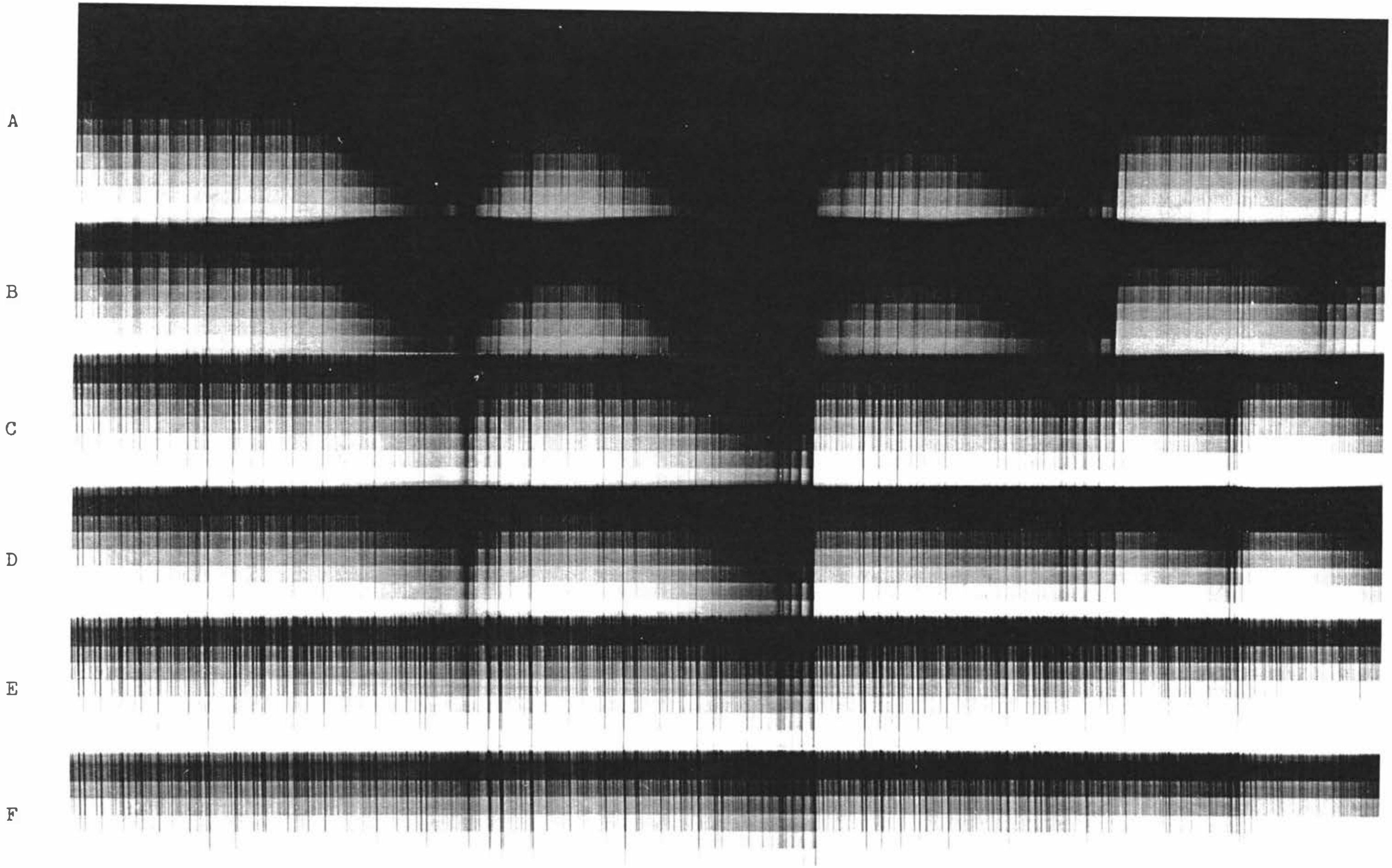


Fig. I-1 Spectrograms of rare earth mixtures (CN band region) arced in various atmospheres.

still the optimum conditions both for background reduction and sensitivity for atmospheres other than carbon dioxide. It was decided, therefore, to investigate the affect of different arcing currents, carriers and carrier concentrations in the 20% argon and 80% oxygen atmosphere.

(iv) Investigation of Sensitivity Limits

AHRENS and TAYLOR (1961) divide the rare earth elements into three volatility groups. Representative elements (lanthanum, cerium, europium, holmium, and ytterbium) from each of these three groups were taken, as well as yttrium and thorium. Solutions of these elements were prepared from their respective "Specpure" oxides. Samples containing 100 ppm of each of these metals were prepared in matrices containing 2%, 4% and 6% sodium chloride, sodium fluoride, caesium chloride and silver chloride respectively and without carrier. The samples were arced at 8A, 10A, 12A and 14A respectively (d.c. with anode excitation) in the 20% argon, 80% oxygen atmosphere with the photographic plate being racked down to expose a fresh area of plate every five seconds. From these volatilisation curves the time taken for complete volatilisation was obtained. The results are given in Table I-2.

For the determination of line-to-background ratios, a further set of samples identical to those above were arced at 8A, 10A, 12A and 14A respectively. Times of arcing were as in Table I-2. It was observed that all carriers increased the line-to-background ratio and improved the detection limit of each element at each of the different concentrations of carrier used as compared with no carrier. Within each carrier concentration range, this effect usually increased to a maximum at 10A and 12A decreasing again at

TABLE I - 2

Times for Complete Volatilisation of Yttrium, Thorium and Rare Earths in Various Matrices

	Carrier												
	NaCl			NaF			AgCl			CsCl			No Carrier
	2%	4%	6%	2%	4%	6%	2%	4%	6%	2%	4%	6%	
Volatilisation time(sec) at 8 amp	35	30	25	25	25	30	20	25	25	30	30	30	35
" " " " " " " 10 "	30	25	25	20	20	25	25	20	20	30	25	30	35
" " " " " " " 12 "	30	25	20	20	20	25	25	25	20	25	30	30	35
" " " " " " " 14 "	25	25	20	15	15	20	25	20	20	25	30	25	35

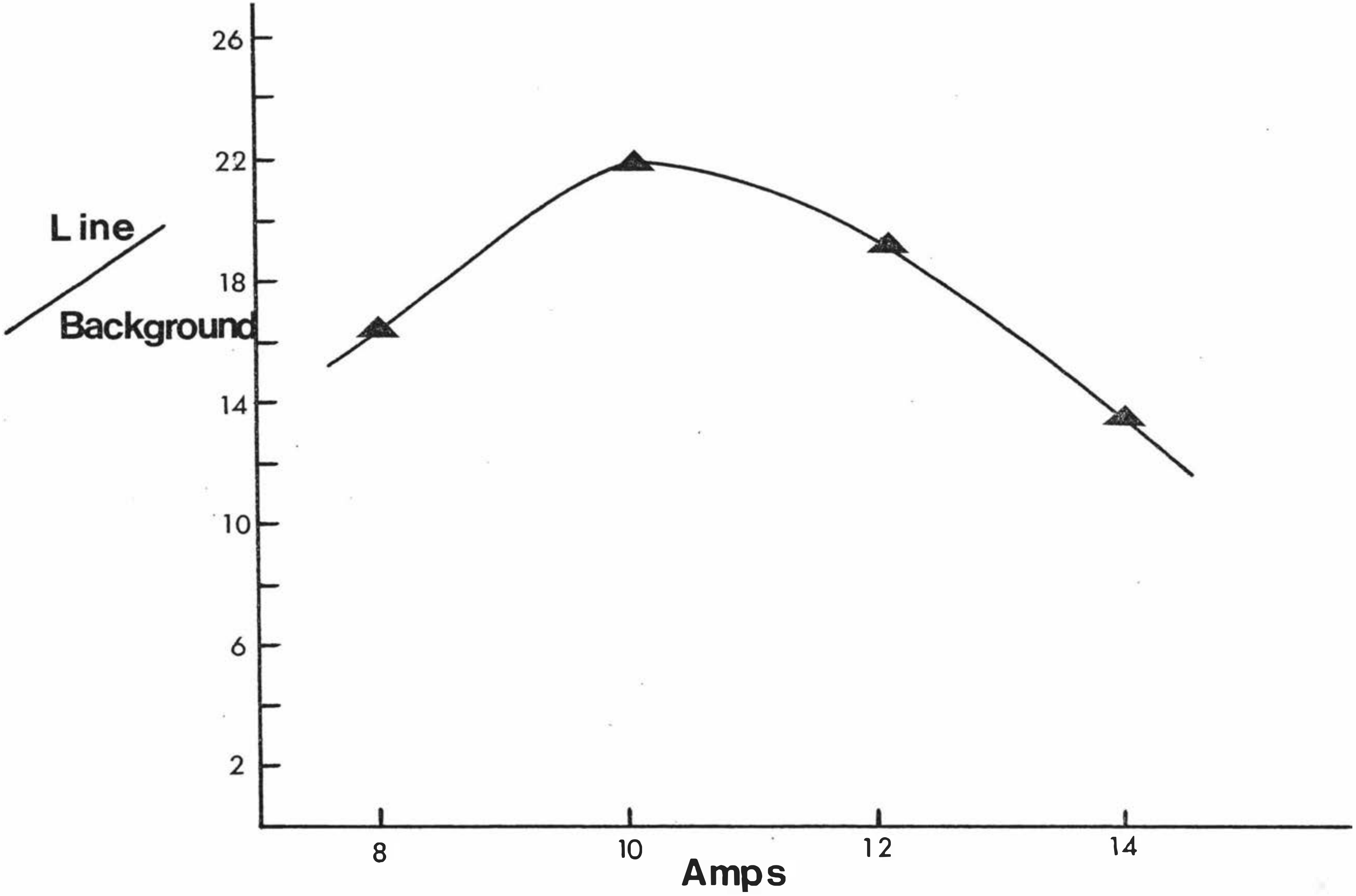


Fig. I - 2 Line-to-background ratio as a function of arcing current.

14A (Fig. I-2). It was observed that 4% sodium chloride and 6% sodium chloride at 10A and 12A respectively provided the largest increase in the line-to-background ratio and improvement in the detection limit for every element as compared with no carrier. Results obtained under these conditions are shown in Table I-3. The limit of detection is taken arbitarily to be that concentration of the element which will give a line intensity equal to that of the background. Since the average background intensities were of the order of 50 B-value units, the limit of detection was taken as that concentration which would give a value of 50 B-value units for the line intensity after correction for background. Table I-3 shows that almost identical results were obtained with either 4% or 6% sodium chloride arced at both 10A and 12A respectively. The final choice of carrier concentration and arcing amperage was determined by the relative volatilisation rates of the analysis elements and internal standard. For accurate, quantitative results it is essential that the behaviour of the analysis elements and internal standard be as similar as possible. As zirconium and palladium had been used by other authors (McCARTY ET AL, 1938; YOUNG, PH.D. THESIS) it was decided to investigate their suitability under these conditions.

(v) The Volatilisation Behaviour of Yttrium, Thorium, Lanthanum, Cerium, Europium, Holmium, Palladium and Zirconium

Samples containing 100 ppm of thorium, yttrium and each of the above rare earths and 1000 ppm of palladium and zirconium were prepared in matrices containing 4% and 6% sodium chloride respectively. Each sample containing a particular concentration of carrier was arced at 10A and 12A in the 20% argon, 80% oxygen

TABLE I - 3

Line-to-Background Ratios and Limits of Detection for Yttrium, Thorium and Rare Earths

	Carrier					
	4% NaCl		6% NaCl		No Carrier	
	A	B	A	B	A	B
Yb3289 at 10 amp	22.2	0.6	36.0	0.6	4.2	5
at 12 amp	33.8	0.6	48.0	0.4	6.2	5
Ho3456 at 10 amp	9.67	1.5	9.5	3.0	2.2	9
at 12 amp	9.00	1.5	12.6	3.0	2.3	6
Y3710 at 10 amp	13.4	0.8	14.1	1.5	2.9	5
at 12 amp	13.5	0.8	17.4	0.8	3.1	5
Th4019 at 10 amp	4.65	5.0	4.0	6	1.4	9
at 12 amp	3.47	5.0	3.2	5	1.4	6
Eu4129 at 10 amp	9.00	1.5	9.6	3	1.2	9
at 12 amp	8.00	1.5	8.8	1.5	1.0	9
Ce4133 at 10 amp	0.81	12.5	0.84	12.5	0.1	25
at 12 amp	0.52	9.0	0.80	12.5	0.2	25
La4333 at 10 amp	1.78	6	1.4	9	0.5	13
at 12 amp	1.54	6	1.7	6	0.2	13

A Line-to-background ratio

B Limit of detection ppm (relative line intensities greater than 50 B-value units).

atmosphere and successive exposures were made at five second intervals. The curves obtained are shown in Fig. I-3. This figure shows that palladium was, in all cases, a better element than zirconium for use as an internal standard as it follows the volatilisation behaviour of the analysis elements more closely. The optimum arcing amperage is 10A with 4% sodium chloride as carrier, because under these conditions all the elements except zirconium have volatilised completely within twenty five seconds without becoming too differentiated. This reason renders the other conditions less suitable.

(vi) Final Spectrographic Operating Conditions

Table I-4 gives the final conditions chosen as a result of the above investigations.

The reproducibility of the spectrographic analysis using these conditions was determined in the following manner. A series of standards containing thorium, yttrium and rare earths with a wide concentration were prepared and arced under the above conditions. Ten replicate arcings were made at each concentration level. The analysis line intensity of each element and that of the internal standard palladium, was measured over the concentration range and the ratio of the two was determined. This ratio was plotted against the coefficient of variation (percent standard deviation) and is shown in Fig. I-4. This curve allows the coefficient of variation to be determined for any element at any concentration and is more meaningful than the value obtained from a single determination. The usual procedure in such work is to calculate the coefficient of variation from replicate analyses of an element at an easily measurable concentration. This naturally presents values better

TABLE I - 4

Spectrographic Operating Conditions

Slit length	12 mm
Slit width	0.015 mm
Wavelength range	2800 - 5000 Å
Photographic plates	Ilford G-30
Current	10A d.c.
Excitation	Anode
Exposure	25 seconds
Electrodes	Johnson-Matthey 4B graphite (1.5 mm internal diameter x 6 mm deep)
Photographic Processing	$4\frac{1}{2}$ min at 20°C in Kodak 19B developer
Optical system	Image of arc focussed at slit with **F958** convex quartz lens
Arc gap	4 mm
Gas	20% argon/80% oxygen

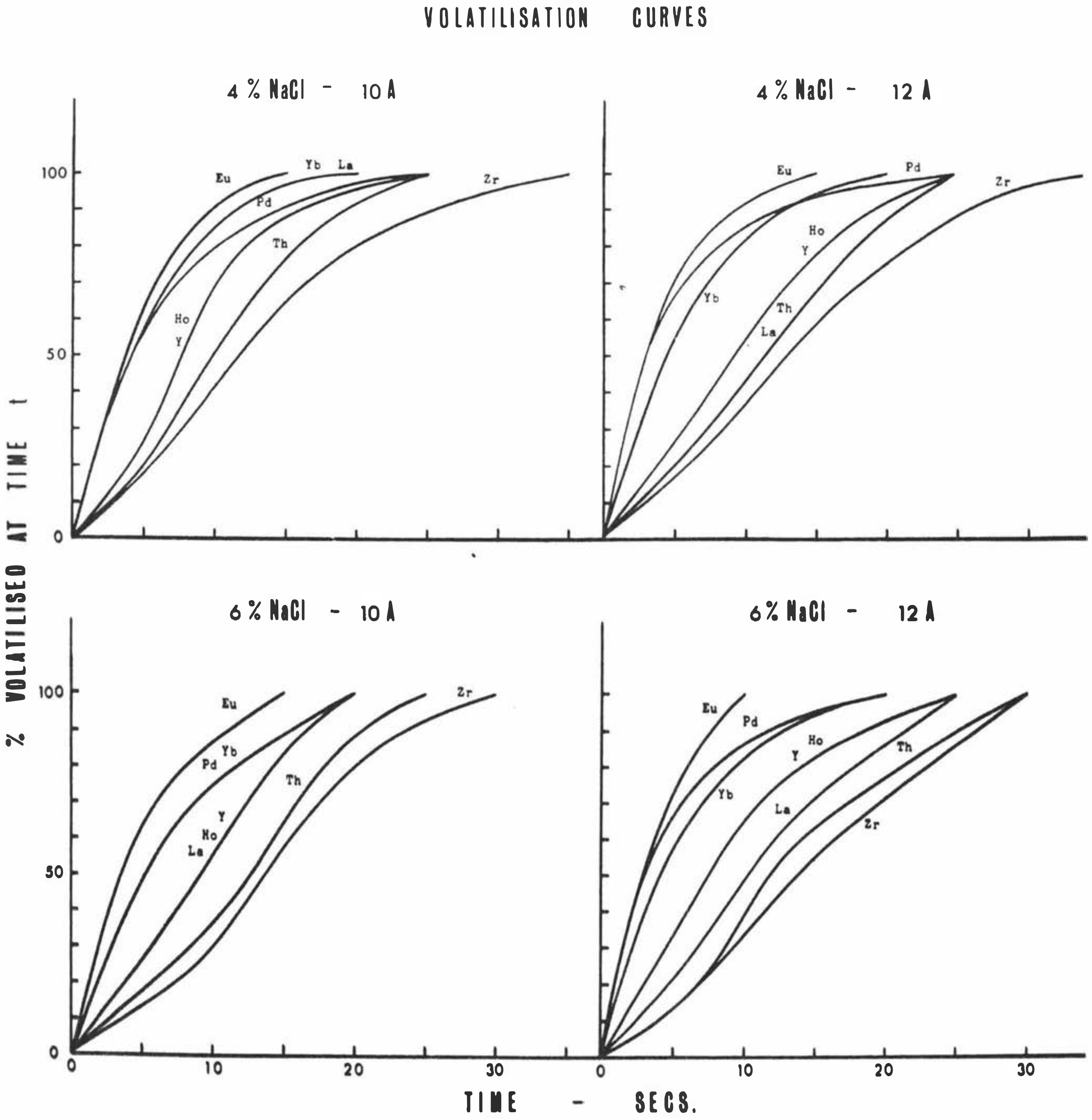


Fig. I - 3 Volatilization curves for rare earths, yttrium, palladium and zirconium.

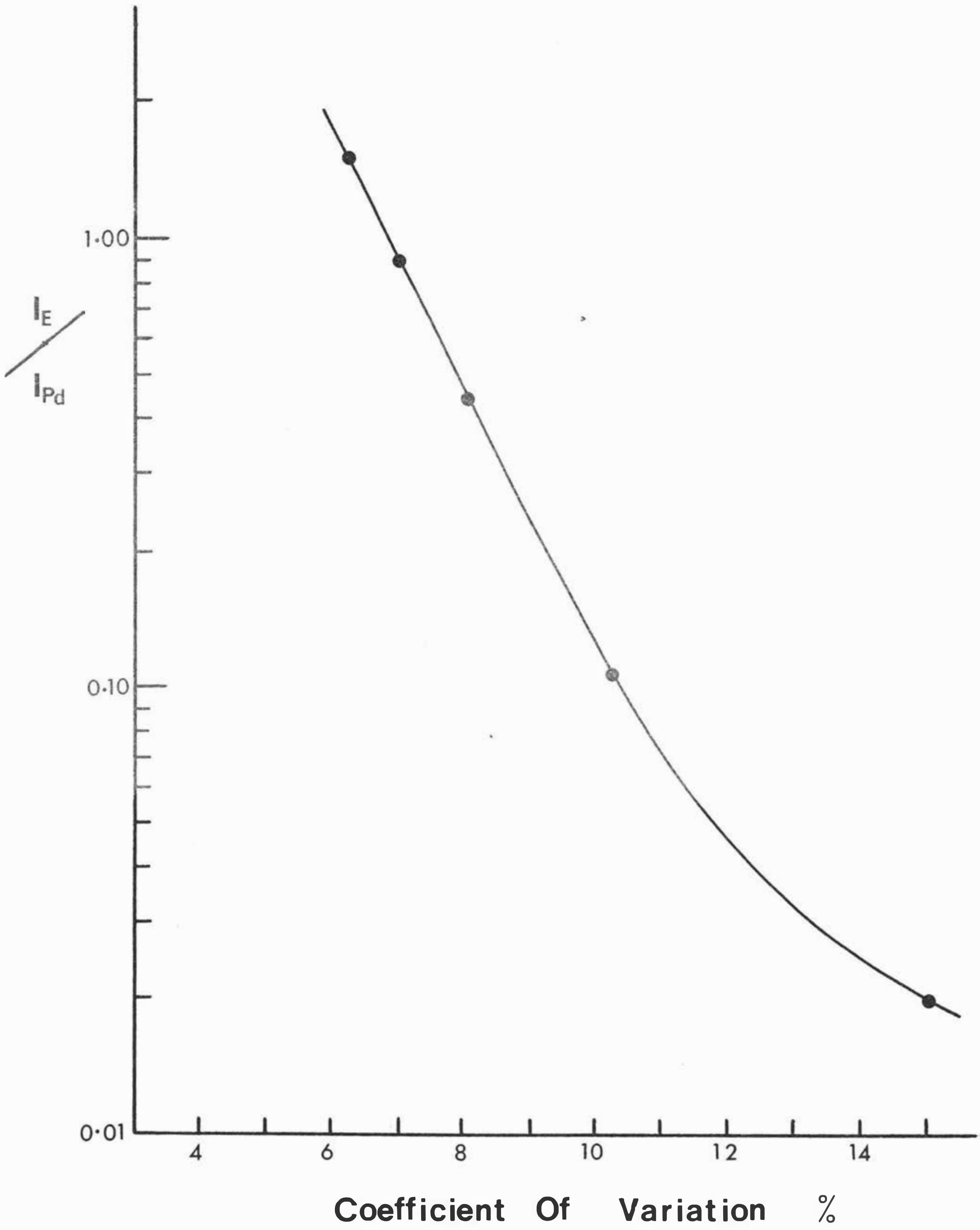


Fig. I - 4 Analysis element intensity/Palladium intensity as a function of the coefficient of variation.

than can be obtained at lower concentration levels.

(b) Studies on the Interference of Thorium, Yttrium and Rare Earth Analysis Lines

I. Development of an Ion Exchange Separation

(i) Separation by Use of the Acetic/Nitric Acid Anion - Exchange System

Solutions were prepared containing macro elements in the proportions found in granite (G-1) as given by FLEISCHER (1965) and 1000 ppm each of uranium, thorium, yttrium and the rare earths. The solvent was a mixture of 90% glacial acetic acid and 10% nitric acid.

The anion-exchange procedure used was a modification of work reported by KORKISCH and ARRHENIUS (1964). The method used was as follows:

Resin: Dowex 1 x 8 (100 mesh), chloride form.

Column Dimension: 15cm x 1cm.

Flow Rate: 0.5 - 0.7 ml/min.

The column was prepared in the normal manner as described by VOGEL (1961) and converted to the nitrate form by passing 5 M nitric acid until the eluant no longer gave a positive test to silver nitrate. The column was then equilibrated with 45 ml of a mixture of 90% glacial acetic acid and 10% 5 M nitric acid which had previously been degassed on a water pump. The previously prepared mixture of elements, in the same solvent, was passed through the column followed by 50 ml of the same solvent to remove any weakly-adsorbed elements. Yttrium, thorium, uranium and the rare earths remained adsorbed on the resin. Uranium was separated from thorium, yttrium and the rare earths by eluting with 35 ml of 6 M hydrochloric acid. This converted the uranium into a chloro-complex which remained adsorbed on the column whereas yttrium, thorium and the rare earths were eluted as they do not form strong chloro-complexes. The uranium was then eluted with 25 ml of 0.1 M hydrochloric acid. The separation took approximately five hours, but several columns could be run simultaneously. In this case a battery of six was found to be suitable.

Several experiments were carried out to investigate the effect of flow rate and element concentration, especially uranium, on the separation procedure. It was found that the separation efficiency was unaffected by flow rates varying between 0.2 ml/min and 1 ml/min. The factor governing flow rate was actually the room temperature as the acetic acid became rather viscous around 18°C. In most cases the flow rate was between 0.5 ml/min and 0.7 ml/min. For the column dimensions given, it was found that solutions samples containing up to 2500 ppm uranium were successfully separated. Element recovery experiments were also performed to determine the efficiency of the separation. The results obtained indicated that there was mutual interference in the rare earth emission spectra, because many elements gave apparent concentrations much higher than the amounts added would have indicated.

Although the above separation successfully concentrates the analysis elements and removes interference from macro constituents, there still exists mutual interference from the rare earths themselves. Results of anion exchange separations reported by CARSWELL (1957) and DANON (1958) indicated that it might be possible to separate uranium, thorium, yttrium and rare earths into several groups, hence reducing interference. The following investigation was carried out.

(ii) Separation by Use of the Nitric Acid Anion-Exchange System

Uranium, thorium, yttrium and rare earths were adsorbed on to the column, as described in the above section, and were, in separate experiments, eluted with 2 M, 4 M and 6 M nitric acid respectively (flow rate 0.5 ml/min.). Aliquots of 5 ml were taken over a volume of 120 ml. Results of these separations are shown in Fig. I-5. From this it is seen that the separation is unsatisfactory and further attempts at separation were discontinued. It is possible to separate the rare earths using ammonium citrate as eluting agent (SPEDDING ET AL, 1950) but the time involved rendered this approach unsatisfactory.

An examination of line spectra of the analysis elements was then made in an attempt to determine the extent of mutual line interference of thorium, yttrium and the rare earths, so that these elements might be analysed together as a group. The following results are essentially those reported by COHEN ET AL (1968).

II. Mutual Interference of Yttrium, Thorium and Rare Earth Analysis Lines

In this study it was necessary to know how the resolution of the large quartz spectrograph varied with wavelength. This was determined in two steps. Firstly, a curve of reciprocal dispersion (Å/mm) against wavelength (Å) was constructed from the NBS card index by measuring the distance (mm) apart of any two lines at

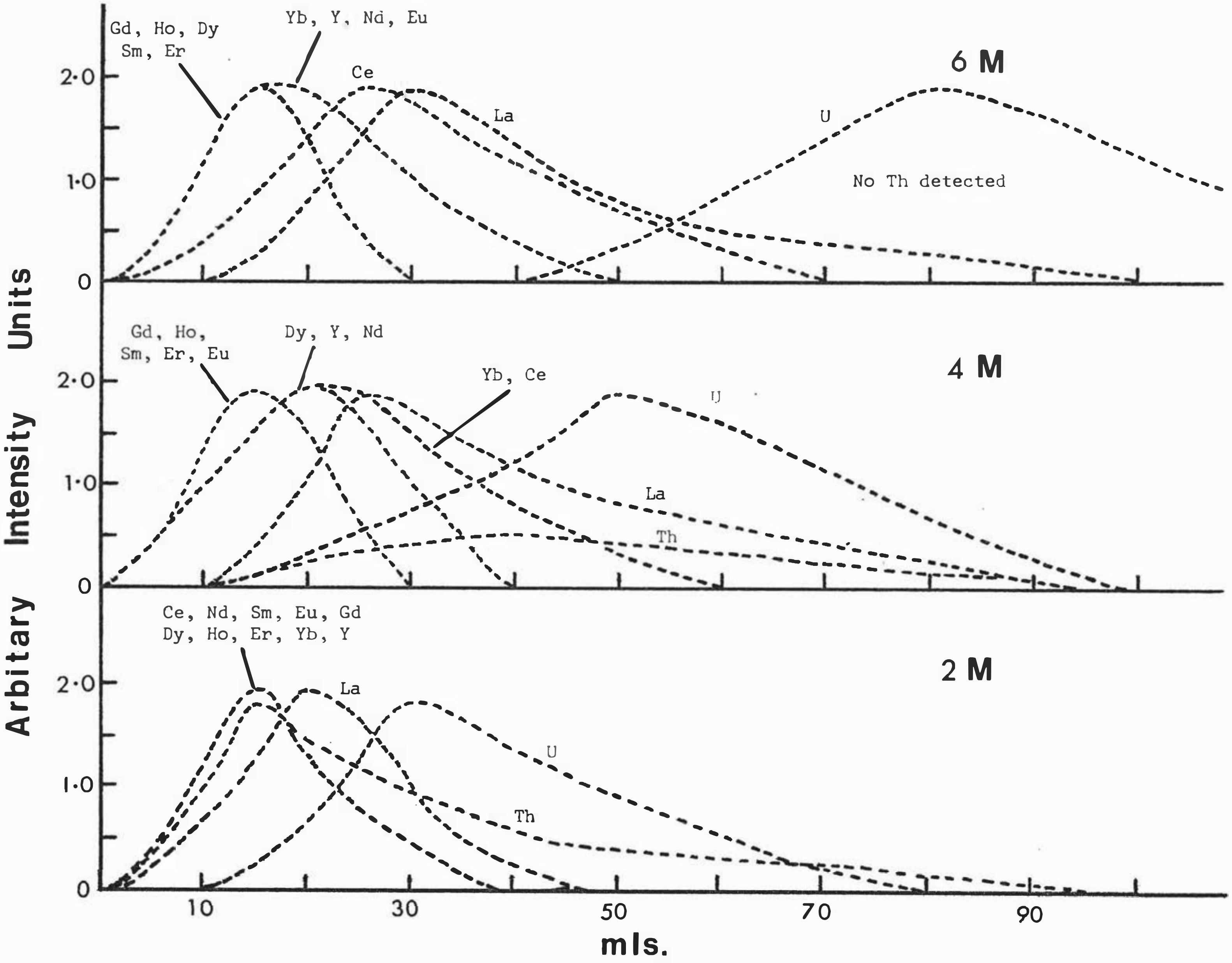


Fig. I - 5   Elution curves for analysis elements in nitrate system.

a particular wavelength. Secondly, the minimum distance between any two resolvable lines on the photographic plate was determined arbitrarily by use of the Hilger microdensitometer, with and without a chart recorder. This distance was found to be about 0.04mm. Using this value, a curve of resolution (Å) as a function of wavelength (Å) was constructed. It is important to add that the term resolvable, as used previously, means that it was just possible to distinguish two separate peaks and depends somewhat arbitrarily on the acuity of the observer. Fig. I-6 shows the respective curves. From these figures it was possible to determine a potential interference band of wavelengths on either side of any particular analysis line at any particular wavelength. From NBS Tables (MEGGERS ET AL, 1961) possible interfering rare earth element lines may be found. The extent to which the elements interfere can be obtained approximately from the formula

$$\% \text{ Interference} = 100 \times \frac{A_i \; I_i}{A_a \; I_a}$$

where A_i, A_a are the respective abundances of the interfering and analysis elements and I_i and I_a are the respective line intensities. It must be emphasised that if intensity values from the NBS Tables are used to compute this interference, the results may be different from those obtained with experimental conditions different from those used by the authors of these tables.

To check the validity of this formula under the conditions used, separate solutions were prepared from "Specpure" chemicals for yttrium, thorium and each lanthanide. Separate samples containing 100 ppm of each element were prepared and arced under the

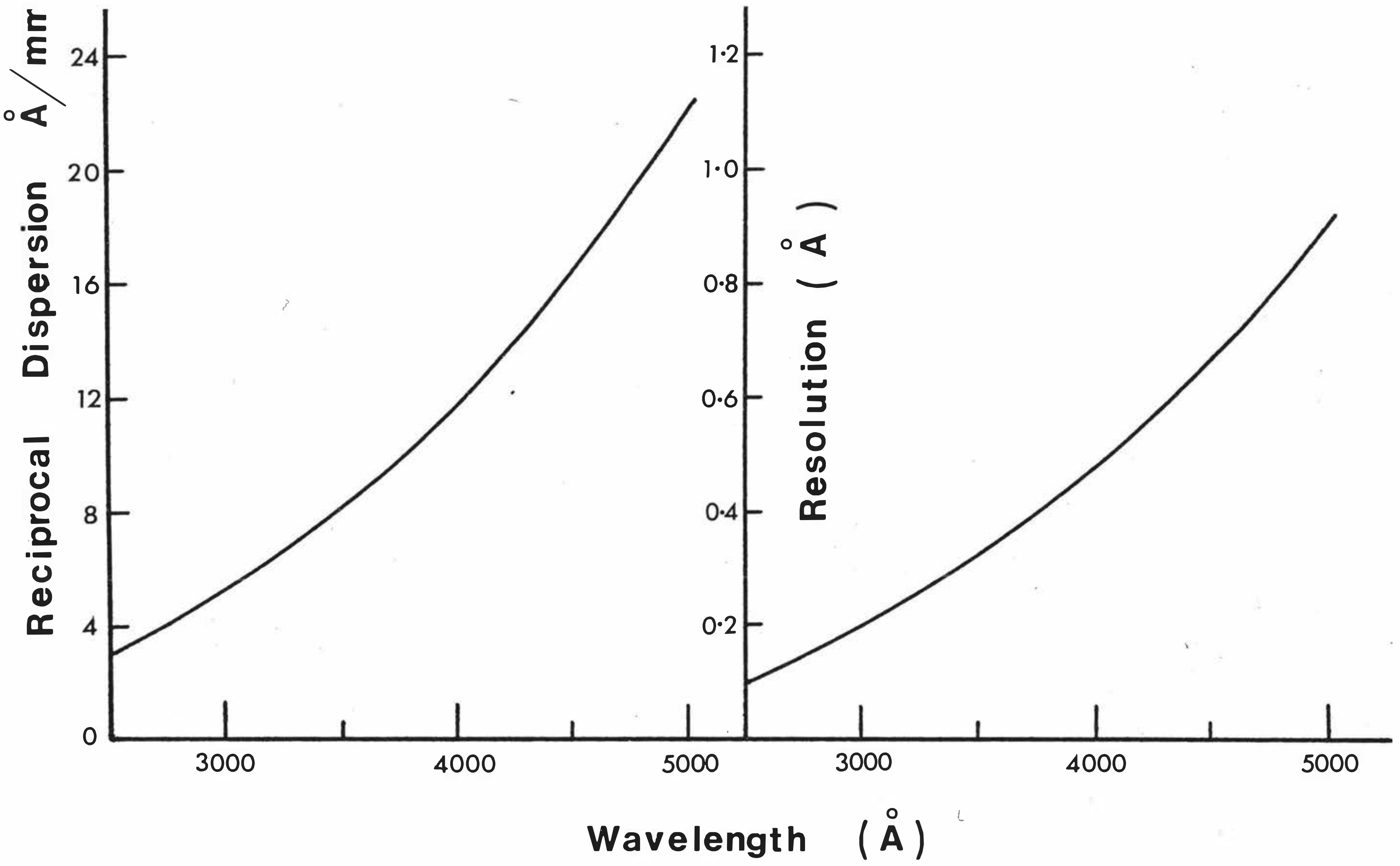


Fig. I - 6 Reciprocol Dispersion (Å/mm) and Resolution (Å) as a function of Wavelength (Å) for the Hilger E742 quartz-optics spectrograph.

standard conditions. The intensity of an analysis line for each element was measured together with the intensity of any potentially interfering lines of other elements. The data showed that for a predicted interference of up to 10%, no interference was detected in the spectrum of any of these elements at the wavelength of the selected analysis lines. This was not the case for predicted interferences greater than 10%. Table I-5 lists the analysis lines used for yttrium, thorium and the rare earths with the respective interfering lines of other rare earth elements and intensity ratios for subsequent correction. The analysis lines tested are not always the recommended R.U. lines but in some cases are lines of lower wavelength which, although of lower sensitivity, may still be used because of the ion exchange enrichment and separation procedure. This use of lower wavelength lines has the obvious advantage of better resolution since dispersion increases with decreasing wavelength. The table does not list all the possible interfering lines as given in the NBS Tables but only those which give a predicted interference of more than 10% from the formula (considering the normal abundance ratios of these elements) and which were detected in the spectrum of the pure element. In all cases, the highest likely concentration of the interfering element was taken in order to allow for maximum interference possible.

When significant interferences are obtained, corrections are made as in the following example. As the neodymium line at 4040.80 Å interferes with cerium 4040.76 Å (this line, although interfered with, was found to be the most suitable cerium line), the intensity ratio of the neodymium lines at 4040 Å and 4061 Å, in the absence of cerium, was measured and found to be 0.732. The

TABLE I - 5

Analytical Lines and Interferences

Analytical lines in Å (intensities)*	Interference range Å (from Fig.I-6)	Interfering lines in Å (intensities)*	Intensity ratios of interfering lines and reference lines
Lu 2911.39 (600)	± 0.18	Th 2911.32 (8)	Th 2911/Th4019 = 0.027
Yb 3289.37 (2600)	± 0.27	None	None
Tb 3324.40 (400)	± 0.27	None	None
Y 3327.89 (600)	± 0.27	None	None
Pd 3421.24 (1400)**	± 0.30	None	None
Gd 3422.57 (700)	± 0.30	None	None
Ho 3456.00 (1800)	± 0.31	None	None
Tm 3462.20 (800)	± 0.32	None	None
Dy 3531.70 (2000)	± 0.33	None	None
Er 3692.64 (700)	± 0.38	None	None
La 3995.75 (360)	± 0.48	None	None
Th 4019.13 (300)	± 0.50	Ce 4019.04 (14)	Ce 4019/Ce 4040 = 0.237
Ce 4040.76 (150)	± 0.50	Nd 4040.80 (180)	Nd 4040/Nd4061 = 0.732
Nd 4061.09 (280)	± 0.50	None	None
Pr 4179.42 (460)	± 0.55	Ce 4179.29 (5)	Ce 4179/Ce4019 = 0.076
Eu 4205.05 (4000)	± 0.57	None	None
Sm 4256.38 (140)	± 0.59	Ce 4256.16 (12)	Ce 4256/Ce4040 = 0.092

* Intensities from NBS Tables

** Internal Standard

corrected cerium intensity at 4040.76 Å is obtained by subtracting 73% of the neodymium intensity at 4061.09 Å (interference free) from the observed value for the cerium line.

The correction of analysis lines for interference should be carried out in the following sequence. Ce 4040 is corrected for Nd 4040 interference, followed by correction of Th 4019 for Ce 4019, using the corrected Ce 4040 intensity value to calculate the correct value for Ce 4019. Having obtained interference-free Ce 4040 and Th 4019 intensities, Pr 4179 can be corrected for neodymium, cerium and thorium interferences.

Working curves for interference-free elements can be prepared by dilution of a common mixed standard, but other working curves must be prepared from individual unmixed standards. Fig. I-7a shows the working curve for Ce 4040 in the presence of various concentrations of neodymium, with and without correction, and the curve obtained from a pure cerium standard. Working curves for other elements (Fig. I-7b) are also given. The low scatter of the points gives an indication of the precision of the method.

(c) The Use of the Combined Anion Exchange-Spectrographic Procedure

(i) Dissolution of Rock Samples

The ease with which rocks are dissolved depends primarily on the nature of the rock (silicate, sulphide etc.), the elements present, and the solvent used. The solvent required for the anion exchange separation, in this case, governed this choice and hence presented certain difficulties. The main one was that 90% glacial acetic acid and 10% 5 M nitric acid is an extremely poor solvent.

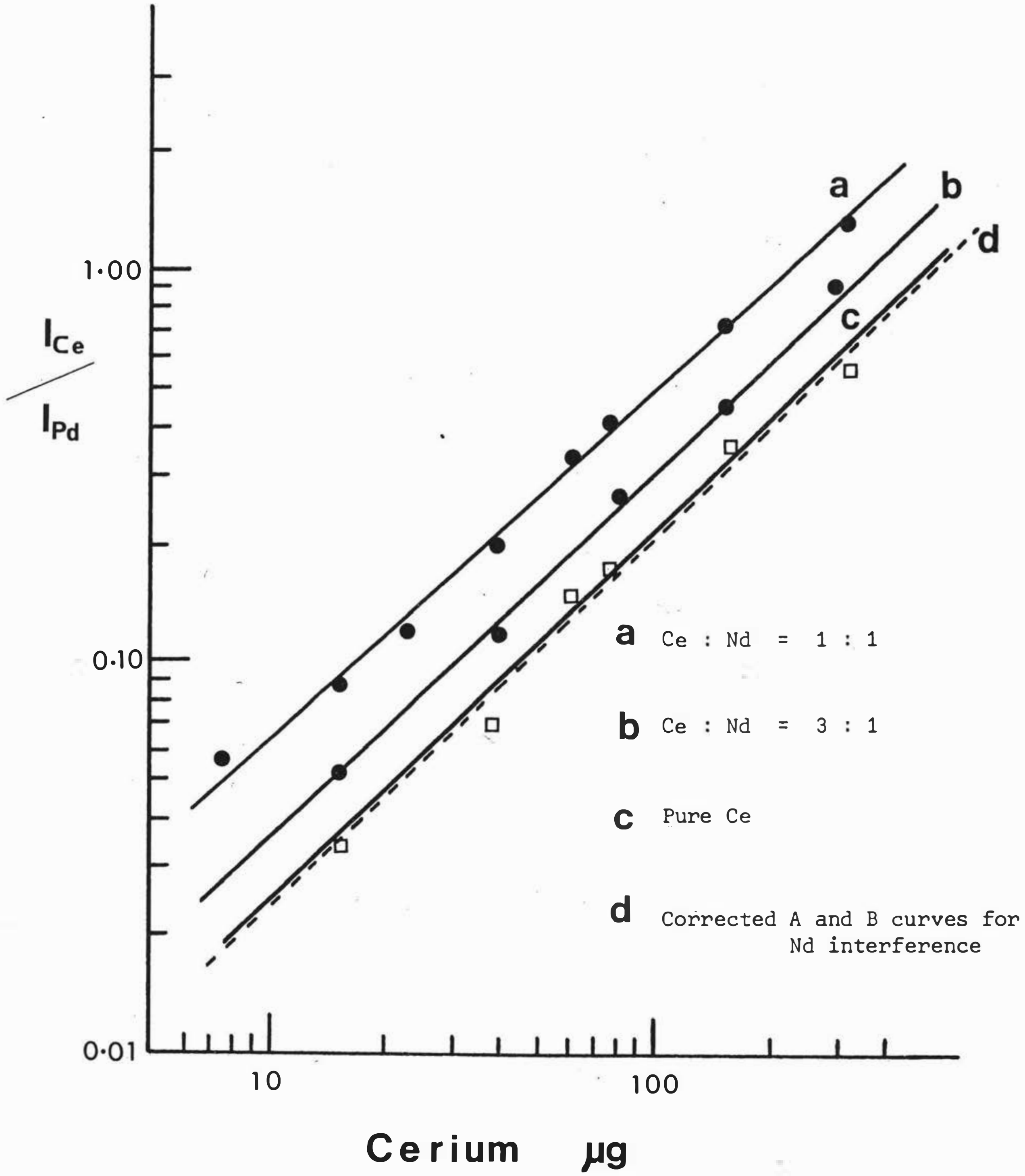


Fig. I - 7a Working curves for cerium (4040) in the presence of various concentrations of neodymium.

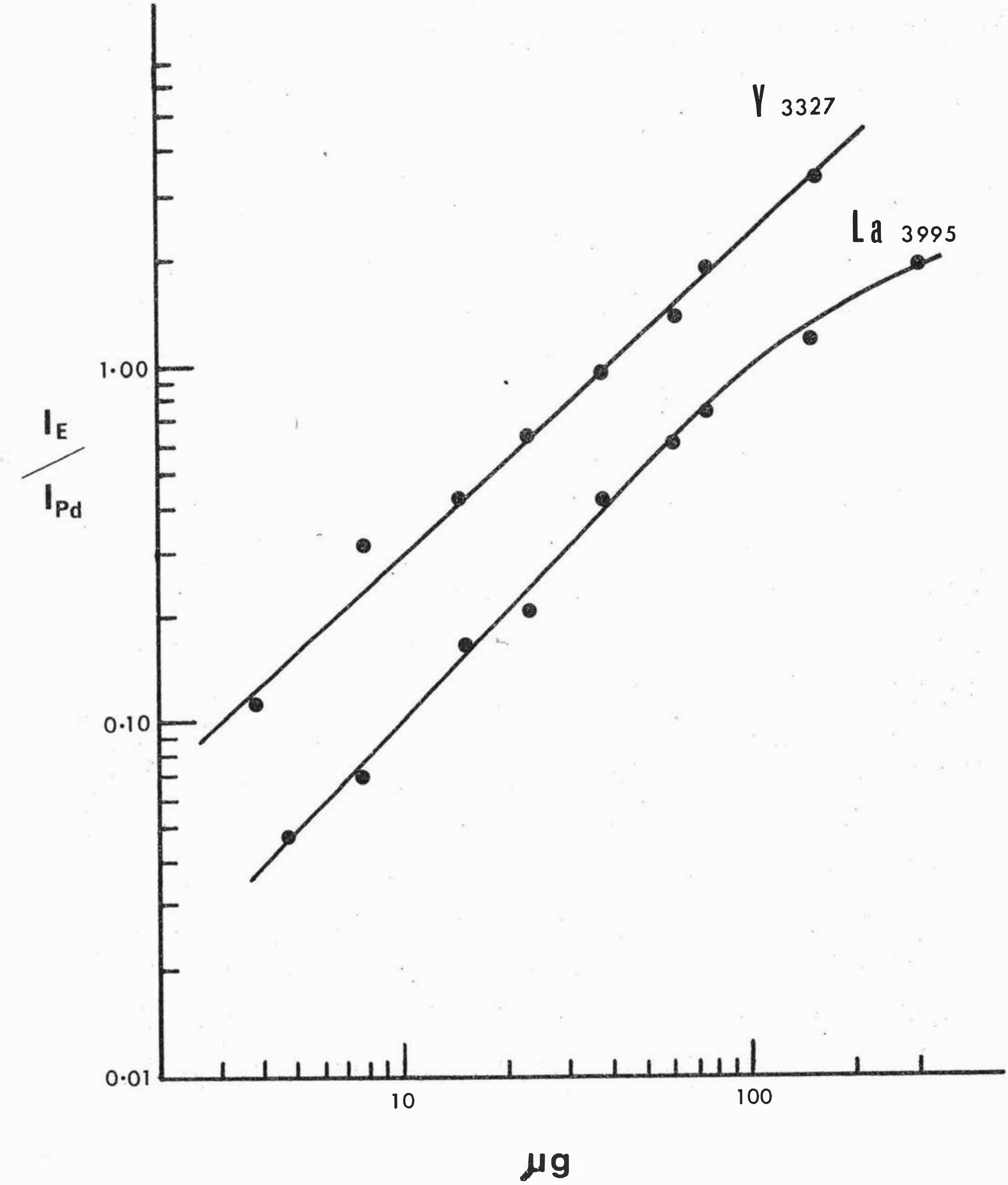


Fig. I - 7b Working curves for Y3327 and La3995.

Also, the elements thorium and cerium are generally very insoluble even in mineral acids. As a result, the following rather tedious scheme had to be used.

Concentrated nitric acid and concentrated hydrofluoric acids (15 ml of each) were added to 1 g of finely-divided rock sample (120 mesh) in a 250 ml teflon beaker and evaporated to dryness over a period of 2-3 hr. Then 15 ml of concentrated nitric acid was added to the residue, which was next transferred to a 150 ml glass beaker and slowly evaporated to dryness. To this residue was added 15 ml of 9:1 mixture of glacial acetic acid and 5 M nitric acid, and the whole was transferred to a tube and centrifuged. The supernatant liquid was retained and the residue was again treated with 15 ml of concentrated nitric acid, evaporated to dryness, taken up in 15 ml of acetic acid-nitric acid mixture and centrifuged. The solution was retained and the residue (usually less than 0.3 g) was dried, weighed, mixed in a 1:3 ratio with sodium peroxide and fused in a platinum crucible at 480° for seven minutes (RAFTER, 1950). The **melt** was neutralised with nitric acid and the solution centrifuged. Any solid remaining was discarded. Sufficient glacial acetic acid to give the correct ratio of acetic acid to nitric acid was added and all three supernatants were combined. The total volume was usually 70-80 ml. The solution was degassed for twenty minutes and then transferred to the prepared ion-exchange column. Complete digestion of the analysis elements was confirmed by arcing the supernatants and residue of a test sample after each stage had been completed.

(ii) Analysis of G-1, W-1 and CAAS Syenite

To evaluate the complete analytical procedure, experiments were carried out to test the recovery of elements from the ion-exchange column. Table I-6 shows the results obtained for some representative elements carried through a complete separation and analysis procedure. Analysis of the standard rocks G-1, W-1 and CAAS Syenite for thorium, yttrium and rare earths was carried out by the developed procedure. Table I-7 compares the results obtained with the most recent recommended values.

(iii) Evaluation of Data

The agreement between the spectrographic results obtained in this work for G-1 and W-1 and those given by FLEISCHER (1969) are good. The neutron activation data of HASKIN and GEHL (1963) also correlates extremely well and is shown in Fig. I-8.

The values obtained for CAAS Syenite give fresh data for nine rare earth elements whose values, as reported by WEBBER (1964) were either doubtful or were below the detection limit of the techniques used. The recent summary of SINE ET AL (1969) includes values obtained by TENNANT and FELLOWS (1967), also using emission spectrography. These values generally correlate well with this work and are shown in Fig. I-9. This figures shows that there is disagreement in the values for samarium, holmium and lutecium. In order to evaluate the correctness of the values obtained, the rare earth abundance ratios for an average acidic rock, an average basic rock and CAAS Syenite were calculated. These values are given in Table I-8. This table shows that whenever the results of this work and those of Tennant and Fellows agree, the abundance ratio (normalised to La = 1.00) of the rare earths in the syenite

TABLE I - 6

Recoveries from Ion-Exchange Separations

Element	Amount added (μg)	Amount recovered (μg)
La	300	280
Ce	300	309
Nd	300	309
Sm	100	102
Eu	100	98
Gd	100	99
Dy	100	102
Ho	100	102
Y	100	100

TABLE I - 7

Comparison of Spectrographic, Neutron Activation and Recommended Values for Thorium, Yttrium, Uranium and the Rare earths in G-1, W-1 and CAAS Syenite (ppm)

Element		G-1				W-1			CAAS Syenite		
	Code	A	B	C	D	A	C	D	A	B	E
La	1	100	80	100	102	10	12	11.7	187	245	220
Ce	2	200	160	170	134	20	23	24	350	625	365
Pr	3	19	16	17	20.9	5	4	3.68	137	140	-
Nd	4	60	43	55	54.6	16	17	15.1	300	305	302
Sm	5	< 5	< 10	9	8.6	< 5	4	3.79	< 5	245	-
Eu	6	0.9	1	1.3	1.04	1.5	1.1	1.09	15	8	-
Gd	7	7	< 10	5	4.88	4	4	4.2	72	58	-
Tb	8	< 2	< 50	0.6	0.5	< 2	0.8	0.75	< 2	< 50	-
Dy	9	2	< 20	2.5	n.d.	2	4	n.d.	100	135	-
Ho	10	0.4	< 1	0.5	0.5	3	1	1.35	21	2	-
Er	11	1.4	< 10	2	1.4	2.5	3	2.57	57	42	-
Tm	12	< 3	< 1	0.2	0.2	< 3	0.3	0.35	< 3	5	-
Yb	13	0.6	0.8	1	0.62	1.5	2.2	2.1	90	57	70
Lu	14	0.1	< 10	0.2	0.17	0.3	0.35	0.33	1.5	< 10	-
Y	15	12	12	13	12.5	11	25	23.8	450	450	450
Th		30	21	52	n.d.	1	2.4	n.d.	710	1300	1338
U		2.6	< 50	4	n.d.	1.5	0.5	n.d.	2380	2700	2500

A - This work.
B - Direct arcing with high dispersion instrument (TENNANT and FELLOWS, 1967).
C - Recommended values for G-1 and W-1 (FLEISCHER, 1969).
D - Neutron activation (HASKIN and GEHL, 1963).
E - Median values for CAAS syenite (SINE ET AL, 1969).
n.d. - Not determined.

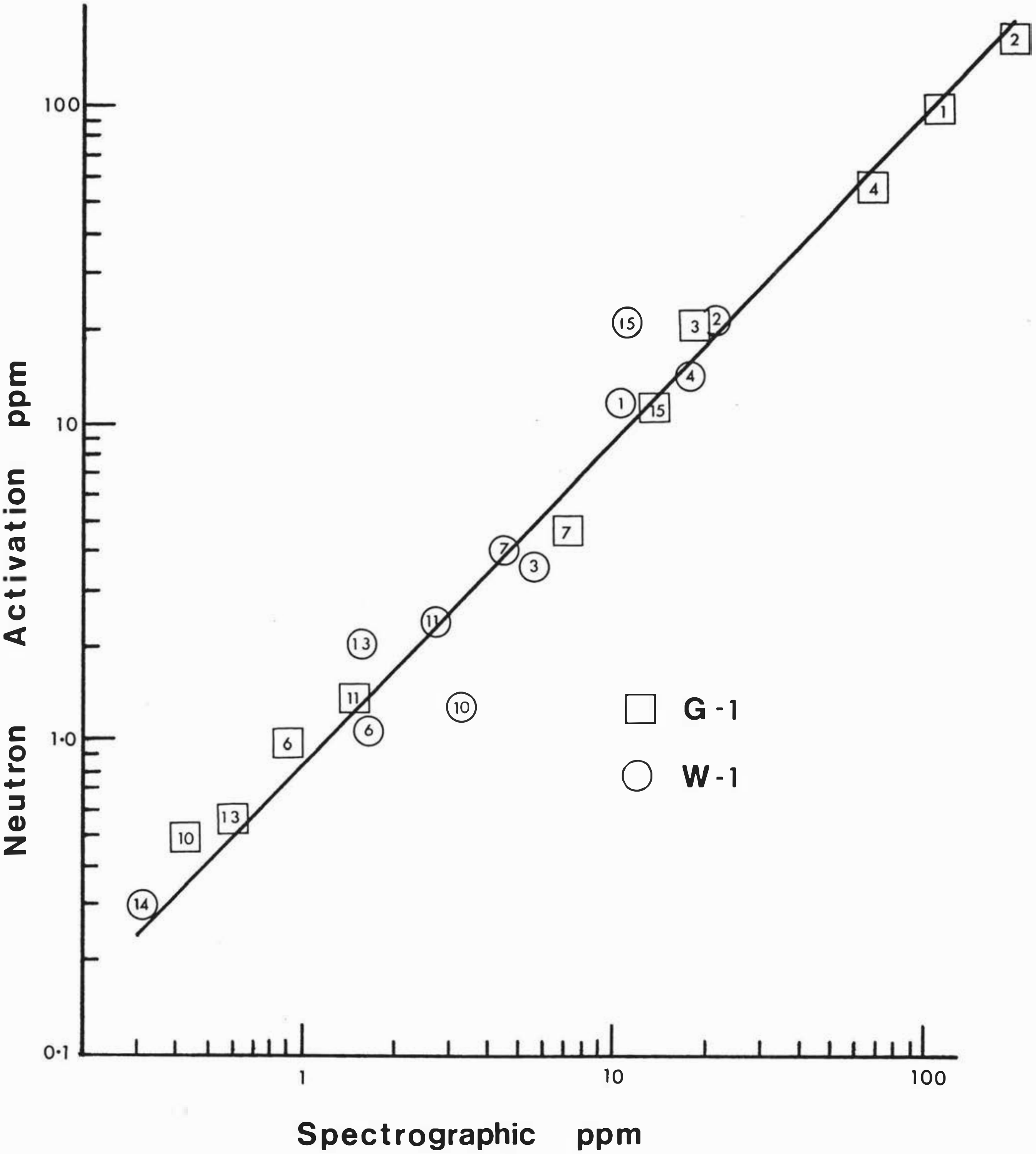


Fig. I - 8 Neutron activation data from HASKIN and GEHL as a function of spectrographic data from the author for G-1 and W-1.

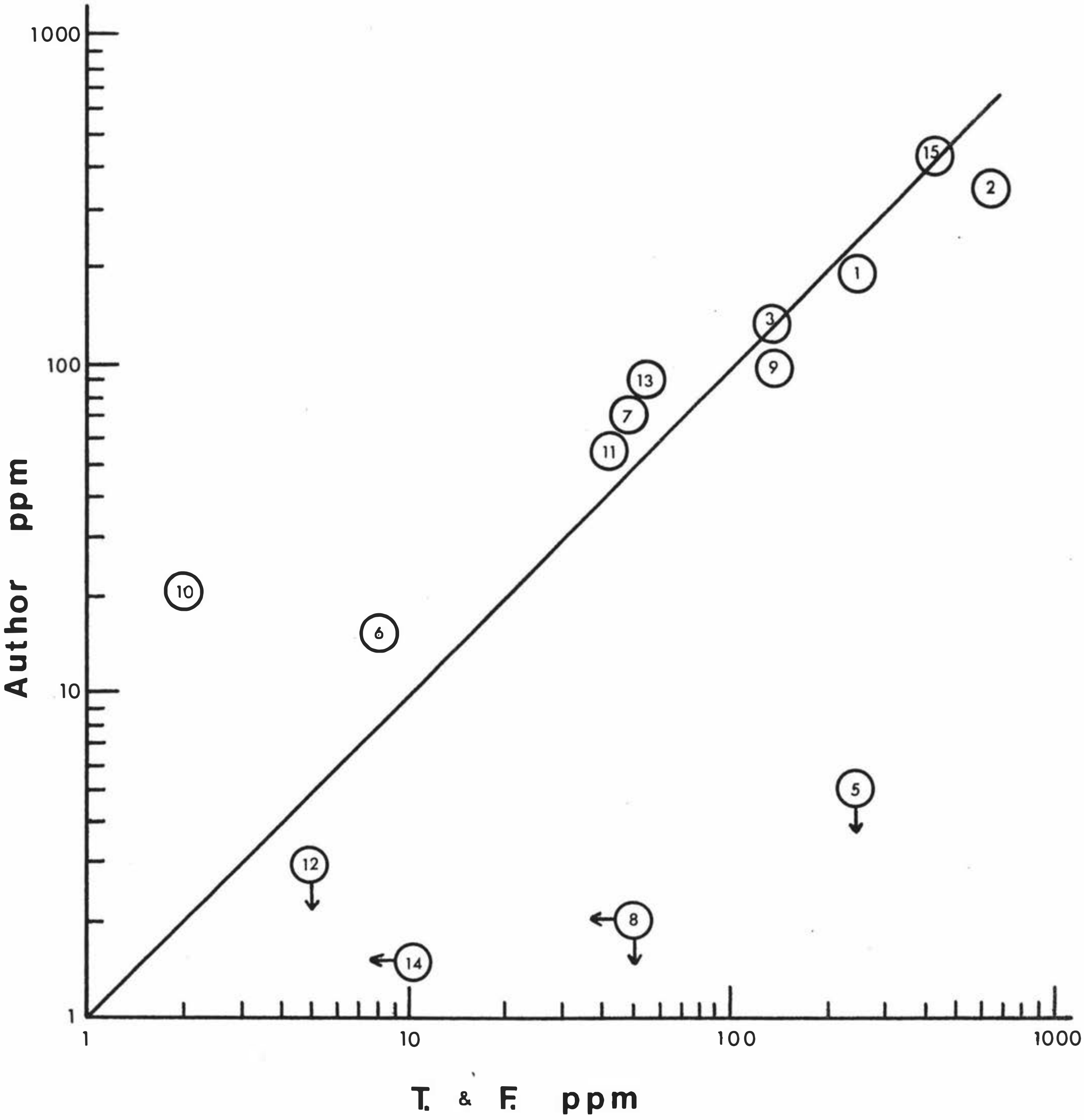


Fig. I - 9 Data from the author as a function of spectrographic data from TENNANT and FELLOWS for CAAS Syenite.

TABLE I - 8

Rare Earth Abundance Ratios for G-1, W-1 and CAAS Syenite. (All Data Normalised to La = 1.00 by weight).

Rare Earth Element	A	Syenite		B
		N.E.C.	T.&F.	
La	1.00	1.00	1.00	1.00
Ce	1.58	1.84	2.46	2.73
Pr	0.20	0.72	0.55	0.35
Nd	0.62	1.57	1.17	1.47
Pm	-	-	-	-
Sm	0.10	0.025	0.96	0.36
Eu	0.0094	0.073	0.029	0.10
Gd	0.057	0.33	0.167	0.39
Tb	0.0030	0.087	0.174	0.06
Dy	0.018	0.45	0.46	0.30
Ho	0.0034	0.092	0.0067	0.081
Er	0.0090	0.25	0.14	0.18
Tm	0.0016	0.013	0.016	0.023
Yb	0.0035	0.38	0.183	0.13
Lu	0.0008	0.0055	0.031	0.021

A - Average Acidic Rock pattern. Average of G-1 (HASKIN and Gehl, 1963) and Kirovograd granite (GAVRILOVA and TURANSKAYA, 1958).

B - Average basic rock pattern. Average of W-1 (HASKIN and GEHL, 1963), and Kilauea-iki (SCHMITT ET AL 1963a).

approximate to that of an average basic rock. A plot of abundance ratio against atomic number for the average granite rock, average basic rock and syenite further confirmed this.

To help evaluate the relative merit of the value of these discordant elements, as shown in Fig. I-9, the abundance ratios of the rare earths in the average basic rock and the results obtained for the syenite in this work, together with those values obtained by Tennant and Fellows, were plotted against atomic number and are shown in Fig. I-10. From this it is clearly seen that the elements samarium, holmium and lutecium do not lie as close to the curve of the average basic rock as do the other rare earth elements. If it is assumed that the rare earth abundance ratio pattern is consistent for all member elements, then the value for the discordant element closer to the curve of the average basic rock is the value which is likely to be more correct. If, as is the case of samarium, both the values lie far from the average basic rock curve, and are widely different, then it is likely that both are incorrect. However, if this happens, the estimated value can be obtained and is in this case approximately 37 ppm. On this basis it is decided that the author's value for holmium (21 ppm) is more likely to be correct than that of Tennant and Fellows (2 ppm) whereas their value for ytterbium (57 ppm) is better (90 ppm). It is also possible that the author's value for lutecium (1.5 ppm) is too low; a value of 3 ppm is more consistent with the average basic rock curve.

It is concluded that the results in Table I-6 and Table I-7 have demonstrated the feasibility of using a large quartz-optics (medium dispersion) spectrograph for the determination of thorium,

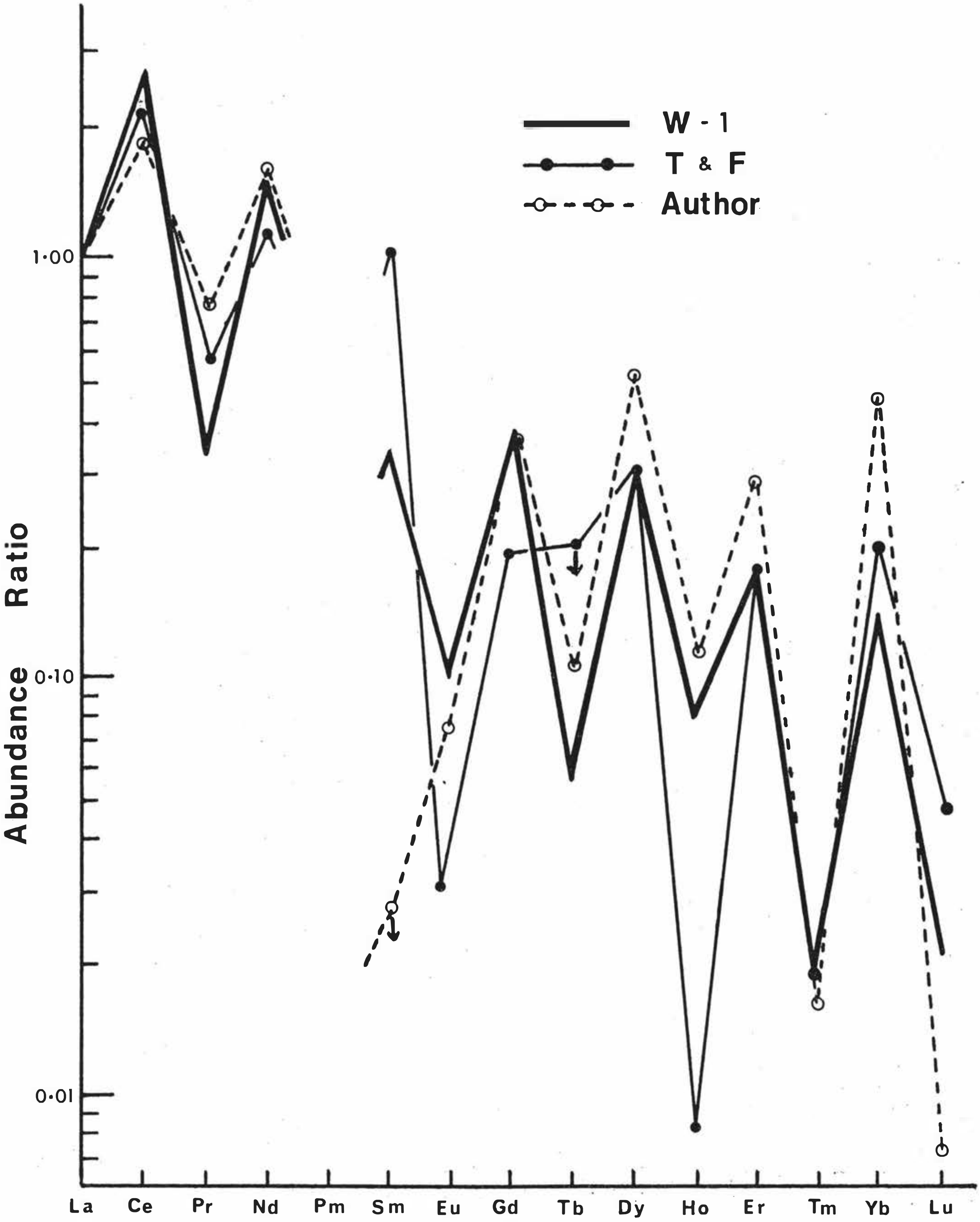


Fig. I - 10 Rare earth distribution for an average basic rock and CAAS Syenite.

yttrium and the rare earths provided that an initial separation is previously carried out.

ANALYTICAL METHODS FOR URANIUM

(a) Spectrographic Procedure for Macro Amounts of Uranium

The uranium spectrum is extremely complex, and because no lines show high transition probabilities the emitted radiation is dissipated among many lines. As a result, the sensitivity is low. Also, when present in high concentrations, uranium emits an intense continuous background radiation which interferes with itself and other elements. Because of these properties uranium is a difficult element to analyse spectrographically.

Uranium was analysed under the same spectrographic conditions established for the analysis of thorium, yttrium and rare earths. However, the limit of detection was only 0.8% uranium, rendering the technique suitable only for the analysis of minerals. Fig. I-11 shows the working curve obtained.

(b) Solution Fluorimetry

Solution fluorimetry was investigated as it is well known that this technique is considerably less sensitive than the extremely-sensitive fusion-bead technique and, as a result, might be a suitable method to analyse for uranium in the intermediate concentration range between that of fusion-bead analysis and spectrographic analysis. SILL and PETERSON (1947) reported the fluorescence of uranium in orthophosphoric acid and used this property to determine uranium visually. As this appeared to be a possible method for analysing uranium in an intermediate concentration range, the following investigation was carried out.

A uranium standard (10 ppm) was prepared in solutions of 5%, 10%, 20%, 50%, 75% and 100% phosphoric acid respectively and the fluorescence measured with a fluorimeter. The results are

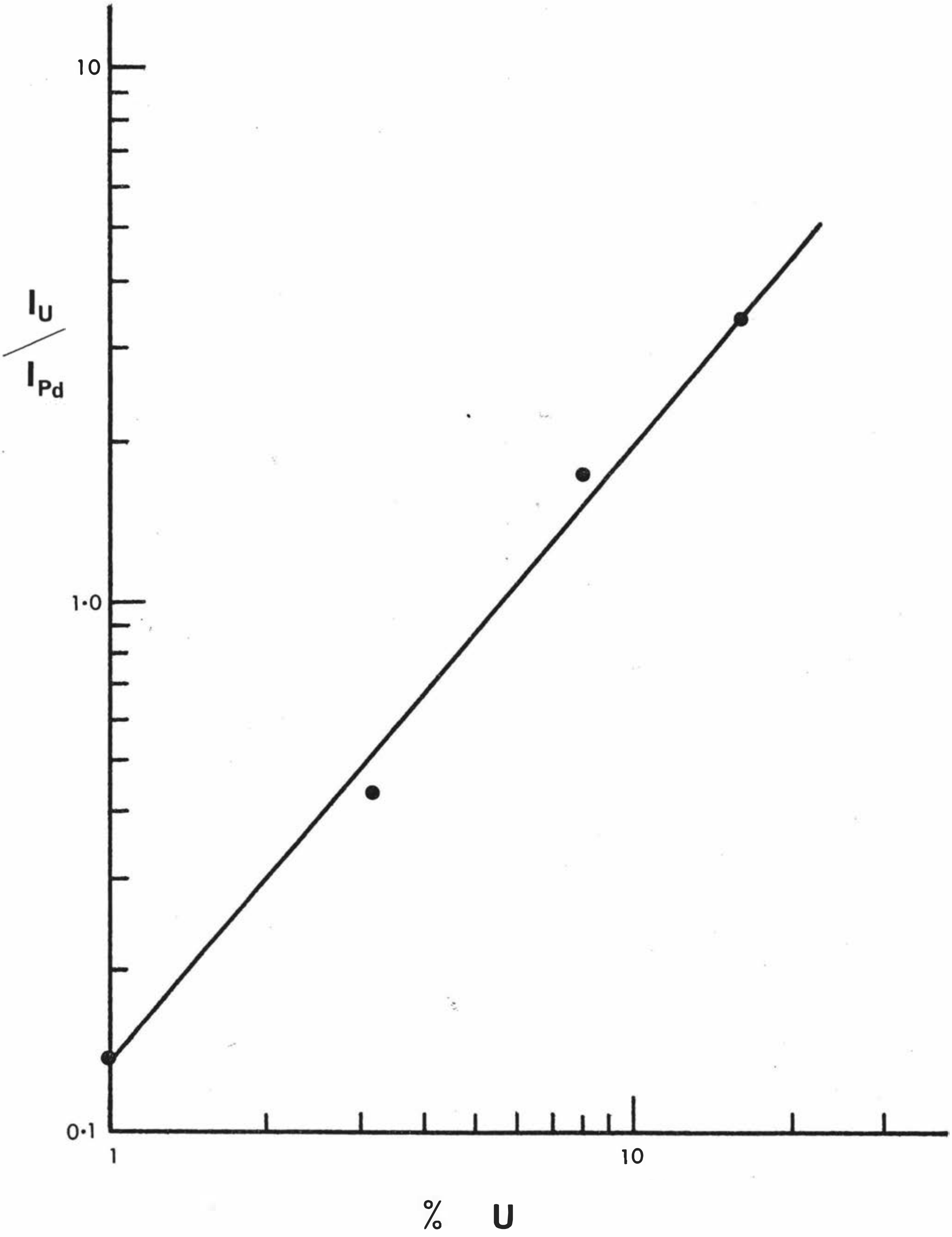


Fig. I - 11   Spectrographic working curve for uranium.

shown in Fig. I-12.

Specifications

Instrument: Aminco-Bowman Spectrofluorimeter with variable excitation and emission monochromators and xenon source.

Excitation wavelength: 264 mμ

Emission wavelength: 518 mμ

From Fig. I-12 it is seen that 5% or 10% phosphoric acid is the optimum phosphoric acid concentration. All further analysis were carried out using 10% phosphoric acid. Preliminary working curves were prepared and it was found that Beer's Law was obeyed up to about 13 ppm uranium. To increase the applicable concentration range, the following dilution scheme was developed. Solutions with 5 μg - 50 μg of uranium were diluted to 5 ml with 10% phosphoric acid, samples with 25 μg - 250 μg were diluted to 25 ml and amounts of 250 μg - 1000 μg required dilution to 100 ml. The results are shown in Fig. I-13. This allowed each analysis to be carried out in such a way that if dilution was necessary, the total uranium present, and not a fraction of it, was diluted. This considerably reduced the absolute error in the analysis due to dilution. The analysis was carried out as follows:

The ion-exchange eluate containing only uranium was taken to dryness, 5 ml of phosphoric acid was added and the solution was examined under an ultra violet lamp (254 mμ). If the fluorescence intensity was too high this volume was further diluted to 25 ml and again examined. If the intensity was still too high after diluting to a volume of 100 ml, then a fraction of this was taken and diluted further. However, this situation was uncommon.

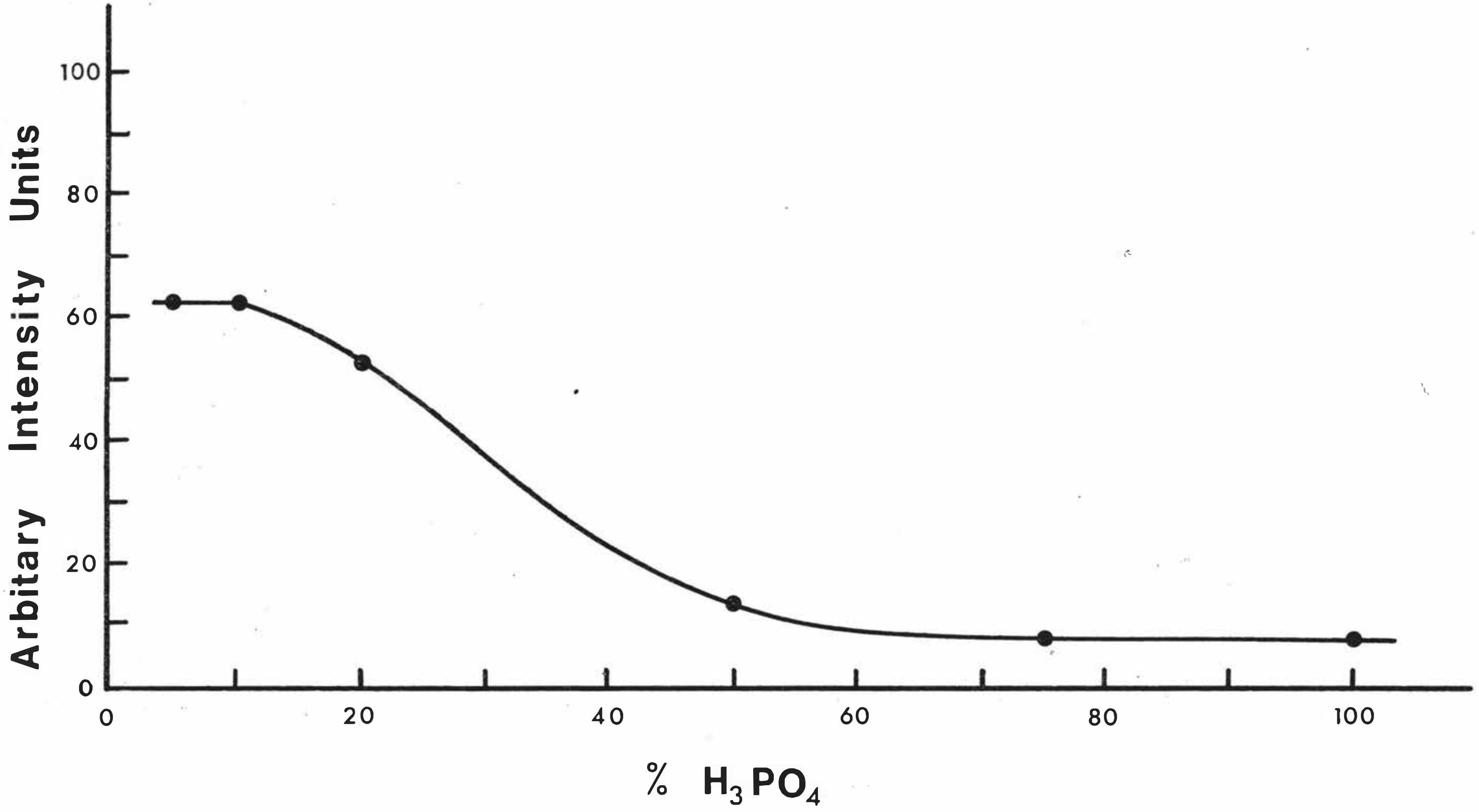


Fig. I - 12 Uranium fluorescence intensity as a function of per cent phosphoric acid.

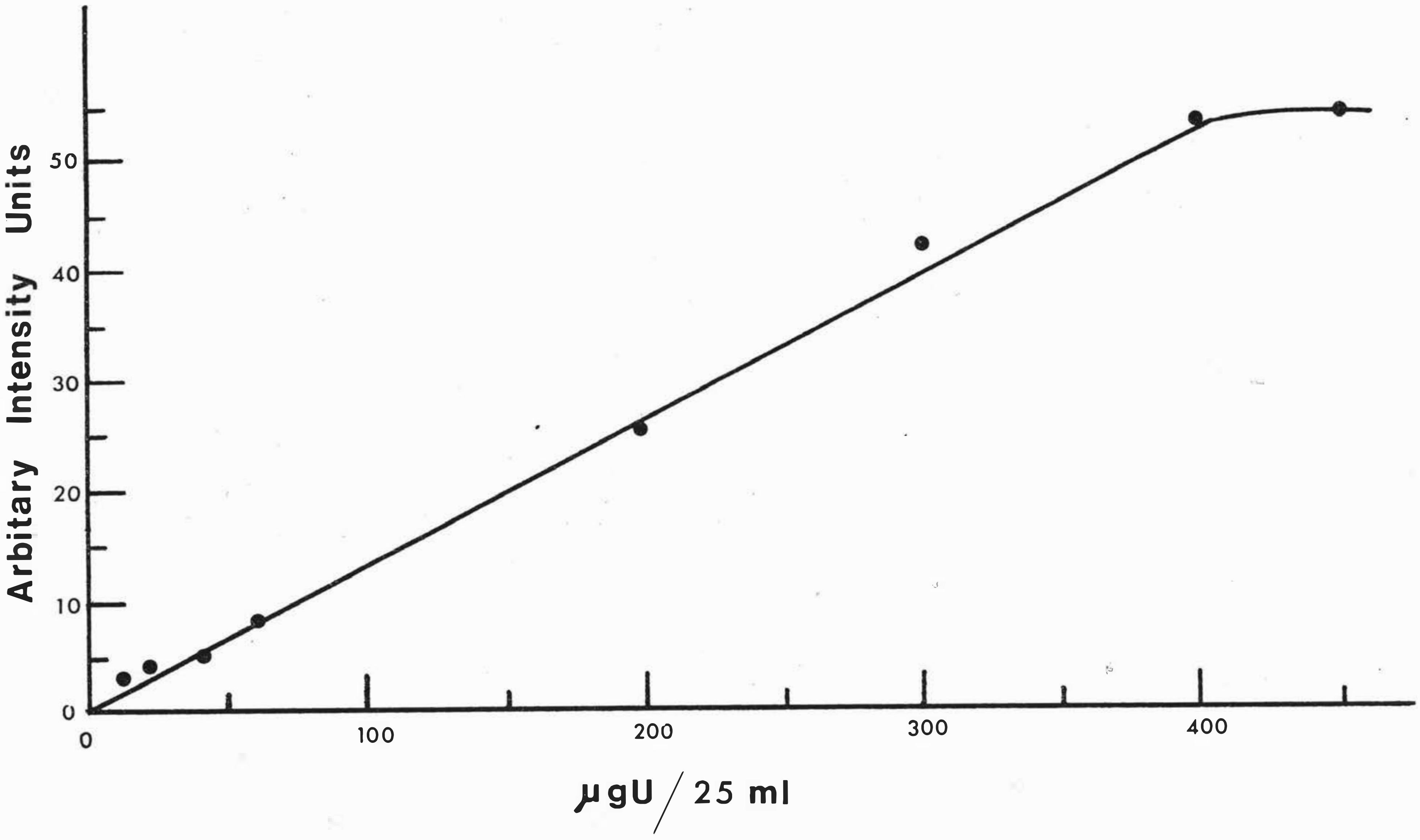


Fig. I - 13 Solution fluorimetry working curve for uranium.

Replicate analysis of samples containing 5 ppm U were analysed and gave a coefficient of variation of ten per cent.

(c) Fusion-Bead Fluorimetry

Melts obtained by fusing uranium salts with sodium fluoride fluoresce a brilliant yellow-green when exposed to ultra-violet light (NICHOLS and SLATTERY, 1926). However, sodium fluoride has a high melting point (992°C) and tends to stick to platinum and gold containers making it difficult to work with. GRIMALDI ET AL (1952) employed a mixture of sodium fluoride, sodium carbonate and potassium carbonate which has the advantages of a lower melting temperature (about 700°C), does not stick to platinum or gold containers and gives about the same fluorescence as sodium fluoride. These authors also discuss the effect of fusion temperature and time of heating on the fluorescence intensity. Details of the procedure used in the present work are as follows.

A mixture of ANALAR sodium fluoride, sodium carbonate and potassium carbonate in the ratio (by weight) 9:45.5:45.5 was prepared. One hundred and eight grams of this mixture was mixed in a Waring blender with 100 ml of water until a smooth paste was obtained. This was then poured into the pellet mould. The mould consisted of a 15 cm^2 x 1 cm teflon slab (to prevent contamination) with one hundred holes (1 cm i.d.). A glass plate, fastened by screw clips, was used as a base and could be unfastened to remove the pellets. The mould was heated for 2-2½ hrs at 105°C and the pellets were extruded, transferred to a glass beaker and dried for a further two days. Finally, before use they were graded into groups according to their weight. Pellets weighing 1.0 ± 0.5 g were used for this work. The ion-exchange eluates were taken to dryness and then redissolved in 2 ml of 2 M nitric acid. One ml of each sample was transferred to each of six 1 ml capacity hemispherical gold micro-dishes. A further three micro-dishes were filled with 1 ml of each of three standards containing 1 µg, 3 µg and 6 µg of uranium. The gold dishes were placed on a vertical section of quartz tubing mounted in a stainless steel holder which was heated in an oven at 105° until the contents of the dishes were evaporated to dryness. On removal, one fusion pellet was added to each micro-dish and the holder was placed in a furnace at 700°C for 10 minutes. After removal, the dishes were placed in a fluorimeter holder and allowed to cool. Analysis was carried out with a specially designed fluorimetric attachment to a Techtron AA3 atomic absorption spectrophotometer (BROOKS and WHITEHEAD, 1968). As a precaution against errors in the fusion procedure, as a result of uneven or variable heating, uranium standards were always included in each set of six analyses. Fig. I-14 shows the slight differences obtained in the working curves from different runs. The useful concentration range is between 0.5 ppm and 6 ppm uranium and replicate analyses gave a coefficient of variation of ten per cent.

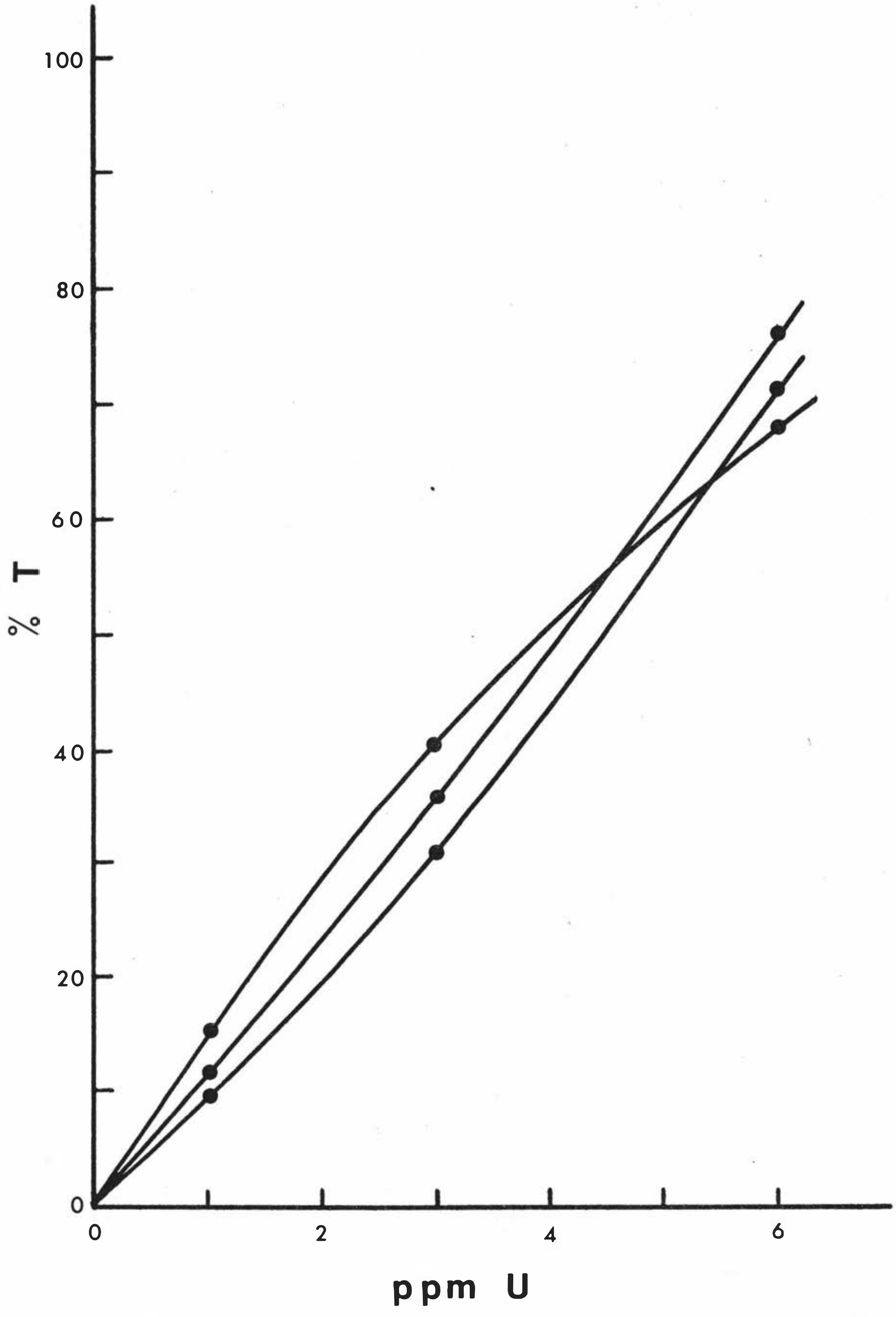


Fig. I - 14 Fusion-bead fluorimetry working curves for uranium.

DISCUSSION

In the introduction to this analytical section it was clearly shown that the use which can be made of results from the analysis of geological samples depends critically on the accuracy of the determinations. For this reason considerable effort and care was exercised to develop the methods available to the author to their utmost precision and sensitivity. The results given in Table I-7 for G-1, W-1 and CAAS Syenite indicate that this was achieved. To the author's knowledge, this is the first time a medium-dispersion quartz-optics spectrograph has been successfully used to analyse rare earths at this level. It is important to note that although the analytical procedure for thorium, yttrium and rare earths was developed specifically for a quartz-optics spectrograph, use of a grating-spectrograph in conjunction with this method should yield even better results. With a grating-spectrograph, better precision would be obtained because of greater dispersion(reciprocal dispersion of the order of 2.5Å - 5.0Å/mm) and the sensitivity should be higher due to the corresponding reduction in background.

During the development of the technique for analysis of the rare earths, fresh data were obtained for the abundance of these elements, and for yttrium and thorium, in standard rocks G-1, W-1 and CAAS Syenite. The good correlation of the data for G-1 and W-1 obtained in this work with that obtained by Haskin and Gehl using neutron activation analysis, a technique which is now generally accepted as probably the most accurate method for trace analysis, implies that emission spectrography is still an extremely useful method for rare earth analysis, provided care is taken to optimise the conditions.

The chemical methods used for uranium analysis in this section enabled a wide concentration range to be covered with a good degree of accuracy. Ion-exchange separation of uranium from all other elements enabled fluorimetric analysis to be carried out without the risk of quenching due to the presence of other ions. This is particularly important, for quenching problems in fluorimetry can be severe. The chemical methods are better than the majority of radiochemical techniques because they determine the absolute amount of uranium present. The precision of radiochemical methods, which usually involve the measurement of the activity of daughter products rather than uranium itself, is heavily dependent on the degree of isotopic equilibrium in the samples analysed.

The separation procedure developed is practical, but suffers as a routine method because of the time involved in dissolution of the rocks in an unfavourable solvent and because of the amount of attention required during separation. The time problem can be improved by operating more columns simultaneously but practical considerations limit this to a maximum of about twelve columns. However, in all techniques used for trace analysis of rare earths there usually exists some tedious operation such as chemical separation, or in the case of direct neutron activation analysis, long "cooling" times.

It is concluded that the analytical procedure developed for the analysis of thorium, yttrium and rare earths compares favourably with other techniques on the basis of time involved and precision obtained.

PART II

GEOCHEMICAL INVESTIGATIONS IN THE HAWKS CRAG BRECCIA

INTRODUCTION

The search for uranium in New Zealand during and following World War Two was extensive but did not at first yield any discoveries. In 1954 GRANGE issued a guide to prospectors in an effort to create interest in the search for uranium. As a result of this, two prospectors, Jacobsen and Cassin, discovered radioactive material in the Middle-Cretaceous Hawks Crag Breccia of the Buller Gorge late in 1955. Since this date, there has been a surge of interest in uranium prospecting in New Zealand, partly due to a greater world demand for this element and partly because of the urgent necessity to find domestic supplies for a nuclear reactor which is proposed for New Zealand in the late 1970's.

The radioactive area is situated in the Lower Buller Gorge region of the South Island of New Zealand and is some fifteen miles east of the township of Westport. This region has been investigated by various workers who have studied extensively the geological, petrological and mineralogical features of the area (BECK ET AL, 1958; WHITTLE, 1960) and recently this whole region has been surveyed by airborne gamma-scintillometry. Except for a study on the suitability of stream water analysis (WODZICKI, 1959a), little or no geochemical work has been carried out.

Many methods have been used in various parts of the world for uranium prospecting with varying degrees of success. The uranium content of residual soil has been used as an ore guide under many different climatic conditions with some success (JONES ET AL, 1956; GANLOFF ET AL, 1958; ILLESLEY ET AL, 1958). Analysis of plants for uranium in the Colorado Plateau, has been one of the most successful of the biogeochemical methods (CANNON and

KLEINHAMPL, 1956; CANNON, 1960a) and has the advantage that this method can give an indication of buried ore through thicknesses of as much as fifty feet of barren overburden. However, a disadvantage of this method is that a specialized knowledge of the uptake behaviour of various plant species is required and an orientation survey must always be carried out before routine sampling can be undertaken. Measurement of the uranium content of stream water has also been shown to be an effective method of reconnaisance exploration (JUDSON and OSMOND, 1955; DENSON ET AL, 1956; FIX, 1956) provided that the deposits are reasonably large compared with the total drainage area. The advantages of sampling soils, stream sediments, plants and stream waters for uranium are that unexposed ore deposits can be more easily located and large areas can be covered at a relatively low cost. However, one major difficulty is that uranium (VI) is extremely soluble, and often in areas of high rainfall, the uranium concentration can be very low. A critical review of scintillometric, geochemical and biogeochemical methods for prospecting for uranium has been given by WHITEHEAD and BROOKS (1969a). The same authors have also carried out biogeochemical prospecting in the New Zealand radioactive areas (1969b).

In potentially uraniferous areas of New Zealand, the rugged topography and dense bush cover would suggest that the analysis of stream sediments and stream waters should be a useful method for the detection of uranium mineralization since streams are often the only means of access to such areas. Unfortunately due to the high rainfall (200 inches per annum), analysis of stream waters draining the known uranium mineralization in the Lower Buller Gorge showed that this approach was unsatisfactory as the concentration of uranium found depended critically on the rainfall and the relative size of the mineralized area in relation to the total drainage area (WODZICKI, 1959a). This prevented direct correlation of results from creeks sampled under different weather conditions as the uranium values would often vary by a factor of three in samples taken before and after several hours of rain. As a result of this high rainfall and the high mobility of the uranium (vi), it was suspected that the direct analysis of stream sediments might also be unsuitable as a prospecting guide for uranium. In such cases, and particularly where stream sediments are the only accessible material available for prospecting purposes, the role of pathfinders for uranium is particularly important. Except for the discovery of radioactive boulders in streams (WODZICKI, 1959b) stream sediment analysis as a method of prospecting has not been used before in this area.

Although the use of general pathfinders in geochemical prospecting has received consideration in the past (WARREN and DELAVAULT, 1959; HAWKES and WEBB, 1962), very little attention has been paid to uranium pathfinders beyond the use of selenium in the uraniferous areas of the Colorado Plateau (CANNON, 1960b). This neglect of pathfinders for uranium probably arises partly from an undue reliance on radiometric data which do not always reliably indicate the presence of uranium (WHITEHEAD and BROOKS, 1969a) and partly from the fact that elemental associations with uranium, vary from area to area and are not consistent.

The main aims of the work reported in this section were:

(1) To investigate the suitability of using the uranium content of stream sediments for direct prospecting for uranium in the Lower Buller Gorge of New Zealand.

(2) To establish any elemental associations which exist in uranium minerals of this area and to study the changes of these associations in the weathering sequence: minerals-soils-stream sediments, to ascertain their suitability as pathfinders for uranium.

Preliminary investigations of the uranium minerals for all elements, using emission spectrography and atomic absorption spectrophotometry, gave evidence that the elements, copper, lead, zinc and beryllium held some association with uranium. Thorium, yttrium and the rare earths could not be analysed directly due to their low concentration and poor detection limit with the instruments used. The analysis of these elements was important because of their likely geochemical association with uranium (GOLDSCHMIDT, 1958) and their frequent occurrence in economic deposits of uranium such as in the Mary Kathleen Mine in Queensland, Australia. These elements were, however, successfully analysed with the methods described in Part I of this thesis.

There was clearly a need for a more detailed geochemical survey of this area and the work reported in this section was carried out with this in view.

THE GEOLOGICAL AND PHYSICAL FEATURES OF THE URANIFEROUS AREA

(a) Physical Features

The area under investigation is situated in the Lower Buller Gorge region of the South Island of New Zealand and is some fifteen miles east of the township of Westport (Fig. II-1). The most striking feature of the climate in this area is the heavy rainfall. This varies from about 80 inches per annum near the coast to 200 inches per annum fifteen miles inland, with periods of up to one month when little or no rain falls. The climate is temperate, average winter and summer temperatures not varying by more than 15°F.

Below 3,500 feet, the area is covered with dense beech forest typical of this part of New Zealand (Fig. II-2). The streams are short and their profiles are steep. The relief varies between 2,000 ft and 4,000 ft making the country rugged and difficult to traverse. Aerial photographs are shown in Fig. II-3a and Fig. II-3b. Access is restricted mainly to the numerous streams which drain the area. The steepness of the topography precludes the accumulation of products of weathering except at the foot of bluffs and in river valleys. Excluding the Ohika beds, which are well jointed, the rocks are massive and weathering extends only a short distance below the surface. The soils in the more stable parts of the terrain have been classified as moderately-weathered, podzolised, yellow-brown earths. Skeletal soils are found on the steeper slopes. The pH ranges between 4.5 and 6.5 in all horizons of the soils.

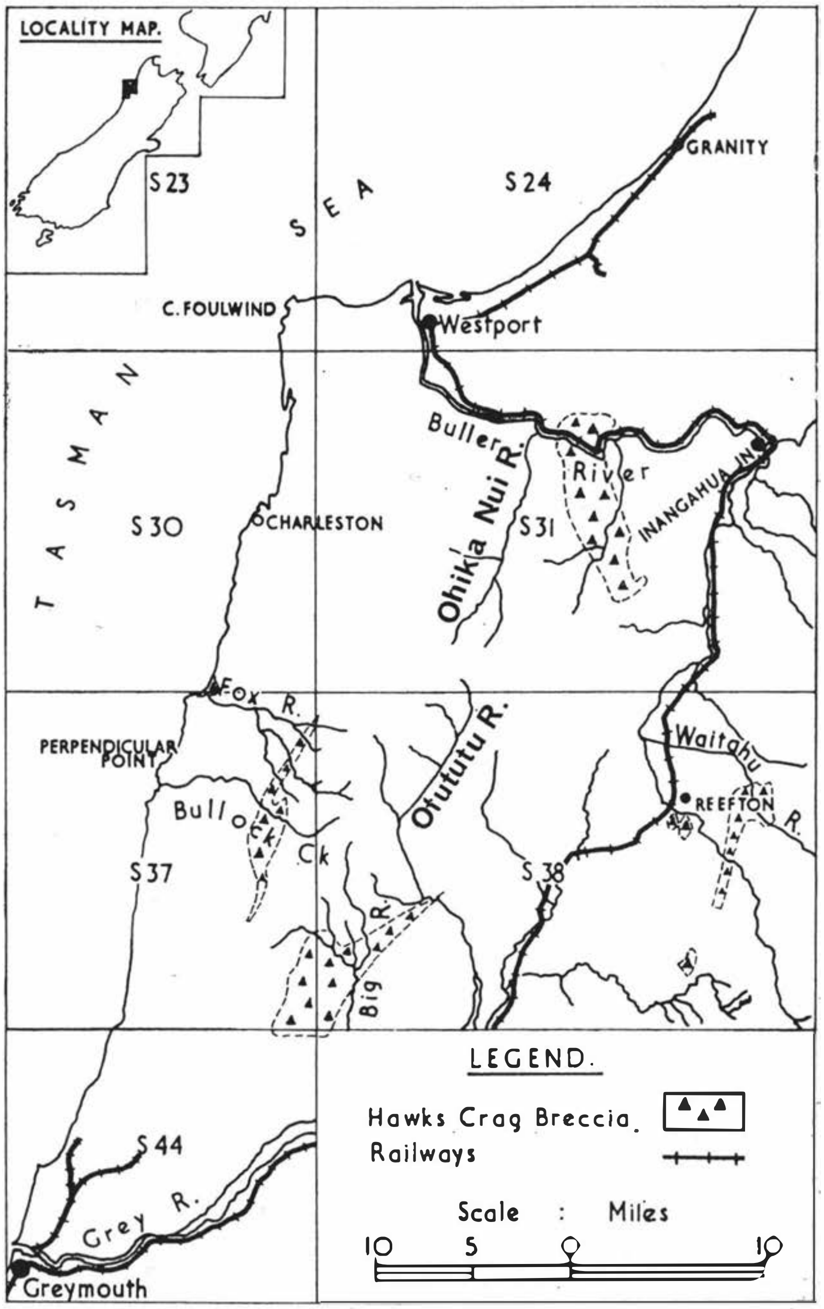


Fig. II - 1 Map Showing Distribution of Hawks Crag Breccia on West Coast of South Island of New Zealand.

Fig. II-2   Photo showing dense beech forest in H.C.B. area.

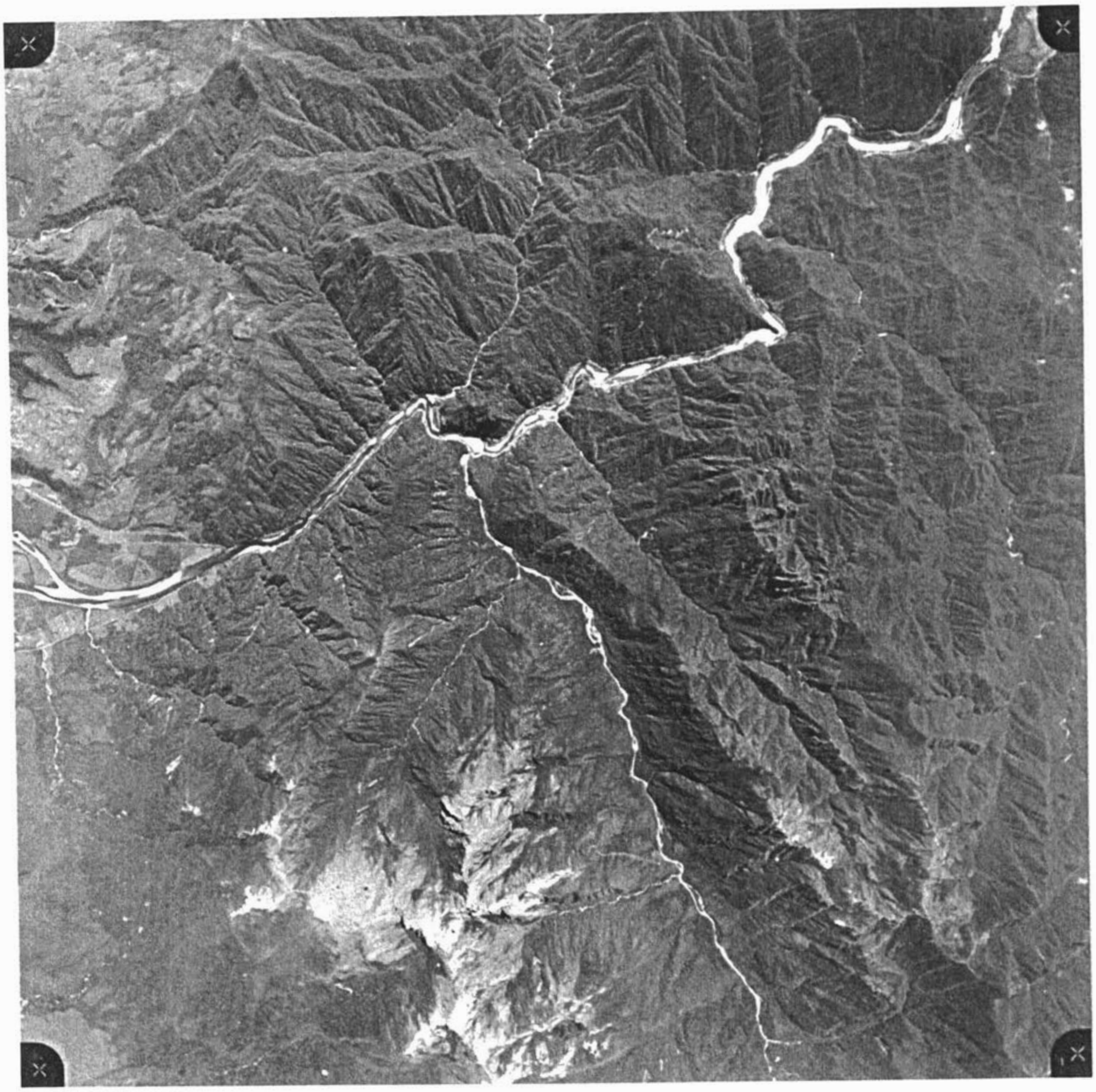


Fig. II-3a Aerial photograph of Lower Buller Gorge including H.C.B. area.

Fig. II-3b Aerial photograph of H.C.B. area from Fig. II-3a.

(b) General Geology

The geology of the Lower Buller Gorge has been described by MORGAN and BARTRUM (1915), WELLMAN (1950) and BECK ET AL (1958) and is shown in Fig. II-4. Table II-1 gives the stratigraphic sequence of rocks in this area. A brief outline of the geology is given below for completeness.

The basement rocks include Paparoa granite-gneiss which varies in composition from granitic to granodioritic, Greenland Series sediment, and quartz-phorphyry instrusives. Gneissic banding is common and in some localities the gneiss is porphyritic.

Greenland Series consist of well-indurated phyllitic greywackes of Paleozoic age and Ohika beds, of Upper Jurassic age, which rest uncomformably on the basement rocks and consist of non-marine shales, tuffs, sandstones and conglomerates.

The Hawks Crag Breccia (Middle to Upper Cretaceous) rests unconformably on the Ohika beds and has been divided into three facies depending on the relative amounts of parent material present. These are: (1) The Tiroroa facies consisting of rounded to sub-rounded granite pebbles and boulders which are set in a coarse, angular, arkosic matrix.

(2) Dee Point facies consisting of angular to sub-angular greywacke fragments set in a silty matrix.

(3) Blackwater facies consisting of granite and greywacke pebbles and boulders set in a silty matrix.

(c) The Petrology and Mineralogy of the Uranium Deposits

A more detailed description of the petrology and mineralogy of the deposits is given than was for the geological and physical

TABLE II - 1

Stratigraphic Sequence in Lower Buller Gorge

	Lithology	Age
Tertiary	Non-marine at base	Eocene-Pliocene
	UNCONFORMITY	
Porphyry	Soda trachyte	Upper Cretaceous(?)
Lamprophyre	Camptonite, vogesite monchiquite	Upper Cretaceous(?)
Hawks Crag Breccia	Conglomerate, breccia, sandstone, siltstone	Middle Cretaceous
	UNCONFORMITY	
Ohika	Shales, conglomerates, vitric tuffs	Jurassic
	UNCONFORMITY	
Quartz porphyry	Quartz porphyry, granite porphyry	Jurassic(?)
Granite	Granite Gneiss, diorite gneiss, pegmatite, hornfels, schist	Lower Paleozoic and/ or Pre-Cambrian(?)
Greenland	Greywacke, phyllite, schist	Lower Paleozoic or Pre-Cambrian(?)

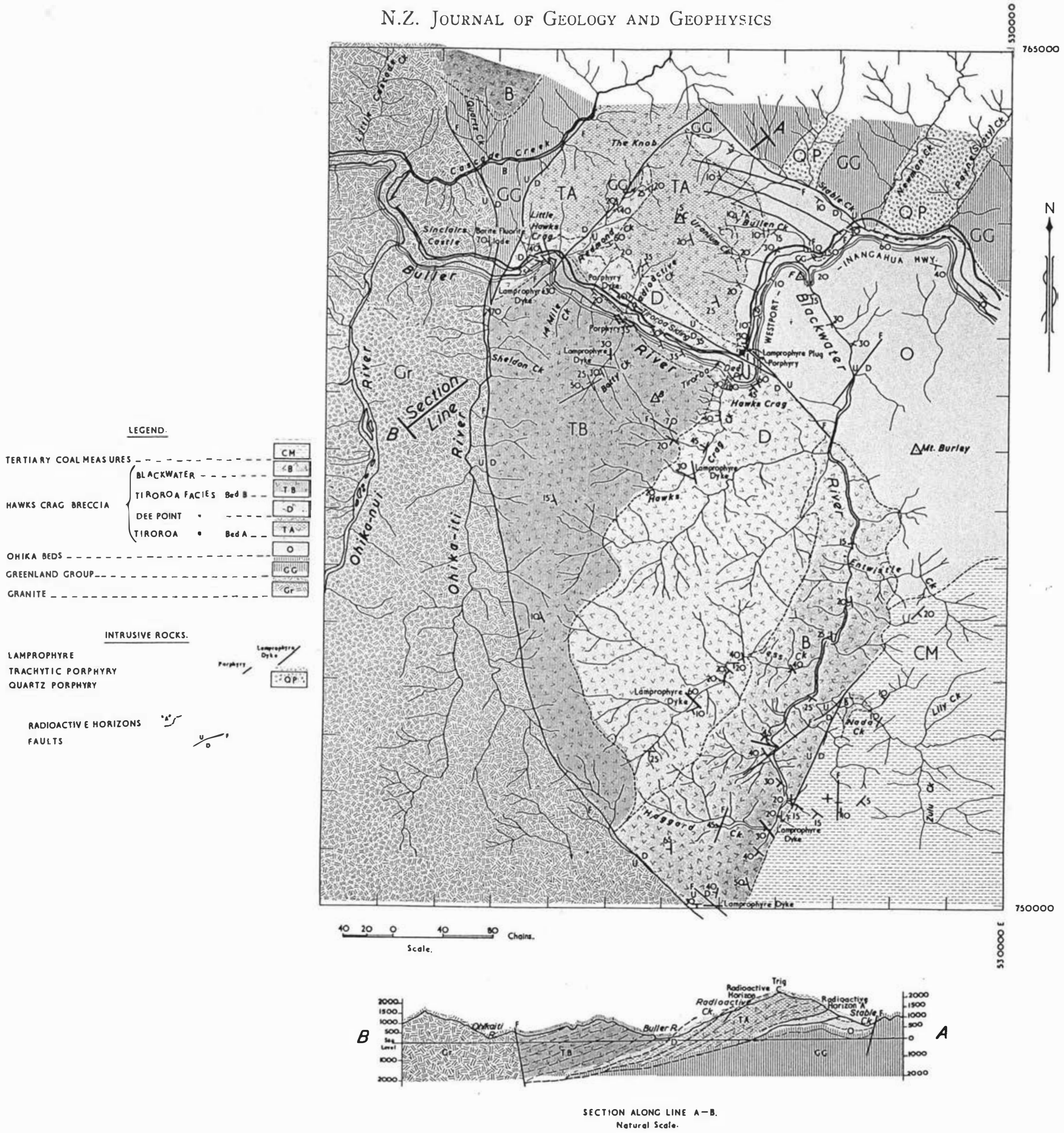


Fig. II-4 Detailed geological map of the H.C.B. area (From BECK ET AL, 1958).

features as the petrology and mineralogy is pertinent to both this Part and Part III of the Thesis.

The greater proportion of the uranium mineralization in the Buller Gorge occurs in the bedded deposits in the Tiroroa facies on both the North and South sides of the Buller River. Mineralization on the North side is primarily coffinite (hydroxyl-substituted uranous silicate) whereas mineralization on the South side is mainly uraninite.

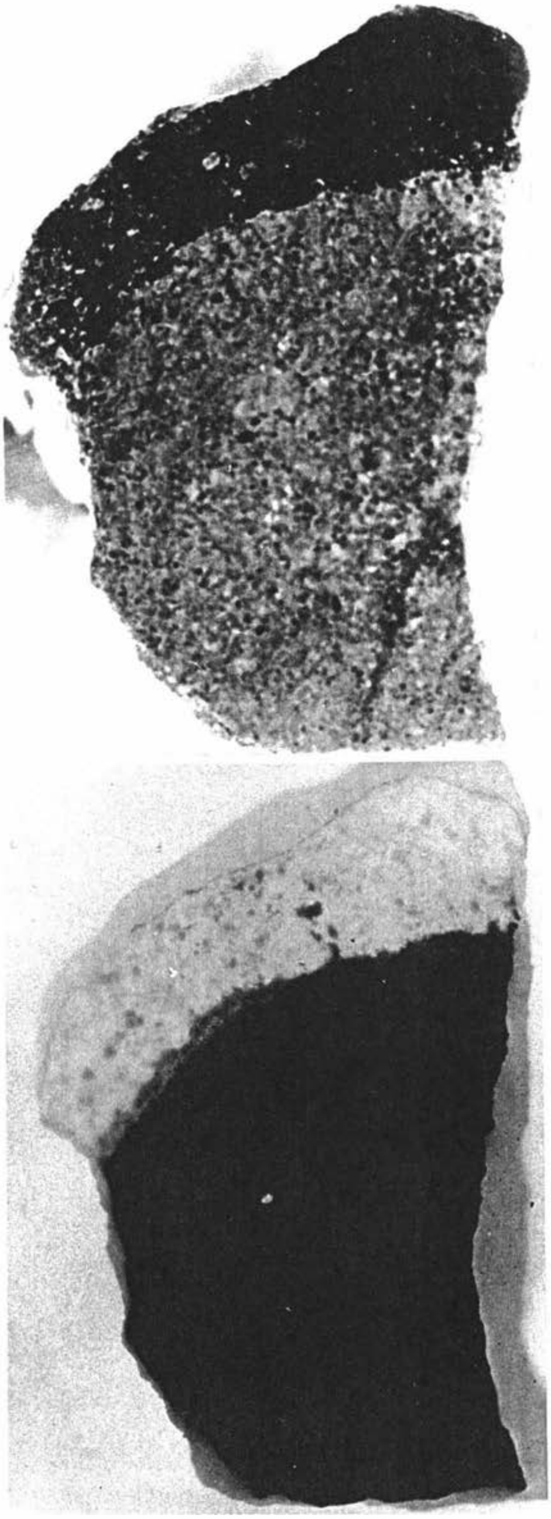
(i) The North Side Deposits: The mineralization on the North side is found in horizons which occur within the arkose and vary in width from a few inches to several feet. The horizons, although disposed parallel to bedding are lensoid and discontinuous, with uranium concentrations varying from less than 0.025% to 6.4% U_3O_8 (BECK ET AL, 1958). The country rock is a medium-grained arkose which consists of angular quartz, potash feldspar, acid plagioclase, calcite, sericite, biotite, chlorite and tourmaline. The interstial material or matrix, which binds the ditrital grains together is predominantly fine-grained calcite with sub-ordinate chlorite and sericite. These minerals form a country rock which is light grey in colour and granular in appearance. The radioactive horizons are distinguished by a dark grey colour which deepens with increasing radioactivity and the white or pink feldspars, which are characteristic of the country rock, change to a red colour within the radioactive bands. No other lithological or structural feature distinguishes the ore-bearing rock from inactive country rock. The contact between ore and country rock may be quite sharp and distinguished by sudden colour change, or it may be gradational and characterised by darkening of the arkose over a transitional zone of an inch or so thickness.

The change from country rock arkose to ore through the gradational zone has been studied by WHITTLE (1960) who then observed that the darkening of the arkose and the formation of ore is due to the progressive emplacement of black opaque coffinite in the interstices between detrital grains, along their borders and in cracks which intersect them. Coffinite in the interstial areas, i.e. within the matrix, replaces the calcite and penetrates the micas along their cleavages. The introduced coffinite forms thin discontinuous sheets, wrapping round the grain boundaries and locally thickening or thining. Large-scale or complete replacement of the matrix is rare. The darker colour of the more active bands is simply due to a greater multiplicity of **thin** coffinite replacement masses.

(ii) The South Bank Deposits: Uranium mineralization on the South Side of the Buller Gorge is concentrated in two horizons named T-J and S-C respectively. The T-J horizon is situated across Centre Creek about 1100 ft above the road and the S-C horizon stretches between Centre Creek and Big Tick Creek about 800 ft above the road (Fig. II-10).

T-J Horizon: A cleared quarry face in the T-J horizon disclosed three radioactive horizons some 4'6" apart. About 1958 an adit was driven into non-folded conglomerate and arkose which dips at a flat angle into the hillside. The ore band which the adit follows varies in thickness from 1" - 3" and follows an interface between pebbly arkose above and granite boulder conflomerate below. The ore bed has not a flat contact but is crenulated as it passes over and round large granite boulders which project upwards into the pebbly arkose. The ore horizon is not located on a shear plane but merely on an interface between slightly differing sedimentary facies. This is indicated by the absence of rotated boulders or of boulders which are stressed or shattered in areas where they project above the average plane of the interface. The arkose adjacent to the ore band is an irregularly-grained rock composed of angular quartz, feldspars and **muscovites**, some of which is quite coarse-grained. These occur in a matrix of finer quartz, feldspar and micas with sericite and clay. Calcareous material is absent, a factor which provides an immediate distinction from the arkose of the North side. The contact with the ore band is very sharp and is due to the sudden appearance of uraninite in the matrix in such great quantities as to change the rock colour quite black. The uranium content of the ore band in such instances can be as high as 35% U_3O_8 over a width of an inch or more. Fig. II-5 shows an autoradiograph and clearly illustrates this. Uraninite replaces only the clays and sericitic material while the finer detrital quartz and feldspar of the matrix are preserved as inclusions in the uraninite. There is an abundance of chalcopyrite in the areas where uraninite is emplaced and in the siliceous detrital material but to a lesser extent. Both uraninite and chalcopyrite were observed to have penetrated mica cleavages (WHITTLE, 1960).

S-C Horizon: This horizon is intersected in Big Tick and in Centre Creek and the following describes samples taken from these intersections (WHITTLE, 1960).



Photograph

Autoradiograph

Fig. II-5 Photograph and autoradiograph of arkose containing uraninite.

The material from Big Tick Creek is a pebbly arkose comparable with that in the vicinity of the adit and it contains granitic, schistose and phyllitic pebbles but no carbonate minerals are present. The rock is very extensively altered and is impregnated with limonite which exists with arsenopyrite remnants mainly in the matrix. Radioactivity is due to secondary minerals occurring with limonite in the matrix and along the surfaces and cracks within boulders. Skeletal residuals of highly altered primary mineral within the matrix probably supplied this secondary material.

The material from Centre Creek is pebbly arkose similar to that at the adit. It contains granitic, schistose and phyllitic fragments in a strongly micaceous arkosic host rock. Samples were selected from the east and west sides of the creek for comparison. The rock on the West side is a dominantly granite conglomerate with large, thin pebbles of phyllite or schist. The matrix contains calcite which is unevenly distributed, being absent in some areas and heavily concentrated in others. Radioactivity is spread throughout the specimen due to dispersed secondary minerals, but is concentrated principally in the dark-coloured areas where uraninite and its included suphides impregnate the matrix. Calcite and chlorite are present in both the weakly and strongly radioactive areas.

The material from the S-C horizon on the east side of Centre Creek is by contrast, a dark grey, almost black, irregularly-grained, micaceous arkose which contains abundant chlorite and sericite but no carbonate in its matrix. The dark colour of this arkose is due to disseminated organic matter, abundant chlorite and general staining by iron oxide. Some of the organic matter is homogeneous and anistropic and appears to be extrinsic hydrocarbon. It has a textural relationship to the host arkose which suggests it is epigenetic in origin. The major radioactivity is concentrated along the edges of the long vein-like hydrocarbon bodies although they themselves are not radioactive. This radioactivity is due to relicts of uraninite which occurs in the arkose matrix in juxtaposition to the carbonaceous masses. Most of the uraninite has vanished due to leaching, but areas in which relicts remain are clearly marked by hosts of minute sulphide minerals. The texture of this rock indicates that it has been subjected to mild shearing and the vein-like hydrocarbons are dispersed parallel to the direction of strain.

The geochemical survey reported in this part of the thesis was confined to the Tiroroa facies on the South Side of the Buller River. This side was chosen because only a minimum of prospecting had been done in this area. This lack of exploration was due to two reasons. Firstly, the deposits on the North Side were found first and hence attracted most of the attention. Secondly, the later discovery of the South Side deposits, which are somewhat more extensive than those of the North Side, coincided with the fall in the world price for uranium. The combination of these two factors made the mining of this uranium uneconomic and as a result the interest in uranium prospecting fell considerably at this time. As has been mentioned previously, this trend has been completely reversed in recent years with the advent of an era of intensive activity in the search for uranium.

METHODS

(a) Sampling Procedures

Minerals were ground, dried at 110°C and were sieved to 100-mesh size before further treatment. Samples were taken from the radioactive horizons T-J and S-C on the South Side (uraninite, torbernite, Autunite, gummite) and from the radioactive horizons on the North Side (coffinite).

Soil samples were taken from various points on the drainage slopes of the South Bank horizons and were air dried, passed through a 40-mesh nylon sieve and then ignited at 450°C to remove the organic matter. Further grinding to 100-mesh followed.

Stream sediments were collected from various streams draining and adjoining the uraniferous areas on the South Bank in the following manner. Samples were taken from stream deposits and were wet-sieved through a 40-mesh, nylon cloth stretched over the mouth of a plastic funnel. The fraction passing the sieve was collected in a plastic bag and the fines were allowed to settle for approximately two to three minutes before the water was decanted off. The position of the sampling point and the bag marking was noted. The sediments were dried at 110°C and separated into three fractions by the use of nylon sieves. The fractions were: less than 80 mesh, between 60 and 80 mesh, and between 40 and 60 mesh. Preliminary analysis of these fractions showed that the "less than 80 mesh" contained the highest concentration of nearly all elements investigated(Table II-2).

TABLE II - 2

Analysis of Stream Sediments as a Function of Mesh Size

Sample	Mesh Size	La	Ce	Pr	Nd	Gd	Dy	Yb	Y	Th	U
B1	Less than 80	54	134	15	34	13	4.8	4.1	12.5	11	13.6
	Between 60 and 80	36	67	10	14	8.5	2.7	2.3	14	11	10.0
	Between 40 and 60	42	95	13	16	8.5	3.8	2.4	21	14	9.8
BC4	Less than 80	26	50	11	9	7	2.3	1.0	4.8	3.1	4.8
	Between 60 and 80	20	44	12	11	4.6	1.7	1.1	5.6	6.0	4.8
	Between 40 and 60	2.8	40	2	12	3.2	0.4	0.5	1	1	3.8

(b) Analytical Techniques

Emission spectrography was used to analyse beryllium, thorium, uranium, yttrium and rare earths as described in Part I.

Solution fluorimetry and pellet fluorimetry were used to analyse uranium, the particular method used depending on the uranium concentration.

A Techtron AA3 atomic absorption spectrophotometer was used to analyse copper, zinc and lead. The sample was treated with a mixture of hydrofluoric and hydrochloric acids and taken to dryness. The residue was redissolved in 2 M hydrochloric acid, filtered and stored in plastic bottles until the time of analysis.

(c) Statistical Analysis of Data

To be able to make careful interpretation of the inter-element analytical results, correlation calculations were carried out on a IBM 1620(II) computer.

Correlations between two variables are usually carried out by the method of linear regression, but MIDDLETON (1963) notes that this is applied to determine whether one variable is dependent on the other when the latter is not subject to error. However, in this work, as in most geochemical work, neither variable can be said to be absolutely known. Therefore, it is better to calculate the reduced major axis, rather than the regression lines. The advantages of the reduced major axis are that:

1. it makes no assumptions of independence;
2. it is invarient under change of scale;
3. it is simple to compute;

4. results obtained from its use are intuitively more reasonable than corresponding results obtained from regression analysis. (IMBRIE, 1956).

For all these correlations, the logarithms of concentrations were compared, since the concentrations often spanned several orders of magnitude and appeared to be log-normally distributed (AHRENS, 1954). Thus the position of the reduced major axis on a log-log basis, was calculated for each pair of analytical data, and the significance of the correlation determined by calculation of the correlation coefficient (r) and reference to the tables of FISCHER and YATES (1957).

Cumulative frequency studies of some of the data were also carried out. A plot of the cumulative frequency of the concentrations of the samples, as a percentage of the total number of samples, plotted on probability paper against the concentration value, has been shown to be useful for geochemical and biogeochemical data interpretation (TENNANT and WHITE, 1959; WILLIAMS, 1967c). In particular, log-normal distributions will show a straight line when plotted on log-probability paper, and similarly with normally-distributed data on linear-probability paper. In other cases, curves will ensue. However, if there is more than one distribution set within the data, such as could occur in mineralized and unmineralized soil samples, a distinct change of slope or a point of inflexion in the graph will be observed. This break can be considered to occur at the minimum concentration of mineralized samples, although some overlap of distributions will occur (WILLIAMS, 1967c). It must be remembered that the significance of interpretation from this analysis is somewhat limited unless the set contains about 80 to 100 samples. However, generalised conclusions can be obtained on sets less than 80.

ELEMENTAL ASSOCIATIONS WITH URANIUM IN MINERALS, SOILS AND SEDIMENTS

This section reports on the various elemental associations with uranium and discusses their suitability as pathfinders. This is essentially the same as was reported by COHEN ET AL (1969).

(a) Copper and Uranium

Analysis of copper and uranium in minerals, soils and stream sediments, combined with a statistical interpretation of the data, showed a meaningful correlation between this pair of elements for the whole of the weathering sequence minerals - soils - stream sediments. Correlation coefficients are shown in Table II-3 and plots of the data are shown in Fig. II-6.

Correlation coefficients decrease regularly in the sequence minerals - soils - stream sediments and indicate that association between this pair of elements originates in the minerals and is preserved throughout the weathering sequence. WHITTLE (1960) has observed that chalcopyrite is associated with uranium in the South Bank deposits of the Lower Buller Gorge and this is probably the source of the copper detected. Further mobilisation and transport of both elements is facilitated by the porous nature of the arkosic matrix which allows oxidation and movement to take place.

The preservation of the initial copper-uranium relationship throughout the whole weathering sequence is a fortunate occurrence which renders copper a useful pathfinder in minerals, soils and sediments.

Cumulative frequency plots for copper in soils and

TABLE II - 3

Statistical Data for Various Elements in Minerals, Soils and Stream Sediments

First Correlating Variable	Second Correlating Variable	Minerals		Soils		Sediments	
		r	Sig.	r	Sig.	r	Sig.
Log concn. of U	Log concn. of Be	0.88	S**	0.68	S**	0.07	NS
Log concn. of U	Log concn. of Cu	0.79	S**	0.66	S**	0.42	PS
Log concn. of U	Log concn. of Pb	0.95	S**	0.80	S**	-0.25	NS
Log concn. of U	Log concn. of Zn	0.02	NS	0.34	PS	0.12	NS
Log concn. of Cu	Log concn. of Pb	0.78	S**	0.74	S**	-0.14	NS
Log concn. of Cu	Log concn. of Zn	0.04	NS	0.32	PS	0.20	NS

r = correlation coefficient
Sig. = level of significance

N.B. Levels of significance (BROOKS ET AL, 1966) shown above are as follows:

S** = significant at 0.1% level of probability (very highly significant)
S* = significant at 0.1 - 1% level of probability (highly significant)
S = significant at 1-5% level of probability (significant)
PS = significant at 5-10% level of probability (possibly significant)
NS = not significant

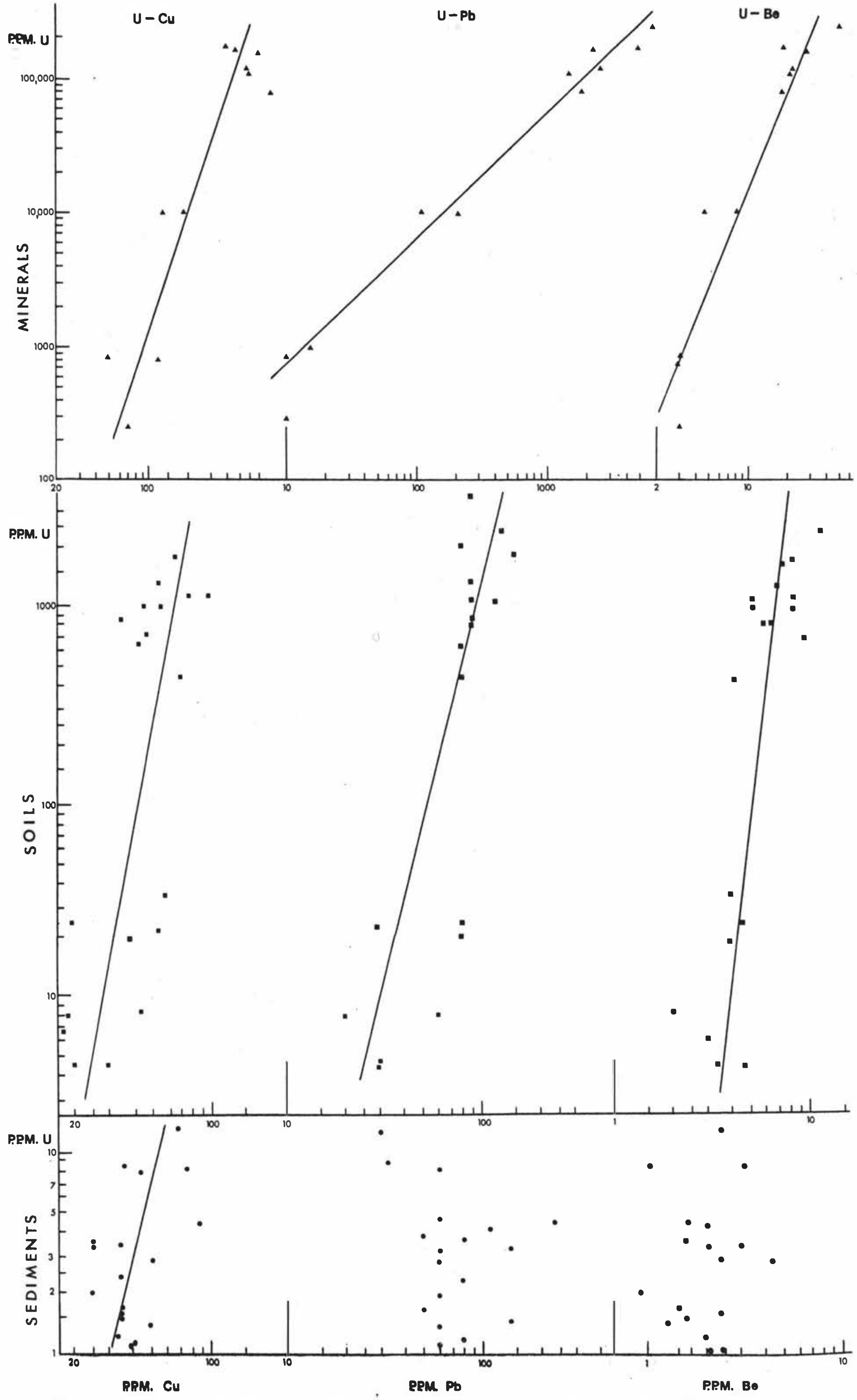


Fig. II - 6 Elemental Relationships in Minerals, Soils and Stream Sediments.

sediments (Fig. II-7) show that anomalous amounts correspond to greater than 60 ppm in soils and greater than 40 ppm in sediments. Such values may represent indirectly the presence of uranium mineralization.

(b) Beryllium and Uranium

Statistical analysis of beryllium and uranium data showed a meaningful correlation between this pair of elements in the minerals, and soils but not in the stream sediments. Correlation coefficients are given in Table II-3 and plots of the data are shown in Fig. II-6. Cumulative frequency plots for the soils are shown in Fig. II-7, from which it is seen that beryllium values above 4 ppm (normal background distribution for granitic rocks) indicate abnormal values and would suggest the presence of uranium.

(c) Lead and Uranium

The association of lead with uranium in the minerals is extremely close (Table II-3 and Fig. II-6). The correlation is so good (r = 0.95) that the author believes that most of the lead is radiogenic in nature.

In the soils, two distinct distributions are evident (Fig. II-7) and a value of 70 ppm appears to indicate the threshold value for anomalous lead. The correlation between uranium and this element in soils is still good (r = 0.80) but not as good as in the minerals whereas in the stream sediments no correlation between these elements exists at all.

(d) Zinc and Uranium

No significant correlation was observed for this pair of

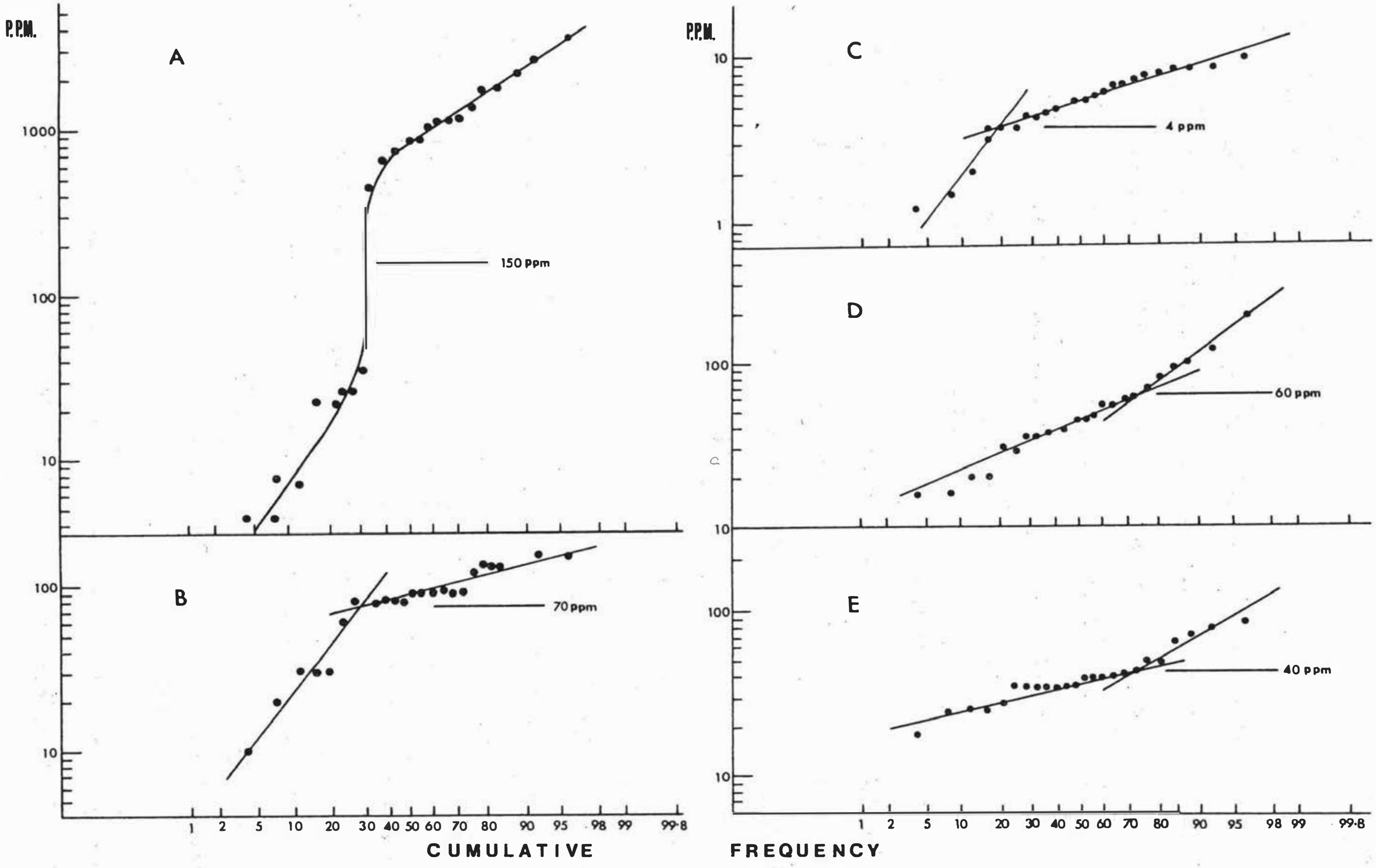


Fig. II - 7 Cumulative Frequency Plots for Various Elements in Soils and Stream Sediments.

A - Uranium in soils
B - Lead in soils
C - Beryllium in soils
D - Copper in soils
E - Copper in sediments

elements in minerals or sediments (Table II-3) but there was a possibly-significant relationship in soils (r = 0.34). A zinc-uranium relationship in soils has also been observed by WHITEHEAD and BROOKS (1969b). However, the author considers zinc as an unsuitable pathfinder for uranium since the value of r is so low.

(e) Rare Earth Elements

The analysis of minerals for yttrium, thorium and the rare earth elements was carried out using the analytical procedure described in Part I of this thesis. The results are shown in Table II-4. This table shows that although the levels of these elements are slightly higher in the mineralized fraction compared with the unmineralized fraction, they are still extremely low. However, despite their low concentration, the normal Oddo-Harkins distribution exists,(Fig II-8), that is,the even-numbered rare earths have a higher concentration than the uneven numbers and thus show that no fractionation has occurred within the group. Statistical analysis of the data was not attempted as in most cases the concentration of the elements was almost at the detection limit.

Visual inspection of the results show that there are no meaningful correlations between any of the elements and uranium and thus yttrium, thorium and the rare earths are unsuitable as pathfinders.

However, the low values obtained are significant in themselves as they suggest that either the original uranium was not associated with rare earths or that the uranium has been mobilised and because of the greater solubility of uranium (VI) compared

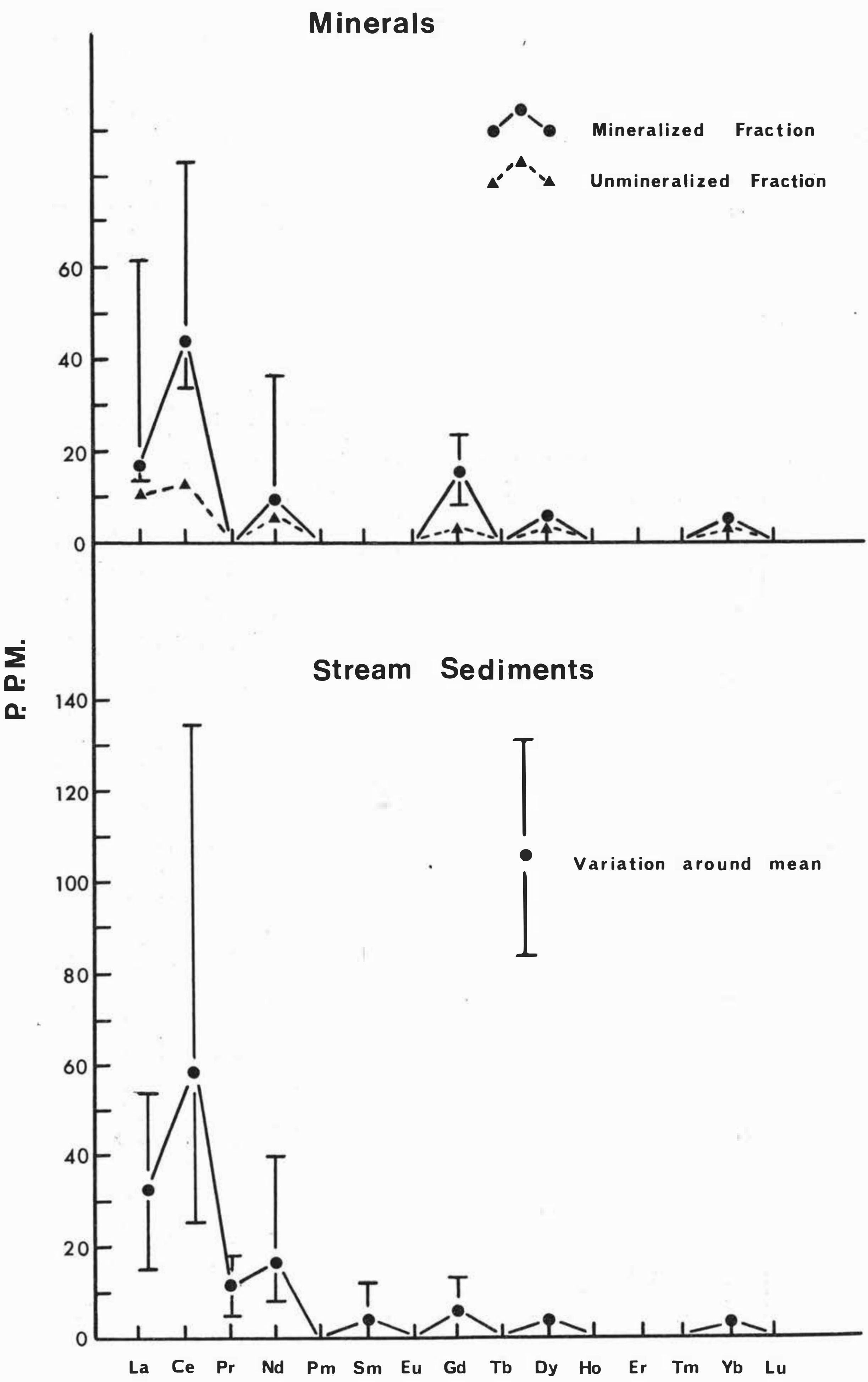


Fig. II - 8 Rare Earth Distribution in Uranium Minerals and in Stream Sediments Draining Hawks Crag Breccia Areas.

TABLE II - 4

Rare Earth Concentrations in Minerals, Matrix and Stream Sediments (ppm)

Sample	La	Ce	Pr	Nd	Sm	Gd	Dy	Yb	Y	Th	U
MINERALS											
Uraninite 1	10	18	n.f.	n.f.	n.f.	7	1.5	1.4	8.5	4	162,000
Matrix 1	6	8	n.f.	n.f.	n.f.	2	0.9	0.5	1.0	n.f.	10,000
Uraninite 2	7	19	n.f.	n.f.	n.f.	8.5	0.6	3.0	14.0	n.f.	120,000
Matrix 2	7	8	n.f.	n.f.	n.f.	6.5	1.1	0.8	3.4	n.f.	10,000
Uraninite 3	n.f.	n.f.	n.f.	n.f.	n.f.	9.5	4.4	4.4	9.5	n.f.	110,000
Matrix 3	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	0.9	0.9	1.9	n.f.	248
Matrix 4	19	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	0.8	n.f.	n.f.	843
Torbenitic Matrix 5	31	42	n.f.	30	n.f.	6.5	n.f.	1.8	4.8	n.f.	750
Autunitic Matrix 6	4	n.f.	n.f.	n.f.	n.f.	5.9	1.7	1.7	6.5	n.f.	8
Gummite	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	n.f.	250,000
STREAM SEDIMENTS											
01	28	50	14	17	n.f.	n.f.	1.6	1.0	2.5	4.6	3.4
02	47	95	18	40	n.f.	n.f.	4.8	1.6	12	18	8.6
03	28	54	12	11	10	3.7	2.2	0.6	3.4	5.6	2.4
04	16	26	5	10	n.f.	n.f.	0.6	0.1	1.9	3.4	2.0
05	30	40	13	16	8	3.6	2.7	1.0	6.0	7.0	1.2
07	15	25	10	14	n.f.	n.f.	0.7	0.5	1.5	4.0	4.5
08	30	38	11.0	16.0	9.0	4.0	2.4	0.9	6.0	6.0	3.4
B13	23	46	12	11	n.f.	5.0	2.5	2.0	8.0	5.4	8.6
B14	20	30	10	7	n.f.	3.6	0.8	1.2	2.6	6.4	0.8
B15	26	45	9	11	n.f.	5.6	1.3	0.7	5	6.4	2.9
B16	54	134	15	34	n.f.	13	4.8	4.1	12.5	11.0	13.6
B17	27	57	12	19	4	7	2.0	0.9	6.5	4.8	1.4
B18	42	60	18	30	n.f.	8.5	2.4	1.3	16	9	1.7

TABLE II - 4 continued

Sample	La	Ce	Pr	Nd	Sm	Gd	Dy	Yb	Y	Th	U
STREAM SEDIMENTS cont.											
BR1	29	90	10	n.f.	n.f.	3.4	n.f.	1.5	4.8	17	8.8
BR2	46	70	14	30	10	11.5	2.5	0.8	9.0	16	0.8
BR3	45	61	10	36	12	10	3.6	1.5	13.0	11	0.4
BC1	25	46	10	13	n.f.	12	1.5	0.7	4	6.0	6.8
BC2	26	52	12	15	n.f.	7	1.8	0.7	4.4	5.6	4.0
BC3	30	60	14	22	n.f.	9	2.6	1.1	6.0	6.5	3.8
BC4	26	50	11	9	4	7	2.3	1.0	4.8	3.1	4.8
BC5	28	74	15	15	6	6	2.3	0.8	4.4	5.0	4.0

n.f.	not found.
O1	represents sample 1 from the Ohika-iti River as shown in Fig. II-9.
B13	represents sample 13 from Tiroroa Creek as shown in Fig. II-9.
BR	represents Big River area (Fig. II-1).
BC	represents Bullock Creek area (Fig. II-1).

Uraninite 1, 2 and 3 represent three different mineral samples and Matrix 1, 2 and 3 represent the associated matrix fraction (Fig. II-5).

with rare earths, fractionation has taken place. This latter reason is believed to be more likely as mineralogical studies by WHITTLE (1960) have also shown evidence for the epigenetic nature of uranium.

During the current investigation, TENNANT and SEWELL (1967) published the results of a survey of the rare earth contents in stream sediments of the adjacent Otututu River and Ohika-Nui River not including the Hawks Crag Breccia drainage area. These results showed that the Otututu area was rich in "cerium-earths" whereas the Ohika-Nui River area was rich in "yttrium-earths". The concentration range of the elements Lanthanum, Cerium, Neodymium, Yttrium and Thorium varied from several tens to several hundred ppm. This variation was generally unpredictable as element concentrations from samples taken within several hundred yards of each other could vary by an order of magnitude. Overall, however, the rare earth pattern for each area was quite distinctive.

The Hawks Crag Breccia is found on both sides of the Ohika-Nui River and Otututu River (Fig. II-1) and although it is generally believed that it has not travelled very far, due to the presence of angular parent rock, its origin is still far from clear. Petrological comparisons of the granites in the Breccia with those in neighbouring areas seems to suggest that the Breccia could possibly be derived from the Otututu granite (NATHAN, pers. comm.). It was hoped that analyses of stream sediments from the Hawks Crag Breccia would reflect characteristic rare earth patterns which when compared with those obtained by TENNANT and SEWELL might show whether the Breccia could have been derived from either the Ohika-Nui granite or the Otututu granite or possibly both. The results obtained are shown in Table II-4 and are discussed later.

ELEMENTAL RATIOS AS PATHFINDERS FOR URANIUM

From Fig. II-7 it appears that an anomalous uranium distribution may be detected by the presence of > 70 ppm lead, > 4 ppm beryllium and > 60 ppm copper in the soils and > 40 ppm copper in the stream sediments. Although the analysis of stream sediments for copper as a pathfinder for uranium appears to be a likely method, the possibility of single anomalous copper values due to other factors is still a danger to the reliability of the method. For this reason various ratios and combination of ratios of all the associated elements were investigated in an attempt to establish a more reliable criterion for the detection of anomalous areas. The use of ratios or combination of ratios tends to lessen the importance of any spurious, anomalous result.

Figure II-9 shows a triangular plot for uranium, lead and copper concentrations in which each constituent is expressed as a percentage of the sum of the three. The data are therefore not based on the absolute percentage of each element in the entire mineral, soil or stream-sediment sample.

A decrease in the uranium content indicates the progression of weathering through the sequence minerals-soils-stream sediments. It is seen that in the sediments, the uranium content decreases to very low values and the importance of the lead-copper relationship becomes much greater. Visual inspection of the data for the stream sediments in Fig. II-9, shows that there is a tendency for certain samples to be grouped together in the copper-rich corner of the graph.This implies higher copper/lead ratios, particularly for sediments 10, 13, 15, 16 and 17, the sampling positions of which are shown in Fig. II-10.

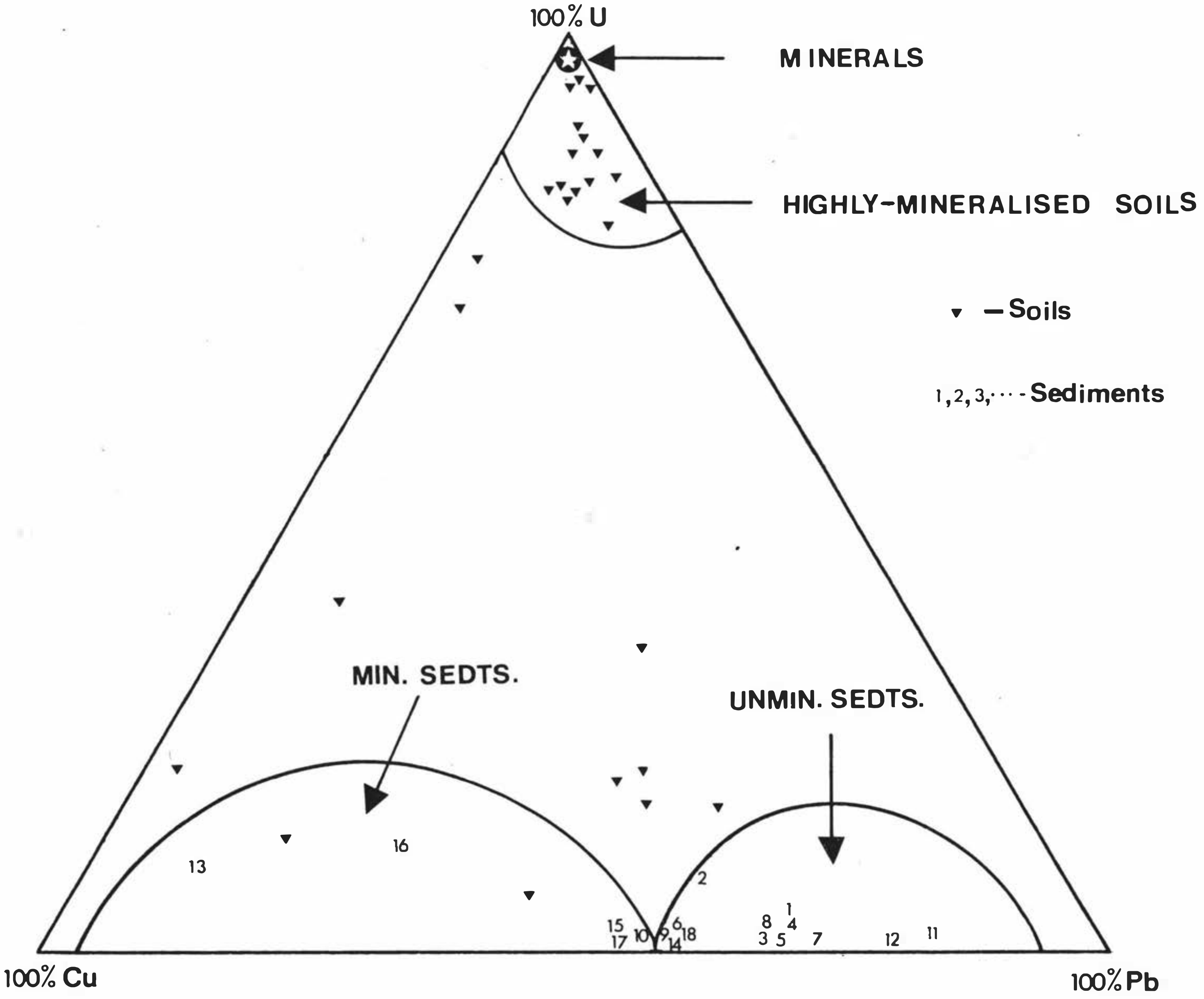


Fig. II - 9 Triangular Plot for Concentration Ratios of Copper, Lead and Uranium in Minerals, Soils and Stream Sediments.

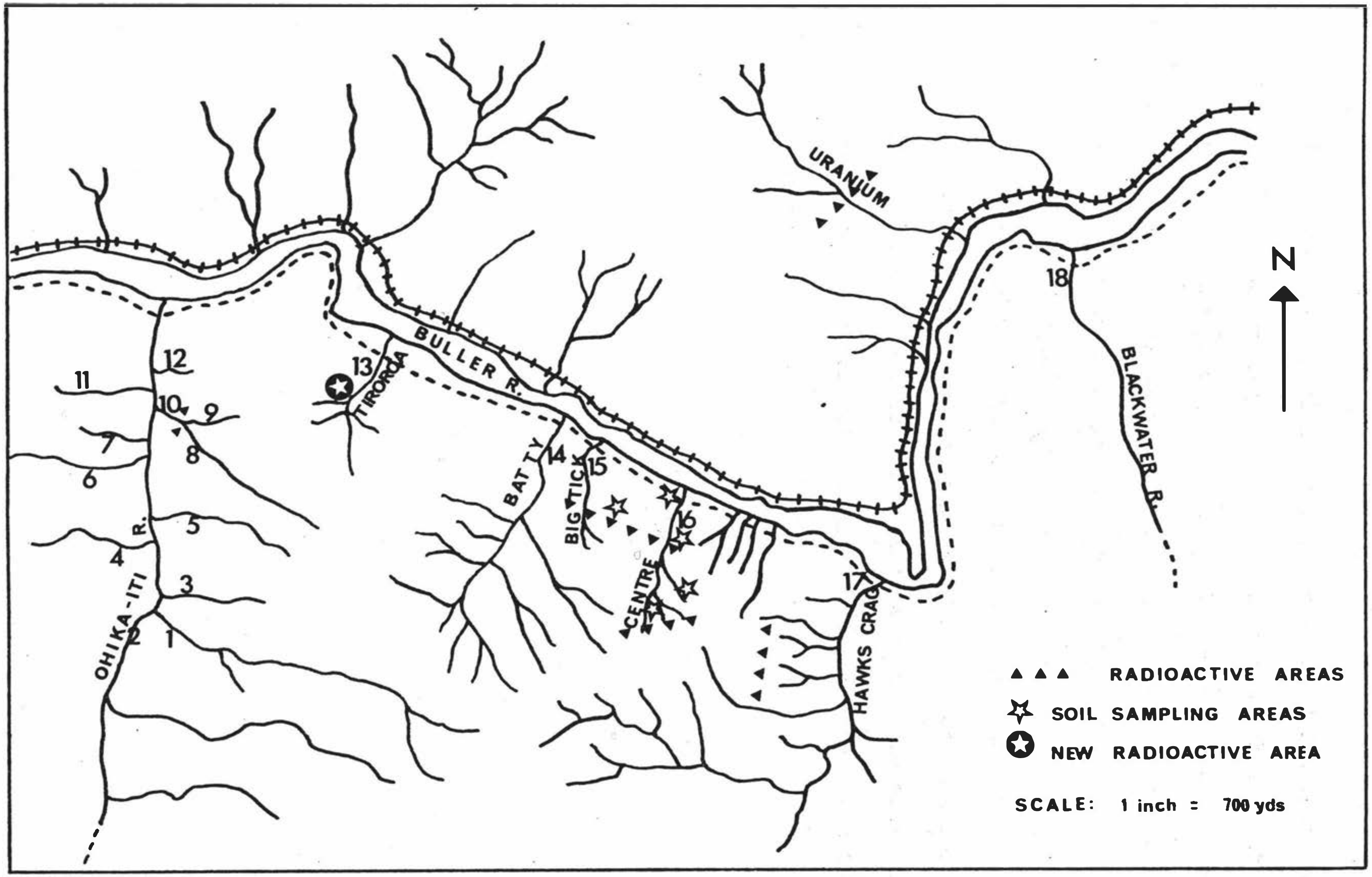


Fig. II - 10 Map of Buller Gorge Area of New Zealand showing Radioactive Horizons and Sampling Points for Soils, and Stream Sediments.

The copper/lead ratios are shown also in Table II-5 which includes the uranium content and indicates whether the stream from which the sample was taken (Fig. II-10) was known to drain a uranium anomaly. As far as was known at the time, Tiroroa Creek (sample 10) was not known to drain a radioactive area.

As it seemed that higher copper/lead ratios in stream sediments might indicate uranium anomalies in the drainage area of the stream, further sampling was carried out in Tiroroa Creek. These samples gave further evidence of uranium mineralization in this area with absolute uranium values ranging from 18-62 ppm and with associated high copper/lead ratios.

TABLE II - 5

Elemental Ratios as Pathfinders for Uranium in Stream Sediments

No.	Name of Stream	Cu/Pb ratio	U concn. (ppm)	Whether mineralization previously known
1	Trib.Ohika-iti R.	0.42	3.4	No
2	Main Stream - Ohika-iti R.	0.58	8.6	No
3	Trib.Ohika-iti R.	0.44	2.4	No
4	Trib.Ohika-iti R.	0.42	2.0	No
5	Trib.Ohika-iti R.	0.44	1.2	No
6	Trib.Ohika-iti R.	0.73	4.3	No
7	Trib.Ohika-iti R.	0.36	4.5	No
8	Trib.Ohika-iti R.	0.44	3.4	No
9	Trib.Ohika-iti R.	0.70	1.6	No
10	Trib.Ohika-iti R.	0.80*	0.8	Yes
11	Trib.Ohika-iti R.	0.18	3.4	No
12	Trib.Ohika-iti R.	0.25	1.5	No
13	Tiroroa Creek	7.69*	8.6	No**
14	Batty Creek	0.67	0.8	Doubtful
15	Big Tick Creek	0.83*	2.9	Yes
16	Centre Creek	2.27*	13.6	Yes
17	Hawks Crag Creek	0.83*	1.4	Yes
18	Blackwater R.	0.70	1.7	No

* Ratio indicating presence of mineralization in drainage area.

** Evidence of mineralization found at later date.

DISCUSSION

Geochemical prospecting is concerned with the detection of anomalous amounts of any element as a guide to the detection of its ore. This problem may essentially be approached in two ways. Samples collected from a grid survey may be analysed either directly for the element concerned or for its associated elements. The choice of either of these two approaches depends on the answers to the following questions. Firstly, is the metal being sought capable of being transported far enough from its source and in sufficient quantities, to justify direct geochemical search? Secondly, will normal variations in the background of the area render any geochemical method unreliable. In view of these questions, pathfinder elements may be defined as elements which, because of some particular property or properties, provide anomalies or halos more readily usuable than the sought-after element with which they are associated.

Uranium is well known for its solubility and extreme mobility and as discussed previously, is a difficult element to prospect for directly in areas of rugged topography and high rainfall. Hence the important role of pathfinders in this instance. However, it is interesting to note that Table II-4 shows a uranium value which is distinctly higher in a sample from a known mineralized stream (B16, Centre Creek) and three other high values (Big River 1, Tiroroa Creek /B13/ and Ohika-iti River /O$_2$/). It was found that BR1 was taken thirty yards downstream from an isolated uranium anomaly (FOSTER, pers. comm.) and more detailed investigation in Tiroroa Creek indicated a general radiation level two or three times background. The sample from the Ohika-iti River was taken in the main stream and the high value obtained is thought to be due to an unrepresentative fraction.

All these anomalies detected by the direct analysis of uranium have two features in common. These are:

1) the sample taken was very close (within fifty yards) of the uranium anomaly, and

2) the uranium anomaly was a considerable part of the drainage area and registered at least three times above background on a scintillometer.

Although direct analysis of uranium in stream-sediments registered some success, this survey has shown that generally in an area of rugged topography and high rainfall this approach is unsuitable.

Statistical evaluation of the elements associated with uranium throughout the weathering sequence minerals, soils, stream-sediments, showed that only copper was suitable as a pathfinder in the stream-sediments whereas lead, beryllium and copper were suitable pathfinders in minerals and soils. To understand these results it is necessary to consider the different weathering processes involved and to evaluate their relative significance.

Three main types of weathering may be distinguished: physical, chemical and biological. Physical processes include those that cause rock disintegration without appreciable chemical or mineralogical changes. As the rock disintegrates, the surface area becomes larger and this facilitates chemical weathering due to reactions with water, oxygen and carbon dioxide. Biological activity can contribute either directly or indirectly to both physical and chemical weathering. Generally, these processes take place side by side and their relative importance varies according to the environment.

In the Buller Gorge region, although the topography is rugged and the annual rainfall is high, both conditions being suitable for physical weathering, the area is densely covered with vegetation whose natural rain shield and large root network successfully prevents erosion. This dense vegetation cover may also play an important role in the biological weathering process as uptake of elements such as copper, zinc and uranium by the flora has been shown to be quite significant (WHITEHEAD and BROOKS, 1969b).

Although biological effects can make an appreciable contribution to the overall weathering process, as does physical weathering, the author feels that the contribution of this effect is low as the levels of element concentrations found in the soil are too high to have accumulated from decayed vegetation.

Evaluation of the effect of physical and biological weathering processes for the distribution of the elements indicates that the largest contribution comes from chemical weathering. Acceptance that chemical weathering is the major factor is strengthened when it is remembered that the Hawks Crag Breccia is a porous sandstone matrix and as a result of the high rainfall, oxidation and transport of the soluble elements is easily facilitated.

A comparison of the solubilities of the elements uranium, copper, lead and beryllium shows that uranium (VI) is the most soluble followed by copper, lead and then beryllium. Further evidence substantiating the importance of chemical weathering is shown by the fact that because of solubility differences, lead and beryllium do not correlate with uranium beyond the soils whereas copper does. Because copper is less soluble than uranium it is more suitable for analysis in stream-sediments than this element and is hence a suitable pathfinding element for uranium.

Analysis of uranium minerals for yttrium, thorium and the rare earths did not provide any useful information concerning possible pathfinders for uranium. In all cases the levels of these elements in the mineralized rocks were extremely low, with the levels in the mineralized fraction being slightly higher than those in the unmineralised fraction. Stream sediment concentrations were higher again and probably reflect the greater proportion of granitic material in the Breecia. The results presented in Table II-4 for the analysis of stream sediments from the Hawks Crag Breccia for yttrium, thorium and rare earths show that overall the concentrations of these elements are low compared with the majority of those values obtained by TENNANT and SEWELL from the Otututu and Ohika-Nui granitic areas. The generally low levels obtained for yttrium, thorium and the rare earths are probably due to dilution with the weathered matrix material which, as shown by results in Table II-4 for the matrix, is deficient in rare earths. An attempt was made to compare the rare earth distributions found in the Hawks Crag Breccia areas with those found in the Ohika-Nui and Ototutu River areas by computing the amounts of lanthanum, yttrium and thorium in each sample as a percentage of the sum of the three, and by plotting these values on triangular graph paper. The elements, lanthanum yttrium and thorium were chosen because they were shown by TENNANT and SEWELL to be the most discriminating for the respective areas. Fig. II-11 shows the results obtained. The overlap of samples from the Ohika-Nui area into that area on the graph representing the Otututu area and vice versa, is a result of the fluctuation of the element concentration within each area. It is seen however, that the greatest concentration of samples from both the Ohika-Nui and Otututu areas do fall into separate areas on the graph which may be taken as "characterising" that particular area sampled. It is clearly seen that the samples from the Hawks Crag Breccia fall closer to the area characterised as Otututu than that characterised as Ohika-Nui River. This would indicate that the Hawks Crag Breccia was derived from the Otututu granite.

The author considers, however, that for a more definite indication of this relationship, analysis of a large number of samples from all the Hawks Crag Breccia areas would be required.

In summary, it is concluded that this work has shown that in the Hawks Crag Breccia area, prospecting for uranium by use of pathfinder elements, lead, beryllium and copper in soils and copper in stream sediments provides a relatively speedy and simple method. Direct analysis for uranium was shown to be, in general, unsuitable unless the sampling site was close to the radioactive area. Although yttrium, thorium and rare earths did not prove suitable as pathfinders for uranium, the analysis of stream sediments for these elements did provide new evidence to support the suggestion that the Hawks Crag Breccia was derived from granite from the Otututu area.

The uncertainty concerning this origin is reflected in the various theories for the origin of the uranium mineralization

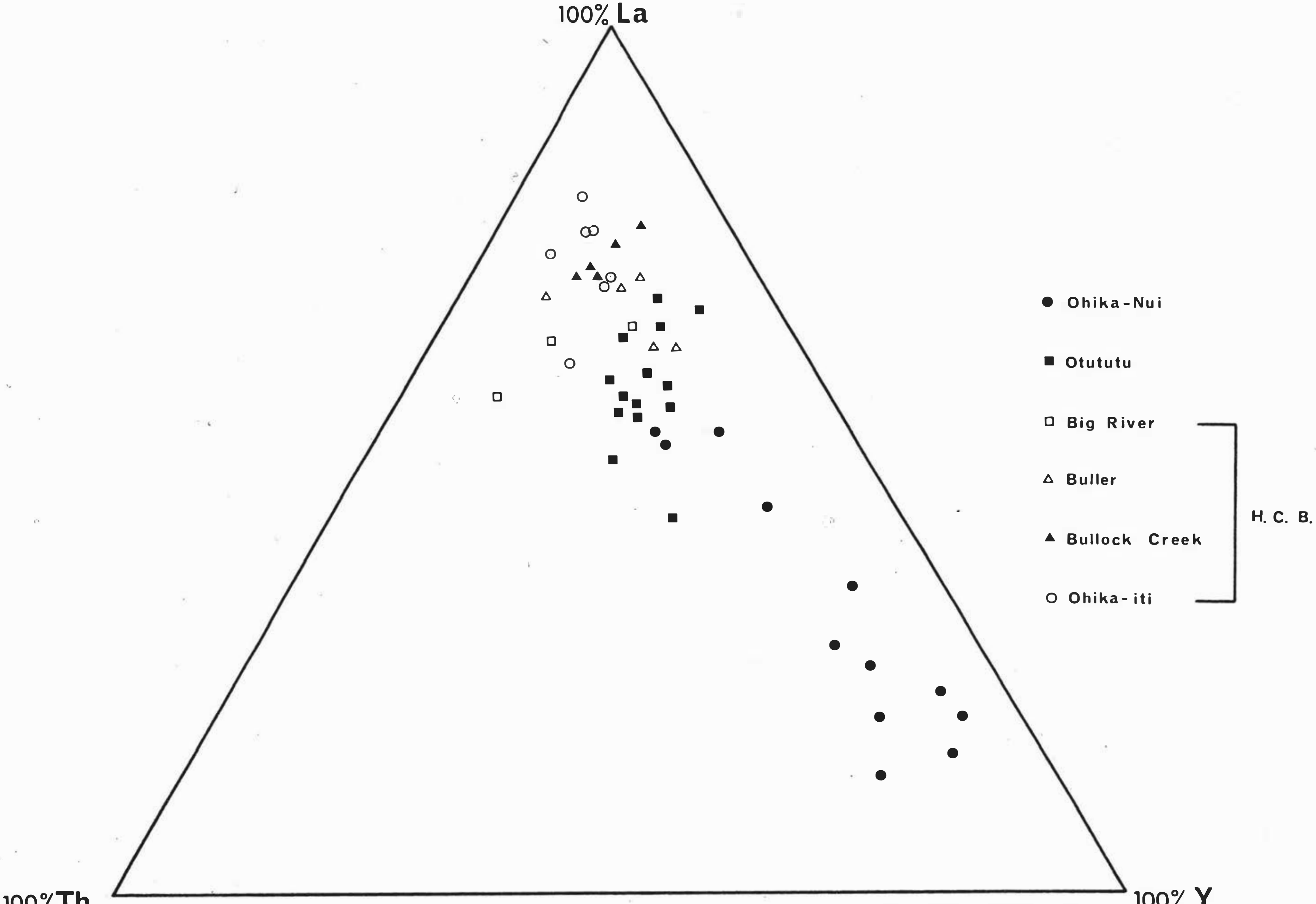


Fig. II - 11 Triangular Plot for Concentration Ratios of Lanthanum, Yttrium and Thorium from Stream Sediments in Drainage Areas; Ohika-Nui River, Otututu River, and Hawks Crag Breccia.

itself (BECK ET AL, 1958; WODZICKI, 1959b). The final part of the thesis inter alia reports on low energy gamma ray studies carried out with the minerals to determine their composition and state of equilibrium; an important consideration for any discussion concerning the origin of these radioactive deposits.

PART III

EQUILIBRIUM STUDIES ON URANIUM MINERALS BY HIGH-RESOLUTION GAMMA SPECTROMETRY

INTRODUCTION

Natural uranium, consisting of 99.28% U^{238}, 0.71% U^{235} and 0.01% U^{234}, is an unstable element whose isotopes decay to simpler nuclides with emission of alpha, beta and gamma radiation. The recording of this radioactivity with appropriate electronic instruments has, for many years, been a convenient method for the detection of uranium and has formed the basis of a method used extensively in exploration for uranium mineralization. At first, hand-borne Geiger-Muller counters, which detect alpha and beta radiation, were used, but these instruments have now been superseded by the more sensitive scintillometer. The scintillometer detects gamma radiation, which is considerably more energetic than alpha or beta radiation, and hence facilitates detection of radioactive substances at a much greater range than does the Geiger counter. Because of the higher sensitivity achieved, the scintillometer can be operated from moving vehicles. The latest development in radiometric survey techniques is the use of highly-sensitive scintillometers capable of differentiating between radiations from uranium, thorium and K^{40}.

It is well known that the major fraction of gamma radiation of the uranium series comes from the decay of daughter products of Ra^{226}. An approximate determination of the amount of uranium present can be made directly from the measurement of the gamma radiation if it is assumed that the mineral is in radioactive equilibrium. In this, it is implied that the rate of production of Ra^{226} from U^{238} must equal the rate of decay of Ra^{226}, a condition which is not always satisfied in practice. For the purpose of ore detection, however, where we are concerned with the order of magnitude of the uranium concentration, the state of equilibrium is unimportant. As it has been found that many uranium minerals are not in equilibrium, direct measurement of the gamma radiation for uranium content leads to incorrect values. This problem can be overcome by measuring both beta and gamma radiation (EICHHOLZ ET AL, 1953). However, the importance of knowing the state of equilibrium of a uranium mineral is not confined to the quantitative analysis of uranium. In order to obtain the age of a uranium mineral it is also necessary to know its state of equilibrium, as deviations from the equilibrium state change the Pb^{206}/U^{238} or Pb^{207}/U^{235} ratios. (Pb^{206} and Pb^{207} are the stable end products of the decay of U^{238} and U^{235} respectively, as shown in Fig. III-1).

The term generally accepted to describe the state of equilibrium of a uranium mineral is "percentage equilibrium radium". This is defined as the amount of radium actually present in a sample expressed as a percentage of the amount of radium which would be present if a state of radioactive equilibrium existed between the uranium and the products of its decay. As has been mentioned previously, this stage is reached when the rate of radium decay becomes equal to the rate of radium formation. There are two main reasons for the "percentage equilibrium radium" deviating from one hundred percent.

(a) Insufficient time may have elapsed since the deposition of the uranium to allow the formation of the equilibrium amount of radium. The rate at which the Ra^{226} activity builds up to that of the U^{238} parent is limited by the half-life of one of the intermediate members of the series, U^{234} ($t\frac{1}{2} = 2.0.10^5$ yr). Only

Uranium Series

Element	Symbol	Radiation	Half-Life
Uranium I	^{238}U	α	$4.5X10^{10}$ years
Uranium X_1	^{234}Th	β	24 days
Uranium X_2	^{234}Pa	β	1.1 minutes
Uranium II	^{234}U	α	$2.3X10^{5}$ years
Ionium	^{230}Th	α	$8.0X10^{4}$ years
Radium	^{226}Ra	α	$1.6X10^{3}$ years
Radon	^{222}Rn	α	3.8 days
Radium A	^{218}Po	α,β	3.0 minutes
Radium B	^{214}Pb	β	27 minutes
Astatine	^{218}At	α	2 seconds
Radium C	^{214}Bi	β,α	20 minutes
Radium C'	^{214}Po	α	$1.5X10^{-4}$second
Radium C"	^{210}Tl	β	1.3 minutes
Radium D	^{210}Pb	β	22 years
Radium E	^{210}Bi	β,α	5.0 days
Radium F	^{210}Po	α	140 days
Thallium	^{206}Tl	β	4.2 minutes
Radium G (end product)	^{206}Pb	-	Stable

Actinium Series

Element	Symbol	Radiation	Half-Life
Actinouranium	^{235}U	α	$7.1X10^{8}$ years
Uranium Y	^{231}Th	β	24 hours
Protactinium	^{231}Pa	α	$3.2X10^{4}$ years
Actinium	^{227}Ac	β,α	22 years
Radioactinium	^{227}Th	α	19 days
Actinium K	^{223}Fr	β	21 minutes
Actinium X	^{223}Ra	α	11 days
Actinon	^{219}An	α	3.9 seconds
Actinium A	^{215}Po	α,β	$1.8X10^{-3}$second
Actinium B	^{211}Pb	β	3.6 minutes
Astatine	^{215}At	α	10^{-4} second
Actinium C	^{211}Bi	β,α	2.2 minutes
Actinium C'	^{211}Po	α	$5X10^{-3}$second
Actinium C"	^{207}Tl	β	4.8 minutes
Actinium D (end product)	^{207}Pb	-	Stable

Fig. III-1

Thorium Series

Element	Symbol	Radiation	Half-Life
Thorium	^{232}Th	α	1.4X10^{10} years
Mesothorium I	^{228}Ra	β	6.7 years
Mesothorium II	^{228}Ac	β	6.1 hours
Radiothorium	^{228}Th	α	1.9 years
Thorium X	^{224}Ra	α	3.6 days
Thoron	^{220}Tn	α	54 seconds
Thorium A	^{216}Po	α	0.16 second
Thorium B	^{212}Pb	β,α	10 hours
Astatine	^{216}At	α	3X10^{-4}second
Thorium C	^{212}Bi	β,α	60 minutes
Thorium C'	^{212}Po	α	3X10^{-7}second
Thorium C"	^{208}Th	β	3.1 minutes
Thorium D (end product)	^{208}Pb	-	Stable

Fig. III-1 Decay Schemes for ^{238}U, ^{235}U, ^{232}Th

after a little more than one million years does the Ra^{226} activity reach 97% of its equilibrium value.

(b) There may have been some preferential loss (e.g. by leaching) of one or more of the isotopes in the decay series. If radium has been lost preferentially, a "percentage equilibrium radium" value of less than one hundred percent is to be expected, whereas preferential loss of uranium will lead to values of "percentage equilibrium radium" greater than one hundred percent.

The most common method used to determine the "percentage equilibrium radium" relies on the measurement of the known types of radiation arising from the disintegration of uranium and its daughter products. It is necessary in this method to measure both beta and gamma radiation. The beta radiation arises from both the immediate uranium daughter products and also from radium. The major fraction of the gamma radiation arises from radium and its daughters. The gamma radiation figure is used to calculate the amount of beta radiation due to radium, and this is then deducted from the total beta measurement to determine the amount of beta radiation arising from the uranium. From this corrected figure, the amount of uranium is determined and the "percentage equilibrium radium" calculated. This is essentially the method used by BOSIN and BOGDAN (1960) and STERN and STIEFF (1959). Another approach is that of GRACE and BATES (1959) who determined the equilibrium using alpha and fission-fragment radiography. This technique has the advantage that it can be applied on a micro scale but suffers from the disadvantage that it can not be used in the presence of natural thorium.

The main weakness in the method involving the measurement of both beta and gamma radiation is the assumption that all the gamma radiation detected is due to the decay of radium or its daughters. This is not so, as Th^{234} and U^{235} both produce gamma radiation, and although the activity is only a fraction of that from radium and its daughters, it is still significant. As a result of this, the corrected beta figure for uranium would be too low, and therefore the associated "percentage equilibrium radium", value would be rather too high. The advantage offered by a method which independently measures the radiation from only Ra^{226} and a uranium isotope is clearly seen (U^{235} is the most suitable uranium isotope for a gamma ray study as the decay of U^{238} to Pa^{234} does not involve gamma emission and U^{234} is insufficiently abundant). LEDERER (1969) states that the principal gamma rays from both U^{235} and Ra^{226} have an energy of 185 KeV and the principal gamma rays from Pb^{214} (a daughter of Ra^{226} always in equilibrium, due to its short half-life) have energies of 242, 295 and 352 KeV respectively. From these gamma rays it is theoretically possible to calculate the "percentage equilibrium radium". To achieve this experimentally, however, it is necessary to resolve the three Pb^{214} gamma rays, and to determine the extent to which the Ra^{226} 185 KeV gamma ray interferes with the 185 KeV gamma ray from U^{235}.

Prior to the development of the Ge(Li) detector, the Pb^{214} gamma rays could not be satisfactorily resolved, as the NaI(Tl) detector did not possess sufficient resolution in this energy region. Fig. III-2 clearly illustrates this point. Although the Ge(Li) detector was developed primarily for the

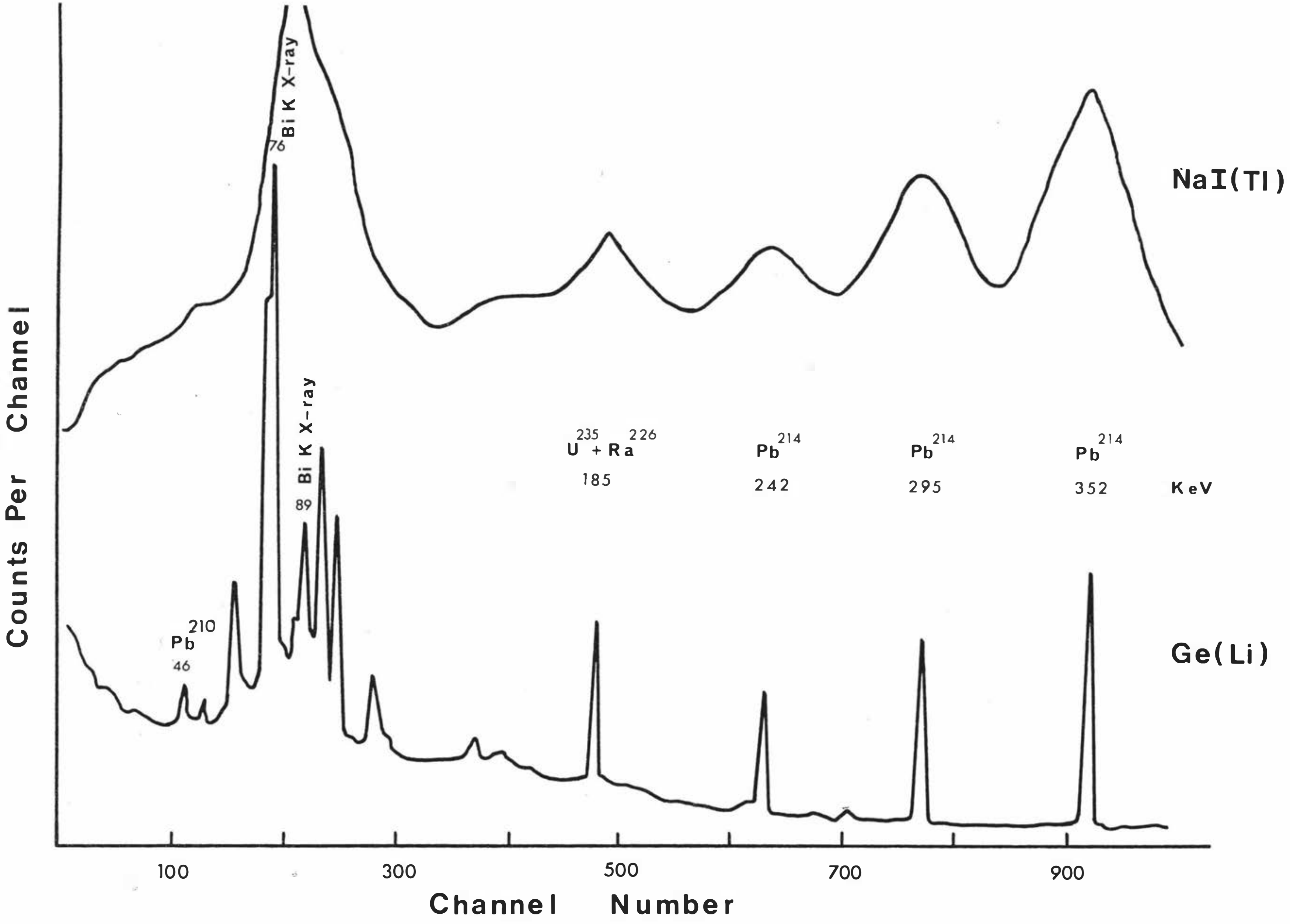


Fig. III - 2 Comparison of uraninite spectra recorded with NaI(Tl) and Ge(Li) detectors benefit of the nuclear spectroscopist, it has been used in many other fields of research. These include decay-scheme studies with radioactive isotopes, beam spectroscopy, low-temperature nuclear orientation and activation analysis. An excellent review of the impact of semiconductor detectors on gamma-ray and electron spectroscopy is given by HOLLANDER (1966). The preparation, maintenance and relevant theory of the semiconductor detector is given by MANN ET AL (1966), DEARNALY and NORTHROP (1966) and COOTE (1967).

The geochemist and analytical chemist have gained most benefit from the Ge(Li) detector in the field of activation analysis because the high resolution obtained has, in many cases, made possible the direct measurement of the irradiated sample. Previously, using the NaI(Tl) detector, tedious chemical separations were required. To the author's knowledge, the only application of the Ge(Li) detector to naturally-occurring radioactive material, is that of MATHEVON ET AL (1967), who used the gamma radiation of specific isotopes to determine uranium, thorium and radium content of such samples. The method used by these authors required that the sample was in radioactive equilibrium and that an accurately known uranium standard, also in equilibrium, was available as reference. MATHEVON ET AL also developed a method to compare the radioactive equilibrium of each sample with that of the standard rock. However, due to an error in the assignment of the 185 KeV gamma radiation by the above authors, the present author considers that the reported work is in serious error and requires further elucidation.

The aim of this part of the thesis was three-fold:

(1) To identify the various peaks in the low energy region of the gamma spectrum (30-360 KeV) of naturally occurring uranium ores.

(2) From the results of (1), to develop a method for determining the "percentage equilibrium radium".

(3) To investigate the equilibrium state of uranium minerals in the Buller Gorge in order to provide more information on the history of these deposits.

INSTRUMENTATION

All measurements were obtained via a high-resolution gamma spectrometer at the Institute of Nuclear Sciences, Department of Scientific and Industrial Research, Wellington.

High resolution in the low-energy region (40-360 KeV) was obtained by using a 5 cm^3 Ge(Li) detector, drifted from five sides and with the open end facing the radiation. In a germanium detector only 3eV is required to produce an electron-hole pair, whereas a NaI(Tl) crystal requires about 300 eV per photo-electron from the cathode and hence has a much poorer resolution.
Fig. III-2 clearly illustrates the difference in resolution of these detectors.

The Ge(Li) detector was coupled to a SIMTEC P-11, low-noise Field-Effect-transistor pre-amplifier; the combination provided resolution of 2.5 KeV. These two components were housed in the radiation area thirty to forty feet from the control room. Coaxial cables from the pre-amplifier lead to the control room, where the pulses were amplified by an ORTEC 410 transistor main amplifier which was connected to an RCL 256-channel pulse-height analyser (P.H.A.). For very accurate calibration work a KICKSORT 4096-channel pulse-height analyser was used. Data stored in the memory of either P.H.A. were recorded as a spectrum listing via a typewriter, for later manual plotting, or were punched directly onto paper tape which provided the input information for computer-assisted analysis. Figures III-3 and III-4 show schematic diagrams of the gamma spectrometer, and the system used for computer-assisted analysis of gamma spectra, respectively.

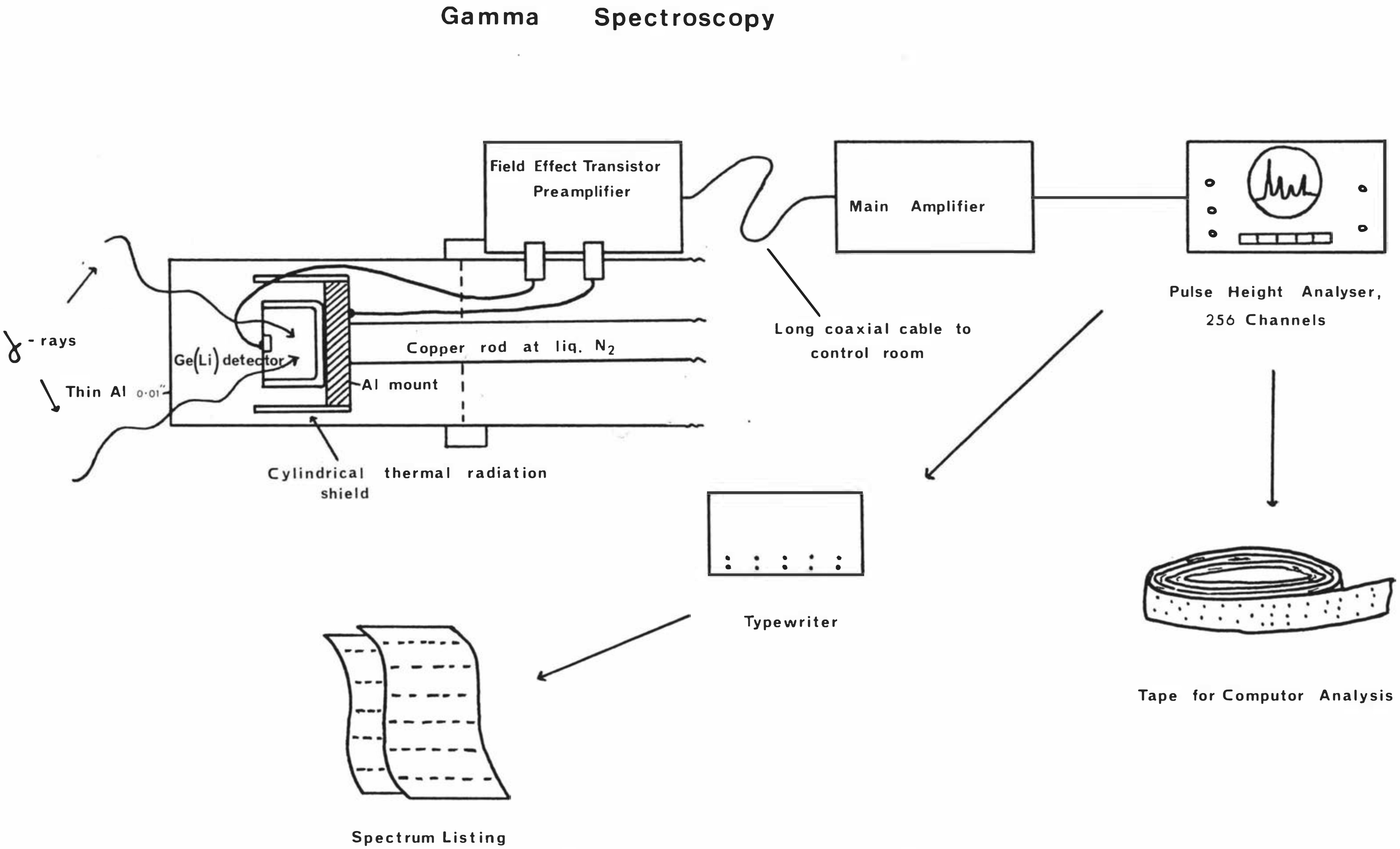


Fig. III - 3 Gamma spectroscopy - schematic diagram

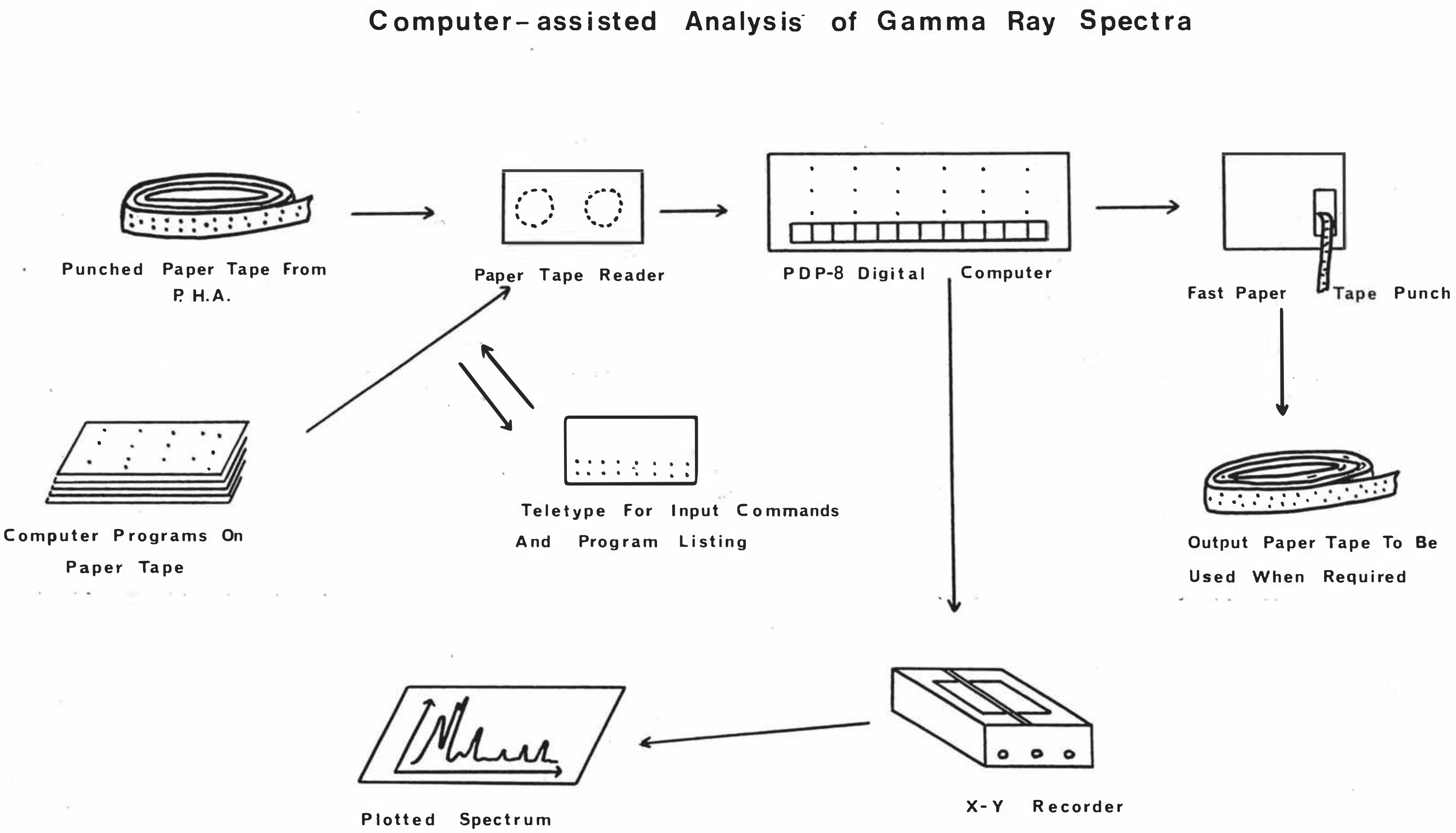


Fig. III - 4 Computer-assisted analysis of gamma spectra

Operation Procedure

Five to fifteen grams (depending on the activity) of powdered rock (less than 80 mesh) was placed in a cylindrical glass phial (5cm x 2cm diam.) and positioned in front of the detector next to the thin aluminium window. The sample was counted for a sufficient time to allow a well-defined spectrum to be obtained. For most uranium minerals this was between fifteen and thiry minutes. A check on the number of counts per channel in each channel comprising the spectrum was easily obtained at any time via an oscilloscope in the P.H.A. When a well-defined spectrum had been obtained, the number in each channel was either listed by the typewriter or punched on to paper tape and then analysed with the computer as has been previously described. A typical spectrum obtained is shown in Fig. III-2.

IDENTIFICATION OF SPECTRA

(a) Calibration of Pulse Height Analyser

As has been previously mentioned, the gamma spectrum is recorded by the P.H.A. as counts in a given time for each channel. In order to assign specific energies to each peak a calibration curve of energy as a function of channel number must be determined. The calibration curve was constructed from the gamma spectrum of a standard source, consisting of several isotopes, by plotting the known energies of the gamma rays from these isotopes against their corresponding channel numbers. Table III-1 shows some of the isotopes used, with their respective gamma ray energies, and Fig. III-5 shows a typical calibration curve obtained. Provided that the settings on the spectrometer are kept constant, the calibration curve can be used for all spectra taken over several hours. If, however, an assignment of an energy to a peak is doubtful the calibration curve is redetermined either immediately before or after the particular spectrum being studied.

(b) Analysis of Spectra

The analysis of the low-energy gamma ray region (30-400 KeV) was carried out in two parts. The first, and most important to this work, was a qualitative and quantitative study confined to the region 180-360 KeV. This region includes the main gamma radiation from U^{235} and Ra^{226} (185 KeV) and the main gamma radiation from Pb^{214} (242, 295, and 352 KeV). These are the most important gamma radiations for the calculation of radioactive equilibrium. The second part was concerned only with identification of the observed peaks in the region 30-180 KeV. The energy region above 360 KeV was not considered because it contains only gamma rays from Bi^{214} and yields no new information. Use of one of these

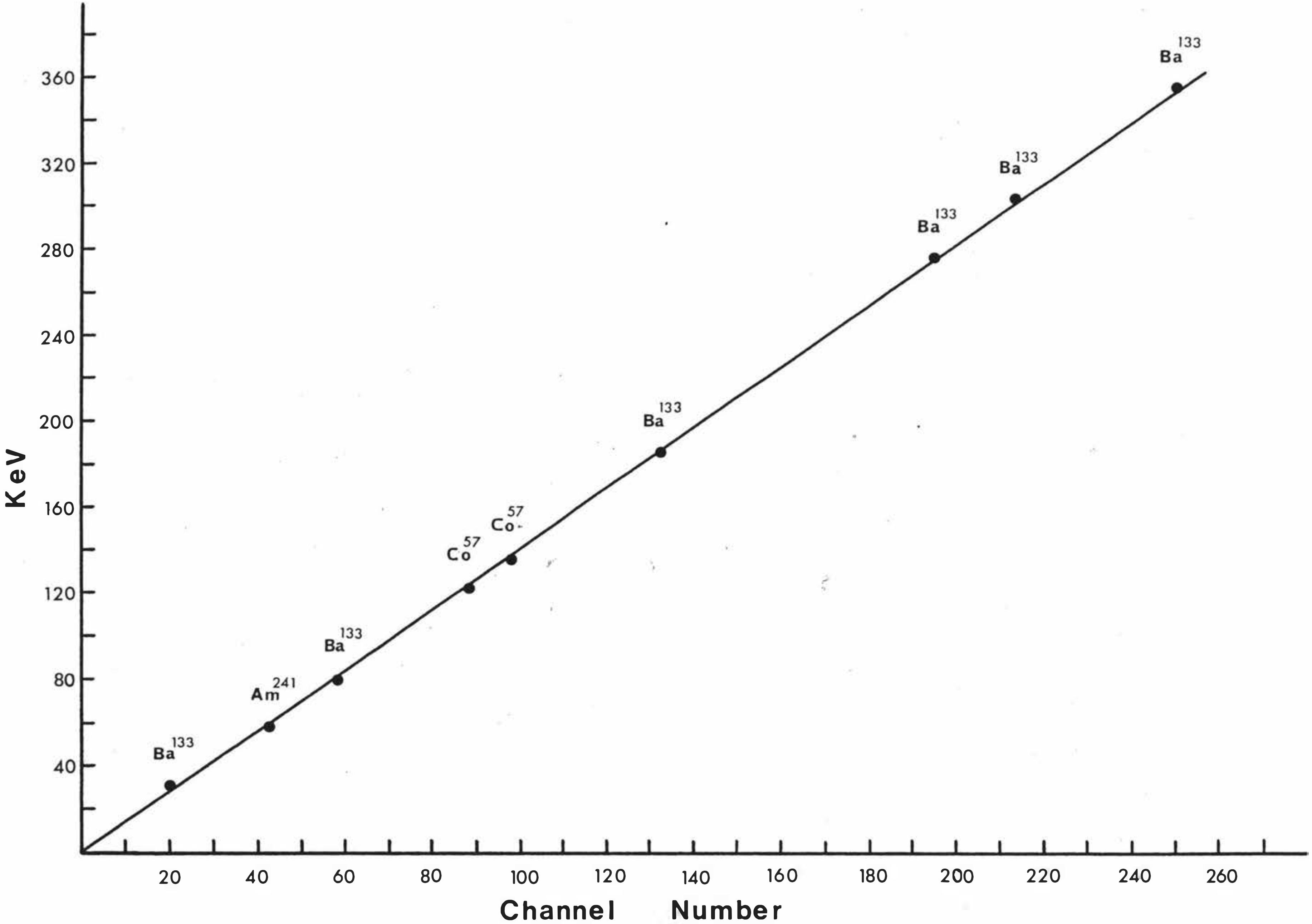


Fig. III - 5 Calibration curve, keV as a function of channel number

TABLE III - 1

Isotopes and Respective Gamma Ray Energies Used for Calibration of a Pulse Height Analyser

Isotopes	Energies (KeV)
Ba^{133}	30.9, 81.1, 276.5, 303.0, 356.3, 384.1
Ra^{226}	185.7, 241.9, 295.2, 352.0
Am^{241}	26.35, 59.54
Co^{57}	121.97, 136.33
Co^{60}	1173.2, 1332.4
Pb^{210}	46.5

gamma rays as a determination of Ra^{226} was not attempted because of the very low detector efficiency in this energy range. Although no appreciable amounts of the thorium series were detected in the uranium minerals from the Buller Gorge (a situation which reduced the complexity of the spectrum), the quantitative study carried out included the possibility of the presence of thorium in order to ensure that this method of calculating radioactive equilibrium had general application.

(i) 180-360 KeV Region

Fig. III-6 shows (i) the gamma spectra obtained from a uranium mineral (uraninite), (ii) Ra^{226} in equilibrium with Pb^{214} and Bi^{214}, (iii) "uraninite minus Ra^{226}" and (iv) an aged thorium nitrate sample. The spectrum labelled "uraninite minus Ra^{226}" was obtained by counting the uraninite for two hours and subtracting the counts obtained from the radium source over the same time. To normalize the two count rates, the position of the radium source in front of the detector was altered until the "percentage live time" meter registered the same value as when the uraninite sample was counted. This approach was considered to be the most suitable way to determine the extent of interference of the Pb^{214} peaks in natural samples, arising from U^{235} or other decay products. It is estimated that the error incurred by this procedure would not be greater than one percent.

From Fig. III-6 it is clearly seen that the 185 KeV gamma ray from Ra^{226} cannot be distinguished from the 185 KeV gamma ray from U^{235}, and that the 239 KeV gamma ray from Pb^{212} (a daughter of Th^{232}) interferes strongly with the 242 KeV gamma ray from Pb^{214} As a result of a systematic search through TABLE OF ISOTOPES

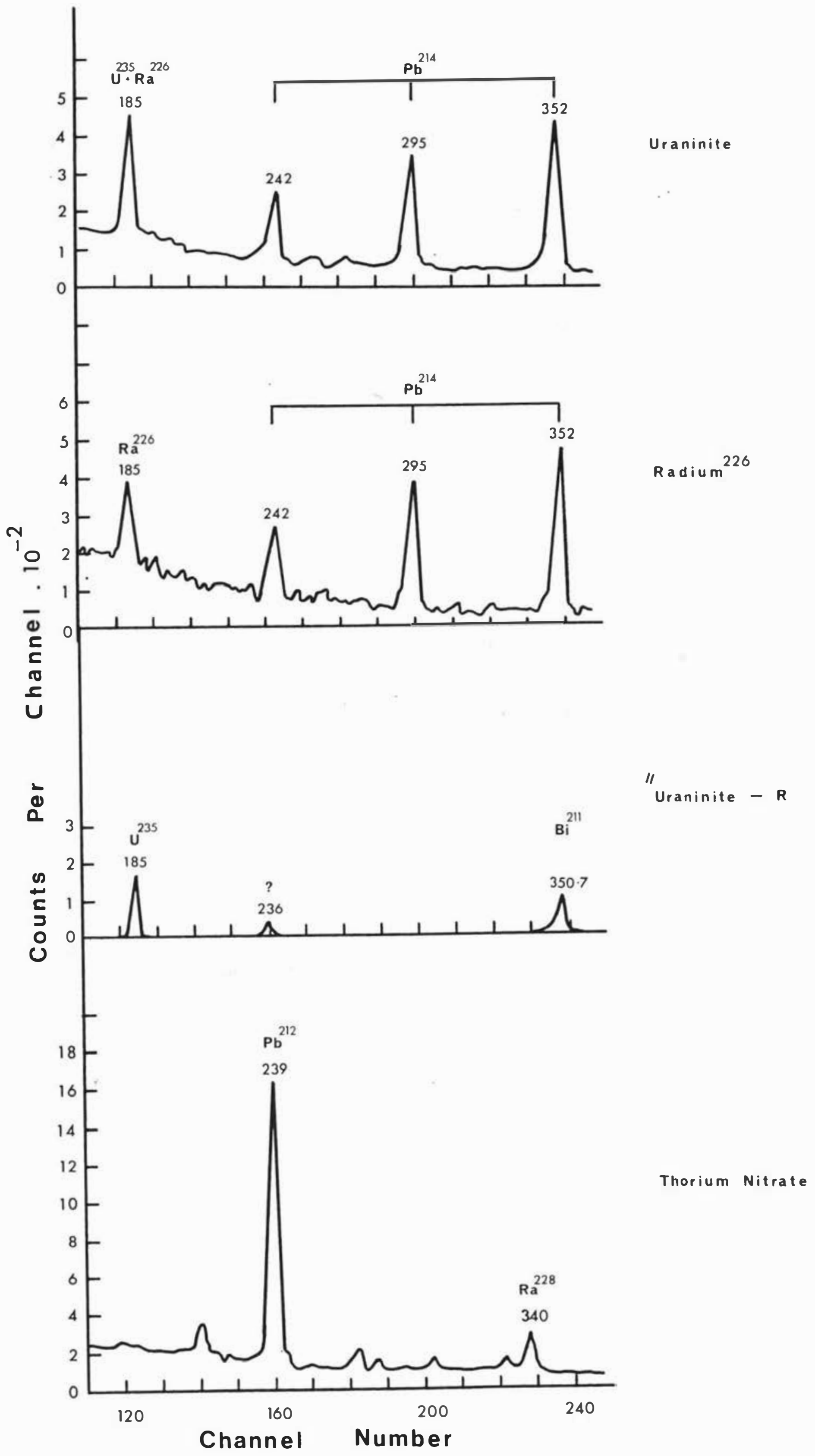


Fig. III - 6 Gamma spectra of uraninite, Ra^{226}, Th^{232} (Energies of peaks in keV).

(LEDERER, 1969) these interferences were expected but their respective quantitative contributions were unknown. The "uraninite minus Ra^{226}" spectrum shows a peak at 350.7 KeV. This is probably due to Bi^{211}, a daughter of U^{235}, as Bi^{211} is the only isotope present which has a favourable decay path to produce a gamma ray of this energy. Hence there is interference of the Pb^{214} 352 KeV peak by the Bi^{211} 350.7 KeV peak. This Bi^{211} interference prevents the Pb^{214} 352 KeV peak from being used as a measure of Ra^{226} present in the sample because the Bi^{211} contribution to the Pb^{214} peak will vary according to the amount of U^{235} present in the sample. Further confirmation that the Pb^{214} 352 KeV peak is contaminated is shown by comparing the ratio - 352 KeV peak/295 KeV peak from the uraninite with the same ratio from the Ra^{226} spectrum. The values of this ratio are 1.319 and 1.257 respectively, which shows that the value of the 352 KeV peak from the uraninite is higher than would be expected if it was free from interference. The spectrum obtained from the aged thorium nitrate sample shows a strong peak due to Pb^{212} at 239 KeV. As the resolution of the system used is 2.5 KeV, it is seen that the Pb^{212} 239 KeV peak will interfere with the Pb^{214} 242 KeV peak and render it unsuitable as a measure for Ra^{226}. These results show that only the Pb^{214} 295 KeV peak is free from interference, and is suitable for use as a measure of Ra^{226} activity.

(ii) 30-180 KeV Region

The identification of peaks from uranium samples in this energy range of the spectrum was attempted as little information is available in the literature. Preliminary experiments, with dissolved uraninite as sample, were carried out to investigate the suitability of using solvent extraction techniques to separate the various isotopes and hence facilitate identification of their gamma radiations. The system chosen was tributyl phosphate/HCl as this was the best documented (SATO, 1966). However, incomplete separations were obtained with this system. A successful separation was achieved by using the anion-exchange technique reported in Part II of this thesis for the separation of uranium and thorium. Fig. III-7 shows the spectra obtained. The excellent separation of uranium from thorium assisted identification of U^{235} gamma radiation and Th^{234} gamma radiation in this energy region. The spectrum of the uranium fraction shows that U^{235} emits the following gamma radiation and X-rays in the 30-180 KeV region: 49, 68, 85, 93, 98, 110, 143, 163 KeV. The spectrum of the thorium fraction shows two peaks due to the 63 KeV and 93 KeV gamma rays from Th^{234}. The U^{235} spectrum obtained in this work compares well with that obtained by MANN ET AL (1966), also using a Ge(Li) detector, from a U^{235} source of 93% purity. The uraninite spectrum (Fig. III-2 shows two peaks at 76 and 89 KeV which are absent from the uranyl nitrate spectrum. These peaks are Bi K x-rays, following the decay of Pb^{214}. Their absence from the uranyl nitrate spectrum is due to the absence of Pb^{214}, because of the young age of the sample. Similarly, a peak at 46.5 KeV, due to Pb^{210}, appears in the uraninite spectrum, but not in that of the uranyl nitrate.

The above results show that this low-energy region (30-180 KeV) is extremely complex. The features with the best

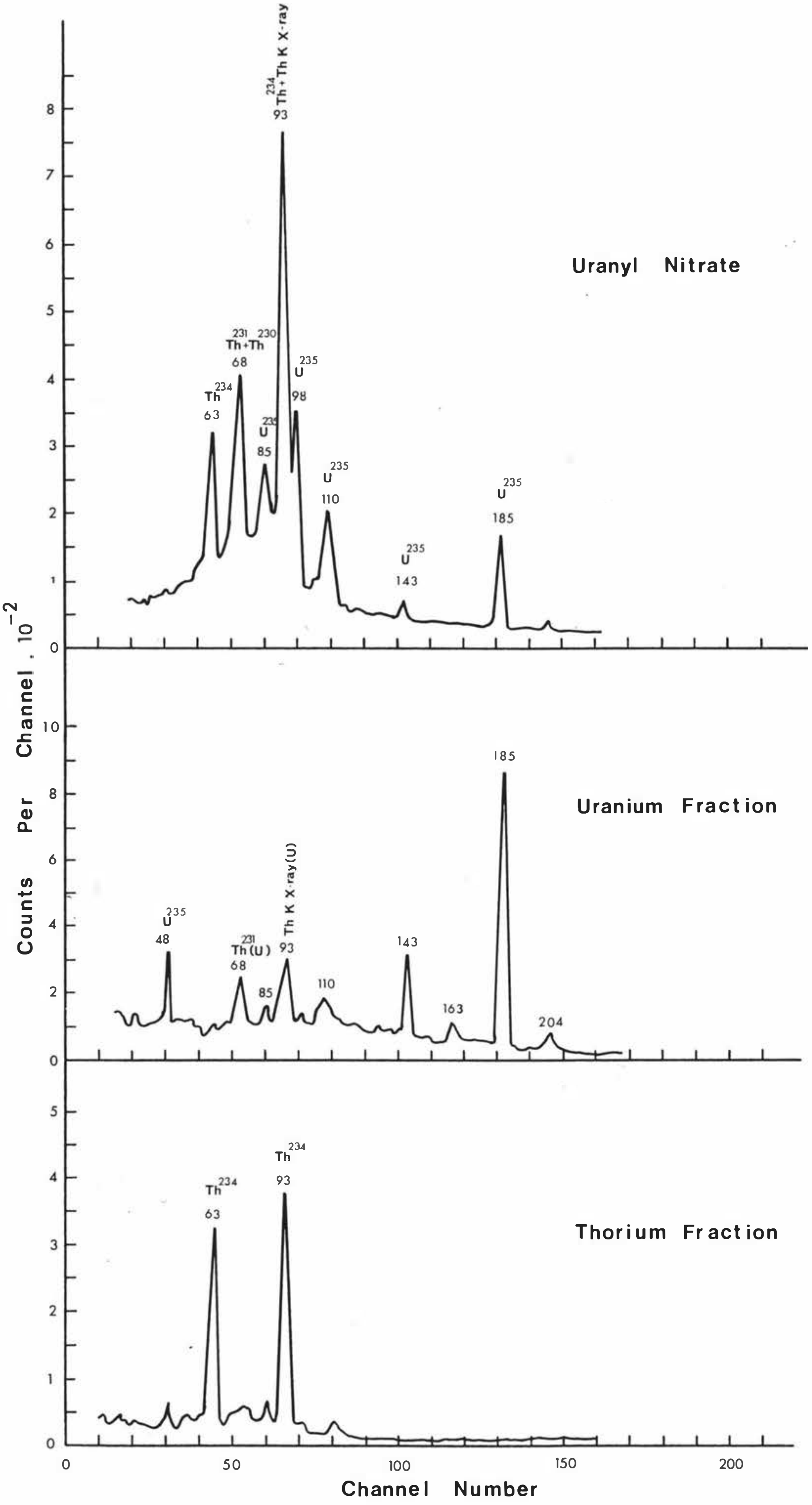


Fig. III - 7 Gamma spectra of uranyl nitrate, extracted uranium fraction and thorium fraction (Energies of peaks in keV).

possibilities for useful applications are the 63 KeV gamma radiation from Th^{234} (as an indication of U^{238}), and the 46.5 KeV gamma radiation (as a measure of Pb^{210}). However, the higher energy end (180-360 KeV) of this low energy region appears to contain the most significant information.

EQUILIBRIUM STUDIES ON MINERALS

(a) Derivation of the Equilibrium Relationship

As has been previously mentioned, the term "percentage equilibrium radium" is the accepted way of expressing the state of equilibrium of a uranium mineral. This term is defined as the amount of radium actually present in the sample, expressed as a percentage of the amount of radium which would be present if the sample was of sufficient age to have attained a state of equilibrium between the uranium and the products of its decay.

From the previous results it is seen that it is possible to determine the number of radium atoms present from the count rate obtained from the Pb^{214} 295 KeV peak. The number of counts in unit time at an energy of 295 KeV, C(295), is given by

$$C(295) = \lambda_{Pb} N_{Pb} P_{Pb}(295) E(295)$$

where λ_{Pb}, N_{Pb} are the decay constant and number of atoms respectively, of Pb^{214}, $P_{Pb}(295)$ is the fraction of disintegrations from Pb^{214} giving a gamma ray of 295 KeV, and E(295) is the Ge(Li) detector efficiency at this energy.

When Ra^{226} is in radioactive equilibrium with Pb^{214},

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

where λ_{Ra}, N_{Ra} are the decay constant and number of atoms respectively, of Ra^{226}. This equilibrium is attained in a Ra^{226} sample after only a few weeks have elapsed.

Hence the number of radium atoms in the sample is given by

$$N_{Ra} = \frac{C(295)}{\lambda_{Ra} P_{Pb}(295) E(295)}$$

However, the absolute value of the detector efficiency, which is difficult to obtain with better than ten percent accuracy, must be determined experimentally for each detector used. As a result, this approach is considered unsatisfactory. To overcome this problem an attempt was made to obtain a relationship between the "percentage equilibrium radium" and the ratio of the 185 KeV (U^{235} + Ra^{226}) peak to the 295 KeV (Pb^{214}) peak in which the detector efficiency term is not involved. The following shows how this relationship was developed.

Let C(185) be the number of counts in unit time at an energy of 185 KeV, and let the detector efficiency at this energy be E(185).

Then $C(295) = N_{Ra}\lambda_{Ra}P_{Pb}(295)\ E(295)$ --- (1)

and $C(1\overset{8}{9}5) = N_{Ra}\lambda_{Ra}P_{Ra}(185)E(185) + N_U\lambda_U P_U(185)E(185)$ --- (2)

where λ_U, N_U are the decay constant and number of atoms, respectively, of U^{235}, $P_{Ra}(185)$, $P_U(185)$ are the fractions of the disintegrations from Ra^{226}, U^{235} giving a gamma ray of the stated energy.

Let $\lambda_{Ra}\ P_{Pb}(295)\ E(295) = k_1$

$\lambda_{Ra}\ P_{Ra}(185\ E(185) = k_2$ --- (3)

$\lambda_U P_U(185)\ E(185) = k_3$

then $C(295) = k_1 N_{Ra}$ --- (4)

$C(185) = k_2 N_{Ra} + k_3 N_U$ --- (5)

$\therefore\ N_{Ra} = C(295)/k_1$

and $N_U = \frac{1}{k_3}\left[C(185) - \frac{k_2}{k_1}\ C(295)\right]$

hence $\frac{N_U}{N_{Ra}} = \frac{k_1 C(185) - k_2\ C(295)}{k_3 C(295)}$

$$= \frac{k_2}{k_3}\left(\frac{k_1}{k_2} \cdot \frac{C(185)}{C(295)} - 1\right)$$

$$= \frac{k_2}{k_3}\left(\frac{k_1}{k_2}x - 1\right) \qquad \text{--- (6)}$$

where $x = \frac{C(185)}{C(295)}$.

Now $\frac{k_1}{k_2}$ involves the relative efficiency of the detector at 185 and 295 KeV, and must be determined experimentally by measuring x_{Ra}, the value of x for the spectrum of pure Ra^{226} in equilibrium with its daughters. In this case, $N_U = 0$ and hence

$$x_{Ra} = \frac{k_2}{k_1} \qquad \text{--- (7)}$$

Thus (6) becomes

$$\frac{N_U}{N_{Ra}} = \frac{k_2}{k_3}\left(\frac{x}{x_{Ra}} - 1\right) \qquad \text{--- (8)}$$

From (3), $\frac{k_2}{k_3} = \frac{\lambda_{Ra}P_{Ra}(185)}{\lambda_U P_U(185)} = \frac{4\cdot32.10^{-4}.4}{9\cdot75.10^{-10}.54} = 3.29.10^4$

where $P_{Ra}(185)$ and $P_U(185)$ are obtained from LEDERER (1969).

$$\therefore \quad \underline{\frac{N_U}{N_{Ra}} = 3\cdot29.10^4\left(\frac{x}{x_{Ra}} - 1\right)} \qquad \text{--- (9)}$$

When radioactive equilibrium exists between U^{238} and Ra^{226},

$$N_{Ra}\lambda_{Ra} = N_{U1}\lambda_{U1}$$

where λ_{U1}, N_{U1}, are the decay constant and number of atoms respectively, of U^{238}.

But $\frac{N_U}{N_{U1}} = \frac{0.71}{99.28}$

$$\therefore \left(\frac{N_U}{N_{Ra}}\right)_{eq} = \frac{\lambda_{Ra}}{\lambda_{U1}} \cdot \frac{0\cdot71}{99\cdot28} = \frac{4\cdot32.10^{-4}}{1\cdot53.10^{-10}} \cdot \frac{0\cdot71}{99\cdot28} = 2\cdot01.10^4$$

and the value of x for a sample in equilibrium, x_e, from (9) is given by

$$2\cdot01.10^4 = 3\cdot29.10^4\left(\frac{x_e}{x_{Ra}} - 1\right)$$

$$\therefore \quad \underline{x_e = 1\cdot61x_{Ra}} \qquad \text{--- (10)}$$

Consider a sample containing N_U atoms of U^{235}. If the sample were in radioactive equilibrium,

$$(N_{Ra})_{eq} = \frac{N_U}{3\cdot 29.10^4 \left(\frac{x_e}{x_{Ra}} - 1\right)} = \frac{N_U}{2\cdot 01.10^4}$$

In general, however, N_{Ra} will be

$$N_{Ra} = \frac{N_U}{3\cdot 29.10^4 \left(\frac{x}{x_{Ra}} - 1\right)}$$

Hence the percentage equilibrium radium, R, is

$$R = \frac{N_{Ra}}{(N_{Ra})_{eq}} = \frac{0.61}{\left(\frac{x}{x_{Ra}} - 1\right)} .100\% \qquad \text{--- (11)}$$

For the spectrometer system used in the present work the value of x_{Ra} was found to be 0·607 (Fig. III-6). It may be noted that the relative detector efficiency can now be calculated, that is

$$\frac{E(185)}{E(295)} = \frac{P_{Pb}(295)}{P_{Ra}(185)} \cdot 0\cdot 607 = 2.86$$

Substitution of the value $x_{Ra} = 0.607$ in equation (10) gives

$$\underline{x_e = 0.98}$$

This allows a graph to be drawn giving percentage equilibrium radium, R, as a function of x, using (11). This is shown in Fig. III-8. From this graph, R can be determined directly from the experimental count-rates C(185) and C(295). The appropriate value of x_{Ra} for any other Ge(Li) detector can be found by measuring the ratio $\frac{C(185)}{C(295)}$ for a pure Ra^{226} source.

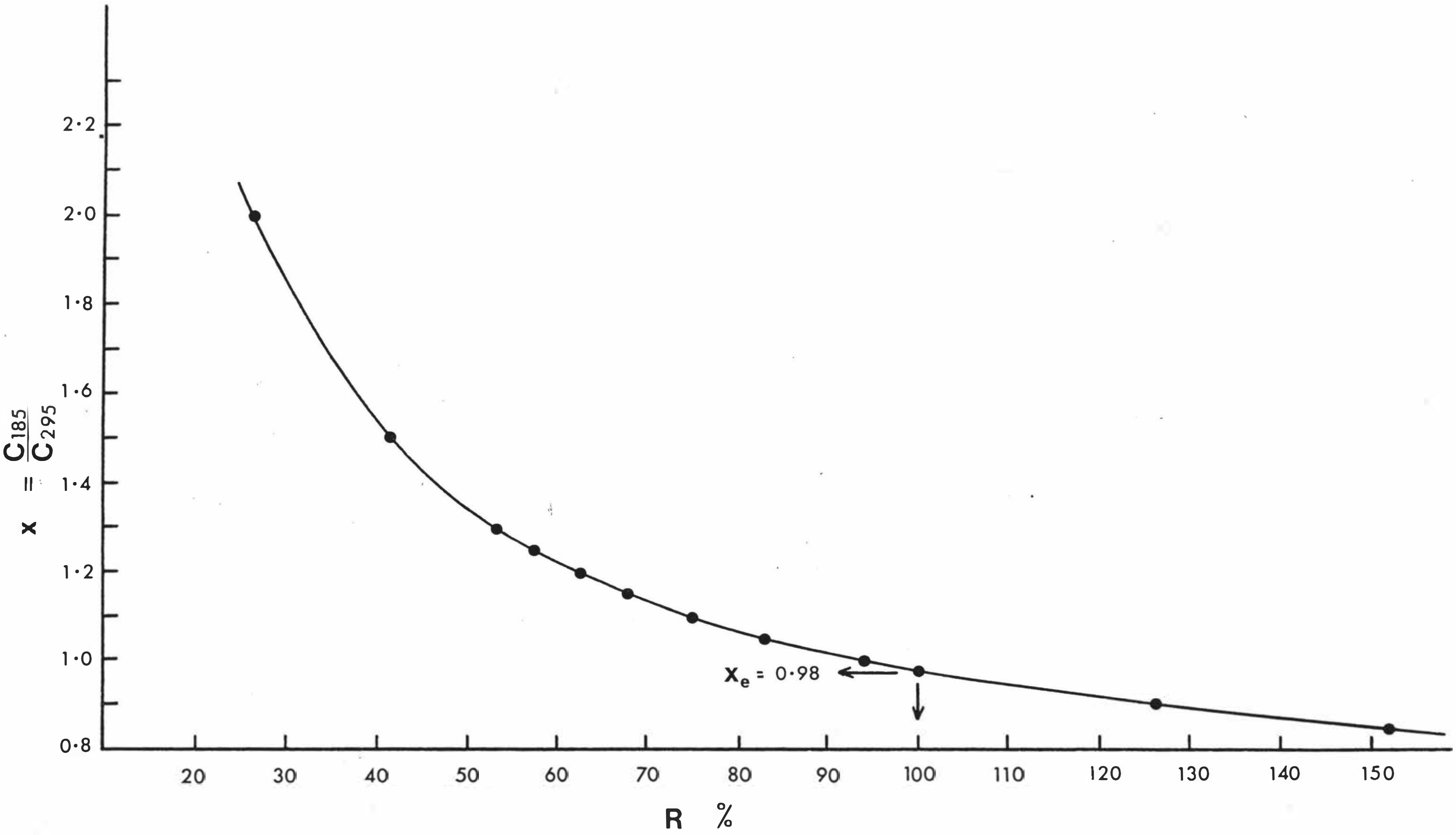


Fig. III - 8 Theoretical curve of $\frac{C(185)}{C(295)}$ as a function of the percentage equilibrium radium

(b) The Isotopic Composition of Uranium Minerals from the Lower Buller Gorge

The gamma spectra of three uranium standards and various primary and secondary minerals, selected from both the North and South Side deposits were obtained, and their respective C(295)/C(185) ratios were measured. From this ratio the "percentage equilibrium radium", R, was calculated. Table III-2 shows the values obtained.

As has been previously mentioned, the mineralogy of the uranium deposits has been thoroughly investigated and has been shown to consist mainly of coffinite on the North Side and uraninite on the South Side, with both sides containing the secondary minerals, gummite, torbernite, autunite and uranophane. However, because of the physical differences observed among many of the "uraninite" samples measured, it was considered necessary to investigate their mineral form. For example, the samples labelled 4 and 5 in Table III-2 were in fact obtained from the same rock, the top half of which was black and the bottom half bright yellow. Analysis of each fraction gave 17.5 and 16.0 percent uranium respectively. The corresponding values of R show that the black fraction is nearer to equilibrium than is the yellow fraction.

Mineral identification was effected by the use of an X-ray powder diffractometer. The samples studied had previously been separated into three density fractions by use of bromoform, methylene iodide and clerici solution. The fraction of the original sample which had a density greater than clerici solution was used for the powder mount. The identifications obtained are given in Table III-2. From this table it is seen that none of the uranium

TABLE III - 2

The Equilibrium State of Various Uranium Minerals from the Lower Buller Gorge

Sample No.	Mineral Form	185	295	185/295	R%
1	β - UO_2	3.14	3.00	1.045	83
2	β - UO_2	6.75	5.50	1.225	59
3	β - UO_2	11.60	11.30	1.030	85
4	β - UO_2	13.10	12.90	1.02	86
5	Ianthinite $UO_2.5UO_3.10H_2O$	8.30	7.55	1.170	65
6	Coffinite	8.40	7.10	1.185	64
7	Coffinite	10.30	8.48	1.215	61
8	Torbernite*	7.80	6.90	1.130	70
9	$UO_3.2H_2O$	4.80	4.78	1.050	83
10	Autunite*	4.83	2.80	1.725	33

Samples 1-5 and 9 taken from T-J horizon (See Fig. II-10).

Samples 6 and 7 taken from North Side.

Samples 8 and 10 taken from S-C horizon.

*Identified visually.

minerals taken are in equilibrium. This is not unexpected, as petrological studies by WHITTLE (1960) showed that in many cases the uranium minerals were altered due to weathering processes. The fact that the value of R is less than one hundred percent means that either radium has been lost from the sample or the sample is less than one million years old, the time taken to attain equilibrium. WILLIAMS (1957) quotes an age determination of the Rio Tinto Company on a sample of coffinite from the North Bank as lying within the range of one hundred million to one hundred and fifty million years. This indicates a Cretaceous age for the mineralization. Approximate age determinations were obtained for a selection of uraninite samples, from the South Side, by using the Pb^{206}/U^{238} method (KULP ET AL, 1954; ECKELMANN and KULP, 1957) and by making the following assumptions:

(1) The total uranium measured was taken to be U^{238}.

(2) The total lead measured, less an estimated background value, was taken to be Pb^{206}. The background value was obtained by analysing lead in a non-radioactive portion of the matrix materials. With these assumptions the ages of four uraninite samples were calculated to be 77, 97, 130 and 180 million years. These values, supported by the value obtained for the North Bank coffinite, indicate quite clearly that the mineralization is of the order of one hundred million years old and therefore the "percentage equilibrium radium" values of less than one hundred percent must be due to preferential loss of radium. It is usually assumed that uranium is leached preferentially to radium because of its greater solubility. However, if this sequence held for the samples studied, the value of the "percentage equilibrium radium" obtained would be

greater than one hundred percent. Therefore it is concluded by the author that preferential leaching of radium has taken place. This conclusion is supported by the results obtained from two separate experiments carried out by STARIK ET AL (1951) to investigate the relative difficulty of leaching of uranium and radium from uraninite. These authors showed that when uraninite was leached with distilled water, or with various concentrations of nitric acid, or with sodium carbonate solutions, the radium was leached preferentially with respect to uranium in all cases. The second experiment involved the analysis for uranium and radium of the outer-surface, middle-portion and central core of both intact and deformed uraninite samples. The intact samples showed no differences but the deformed samples showed that radium had been preferentially removed with respect to uranium. As WHITTLE has shown that the uraninite samples are slightly weathered, the author's explanation of the values of the "percentage equilibrium radium" obtained for these samples appears consistent. Table III-2 also shows that uranium samples in which the uranium exists as U(VI) are often further from equilibrium than those samples in which the uranium exists as U(IV). The low values of "percentage equilibrium radium" obtained for such samples, may be due to continuous leaching or as a result of insufficient time to attain equilibrium since the initial deposition of the uranium from its original primary mineral. Because of the complexity of this situation, it is considered by the author, that equilibrium studies on secondary uranium minerals provide little information concerning the history of these minerals. This is not so with primary minerals where a knowledge of this equilibrium is most informative.

DISCUSSION

The results presented in Part III of this thesis clearly show that the development of the reported technique for the determination of the "percentage equilibrium radium" was primarily dependent on the elucidation of the low-energy gamma ray spectrum. The successful identification of most peaks was obtained as a result of efficient chemical separations, which reduced the number of interferences from the various isotopes present, accurate pulse-height analyser calibrations, judicious use of standard sources and careful, systematic evaluation of the data of LEDERER (1969). These results showed that the Pb^{214} 295 KeV gamma ray was the most suitable to measure, as an indication of Ra^{226}, as it was free from interference. This made it possible to derive the relationship between the 185 KeV peak (U^{235} and Ra^{226}) and 295 KeV peak in terms of the "percentage equilibrium radium". This method will be referred to in future as the "Direct Gamma Method" (D.G.M.).

The advantages of this method over previous methods are threefold. Firstly, and most important, only radiation from specific isotopes is measured whereas in previous procedures, the total beta and total gamma radiation of all isotopes present is measured. Secondly, the derivation of the equilibrium relationship shows that the "D.G.M." is independent of detector efficiency and as such is superior to the previous methods which require this to be accurately known, a determination which is difficult to obtain. Thirdly, the "D.G.M." is simple to use and requires, depending on the activity of the sample, only fifteen to thirty minutes counting time. The main disadvantage is that it requires a Ge(Li) detector, high resolution pre-amplifier and reasonably sophisticated electronics.

The use of the "D.G.M." for determining the "percentage equilibrium radium" of uranium ores from the Buller Gorge showed that in no instance were any of them in radioactive equilibrium. The significance of this has been discussed and apart from re-emphasing that the mineralization appears to be of Cretaceous age and has undergone slight weathering, will not be discussed further, as the origin and history of the mineralization is outside the scope of this thesis.

It is important to add that the "D.G.M." can also be applied for the quantitative determination of uranium. This simply involves obtaining a spectrum of the uranium sample, measurement of the 295 and 185 KeV peaks and the calculation of the actual number of 185 KeV gamma rays from U^{235} as described earlier in this section. A plot of the number of counts per unit time as a function of uranium content, obtained either by chemical methods or from standards, allows a working curve to be constructed which is applicable to any uranium ore irrespective of its state of equilibrium.

To summarise, this part of the thesis reports on the identification of gamma radiation in the low energy region of the spectrum, 30-360 KeV for naturally-occurring uranium minerals. To the author's knowledge, this is the first time that this has been successfully achieved. Reported also, is the development and successful use, of a new method for the determination of "percentage equilibrium radium", an important quantity in the study of uranium mineralization.

GENERAL DISCUSSION

The aims of this thesis, as mentioned in the General Introduction were threefold:

(1) To develop a method for the analysis of low concentrations of yttrium, thorium and rare earths with the use of a large quartz-optics spectrograph.

(2) To investigate the possible association of the above elements, and any other elements, with uranium in the minerals from the South Side of the Buller River and to study the distribution of these elements in the weathering sequence: minerals, soils, stream sediments. From these results, to examine critically the relative merits of direct analysis of uranium and of associated elements in stream sediments, as a geochemical prospecting method for uranium mineralization.

(3) To develop a method, using only gamma radiation from U^{235} and Ra^{226}, to determine the "percentage equilibrium radium" of uranium minerals.

The results presented in Parts I, II and III of this thesis show that the above aims have largely been achieved.

The analytical section in Part I showed that, by careful selection of conditions, together with an efficient separation scheme, a large quartz-optics emission spectrograph could be successfully used to analyse low concentrations of yttrium, thorium and rare earths. The results obtained for the standard rocks G-1 and W-1 substantiated this claim and indicated the accuracy that can be obtained. Fresh data for the above elements in CAAS syenite were also provided and these agreed well with the results of TENNANT and FELLOWS (1967) and CHAMP (1968), the only other results obtained for these elements in this standard rock. The main disadvantage of the reported technique is that it is not readily applicable as a routine method for the rapid analysis of yttrium, thorium and rare earths in geological samples. This is due to the limitation of the dissolution stage in the preparation of the sample for the ion-exchange column. The solution necessary to ensure separation on the resin, a mixture of acetic acid and nitric acid, is an extremely poor solvent for geological samples. However, if the separation stage of the analytical procedure could be improved, this would then render the method quite suitable for rapid, routine analysis.

Although the geochemical study in Part II showed no apparent association of yttrium, thorium and the rare earths with uranium, the data were, nevertheless, important as they provided new evidence for the possible origin of the Hawks Crag Breccia from the Paparoa Range. Copper, beryllium and lead did, however, show good correlations at various stages down the weathering sequence; of these elements, copper showed the best correlation in the stream sediments. This study showed that in this area of high rainfall and rugged topography, the analysis of copper as a "pathfinder" for uranium appeared to be a better indication of the known mineralization than was the analysis of uranium. This was explained by the lower solubility of copper compared with uranium. However, the use of copper alone as an indication of uranium mineralization was not considered completely reliable because of unrepresentative sampling and the presence of different amounts of unmineralized matrix material. This variation in sampling often arose as a result of a lack of fine sediment in the main flow of the streams. To overcome these two problems, ratios of lead, zinc and copper were taken in an attempt to minimise such fluctuations. In general the results obtained from these ratios showed similar patterns to those reflected by the analysis of copper alone. It is considered by the author, however, that although the results appear promising, a more detailed stream-sediment sampling programme would need to be carried out before this technique could be considered completely reliable. With regard to direct analysis of uranium in stream sediments, this study did show that, except when samples were taken within thirty to forty yards of a reasonably large, active outcrop of uranium mineralization, the analysis of stream sediments for uranium gave no indication of surrounding mineralization. In fact, uranium anomalies in stream sediments could only be detected over distances similar to those for which radiometric instruments were useful.

It is considered that Part II of this thesis has clearly shown that, because of climatic or topographical differences, techniques which are used for geochemical prospecting of uranium mineralization in other parts of the world may not be invariably applicable in other areas. It is to be expected that the pathfinder elements will also vary from one uranium deposit to another and it is therefore always necessary to carry out a preliminary orientation survey of each new area. From a knowledge of the geology of the area, elements likely to be associated with the mineral being sought can be chosen.

Part III of this thesis is largely a study of the gamma ray spectra of uranium minerals, and shows the development of a new technique for the determination of "percentage equilibrium radium" (in this thesis called the "Direct Gamma Method"), which will provide geologists with a useful tool for the study of the origin and history of uranium mineralization. Other methods are available to determine the "percentage equilibrium radium", but the "D.G.M." has two main advantages. Firstly, it measures only radiation arising from the isotopes concerned, whereas the previous methods involve assumptions concerning the assignment of radiation to the parent isotopes. Secondly, the "D.G.M." is independent of detector efficiency and relies only on a ratio of the number of counts obtained from the 185KeV and 295KeV gamma rays respectively and not on the absolute determination of the number of beta and gamma radiations emitted. The accuracy of the "D.G.M." depends only on the accuracy of the values for the decay constants, λ_{Ra} and λ_{W}, and on the accuracy of the values determined for the respective gamma ray decay path $P_{Ra}(185)$ and $P_{U}(185)$. The accuracy of these values is considered to be ± 2%, which yields an error of ± 5% in the value for the "percentage equilibrium radium". The error due to counting statistics can be made almost negligible by increasing the counting time. At the present stage of development, the "D.G.M." can be used to determine the "percentage equilibrium radium" for minerals containing 0.1% U_3O_8 or greater with an accuracy of ± 5%.

The results from age determinations and the values obtained for the "percentage equilibrium radium" suggested, quite strongly, that the uranium mineralization has remained in its original site of deposition over a period of approximately one hundred million years. These results do provide information concerning the history of the uranium but they do not tell us anything about its origin. Although some consideration of the origin was made in Part II, a fuller discussion of this subject is outside the scope of this thesis.

To summarise, this thesis has developed two analytical methods, one in the field of elemental analysis and the other in the field of radiochemistry, which should find applications in the fields of analytical chemistry, geochemistry and geology. The critical evaluation of geochemical prospecting methods, discussed in this thesis, should provide the basis for the development of such techniques for use in further uranium prospecting in New Zealand.

The author considers that future studies in the uraniferous, Buller Gorge region should be carried out with the following aims:

(1) To substantiate further the validity of the use of copper as a pathfinder for uranium by a more detailed and comprehensive survey of the streams draining this area.

(2) To test the hypothesis that uranium was leached from its origin in the granite of the Paparoa Range and redeposited in the present site in the Hawks Crag Breccia. Such a study would include the analysis of the trace-element content of the granites from both the Paparoa Range and Hawks Crag Breccia in conjunction with petrological investigations.

The results of this research should provide valuable information which would indicate suitable areas for further uranium prospecting in New Zealand.

REFERENCES

AHRENS L. H. A survey of the quality of some of the principal abundance data of geochemistry. Progress in Physics and Chemistry of the Earth 2, 30, (1957).

AHRENS L. H. The lognormal distribution of the elements. Geochim. Cosmochim. Acta 5, 49, (1954).

AHRENS L. H., EDGE R. A. and BROOKS R. R. Investigations on the development of a scheme of silicate analysis based principally on spectrographic and ion exchange techniques. Anal. Chim. Acta 28, 551, (1963).

AHRENS L. H. and TAYLOR S. R. Spectrochemical Analysis. 2nd Ed., (1961). Addison-Wesley.

ALEKSIEV E. and BOYADJIEVA R. Content of rare earths in the standard igneous rocks G-1, W-1 and G-B. Geochim. Cosmochim Acta 30, 511, (1966).

ANDERSON N. R. and HERCULES D. M. Flurometric determination of uranium with Rhodamine B. Anal. Chem. 36, 2138, (1964).

BALASHOV Y. A., RONOV A. B. and MIGDISOV A. A. The effect of climate and facies environment on the fractionation of the rare earths during sedimentation. Geochemistry No. 1, 951, (1964).

BECK A. C., REED J. J. and WILLETT R. W. Uranium mineralization in the Hawks Crag Breccia of the Lower Buller Gorge region, South Island, New Zealand. N.Z. Jl. Geol. and Geophys. 1, 432, (1958).

BOSIN S. and BOGDAN R. The interpretation of radiometric mineral determinations. Rev. minerlor. (Buckarest) 11, 412, (1960).

BOSWELL C. R. and BROOKS R. R. Improved methods for the measurement of spectral line intensities. Appl. Spectr. 19, 147, (1965).

BROOKES C. J., BETTELEY I. G. and LOXSTON C. M. Mathematics and Statistics for Chemists. Wiley, N.Y. (1966).

BROOKS R. R. and WHITEHEAD N. E. A fluorimetric attachment for an atomic absorption spectrophotometer. Jl. Scientific Instruments 1, 879, (1968).

BROWN R. and WOLSTENHOLME W. A. Analysis of geological samples by spark source mass spectrometry. Nature 201, 598, (1964).

BRUNFELT A. O. and STEINNES E. Instrumental neutron-activation analysis of standard rocks. Geochim. Cosmochim. Acta 30, 921, (1966).

CANNON H. L. The development of botanical methods of prospecting for uranium on the Colarado Plateau. U. S. Geol. Survey Bull. 1085-A, 1, (1960a).

CANNON H. L. and KLEINHAMPL F. J. Botanical methods of prospecting for uranium. United Nations 801, (1956).

CARSWELL D. J. Separation of thorium and uranium nitrates by anion exchange. J. Inorg. Nucl. Chem. 3, 384, (1957).

CHAMP W. H. Private communication. Geol. Survey, Ottawa, Canada.

CHERRY R. D. The determination of thorium and uranium in geological samples by an alpha-counting technique. Geochim. Cosmochim. Acta 27, 183, (1963).

CHERRY R. D. and ADAMS J. A. Gamma-spectrometric determination of thorium, uranium and potassium in tektites. Geochim. Cosmochim. Acta 27, 1089, (1963).

COBB J. C. Determination of lanthanide distribution in rocks by neutron-activation analysis of standard rocks. Anal. Chem. 39, 127, (1967).

COHEN N. E., BROOKS R. R. and REEVES R. D. Pathfinders in geochemical prospecting for uranium in New Zealand. Econ. Geol. (in press), (1969).

COHEN N. E., REEVES R. D. and BROOKS R. R. Use of a large quartz spectrograph for the determination of thorium, yttrium and the rare earths in silicates. Talanta 15, 1449, (1968).

COOTE G. Ge(Li) gamma ray detectors : Their fabrication, commissioning and maintenance. Institute of Nuclear Sciences Rept.No. INS-R-42, (1967).

ECKELMANN W. R. and KULP J. L. Uranium-lead method of age determination. Bull. Geol. Soc. Am. 68, 1117, (1957).

EICHHOLZ G. G., HILBORN J. W. and McMAHON C. The determination of uranium and thorium in ores. Can. Jl. Phys. 31, 613, (1953).

DANON J. Separation of thorium and rare earth elements in nitric acid media by anion exchange. J. Inorg. Nucl. Chem. 5, 237, (1958).

DEARNALY G. and NORTHROP D. Semi-conductor counters for nuclear radiations. Spon (1966).

DENSON N. M., ZELLER H. D. and STEPHENS J. G. Water sampling as a guide in the search for uranium deposits and its use in evaluating widespread volcanic units as potential source beds for uranium. United Nations 794, (1956).

FAIRBAIRN H. W., SCHLECHT W. G., STEVENS R. E., DENNEN W. H., AHRENS L. H. and CHAYES F. A. A cooperative investigation of precision and accuracy in chemical, spectrochemical and modal analysis of silicate rocks. U.S. Geological Survey Bulletin No. 980, (1951).

FARIS J. P. and WARTON J. W. Anion exchange resin separation of the rare earths, yttrium and scandium in nitric acid-methanol mixtures. Anal. Chem. 34, 1077, (1962).

FARIS J. P. Spectrographic determination of scandium, yttrium and the rare earths in thorium. Appl. Spectr. 12, 157, (1958).

FASSEL V. A. and WILHELM H. A. The quantitative spectrographic analysis of the rare earth elements. J. Opt. Soc.Am. 38, 518, (1948).

FASSEL V. A. The quantitative spectrographic analysis of the rare earth elements III. Determination of major constituents in complex mixtures. J. Opt. Soc. Am. 39, 187, (1949).

FIX P. F. Hydrogeochemical exploration for uranium. United Nations 788, (1956).

FISCHER R. A. and YATES F. Statistical Tables for Biological, Agricultural and Medical Research. Oliver and Boyd, London (1957).

FLEISCHER M. Additional data on rocks G-1 and W-1, 1965-1967. Geochim. Cosmochim. Acta 33, 65, (1969).

FLEISCHER M. Summary of new data on rock samples G-1 and W-1, 1962-1965. Geochim. Cosmochim. Acta 29, 1263, (1965).

FRITZ J. S. and GARRALDA B. B. Anion exchange separation of thorium using nitric acid. Anal. Chem. 34, 1387, (1962).

GANLOFF A. M., COLLIN C. R., GRIMBERT A. and SANSELME H. Application of geophysical and geochemical methods to the search for uranium. United Nations 140, (1958).

GAVRILOVA L. K. and TURANSKAYA R. V. Distribution of rare earths in rock forming and accessory minerals of certain granites. Geochemistry No. 2, 163, (1958).

GOLDSCHMIDT V. M. Geochemistry. Oxford University Press, London, (1958).

GORDON G. E., RANDLE K., COLES G. G., CORLISS J. B., BEESON M. H. and OXLEY S. S. Instrumental activation analysis of standard rocks with high-resolution gamma ray detectors. Geochim. Cosmochim. Acta 32, 369, (1968).

GRACE J. D. and BATES T. F. Determination of uranium equilibrium in rocks, using α and fission fragment radiography. Geochim. Cosmochim. Acta 17, 226, (1959).

GRANGE L. I. Prospecting for radioactive minerals in New Zealand. N. Z. Geol. Survey, (1954).

GRIMALDI F. S., MAY I., FLETCHER M. H. and TITCOMB J. Collected papers on methods of analysis for uranium and thorium. U.S. Geol. Survey Bull. 1006, (1954).

GRIMALDI F. S., MAY I. and FLETCHER M. H. Fluorimetric methods of uranium analysis. U.S. Geol. Survey Circular 199, (1952).

GROVES A. W. Silicate Analysis. 2nd Ed., 1951. Thomas Murby, London.

HASKIN L. and GEHL M. The rare earth contents of standard rocks G-1 and W-1 and their comparison with other rare earth distribution patterns. J. Geophys. Res. 68, 2037, (1963).

HAWKES H. E. and WEBB J. S. Geochemistry in Mineral Exploration. Harper and Row, N.Y. Weatherhill Inc., Tokyo, (1965).

HEIR K. S. and ROGERS J. J. Radiometric determination of thorium, uranium and potassium in basalts and in two magmatic differentiation series. Geochim. Cosmochim. Acta 27, 137, (1963).

HILLEBRAND W. F. and LUNDELL G. E. F. "Applied Inorganic Analysis", with special reference to the analysis of metals, minerals and rocks. John Wiley N.Y., (1953).

HILLEBRAND W. F. Some principles and methods of rock analysis. U. S. Geol. Surv. Bull. 176, (1900).

HOLLANDER J. M. The impact of semiconductor detectors on gamma ray and electron spectrography. Nucl. Instrum. Methods 43, 65, (1966).

ILLSLEY C. T., BILLS C. W. and POLLOCK J. W. Geochemical methods of uranium exploration. United Nations 126, (1958).

IMBRIE J. Biometrical methods in the study of Invertebrate fossils. Bull. Am. Museum Natural History 108, 211, (1956).

JONES R. W., FROST I. C. and RADER L. F. A comparison of chemical analyses of plants and soils as aids to prospecting for uranium in the Southern Black Hills, South Dakota. Int. Geol. Cong. XX Session 366, (1956).

JUDSON S. and OSMOND J. K. Radioactivity in ground and surface water. Am. Jl. Sci. 253, 104, (1955).

KNISELEY R. N., FASSEL V. A., QUINNEY B. B., TREMMEL C., GORDON W. A. and HAYES W. J. Quantitative spectrographic analysis of the rare earth elements IX. Spectrochim. Acta 12, 332, (1958).

KORKISCH J. and ARRHENIUS G. Separation of uranium, thorium and the rare earths by anion exchange. Anal. Chem. 36, 850, (1964).

KULP J. L., BATE G. L. and BROECKER W. S. Present status of the lead method of age determination. Am. Jl. Sci. 252, 345, (1954).

LEDERER C. M., HOLLANDER J. M. and PERLMAN I. Table of Isotopes. (1969) Wiley.

MANN H. M., JANARKEK F. J. and HELENBERG H. W. Preparation of large volume planar Germanium detectors and results of their use in nuclear physics experiments. IEEE Transactions on Nuclear Science 13, 336, (1966).

MATHESON G. ROTHE J. P., SIFFERT P. and COCHE A. Determination of radioactivity in rocks by gamma spectrometry with the aid of a Ge(Li) detector. (In French). C.R. Acad. Sc. Paris t. 264, (1967).

McCARTY C. N., SCRIBNER L. R., LAWRENZ M. and HOPKINS B. S. Quantitative estimation of the rare earths by means of their arc spectra. Ind. Eng. Chem. Anal Ed. 10, 184, (1938).

MEGGERS W. F., CORLISS C. H. and SCRIBNER B. F. Tables of Spectral-Line Intensities. NBS Monograph 32-Part II, (1961).

MIDDLETON G. V. Statistical Inference in Geochemistry from Studies in Analytical Geochemistry, D. M. Shaw. University of Toronto Press, (1963).

MITCHELL R. L. The spectrographic analysis of soils, plants and related materials. Tech. Comm. No. 44 of the Commonwealth Bur. Soil Science, Harpenden, England. (1948).

MORGAN P. G. and BARTRUM J. A. The geology and mineral resources of the Buller-Mokihinui subdivision, Westport Division. N.Z. Geol. Survey Bull. 17, (1915).

MYKYTIUK A., RUSSELL D. S. and BERMAN S. S. Direct determination of small quantities of rare earth and yttrium oxides in thoria by emission spectroscopy. Talanta 13, 175, (1966).

NELMS J. R. and VOGEL R. S. Direct spectrometric determination of Dy, Eu, Gd, and Sm in high-purity thorium dioxide. Appl. Spectr. 21, 242, (1967).

NICHOLS E. L. and SLATTERY M. K. Uranium as an activator Jl. Am. Opt. Soc. 12, 449, (1926).

NICHOLIS G. D., GRAHAM A. L., WILLIAMS E. and WOOD M. Precision and accuracy in trace element analysis of geological materials using solid-source, spark mass spectrography. Anal. Chem. 39, 584, (1967).

NIETZEL O. A., WESSLING B. W. and DESESA M. A. Ion exchange-spectrophotometric determination of thorium. Anal. Chem. 30, 1182, (1958).

PRICE G. R., FERRETTI R. J. and SCHWARTZ S. Fluorophotometric determination of uranium. Anal. Chem. 25, 322, (1953).

RADWAN Z., STRZYZEWSKA B. and MINCZEWSKI J. Analysis of lanthanum, yttrium, europium, praseodymium, neodymium and samarium by the carrier-distillation method. Appl. Spectr. 17, 60, (1963).

RAFTER T. A. Sodium peroxide decomposition of minerals in platinum vessels. Nature 75, 485, (1950).

ROSE H. J.Jr., MURATA K. J. and CARRON M. K. A chemical-spectrochemical method for the determination of rare earth elements and thorium in cerium minerals. Spectrochim. Acta 6, 161, (1954).

SATO T. Extraction of uranium and thorium from HCl solutions by Tributyl Phosphate. J. Appl. Chem. 16, 53, (1966).

SCHMIDT R. A., SMITH R. H., LASCH J. E., MOSEN A. W., OLEHY D. A. and VASILEVSKIS J. Abundances of the fourteen rare earth elements, scandium and yttrium in meteoritic and terrestial matter. Geochim. Cosmochim. Acta 27, 577, (1963).

SCRIBNER B. F. and MULLIN H. R. Carrier-distillation method for spectrographic analysis and its application to the analysis of uranium-base materials. Jl. of the Research of the N.B.S. Res. Paper R.P. 1753 37, (1946).

SILL C. W. and PETERSON H. E. Fluorometric behaviour of uranium in H_3PO_4. Anal. Chem. 19, 646, (1947).

SINE N. M., TAYLOR W. D., WEBBER G. R. and LEWIS C. L. Third report of analytical data for CAAS Sulphide ore and Syenite rock standards. Geochim. Cosmochim. Acta 33, 121, (1969).

SPEDDING F. H., FULMER E. I., POWELL J. E. and BUTLER T. A. The separation of rare earths by ion exchange V. Investigations with one-tenth per cent citric acid - ammonium citrate solutions. J. Am. Chem. Soc. 72, 2354, (1950).

STARIK I. E., MELIKOVA O. S. and SOBOTOVITCH E. V. Distribution of radioelements in various parts of uraninite. C.A. 51, 6460h.

STARIK I. E., STARIK F. E. and PETRYAEV E. P. Relative leaching of uranium and radium isotopes from uraninite. C.A. 51, 6461b.

STEADMAN L. T. The carbon arc in oxygen for the spectrochemical determination of potassium. Phys. Rev. 63, 322, (1948).

STERN T. W. and STIEFF L. R. Radium-uranium equilibrium and radium-uranium ages of some secondary minerals. U.S. Geol. Survey Professional Papers 320, 151, (1959).

STRELOW F. W. E. An accurate determination of rare earths and scandium in South African Carbonatites using separation by ion exchange. Anal. Chem. 38, 127, (1966).

TAKETATSU T. Anion exchange separation of rare earth elements and thorium from uranium carbonate solutions. Talanta 10, 1077, (1963).

TAYLOR S. R. Geochemical analysis by spark source mass spectrography. Geochim. Cosmochim. Acta 29, 1243, (1965).

TENNANT C. B. and WHITE M. L. Study of the distribution of some geochemical data. Econ. Geol. 54, 1281, (1959).

TENNANT W. C. and FELLOWS S. K. Spectrochemical determination of trace amounts of rare earths. Geochim. Cosmochim. Acta 31, 1473, (1967).

TENNANT W. C. and SEWELL J. R. A survey of the rare earth contents in stream sediments of the Paparoa Range, New Zealand. N. Z. Jl. Sci. 10, No. 3 (1967).

TOWELL D. G., VOLFOVSKY R. and WINCHESTER J. W. Rare earth abundances in the standard granite G-1 and standard diabase W-1. Geochim. Cosmochim Acta 29, 569, (1965).

VALLEE B. L., REIMER C. B. and LOOFBOUROW J. R. The influence of argon, helium, oxygen and carbon dioxide on emission spectra in the D.C. arc. J.Opt.Soc.Am. 40, 751, (1950).

VASSILAKI M., SALMON L. and GIBSON J. A. Measurement of radioactivity in soil. Geochim. Cosmochim. Acta 30, 601, (1966).

WARREN H. V. and DELAVAULT R. E. Pathfinding elements in geochemical prospecting. Congress Geologico International XX Sesion Cuidad De Mexico, (1956).

WASHINGTON H. S. The Chemical Analysis of Rocks. John Wiley, N.Y., 1930.

WEBBER G. R. Second report of analytical data for CAAS syenite and sulphide standards. Geochim. Cosmochim. Acta 29, 229, (1965).

WELLMAN H. W. Ohika beds and post Hokonui Orogeny. N.Z. J. Sci. Tech. B. 32, 228, (1950).

WHITEHEAD N. E. and BROOKS R. R. A comparative evaluation of scintillometric, geochemical and biogeochemical methods of prospecting for uranium. Econ. Geol. 64, 50, (1969a).

WHITEHEAD N. E. and BROOKS R. R. Radioecological observations on plants of the Lower Buller Gorge Region of New Zealand and their significance for biogeochemical prospecting. Jl. App. Ecology 6, 301, (1969b).

WHITTLE A.W.G. Mineralogy and petrology of the Buller Gorge uranium field. ANDEL Rept No. 33, 29pp., (1960).

WILLIAMS G. J. Economic Geology of New Zealand. Eighth Commonwealth Mining and Metallurgical Congress, Australia and New Zealand, 1965.

WILLIAMS X. Statistics in the interpretation of geochemical data. N.Z. Jl. Geol. and Geophys. 10, 771, (1967).

WODZICKI A. Geochemical prospecting for uranium in the Lower Buller Gorge, New Zealand. N.Z. Jl. Geol. and Geophys. 2, 602, (1959a).

WODZICKI A. Radioactive boulders in Hawks Crag Breccia. N.Z. Jl. Geol. and Geophys. 2, 385, (1959b).

YOUNG E. J. Studies of trace elements in sediments. Ph.D. Thesis, M.I.T. Cam. Mass. (1954).