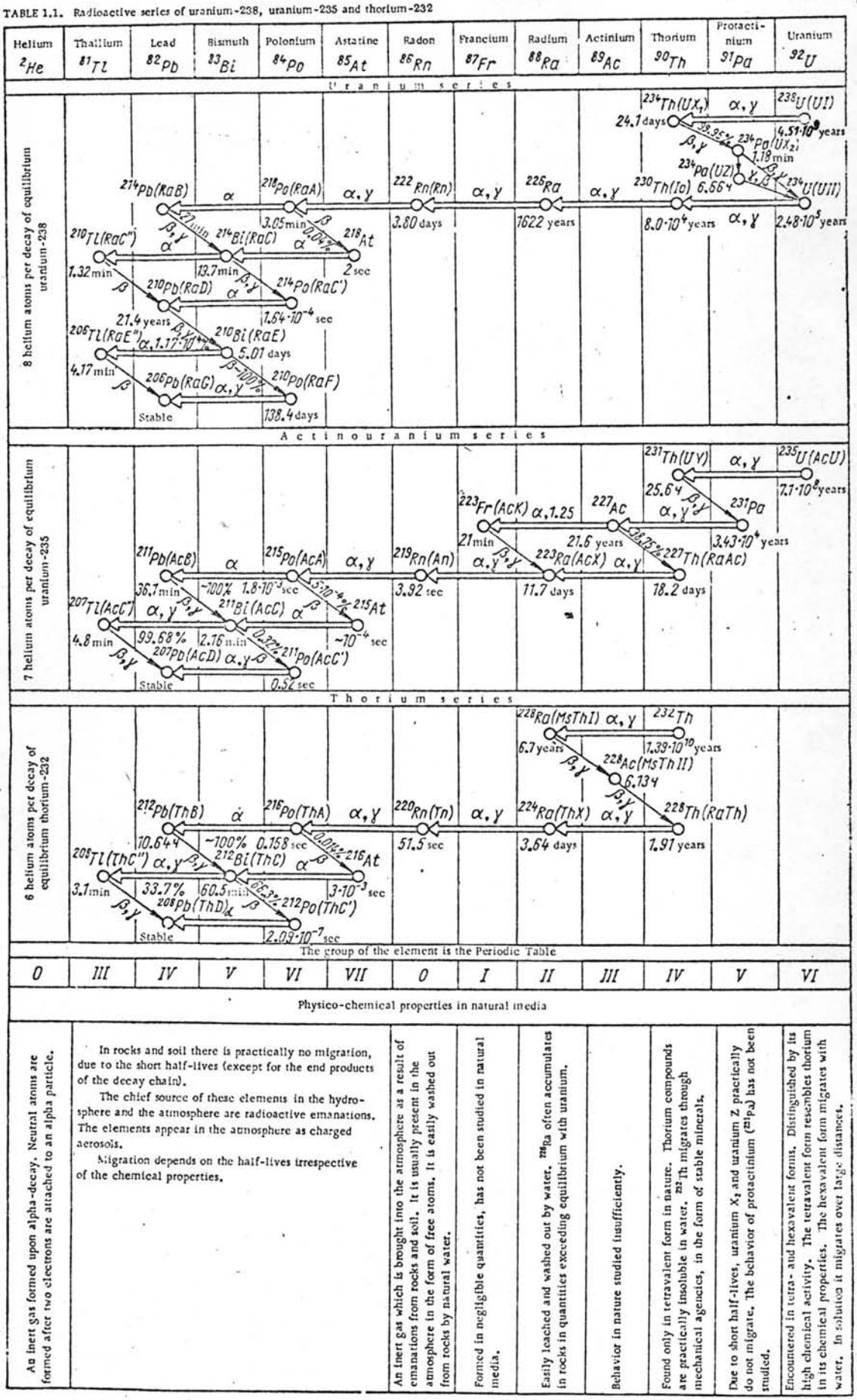
# CHAPTER I

## INTRODUCTION

Uranium and thorium are both natural radioactive elements which were discovered by a German chemist, Martin Heinrich Klaproth in 1789 and by the Swedish chemist, Berzelius in 1828. respectively. Uranium found in nature consists of three isotopes, $U^{238}$(main isotope, abundant 99.276%), $U^{235}$(0.718%) and $U^{234}$ (0.0056%) whereas thorium consists of only one isotope, $Th^{232}$ (100%). Thorium is several times more abundant than uranium. Uranium - 238, uranium - 235 and thorium - 232 are the first members of the three natural occurring radioactive disintegration series, which members and modes of decay are shown in Table 1.1 (1)

TABLE 1.1. Radioactive series of uranium-238, uranium-235 and thorium-232



## 1.1 Uranium and thorium minerals and ores

1.1.1 Uranium Uranium makes up about 0.0004% of the earth's crust. Its crustal abundance varies with the types of rock. The uranium content of basic igneous rocks is considerably smaller than that of acidic ones. Primary uranium minerals such as uraninite ($UO_2$) are found in the high silica igneous rocks called pegmatites. Pitchblende is the most important source of uranium as well as radium, actinium, polonium and helium. It often contains as much as 60% uranium. Carnotite, a hydrated potassium uranyl vanadate, is also an important source containing up to about 7% uranium. Other rarer uranium ores are thorite, autunite, curite, brannerite, betafite and euxenite.

1.1.2 Thorium Thorium is widely distributed in the earth's crust of which it comprises 0.001 - 0.002%. It is found in many minerals, usually associated with rare earths, and often with Ti, Nb, Ta and U. Thorium minerals are mostly encountered in igneous rocks, pegmatites, veins and alluvia, of which the last one is the most important industrial source. The two richest thorium minerals are thorite, a thorium silicate ($ThSiO_4$) containing 62% thorium and thorianite $\{(Th, U)O_2\}$, a thorium-uranium oxide containing 88% thorium. At present the most important source of thorium is monazite, a rare-earth-thorium orthophosphate $\{(Ce, La, Y, Th)PO_4\}$ in addition to the presence of small amounts of Ca, Al, Mg, Si, Ti, Zr and trace amounts of U.

The commercial monazite contains 5 - 9% thorium dioxide. It is found in many countries, primarily in beach deposits, such as India, Brazil, Malaysia, Australia, Union of Africa and the United States. Informations presented at the First Geneva Conferences on the Peaceful Uses of Atomic Energy reveal that new sources of thorium have been found in South Korea (2), Sweden (3), Norway (4), Jugoslavia (5), Greece, Thailand and Australia (6).

Monazite usually occurs in association with other heavy minerals such as rutile, zircon, ilmenite, magnetite, cassiterite and garnet. To separate monazite from these minerals, the processes either by gravity concentration, floatation or magnetic separation are used.

1.1.3 Characteristics of monazite (7) Monazite is brittle and, owing to the presence of thorium, small amounts of uranium and their daughter products, is radioactive. It appears as monoclinic crystals with colors ranging from light brown to hyacinth red but the yellowish-brown to honey-yellow is the most characteristic. It has an index of refraction of 1.786 to 1.837, a specific gravity of 4.6 to 5.3; the hardness varies between 5 and 5.5. Monozite is the only common radioactive mineral found in Thailand (8). It occurs in association with many other heavy minerals, for examples, cassiterite, ilmenite, colombite-tantalite and zircon in the tin dredging areas of Southern Thailand such as the Phuket and the

Phang-Nga tin districts which are situated on the western side of the Kra Isthmus in Peninsular. These areas which extend from $7^{\circ}45'$ to $9^{\circ}10'$ north latitude, are bound on the west by the Andaman Sea and on the South-east by the Phang-Nga Bay (9). It is found that nearly 40% of the mines along the west coast of the Peninsular provinces, Southern Thailand from Ranong down to Phuket, show variable amount of radioactive minerals which will certainly be of economic importance in the future.

## 1.2 Uses of thorium and uranium

Thorium is of commercial importance (10). About 50% of the total consumption are used for the manufacture of Welbach-type incandescent gas mantles, 30% are used in producing magnesium alloys and 10% are used for the production of dispersion-hardened metals, such as nickle, stainless steel and tungsten. The development of thorium as a source of nuclear energy began in 1947 when it was discovered that thorium - 232 ($Th^{232}$) can be converted to uranium - 233 ($U^{233}$) after the capture of a neutron. The reaction and the disintegration process can be represented by the following equation

$$Th^{232} + {}_{0}n^{1} \longrightarrow Th^{233} \xrightarrow[22.4\ min.]{\beta^-} Pa^{233} \xrightarrow[27.4\ d]{\beta^-} U^{233}$$

The produced $U^{233}$ is used as a fissionable material in the breeder reactor which produces the energy being useful for many fields.

Uranium is a minor commercial importance, mostly used in the manufacture of color glass ceramics and nickel-base alloy for electron tubes.

## 1.3 Methods for the determination of uranium and thorium

The techniques of analysis for the determination of the uranium and thorium contents in natural radioactive ores may be divided into two groups. To the first belong those devoted to pure geophysical and geological investigations for which either chemical or instrumental method is acceptable only in relation to its precision and sensitivity. To the second group belong those methods which are connected with the problem of the extraction of fissionable materials from ores. Here the choice is limited by the requirements of speed and simplicity characteristic of such types of research and it is therefore not advisable to use methods, such as chemical analyses, which require long analysis times.

1.3.1 Chemical methods for the determination of uranium and thorium Chemical methods for the determination of the uranium and the thorium contents in minerals are various and well-studied but they are tedious and complicate since the mineral must be opened first. In the monazite opening process either acids such as hydrofluoric acid (11), potassium hydrogen fluoride (12), sulphuric acid or alkalines such as sodium hydroxide (13) can be used. After digestion, the separation of uranium and thorium from each

others and from interfering elements may be followed by precipitation with hydrogen peroxide in slightly acid solution (14), by organic solvent extraction with mesityl oxide (15), or by ion exchange (16, 17). The quantitative determination of uranium and thorium by gravimetric, titrimetric and spectrophotometric methods are briefly summarized.

1.3.1.1 Gravimetric method. In the gravimetric method, uranium and thorium may be precipitated with hydrogen peroxide at pH $\sim$ 1.8 in the absence of impurities that form insoluble peroxides. The peroxides are ignited to $U_3O_8$ at 900°C and to $ThO_2$ at 1100°C. Then they are weighed directly after drying. Complexing ions such as, fluoride, chloride, sulphate and oxalate as well as iron must be absent. The method is suitable for samples containing large amounts of uranium and thorium.

1.3.1.2 Titrimetric method. In complexiметric titration, EDTA is most frequently used as the complexing agent for uranium and thorium in forming soluble complexes. The thorium complex formed contains 1 mole of EDTA per 1 mole of thorium and the end point which is reached at pH 2.5 to 3.5 in nitric acid medium can be detected with alizarin red S (18) or with xylenol orange (19). In the former case, the color changes from red to lemon yellow, whereas in the latter case the color changes from red to pale yellow.

The complex formed between uranium and EDTA contains 2 moles of EDTA per mole of uranium. Best end-point sensitivity is

at pH 4.4 to 4.6 in a 50% isopropyl alcohol medium with 1-(2-pyridylazo)-2-naphthol (PAN) as indicator.

1.3.1.3 Spectrophotometric method. In the spectrophotometric method, several chromogenic reagents can be used to form complexes with thorium. Among the important ones are bromopyrogallol red (BPR) (20), Eriochrome black T (21), thoron (22), methyl thymol blue and xylenol orange. Their molar absorptivities and sensitivities of detection are given in Table 1.2

Table 1.2

Molar absorptivities and sensitivities of some chromogenic reagents with thorium (20)

| Reagents | Molar absorptivity X $10^4$ | Sensitivity $\mu g/cm^2$ |
|---|---|---|
| Thorin | Not reported (545 nm) | 0.03 |
| Eriochrome black T | 3.50 (700 nm) | 0.004 |
| BPR | 5.08 (645 nm) | 0.004 |
| Methyl thymol blue | 3.93 (568 nm) | 0.006 |
| xylenol orange | 7.70 (568 nm) | 0.003 |

In the case of uranium, dibenzoyl methane (DBM), 1-(2-pyridylazo)-2-naphthol (PAN) and thoron (23) are widely used.

1.3.2 Instrumental analysis of uranium and thorium For rapid assay of uranium and thorium, instrumental methods such as radiometric methods, neutron activation analysis and x-ray fluorescence (24, 25, 26) are in preference. Since the first two mentioned methods are examined in the present work, their principles are discussed briefly.

1.3.2.1 Principle of the radiometric analysis. Radiometric methods can be classified into three groups; the methods of integral measurements, the method of differential measurements and the method of counting the $U^{235}$ and the $Th^{232}$ fission products. In the case of the integral methods in which the $\alpha$, $\beta$ and $\gamma$ radiation emitted by the radioactive families are simultaneously measured, the percentages of uranium and thorium in a sample could be obtained independent of the radioactive equilibrium (RE). The $\beta$-$\gamma$ method from Eichholz (24) and the $\beta$-$\gamma$-$\gamma$ method from S. Sciuti et al. (27) belong to this category. The differential methods consist of the analysis of the energy spectrum of the $\alpha$ or the $\gamma$ components of the radioactive family. In this case, the existence of RE in the sample must be assumed. The methods of counting the $U^{235}$ fission products make use of a fission ion chamber. The sample is irradiated with neutrons and from the fission pulse rate, it is possible to determine the contents of uranium (from thermal fission) and thorium (from fast fission).

In general, minerals containing thorium such as monazite, the existence of RE in the $Th^{232}$ family can be usually assumed since

the longest lived daughter of thorium - 232 is radium - 228 ($Ra^{228}$) with a half-life of 6.7 years, so that RE can be established in about 60 years. The only member of the family that can be lost easily from the sample owing to its emanation property is thoron ($Rn^{220}$). This lost is generally accepted to be insignificant (28) in view of the very short half-life ($t_{\frac{1}{2}}$ = 54 sec.) of this nuclide.

On the other hand, in the uranium - 238 family, there are several long-lived daughter products. Even in radioactive ores which have a geological age of $\geq 10^6$ years where the attainment of the secular equilibrium can be guaranteed, disturbances which perturb the equilibrium of the uranium family can occur. The most frequent equilibrium disturbances are the following:

a) Separation of uranium from radium due to chemical or physical agents.

b) Loss of radon by diffusion.

In the first case, two fractions are separated:- a fraction enriched with radium which puts itself quickly in equilibrium with its daughters, but not with the fraction of uranium; another part is enriched with uranium which is in equilibrium at least with $UX_1$ ($Th^{234}$) and $UX_2$ ( $Pa^{234}$).

In the second case, the secular equilibrium up to radium is maintained, while the internal equilibrium among the daughters of radon is dependent upon the diffusion coefficient of the gas in the internal.

Four major types of samples based upon the nature of the RE in the mineral can be differentiated.

a) Samples contain only uranium in RE. The uranium content in such samples can be determined by comparing the gross $\beta$ - or the gross $\gamma$ - activity of the sample with the corresponding activity of a standard uranium ore in which the uranium family is known to be in RE. The relation will be obtained as the following:

$$\frac{\beta \text{ - activity of sample}}{\beta \text{ - activity of standard}} = \frac{\gamma \text{ - activity of sample}}{\gamma \text{ - activity of standard}} = \frac{\% \ U_3O_8 \text{ content of sample}}{\% \ U_3O_8 \text{ content of standard}}$$

These values are generally referred to as equivalent $U_3O_8$ values and are denoted by e $(U_3O_8)_\beta$ and e $(U_3O_8)_\gamma$, respectively.

b) Samples contain only uranium out of RE. Such samples may be broadly classified into two groups. The first group contains uranium in excess of that required to support the daughter products whereas the second group does not contain enough uranium to support the daughter products. In the uranium family most of the high energy $\gamma$ - radiations are emitted by radium and its daughter products which are called the radium groups ($Ra^{226}$ - $Pb^{206}$) while the high energy $\beta$ - radiations are emitted both by the uranium group ($U^{238}$ - $Th^{230}$) as well as by the radium group. Hence when the equivalent $U_3O_8$ content of the sample is determined by comparing the activity of the sample with that from a standard uranium ore

in RE, the e $(U_3O_8)_\beta$ will be smaller than the e $(U_3O_8)_\gamma$ in the case of samples having parent deficiency, whereas in the case of samples having daughter product deficiency, the e $(U_3O_8)_\beta$ will be larger than the e $(U_3O_8)_\gamma$. Hence simple radiometric analysis based on the gross $\beta$ - or $\gamma$ - activity measurements can indicate the type of equilibrium in the samples.

c) Samples contain both uranium and thorium in RE. When the e $(U_3O_8)$ content of such samples are determined using standard uranium ore in RE, the relation e $(U_3O_8)_\gamma >$ e $(U_3O_8)_\beta$ is usually found. Hence, care should be taken not to interpret the results as indication of a disequilibrium sample.

d) Samples contain both thorium and uranium out of RE. If the uranium is out of RE, with a preponderance of the uranium group and is present along with the right proportion of thorium: e $(U_3O_8)_\beta$ can agree with e $(U_3O_8)_\gamma$. Normally these values will not agree and it will be difficult to make an assessment of the type of disequilibrium obtaining in the uranium part of the sample.

The most simple radioactive method for the determination of the uranium and thorium contents is the $\gamma$ - ray spectrometric method. The principle of the method is briefly described.

The $\gamma$ - rays of the uranium series are distributed in the energy interval from several tens of Kev to 2.446 Mev, while those of the actinouranium series to 0.89 Mev and those of the thorium series to 2.61 Mev. Since the normal contribution of the $\beta$ - or the $\gamma$ - activities of the $U^{235}$ series to the total activity of

uranium does not exceed 4%, they are usually neglected.

On comparing the $\gamma$ - ray spectra of a one year old uranium oxide, a uranium ore in RE and a thorium ore (29, 30), it is observed that

a) in the case of the uranium oxide, the major $\gamma$ - activity is in the 80 - 100 Kev region which arise from the decay of $Th^{234}$,

b) in the case of the uranium ore in RE, there are additional peaks of high intensities in the 0.35, 0.61, 0.76, 1.12 and 1.76 Mev regions which arise from the decays of $Pb^{214}$ (RaB) and $Bi^{214}$ (RaC),

c) in the case of the thorium ore, there are additional peaks in the 0.23, 0.91 and 2.61 Mev regions which arise from the decays of $Pb^{212}$(ThB), $Ac^{228}$(Ms ThII) and $Tl^{208}$(Th C").

Hence the uranium and the thorium contents of a sample can be determined by measuring the intensity of any of the $\gamma$ - peaks listed in b) and c) respectively.

In the case of samples containing both uranium and thorium in RE, the individual components can be analysed by intensity measurements at two energy regions, preferably one from each of the two groups listed under b) and c) mentioned above. The simultaneous equations used to evaluate the contents of uranium and thorium are set as follows (31)

$$A_{E_1} = K_{UE_1} \cdot C_U + K_{ThE_1} \cdot C_{Th} \quad \ldots\ldots\ldots\ldots\ldots 1$$

$$A_{E_2} = K_{UE_2} \cdot C_U + K_{ThE_2} \cdot C_{Th} \quad \ldots\ldots\ldots\ldots\ldots 2$$

where $A_{E_1}$ and $A_{E_2}$ are the observed activities per gram of the sample at the energy peaks $E_1$ and $E_2$;

$K_{UE_1}$ and $K_{UE_2}$ are the specific activities per 1% $U_3O_8$ of a standard U - ore in RE at $E_1$ and $E_2$;

$C_U$ and $C_{Th}$ are the concentrations of uranium and thorium expressed as the percentage in the sample. In order to solve the above equations for $C_U$ and $C_{Th}$, the constants $K_{UE_1}$, $K_{UE_2}$, $K_{ThE_1}$ and $K_{ThE_2}$ must be determined first using standards with known amount of uranium and thorium in RE.

The equilibrium spectral composition of the gamma quanta as well as the $\gamma$ -energy of the distributions of the three natural radioactive series are shown in Table 1.3 -1.7 (1).

TABLE 1.3 Equilibrium spectral composition of the gamma quanta of the uranium series

| Isotope | Gamma-quanta energy $E_\gamma$, MeV | Per decay event: number of quanta, n | Per decay event: energy $nE_\gamma$, MeV | In $10^{-4}$ of uranium: number of quanta per second, $\bar{n}$/sec | In $10^{-4}$ of uranium: energy per second, $\bar{n}E_\gamma$, MeV/sec |
|---|---|---|---|---|---|
| $^{238}_{92}$U(UI) | 0.112 | 0.00023 | 0.00003 | | |
| | 0.048 | 0.187 | 0.0089 | | |
| | Total | 0.1872 | 0.0090 | 0.23 | 0.011 |
| $^{234}_{90}$Th($UX_1$) | 0,093 | 0.148 | 0.0137 | | |
| | 0,064 | 0.065 | 0.0041 | | |
| | 0,029 | 0.065 | 0.0018 | | |
| | Total | 0.278 | 0.0197 | 0.34 | 0.024 |
| $^{234}_{91}$Pa($UX_2+UZ$) | 0.250 | 0.0019 | 0.00047 | | |
| | 0.750 | 0.0012 | 0.00090 | | |
| | 0.760 | 0.0060 | 0.0045 | | |
| | 0.910 | 0.0007 | 0.00064 | | |
| | 1.000 | 0.0037 | 0.0037 | | |
| | 1.680 | 0.0002 | 0.00034 | | |
| | 1.810 | 0.0004 | 0.00073 | | |
| | Total | 0.0141 | 0.011 | 0.017 | 0.014 |
| $^{234}_{92}$U(UII) | 0.121 | 0.0003 | 0.00004 | | |
| | Total | 0.0003 | 0.00004 | 0.00037 | 0.00005 |
| $^{230}_{90}$Th(Io) | 0.253 | 0.00017 | 0.00004 | | |
| | 0.184 | 0.00014 | 0.00003 | | |
| | 0.142 | 0.0007 | 0.00010 | | |
| | 0.068 | 0.0059 | 0.00040 | | |
| | Total | 0.00691 | 0.00057 | 0.00857 | 0.00071 |
| $^{226}_{88}$Ra(Ra) | 0.184 | 0.012 | 0.0022 | | |
| | Total | 0.012 | 0.0022 | 0.014 | 0.0027 |
| $^{222}_{86}$Rn(Rn) | 0.51 | 0.00064 | 0.00032 | | |
| | Total | 0.00064 | 0.00032 | 0.00079 | 0.00040 |
| $^{214}_{82}$Pb(RaB) | 0.352 | 0.377 | 0.132 | | |
| | 0.295 | 0.189 | 0.0557 | | |
| | 0.285 | 0.052 | 0.014 | | |
| | 0.242 | 0.105 | 0.0254 | | |
| | Total | 0.723 | 0.228 | 0.896 | 0.283 |

TABLE 1.3 (Continued)

| Isotope | Gamma-quanta energy, $E_\gamma$, MeV | Per decay event: number of quanta, n | Per decay event: energy $nE_\gamma$, MeV | In $10^{-4}$ g of uranium: number of quanta per second, $\bar{n}$/sec | In $10^{-4}$ g of uranium: energy per second, $\bar{n}E_\gamma$, MeV/sec |
|---|---|---|---|---|---|
| $^{214}_{83}$Bi(RaC) | 2.446 | 0.016 | 0.039 | | |
| | 2.410 | 0.002 | 0.00482 | | |
| | 2.297 | 0.004 | 0.00919 | | |
| | 2.204 | 0.052 | 0.11 | | |
| | 2.117 | 0.014 | 0.029 | | |
| | 2.090 | 0.001 | 0.002 | | |
| | 2.017 | 0.001 | 0.002 | | |
| | 1.900 | 0.004 | 0.007 | | |
| | 1.862 | 0.008 | 0.014 | | |
| | 1.848 | 0.020 | 0.036 | | |
| | 1.764 | 0.163 | 0.287 | | |
| | 1.728 | 0.024 | 0.041 | | |
| | 1.668 | 0.010 | 0.016 | | |
| 004256 | 1.605 | 0.004 | 0.006 | | |
| | 1.583 | 0.011 | 0.017 | | |
| | 1.541 | 0.008 | 0.012 | | |
| | 1.509 | 0.022 | 0.033 | | |
| | 1.403 | 0.040 | 0.056 | | |
| | 1.378 | 0.048 | 0.066 | | |
| | 1.281 | 0.017 | 0.021 | | |
| | 1.238 | 0.060 | 0.074 | | |
| | 1.207 | 0.006 | 0.007 | | |
| | 1.155 | 0.018 | 0.020 | | |
| | 1.120 | 0.166 | 0.185 | | |
| | 1.050 | 0.005 | 0.0052 | | |
| | 0.960 | 0.005 | 0.0048 | | |
| | 0.935 | 0.033 | 0.0308 | | |
| | 0.885 | 0.004 | 0.0035 | | |
| | 0.837 | 0.009 | 0.0075 | | |
| | 0.806 | 0.015 | 0.012 | | |
| | 0.787 | 0.012 | 0.0094 | | |
| | 0.769 | 0.053 | 0.040 | | |
| | 0.740 | 0.004 | 0.00296 | | |
| | 0.721 | 0.007 | 0.005 | | |
| | 0.703 | 0.008 | 0.005 | | |
| | 0.666 | 0.023 | 0.0153 | | |
| | 0.609 | 0.471 | 0.286 | | |
| | 0.535 | 0.009 | 0.0048 | | |
| | 0.509 | 0.013 | 0.0066 | | |
| | 0.485 | 0.015 | 0.0072 | | |
| | 0.465 | 0.010 | 0.0046 | | |
| | 0.450 | 0.010 | 0.0045 | | |
| | 0.417 | 0.008 | 0.0033 | | |
| | 0.395 | 0.013 | 0.0051 | | |
| | Total | 1.446 | 1.574 | 1.79 | 1.95 |
| $^{210}_{82}$Pb(RaD) | 0.047 | 0.0025 | 0.00012 | | |
| | Total | 0.0025 | 0.00012 | 0.00310 | 0.00015 |
| Total for the whole family . . . . . | | 2.658 | 1.84 | 3.29 | 2.29 |
| Total for the radium series . . . . . | | 2.184 | 1.80 | 2.70 | 2.23 |

Remarks: 1. Lines of intensity $<1 \cdot 10^{-5}$ MeV per decay event are not listed in the table. 2. Quanta with energies of 0.395, 0.417, 0.450, 0.465, 0.485, 0.509, 0.535 MeV are by convention related to the gamma radiation of RaC.

TABLE 1.4 Energy distribution of the gamma radiation of the uranium series

| Energy interval, MeV | Total number of gamma quanta, % | Total energy, % |
|---|---|---|
| Up to 0.5 | 46.5 | 16.3 |
| 0.5 — 1.0 | 26.2 | 24.0 |
| 1.0 — 1.5 | 13.5 | 23.3 |
| 1.5 — 2.0 | 10.3 | 25.7 |
| >2.0 | 3.5 | 10.7 |

TABLE 1.5. Equilibrium spectral composition of the gamma quanta of the actinouranium series /2/

| Isotope | Gamma-quanta energy $E_\gamma$, MeV | Per decay event: number of quanta, n | Per decay event: energy $nE_\gamma$, MeV | In $10^{-4}$ g of actinouranium: number of quanta per second, n/sec | In $10^{-4}$ g of actinouranium: energy per second, $nE_\gamma$, MeV/sec |
|---|---|---|---|---|---|
| $^{235}_{92}$U(AcU) | 0.200 | 0.04 | 0.008 | | |
| | 0.185 | 0.55 | 0.10 | | |
| | 0.165 | 0.04 | 0.0066 | | |
| | 0.143 | 0.12 | 0.017 | | |
| | 0.110 | 0.05 | 0.005 | | |
| | 0.095 | 0.09 | 0.0085 | | |
| | Total | 0.890 | 0.147 | 7.03 | 1.16 |
| $^{231}_{90}$Th(UY) | 0.310 | 0.015 | 0.0046 | | |
| | 0.218 | 0.015 | 0.0032 | | |
| | 0.1693 | 0.0508 | 0.00860 | | |
| | 0.164 | 0.220 | 0.0360 | | |
| | 0.096 | 0.015 | 0.0014 | | |
| | 0.0851 | 0.0509 | 0.00433 | | |
| | 0.0842 | 0.290 | 0.0244 | | |
| | 0.0812 | 0.0282 | 0.00229 | | |
| | 0.0732 | 0.1611 | 0.0117 | | |
| | 0.073 | 0.015 | 0.0011 | | |
| | 0.0665 | 0.0282 | 0.00187 | | |
| | 0.0621 | 0.1611 | 0.0100 | | |
| | 0.0585 | 0.3190 | 0.0186 | | |
| | 0.0579 | 0.0509 | 0.00295 | | |
| | Total | 1.4202 | 0.1314 | 11.2 | 1.03 |
| $^{231}_{91}$Pa | 0.356 | 0.0140 | 0.00498 | | |
| | 0.329 | 0.0275 | 0.00905 | | |
| | 0.302 | 0.0275 | 0.00831 | | |
| | 0.299 | 0.0275 | 0.00822 | | |
| | 0.283 | 0.0275 | 0.00778 | | |
| | 0.260 | 0.0210 | 0.00546 | | |
| | 0.101 | 0.0140 | 0.00141 | | |
| | 0.097 | 0.0490 | 0.0047 | | |
| | 0.064 | 0.2340 | 0.0149 | | |
| | 0.046 | 0.5020 | 0.023 | | |
| | 0.030 | 0.1670 | 0.0050 | | |
| | Total | 1.1110 | 0.0930 | 8.76 | 0.735 |

TABLE 1.5 (Continued)

| Isotope | Gamma-quanta energy $E_\gamma$, MeV | Per decay event: number of quanta, n | Per decay event: energy $nE_\gamma$, MeV | In $10^{-4}$ g of actinouranium: number of quanta per second, n/sec | In $10^{-4}$ g of actinouranium: energy per second, $nE_\gamma$, MeV/sec |
|---|---|---|---|---|---|
| $^{227}_{90}$Th(RaAc) | 0.350 | 0.015 | 0.0052 | | |
| | 0.343 | 0.020 | 0.0068 | | |
| | 0.334 | 0.029 | 0.0096 | | |
| | 0.330 | 0.017 | 0.0056 | | |
| | 0.304 | 0.029 | 0.0088 | | |
| | 0.300 | 0.017 | 0.0051 | | |
| | 0.296 | 0.019 | 0.0056 | | |
| | 0.286 | 0.080 | 0.0228 | | |
| | 0.282 | 0.020 | 0.0084 | | |
| | 0.256 | 0.080 | 0.0204 | | |
| | 0.250 | 0.020 | 0.0050 | | |
| | 0.248 | 0.003 | 0.00074 | | |
| | 0.236 | 0.080 | 0.018 | | |
| | 0.236 | 0.0033 | 0.00078 | | |
| | 0.205 | 0.0033 | 0.00068 | | |
| | 0.174 | 0.0033 | 0.00057 | | |
| | 0.113 | 0.0300 | 0.0033 | | |
| | 0.080 | 0.0540 | 0.0043 | | |
| | 0.061 | 0.0120 | 0.00073 | | |
| | 0.048 | 0.0290 | 0.0013 | | |
| | 0.031 | 0.1200 | 0.00037 | | |
| | 0.030 | 0.2000 | 0.00600 | | |
| | Total | 0.7759 | 0.141 | 6.13 | 1.11 |
| $^{223}_{87}$Fr(AcK) | 0.310 | 0.008 | 0.0024 | | |
| | 0.215 | 0.030 | 0.0064 | | |
| | 0.080 | 0.240 | 0.019 | | |
| | 0.050 | 0.400 | 0.020 | | |
| | Total | 0.6780 | 0.0481 | 5.35 | 0.380 |
| $^{223}_{88}$Ra(AcX) | 0.371 | 0.0028 | 0.0010 | | |
| | 0.338 | 0.0195 | 0.00659 | | |
| | 0.324 | 0.0230 | 0.00745 | | |
| | 0.270 | 0.0465 | 0.01256 | | |
| | 0.180 | 0.0050 | 0.00090 | | |
| | 0.154 | 0.0550 | 0.00847 | | |
| | 0.144 | 0.0410 | 0.00590 | | |
| | 0.122 | 0.0034 | 0.00042 | | |
| | Total | 0.1962 | 0.04333 | 1.550 | 0.342 |
| $^{219}_{86}$Rn(An) | 0.401 | 0.050 | 0.020 | | |
| | 0.272 | 0.130 | 0.0353 | | |
| | Total | 0.180 | 0.0554 | 1.42 | 0.437 |
| $^{211}_{82}$Pb(AcB) | 0.829 | 0.130 | 0.107 | | |
| | 0.764 | 0.010 | 0.0076 | | |
| | 0.487 | 0.003 | 0.0014 | | |
| | 0.425 | 0.060 | 0.025 | | |
| | 0.404 | 0.060 | 0.024 | | |
| | 0.065 | 0.010 | 0.00065 | | |
| | Total | 0.273 | 0.167 | 2.15 | 1.32 |
| $^{211}_{83}$Bi(AcC) | 0.351 | 0.137 | 0.0480 | | |
| | Total | 0.137 | 0.0480 | 1.08 | 0.379 |
| $^{207}_{81}$Tl(AcC") | 0.890 | 0.005 | 0.0044 | | |
| | Total | 0.005 | 0.0044 | 0.035 | 0.035 |
| | Total for the whole family | 5.666 | 0.8803 | 44.76 | 6.955 |

Remark: The table does not list lines having an intensity of $<1 \cdot 10^{-5}$ MeV per decay event.

TABLE 1.6 Equilibrium spectral composition of the gamma quanta of the thorium series /2/

| Isotope | Gamma-quanta energy, $E_\gamma$, MeV | Per decay event | | In $10^{-4}$ g of thorium | |
|---|---|---|---|---|---|
| | | number of quanta, n | energy, $nE_\gamma$, MeV | number of quanta per second, $\bar{n}$/sec | energy per second, $\bar{n}E_\gamma$, MeV/sec |
| $^{232}_{90}$Th | 0.060 | 0.197 | 0.011 | | |
| | Total | 0.197 | 0.011 | 0.080 | 0.0048 |
| $^{228}_{89}$Ac ($MsTh_2$) | 0.960 | 0.100 | 0.0960 | | |
| | 0.908 | 0.250 | 0.227 | | |
| | 0.831 | 0.016 | 0.013 | | |
| | 0.790 | 0.045 | 0.035 | | |
| | 0.779 | 0.008 | 0.0062 | | |
| | 0.338 | 0.095 | 0.032 | | |
| | 0.328 | 0.033 | 0.0108 | | |
| | 0.270 | 0.031 | 0.0083 | | |
| | 0.209 | 0.040 | 0.0083 | | |
| | 0.129 | 0.106 | 0.0136 | | |
| | 0.058 | 0.700 | 0.0406 | | |
| | Total | 1.424 | 0.492 | 0.583 | 0.201 |
| $^{228}_{90}$Th (RdTh) | 0.217 | 0.0027 | 0.00059 | | |
| | 0.205 | 0.0003 | 0.00006 | | |
| | 0.169 | 0.0012 | 0.00021 | | |
| | 0.133 | 0.0023 | 0.00031 | | |
| | 0.084 | 0.0160 | 0.00134 | | |
| | Total | 0.0225 | 0.00251 | 0.00922 | 0.00103 |
| $^{224}_{88}$Ra (ThX) | 0.241 | 0.0303 | 0.00748 | | |
| | Total | 0.0303 | 0.00748 | 0.0124 | 0.00307 |
| $^{220}_{86}$Rn (Tn) | 0.542 | 0.0003 | 0.00016 | | |
| | Total | 0.0003 | 0.00016 | 0.00012 | 0.00006 |
| $^{212}_{82}$Pb (ThB) | 0.415 | 0.0016 | 0.00066 | | |
| | 0.300 | 0.0320 | 0.00960 | | |
| | 0.239 | 0.4700 | 0.11233 | | |
| | 0.177 | 0.0024 | 0.00042 | | |
| | 0.115 | 0.0066 | 0.00076 | | |
| | Total | 0.5126 | 0.1151 | 0.2101 | 0.04720 |

TABLE 1.6 (Continued)

| Isotope | Gamma-quanta energy, $E_\gamma$, MeV | Per decay event | | In $10^{-4}$ g of thorium | |
|---|---|---|---|---|---|
| | | number of quanta, n | energy, $nE_\gamma$, MeV | number of quanta per second, $\bar{n}$/sec | energy per second, $\bar{n}E_\gamma$, MeV/sec |
| $^{212}_{83}$Bi (ThC) | 1.620 | 0.01680 | 0.02722 | | |
| | 1.073 | 0.00648 | 0.00695 | | |
| | 0.953 | 0.00389 | 0.00371 | | |
| | 0.893 | 0.00389 | 0.00347 | | |
| | 0.786 | 0.01040 | 0.00817 | | |
| | 0.727 | 0.06600 | 0.04798 | | |
| | 0.513 | 0.00454 | 0.00233 | | |
| | 0.493 | 0.00127 | 0.00063 | | |
| | 0.453 | 0.00370 | 0.00168 | | |
| | 0.328 | 0.00151 | 0.00050 | | |
| | 0.288 | 0.00366 | 0.00105 | | |
| | 0.040 | 0.0105 | 0.00042 | | |
| | Total | 0.13264 | 0.10411 | 0.05438 | 0.04268 |
| $^{208}_{81}$Tl (ThC″) | 2.620 | 0.337 | 0.881 | | |
| | 0.860 | 0.0404 | 0.0347 | | |
| | 0.763 | 0.0067 | 0.0051 | | |
| | 0.583 | 0.2932 | 0.1709 | | |
| | 0.511 | 0.0842 | 0.0430 | | |
| | 0.486 | 0.0017 | 0.00082 | | |
| | 0.277 | 0.0377 | 0.00933 | | |
| | 0.252 | 0.0034 | 0.00086 | | |
| | 0.233 | 0.0010 | 0.00023 | | |
| | Total | 0.8013 | 1.1464 | 0.3292 | 0.4700 |
| | Total for the whole family | 3.121 | 1.8796 | 1.279 | 0.7706 |

Remark: Lines having an intensity $<1 \cdot 10^{-5}$ MeV/decay event are not given in the Table.

TABLE 1.7. Energy composition of gamma radiation emitted by the thorium series

| Energy ranges and discrete monochromatic lines, MeV | Total number of gamma quanta, % | Total energy, % |
|---|---|---|
| Up to 1.0 | 85 | 50 |
| 1.0 — 2.0 | 7 | 4 |
| 2.62 | 8 | 46 |

1.3.2.2 Non-destructive neutron activation analysis. By irradiating a sample with neutrons which are produced in a nuclear reactor or from other suitable sources, some of the atoms presented in the sample will be converted into different isotopes of the same element or isotopes of different elements, depending on the energy of the neutrons. The isotopes produced are generally unstable and emit radiation. By comparing the radioactivity induced in a sample with those in a standard which is subjected to irradiation together with the sample, the amount of parent element in the sample can be determined. The mathematical relationship for the calculation is represented by the equation

$$\text{weight of element in sample} = \text{weight of element in standard} \times \frac{C_x}{C_s}$$

where $C_x$ is the observe counting rate of the sample and $C_s$ is that of the standard measured under comparable conditions.

During the neutron irradiation of uranium and thorium the following reactions take place:

$$U^{238}(n,\gamma)\,U^{239} \xrightarrow[23.5\ \text{min}]{\beta^-} Np^{239} \xrightarrow[2.35\ \text{d}]{\beta^-} Pu^{239}$$

$$Th^{232}(n,\gamma)\,Th^{233} \xrightarrow[22.4\ \text{min}]{\beta^-} Pa^{233} \xrightarrow[27.4\ \text{d}]{\beta^-} U^{233}$$

Since $U^{239}$ is rather short-lived, the $\gamma$-transitions of $Np^{239}$ are usually measured for the determination of uranium. Owing to its

high intensity (40%), the $\gamma$-transition of $Np^{239}$ at 106 Kev is normally used as the reference peak for the induced activity (32, 33). However, when a pneumatic tube is used for the irradiation, the uranium content may be calculated via the 74.5 Kev peak of $U^{239}$(34).

When $Th^{232}$ is irradiated, the short-lived $\beta$-emitter $Th^{233}$ is produced. As it has only weak $\gamma$-radiations, its decay-product $Pa^{233}$ is usually used as reference nuclide. The $\gamma$-transition at 311.8 Kev with 80% intensity is measured as reference peak for the induced activity. Since in geological materials many interfering matrix elements are present, the sample must be cooled for two to four weeks before the induced activity of $Pa^{233}$ at 311.8 Kev can be accurately measured (35, 36).

In the present investigation the feasibility and the accuracy of determining the thorium content via the 29.2 Kev peak of $Th^{233}$ with an intensity of 2.1 percent have been examined.

## 1.4 Objective of the present investigation

Since uranium, thorium and rare-earths found limited use in the local market, little attention was paid to the mineral monazite. Consequently, at the time being monazite is produced in very low rate and the produced mineral is mainly exported with prices that are based on the content of rare-earths only. Beginning to realize the strategic importance of this mineral, a study programme directed towards obtaining information of a process that could be adapted industrially to the processing of domestic monazite has been

started in the Office of Atomic Energy for Peace. To be able to justify the feasibility of establishing a national monazite processing plant, the total deposit of monazite in the country, one important factor among others, must be known. For the benefit of this surveying-programme, the methods of spectrophotometry , titrimetry , instrumental activation analysis and radiometric analysis for the contents of uranium and thorium in monazite were examined. Special emphasis was put to radiometric methods which provide quick information on uranium concentration, thorium concentration and the state of radioactive equilibrium of the mineral.