

**DETERMINATION OF RARE EARTH ELEMENTS IN BEYLIKAHİR
THORIUM DEPOSITS BY NEUTRON ACTIVATION ANALYSIS TECHNIQUE**

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of

Mechanical Engineering Department

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By

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December, 1988

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**DETERMINATION OF RARE EARTH ELEMENTS IN BEYLIKAHİR
THORIUM DEPOSITS BY INSTRUMENTAL NEUTRON ACTIVATION
ANALYSIS TECHNIQUE**

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ABSTRACT

The Rare Earth Elements (REE) and Thorium contents of deposits in Eskisehir-Beylikahir region were analyzed by instrumental neutron activation analysis technique.

Ore samples provided by Turkish Mineral Research Institute , MTA, were ground to 1 mm particle size. The samples were homogenized, dried and put into quartz ampoules. The TR-1, 5 MW Research Reactor, in Çekmece Research and Training Center was used to irradiate the samples. The IAEA (Soil-5), IAEA (Soil-7) and S-16 standard reference materials were used as standards in calculating concentrations of elements in ore samples. MicroSAMPO gamma-lines analysis source program was used for both qualitative and quantitative analysis.

Elements determined from ore samples are as follows: Na, Sc, Fe, Co, Zn, As, Sr, Y, Zr, Nb, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Yb, Lu, Hf, Ta, Th and U. Some results of these elements were compared with earlier studies in the region.

The REE and Th percentages were found as 3.7 ± 0.2 % and 0.24 ± 0.02 % for Küçükhöyükütepe and 3.5 ± 0.2 % and 0.30 ± 0.02 % for Kocadevebağirtantepe deposits respectively and total REE contents were calculated as 51.0×10^4 and 9.0×10^4 tons. Also , thorium contents were calculated as 4.0×10^5 tons of Th for Küçükhöyükütepe and Kocadevebağirtantepe deposits together with a weighted average concentration 0.25 %.

Key words : Rare earth elements (REE), Estimation of REE's and thorium in Beylikahır thorium deposits.

**BEYLİKAHİR TORYUM YATAKLARINDA NADİR TOPRAK
ELEMENTLERİNİN ALETLİ NÖTRON AKTİVASYON ANALİZ
YÖNTEMİ İLE TAYİNİ**

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ÖZET

Eskişehir-Beylikahır toryum yataklarında nadir toprak elementleri ve toryum Aletli Nötron Aktivasyon Analiz yöntemi ile tayin edildi. Numuneler Türkiye Maden Tetkik ve Araştırma Enstitüsü tarafından sağlandı ve 1 mm'ye kadar öğütüldü.

Numuneleri ışınlamak için Çekmece Nükleer Araştırma ve Eğitim reaktörü kullanıldı. Numunelerdeki nadir toprak elementlerinin konsantrasyonlarını hesaplamak için referans maddeleri olarak IAEA(Soil-5), IAEA(Soil-7) ve S-16 standartları kullanıldı. Gamma ışınları spektrumlarını analiz etmek için microSAMPO paket programı kullanıldı.

Numunelerden tayin edilen elementler aşağıdadır:

Na, Sc, Cr, Fe, Co, Zn, As, Sr, Y, Zr, Nb, Mo, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Yb, Lu, Hf, Ta, Th ve U. Bu elementlerden bazılarının sonuçları Maden Tetkik ve Araştırma Enstitüsü ve Gülovalı' nin sonuçları ile karşılaştırıldı.

Küçükhöyüktepe ve Kocadevebağirtantepe toryum yataklarında nadir toprak elementleri ve toryum ortalama konsantrasyonları hesaplandı. Küçükhöyüktepe için 3.7 ± 0.2 nadir toprak elementleri ve 0.24 ± 0.02 toryum , Kocadevebağirtantepe için 3.50 ± 0.19 nadir toprak elementleri ve 0.30 ± 0.02 toryum bulundu. Her iki yataktaki toplam nadir toprak elementlerinin miktarları tayin edildi ve Küçükhöyüktepe için 51.0×10^4 ton ve Kocadevebağirtantepe için 9.0×10^4 ton nadir toprak elementleri olduğu hesaplandı. Aynı zamanda her iki yatak için 4.0×10^5 ton toryum rezervi hesaplandı ve ortalama toryum tenörü 0.25% olarak bulundu.

Anahtar sözcükler : Nadir Toprak Elementleri , Beylikahır yatagında Nadir Toprak Elementleri ve toryum miktarlarının saptanması.

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CHAPTER I

INTRODUCTION

1.1. Rare Earth Elements

Rare earth elements (REE) consist of sixteen elements including yttrium ($Z=39$). We call elements from $Z=57$ to 71 as lanthanum series and elements from $Z=58$ to 71 as lanthanides. Among these, promethium ($Z=61$) does not occur in nature. It can be isolated in some quantities from fission products of uranium.

As the atomic number increases from lanthanum to lutetium, additional electrons tend to be added into 4f shell, rather than going to complete the 5d shell, thus, leaving the number of valence electrons unchanged. One effect of this inner addition is that the radii of the ions, instead of increasing with atomic number, show a small but definite decrease from 104 pm for La^{+3} to 84 pm for Lu^{+3} . This decrease "lanthanum contraction" is enough to bring the radii of Ho^{+3} and Er^{+3} to 89 pm and 87 pm respectively, close to that of Y^{+3} 88 pm, despite the yttrium's lower atomic number. Yttrium has the same valence electron configuration as holmium and erbium as well as a similar ionic size. Its association with those elements is therefore understandable [1]. Yttrium always occurs with the lanthanum-lutetium group. In addition, in certain classifications, scandium ($Z=21$) which is not directly a REE, is considered as a REE because of its

chemical similarities to the rest of the group. Scandium has an important application with REE. Some properties of REE's are shown in Table 1.1.

Table 1.1. Some Properties of Rare Earth Elements, Thorium and Uranium [2].

Name	Symbol	Atomic Number	Atomic Weight	Crustal Abundance (mg/kg)
Yttrium	Y	39	88.92	28.0
Lanthanum	La	57	138.92	18.0
Cerium	Ce	58	140.13	46.0
Praseodymium	Pr	59	140.92	5.5
Neodymium	Nd	60	144.27	24.0
Promethium	Pm	61	145.00	Nil
Samarium	Sm	62	150.43	6.5
Europium	Eu	63	152.00	0.5
Gadolinium	Gd	64	156.90	6.4
Terbium	Tb	65	158.93	0.9
Dysprosium	Dy	66	162.46	5.0
Holmium	Ho	67	164.94	1.2
Erbium	Er	68	167.20	4.0
Thulium	Tm	69	168.92	0.4
Ytterbium	Yb	70	173.04	2.7
Lutetium	Lu	71	174.99	0.8
Thorium	Th	90	232.12	12.0
Uranium	U	92	238.03	4.0

1.2. Rare Earth Element Deposits

In spite of the name, rare earths are quite abundant in nature but economically viable deposits are rather limited. The biggest REE deposits are located in China, U.S.A and India with approximately 3.0×10^6 tons each have second largest potentials. The REE's usually occur with thorium deposits. There are four main thorium minerals in nature : Monazite, thorianite, thorite and bastnasite. The geological features of these minerals can be expressed as follows:

a) Monazite is a phosphate of light lanthanum series, but always contains thorium, together with some uranium, aluminum, calcium, titanium, zirconium, iron and a little amount of lead. Its formula appears to be $(Ce, La, Th, Y)PO_4$, despite the invariable thorium content.

b) Thorianite is an impure oxide, ThO_2 , which contains uranium. There is a continuous series of isomorphous minerals extending from ThO_2 to UO_2 (uraninite). Thorianite which contains a significant amount of uranium is called uranothorianite. Thorianite and uranothorianite are dark brown to black colored minerals, which may be crystalline or like pitchblende amorphous or crypto crystalline in structure.

c) Thorite is thorium silicate, of ideal formula $ThSiO_4$. It always contains uranium and the name is changed to uranothorite when the uranium content is appreciable.

d) Bastnasite is a light lanthanum series of fluoro carbonate, of ideal formula LnFCO_3 ; commercially exploited deposits contain little thorium.

In industry, monazite mineral can be used for thorium production. It can also be processed to obtain cerium and other REE's. Bastnasite mineral contains about 0.05 % ThO_2 . This makes it more attractive than monazite when production of lanthanum series is envisaged since it is free of the restrictions for handling radioactive minerals. It is however, rarer than monazite. Four major thorium deposits in the world are as follows [3].

- Travancore Deposits (India) are similar to monazite minerals which contain about 3 % ThO_2 .
- Sri-Lanka Deposits (Ceylon) have monazite minerals, the thorium content of these deposits changes from 2 to 47 %.
- Florida, Idaho and California Deposits (USA) have more valuable thorium ores of about 5 %.
- Brazil Deposits (Brazil) have monazite minerals and it has about 6 % ThO_2 .

1.2.1. Thorium Deposits in Turkey

Well known thorium deposits in Turkey are Eskişehir Beylikahır deposits which contain rare earth elements (REE's) and thorium as bastnasite mixed with barite, calcite and fluorite [4]. The REE content of these deposits are approximately 9.53×10^5 tons with 3.14 %

REE's [5] and thorium content is estimated to be 3.84×10^5 tons with weighted average concentration 0.21 % ThO_2 [6].

Several studies have been reported concerning mineralogical analysis and physical enrichment of this ore, as well as thorium recovery [4]. These results indicate that processing this ore only for the thorium recovery is not economically attractive. Other thorium ores were observed in Malatya-Hekimhan and Kayseri-Felahiye regions.

1.2.2. Structure and Mineralization of Eskişehir

Beylikahır Thorium Deposits

Eskişehir Sivrihisar thorium deposits which are located among Kızılcaören Karkın and Okçu Villages called "Eskişehir-Beylikahır complex thorium deposits". These deposits have four mineralization levels [6].

- i) Manganese oxide mineralization.
- ii) Barite mineralization.
- iii) Fluorite mineralization.
- iv) Calcite and carbonate mineralization.

These four mineralization levels have the same elements, but the quantity of these elements are variable in each level. But, in each level, thorium content is approximately the same. The REE and thorium contents are also in considerable amount in Eskişehir-Beylikahır thorium deposits. Therefore, analysis of REE and thorium contents of these deposits will be very important for Turkey because of their economic values in the world.

1.3. Some Selective Applications of REE and Thorium

Superconductivity is not peculiar to a few metals. The REE's are used in alloys to increase the conductivity. Thus, the conductivity of Bi-REE's alloy is greater than pure Bi metal. More than twenty metallic elements, mostly REE's are also used in electronic instruments as superconductors. These are Al, Si, Ti, Zn, Ga, Ge, Zr, Nb, Mo, Tc, Ru, Cd, Hf, Ta, W, Re, Tl, Pb, La, Th, Pa and U [7].

Considerable amount of yttrium and europium are presently being used in making red phosphorous for color television screens. Strontium fluoride containing erbium fluoride is an efficient converter of infra-red radiation into visible radiation [7].

The REE's and thorium are used in arc-carbons, to measure intensity of x-rays in photo-electric cells, in glass polishing and in glass making [6].

Tungsten-thorium alloys increase the efficiency of electric ampoules. They are used as catalyst in chemical reactions. Also some lanthanum series have attracted attention as potential nuclear reactor control materials such as samarium, europium and dysprosium. Cerium is used in refractories. Also the melting point of thorium oxide is high and it is used as a refractor [1]. The REE's are also used extensively in oil refining industry as catalyst.

1.4. Determination of REE by Various Methods

The REE's can be determined by many methods. Among the most used ones are the following:

- X-Ray fluorescence (XRF) can be used to determine twenty or more elements including REE's in samples. The XRF is a nondestructive, rapid and highly automated technique for the analysis of major elements in large number of samples.
- Individual separation of REE's by ion-exchange chromatography simplifies the radiochemistry and results in a much higher selectivity and also improves analytical sensitivity.
- Individual separation of REE's by high voltage electrophoresis. This method is also rapid and free of interferences.
- Also, Atomic absorption spectrometry, Fluorimetry, Emission spectroscopy, Mass spectrometry, Colorimetry and Spectrophotometry are used to determine the REE's.
- Instrumental Neutron Activation Analysis(INAA) can be used to observe about 35 or more elements in most samples. Several elements that are measurable by neutron activation analysis method can be determined more sensitive. The INAA is the time consuming and expensive but sensitive enough to observe many trace elements. Since we have this facility in our Department, we used INAA for REE determination.

1.4.1. General Theory of Instrumental Neutron Activation Analysis (INAA)

Since this is the analysis technique we used in our determination, it will be described in more detail. Instrumental neutron activation analysis is one of the most sensitive and highly specific analytical technique in the determination of very low concentrations of many elements present in various samples. It is well suited for the analysis of geological, environmental and biological samples. INAA technique has several advantages over the competing analytical methods [8,9]. Those advantages can be listed as follows:

- 1) INAA method is based on nuclear properties and the results are independent of the chemical form of the elements in the samples.
- 2) The method requires little sample preparation and no chemical treatment prior to analysis. There is no need to dissolve the samples. Contamination and loss of the trace elements will be avoided during chemical manipulations so that the sample contamination is minimized [10,11,12].
- 3) Samples can be analyzed for one or more elements [13].
- 4) The INAA method is nondestructive, thus as soon as the induced radioactivity has decayed to safe levels, the samples can be analyzed by other methods, such as atomic absorption spectrometry, infrared spectrometry, etc [8].
- 5) For many of the observable elements, this technique is more sensitive, than the others. This method is not

influenced by concentration variations from sample to sample and naturally suited for unambiguous measurement of elemental concentrations [14].

Neutron activation analysis is principally based on the quantitative detection of γ -rays produced from element in samples by neutron-induced reactions. When a sample is bombarded by neutron in a reactor, generator or other suitable sources, some of the nuclei present in the medium interact with these neutrons and produce radioactive isotopes. The radioisotope so formed, would decay with a characteristic half life by emission of alpha, beta and gamma rays with definite energies. Generally, the irradiation is done with thermal neutrons. With few exception most stable isotopes are capable of capturing thermal neutrons, with characteristic reaction cross sections which vary from one nucleus to another. The resulting radioactivity is measured using the gamma spectroscopy of unique gamma rays emitted by each radionuclide [15]. The rate of decay from a sample of any radioactive substance, in principle, is independent of its chemical composition, temperature, pressure or the presence of any other nuclei in the medium but only proportional to the number of nuclei present. In a sample containing N radioactive nuclei, the rate of decay will be expressed as:

$$-\frac{dN}{dt} = \lambda N \quad (1.1)$$

Where λ is the decay constant which is characteristic for a given nucleus. Integration of the above equation gives:

$$N = N_0 e^{-\lambda t} \quad (1.2)$$

Where N_0 is the number of nuclei present at time $t=0$ and N is the number of nuclei present at time t . In INAA, the rate of change of the number of nuclei is given by

$$\frac{dN}{dt} = \Phi \sigma N_0 - \lambda N \quad (1.3)$$

After solving Eqn.1.3 with some assumptions we get:

$$A = \Phi \sigma N_0 (1 - e^{-\lambda t_i}) \quad (1.4)$$

In which A is the activity produced at the end of irradiation. Then, the quantity of radioactivity at the end of cooling is given by:

$$A = \epsilon \Phi \sigma N_0 (1 - e^{-\lambda t_i}) e^{-\lambda t_c} \quad (1.5)$$

where;

A : Activity at the end of the cooling time, t_c

ϵ : Efficiency of detector system

t_i : Irradiation time

t_c : Cooling time

$$\lambda : \text{Decay constant} = \frac{0.693}{t_{1/2}}$$

$t_{1/2}$: Half life of the radioactive isotope produced

Φ : Neutron flux, $\text{n.cm}^{-2}.\text{sec}^{-1}$

σ : Reaction cross section

N_0 : Number of nuclei present = $\frac{Wxf}{M} * 6.02 \times 10^{23}$

W : Weight of the desired element

f : Abundance of the stable parent isotope

M : Atomic weight of the element being determined

In INAA, the rate of change of the activity of nuclide is shown in Figure 1.1.

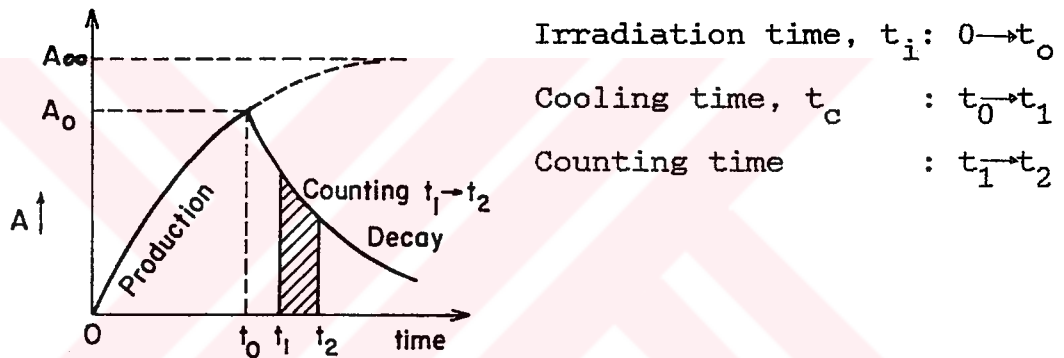


Figure 1.1. Neutron Irradiation and Counting

In activation analysis, quantitative determinations can be done by two methods. One of them is the direct method which employs the above equation and the other is comparative method where the standards are used along with the samples for comparison.

In the direct method, activity is calculated from known values of Φ , σ , t_i , t_c , and all the factors must be known accurately. In many cases, it is difficult to measure neutron flux during irradiation and σ is not precisely known. Therefore, the comparative method is more commonly used in neutron activation analysis in which both

samples and standards are irradiated simultaneously under the same conditions. If the Eqn. 1.5 is written for both sample and reference standard and taking their ratio, we get:

$$\frac{A_{\text{sample}}}{A_{\text{standard}}} = \frac{\epsilon \Phi \sigma}{\epsilon \Phi \sigma} * \frac{N_{0\text{sample}}}{N_{0\text{standard}}} * \frac{(1-e^{-\lambda t_i})}{(1-e^{-\lambda t_i})} * \frac{e^{-\lambda t_c}}{e^{-\lambda t_c}} \quad (1.6)$$

Since Φ , ϵ , σ , and t_i are the same for a given isotope for both sample and reference standard, then, for the same cooling time, equation becomes

$$\frac{A_{\text{sample}}}{A_{\text{standart}}} = \frac{N_{0\text{sample}}}{N_{0\text{standart}}} \quad (1.7)$$

$$Wt_{\text{sample}} = \frac{A_{\text{sample}}}{A_{\text{standart}}} * Wt_{\text{standart}} \quad (1.8)$$

Correction for the decay during counting and percent dead time are given by:

$$A_0 = \frac{(\text{Area}) \lambda e^{\lambda t_c}}{1 - e^{-\lambda t_c}} \quad , \quad \text{DT \%} = \frac{\text{RT} - \text{LT}}{\text{RT}} \quad (1.9)$$

where;

A_0 : Count rate at the end of irradiation

Area: Area of the peak

RT : Real counting time, $\text{RT} = t_2 - t_1$

LT : Live time of the counting.

Then decay corrected activity can be expressed as:

$$A_0 = \frac{(\text{Area})e^{\lambda t_m}}{LT} \quad (1.10)$$

In this equation t_m is the time from the end of irradiation to the midpoint of counting. In order to determine the quantity of the desired element in the sample it is enough to know the amount of element present in the reference standard and activities of both sample and reference standard irradiated under the same conditions. Activities used in the calculations must be the ones corrected for both blank and background contributions. Then the concentration of the unknown present in the sample can be expressed as

$$C_{\text{sam}} = \frac{Wt_{\text{st}} * C_{\text{st}}}{Wt_{\text{sam}}} * \frac{A_{0\text{sam}} - A_{0\text{bl}}}{A_{0\text{st}} - A_{0\text{bl}}} \quad (1.11)$$

A_0 : Decay corrected activity for sample,
standard and blank respectively

C_{sam} : Concentration of the element in the sample

C_{st} : Concentration of the element in the standard

Wt_{st} : Weight of the standard

Wt_{sam} : Weight of the sample

A computer program is written to calculate the concentrations of elements in the sample. Listing of the program is given in Appendix B. By using the program, decay corrected activity is calculated for each sample, standard and blank. Then, concentrations of elements are calculated in the sample together with their absolute and relative errors.

Some important elements such as, Pb and Ni can not be measured by INAA. Thus, the best strategy is to apply both X-Ray Fluorescence (XRF) and INAA as complementary methods to same samples.

1.5. A Computer Program for Activation Analysis;

MicroSAMPO

MicroSAMPO which is a Fortran IV program is one of the computer programs used for analysis of γ -ray spectra obtained as a result of Instrumental Neutron Activation experiments. The early work on SAMPO program was done at the Lawrence Berkeley Radiation Laboratory, University of California [16]. After redesigning and rewriting at the European Organization of Nuclear Research (CERN), in Geneva, Switzerland and at the Helsinki University of Technology in Finland, SAMPO76 [17] and SAMPO80 [18] versions were published. It includes algorithms for line shape, energy and efficiency calibrations as well as peak search and peak fitting routines. The analysis is based upon the study of photopeaks in the spectrum. It has fast interactive graphics capabilities very convenient automatic calibration procedures and data filing system, as well as multichannel analyzer (MCA) control [19].

The main objectives of microSAMPO

1. MicroSAMPO works on IBM Personel Computer (PC)-XT model micro computers with normal or enhanced color graphic display.

2. MicroSAMPO includes flexible multichannel analyzer interface which can be used with new computer controllable Canberra models.
3. Data transfer from and to the MCA is good and reliable. Convenient data storage and retrieval of data is incorporated into the program.

1.6. The Aim of This Work

Eskişehir-Beylikahır thorium deposits are the main sources of REE's in Turkey. These deposits contain bastnasite mixed with barite, calcite and fluorite minerals. Recovery of Only thorium from these deposits is not economically possible. Therefore, the aims of this work are to develop experimental techniques for the determination of REE and Th in these ores, to determine the REE content of these ores as well as thorium and to estimate the amount of REE's and thorium in these deposits. Such studies require simple and accurate analytical methods for simultaneous determination of REE's in a large number of samples. Since REE are becoming important both scientifically and economically, the determination of REE's and thorium in these deposits will play an important role for Turkey.

CHAPTER 2

EXPERIMENTAL

2.1. Collection of Samples

Eskişehir-Beylikahır-Kızılcaören thorium deposits have approximately 1.83×10^8 tons of ThO_2 [6] and 30.4×10^6 tons of REE ores [20]. Average concentrations of ThO_2 and REE's are estimated as 0.21 % and 3.14 % respectively. Consequently, this region is important for the recovery of thorium and REE's. Samples from Eskişehir region were collected from different locations according to their mineral deposits by Turkish Mineral Research Institute (MTA). In addition to these samples, both dolamitte-2 and dolamitte-4 samples were collected from Nevşehir-Hacıbektaş region where uranium ores which are at the surface. The list of samples analyzed are given in Table 2.1.

Eskişehir-Sivrihisar-Kızılcaören deposits have fillite, fillitic silicate stones, microconglomerates. Both bastnasite and brockite minerals contain thorium. Also these deposits have fluorite, barite, manganese and quartz minerals. The names and chemical formulas of the samples from Eskişehir thorium deposits and from Nevşehir-Hacıbektaş uranium ores are shown in Table 2.2.

Table 2.1. The Identification , Location and Mineralization Type of Samples [21].

Sample	Location	Type of Mineralization
KTS-1	Eskişehir-Kızılcaören	Fluorite, Barite, Manganese, Silicate, Bastnasite
KTS-2	Eskişehir-Kızılcaören	Calcite, Fluorite, Barite, Bastnasite, Limonitte, Magnetite
KTS-3	Eskişehir-Kızılcaören	Carbonates
KTS-4	Eskişehir-Kızılcaören	Fluorites, CaF_2
Kocadeve- bağırtantepe	Eskişehir-Sivrihisar Karkın Village	Fluorite, Barite, Bastnasite, Monazite, Xenotime
Küçük- höyüklütepe	Eskişehir-Sivrihisar Beylikahır	Fluorite, Barite, Bastnasite, Monazite, Xenotime
Dolamitte-2	Nevşehir-Hacıbektas	Cryptocrystolene, Dolamitte, Clay, Quartz
Dolamitte-4	Nevşehir-Hacıbektas	Crptocrytolene, Dolamitte, Clay, Quartz

2.2. Preparation of Samples for Irradiation

All the samples were ground to 1 mm particle size (dust particles) prior to activation analysis.

Samples were spreaded on plastic trays, homogenized and dried overnight at 60°C. Approximately 200 mg of sample and reference standard were weighed for irradiation.

Table 2.2. The Name and Chemical Formulas of the Minerals

Mineral Name	Chemical Formula
Barite	BaSO_4
Bastnasite	$(\text{Ce}, \text{La}, \text{Nd}, \text{Th}, \text{Other REE})\text{FCO}_3$
Dolomite	$\text{Ca}, \text{Mg}(\text{CO}_3)_2$
Fluorite	CaF_2
Limonite-Gotite	$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Lanthanum Oxide	La_2O_3
Pirolusite	MnO_2
Monazite	$(\text{Ce}, \text{La}, \text{Y}, \text{Th})\text{PO}_4$
Quartz	SiO_2
Cerium Oxide	CeO_2
Thorite	ThSiO_4
Thorianite	$(\text{Th}, \text{U})\text{O}_2$
Calcite	CaCO_3
Xenotime	$(\text{Y}_2\text{O}_3\text{P}_2\text{O}_5)$

The ore samples and standard reference materials were placed in 5cm long quartz ampoules. These ampoules were cleaned before irradiation with the procedure given below:

- After heat sealing one end of quartz ampoules, they were dipped into a polyethylene container containing concentrated HNO_3 for three days.
- They were etched with 40% HF for 30 minutes to remove impurities which might be present in inner and outer surfaces.

- They were rinsed again with concentrated HNO_3 and washed with double and triple distilled water and dried in an oven at 60°C .

Duplicate analysis were performed for each ore sample. After placing samples and reference standards in quartz ampoules, the other end of the ampoules were heat sealed while the their bottom were immersed in liquid nitrogen. Empty quartz ampoules were also treated similarity for blank determinations.

2.3. Irradiation

After preparation of samples in quartz ampoules, all samples, standards and blanks were enclosed in aluminum cans. Aluminum cans were irradiated in two batches at different days. In the first run, samples were irradiated together with the standard reference materials for 4 hours and 35 minutes (Jan.4,1988). A shorter irradiation time (thirty minutes) was preferred for the second run (Jan.11,1988) in order to reduce the activity level obtained. For both irradiations, the neutron flux was about $2.82 \times 10^{13} \text{ n.cm}^2. \text{ sec}^{-1}$. Both irradiations were carried out at Çekmece Nuclear Research and Training Center (CNAEM) research reactor, TR-1 in Istanbul. The arrangement of samples, reference standard materials and blanks in aluminum cans are shown in Figures 2.1 and 2.2. In Figure 2.1, dotted circles represent the three dif-

ferent standard reference materials and the full circles were used for the samples. Samples were placed diagonally. Three different standards were used to allow the correction of any systematic variations in the observed count rates attributable to the neutron flux gradients in the Al-Can.

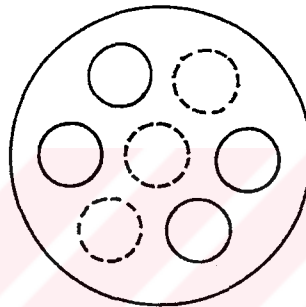




Figure 2.1. The Cross-Sectional Arrangement of Quartz Ampoules at the Bottom of the Cylindrical Aluminum Can. :Samples
:Standard

Standard reference materials used were S-16 [22], IAEA (Soil-5) and IAEA (Soil-7). The certified and recommended values for standard reference materials are given in Appendix A. In the first and second runs, preparation of samples, standard reference materials and blanks were the same. The only difference was the irradiation time in the reactor. This difference is indicated

in Tables 2.3 and 2.4. After 5-15 days of cooling the outer surfaces of the quartz ampoules were cleaned as follows.

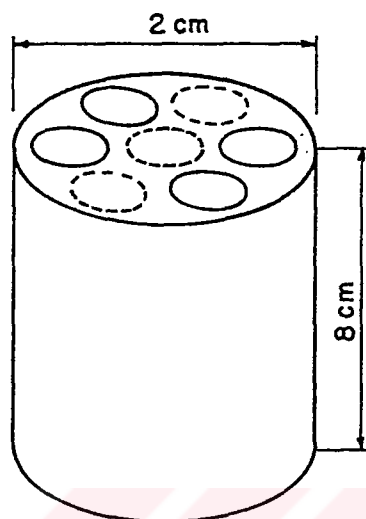


Figure 2.2. Cross-Section of the Aluminum Can

○ : Standards ○ : Samples

Quartz ampoules were etched with 40% HF for thirty minutes, and then were soaked in concentrated HCl for thirty minutes more. After rinsing them with concentrated HNO_3 , they were washed with water and dried. After cleaning, samples, standards and blanks were mounted on cards to attain reproducible geometry during counting. The diagram of a card used for mounting vials is shown in Figure 2.3.

Table 2.3. Content of the first Run; Irradiation at January 4, 1988

First Aluminum Can Second Aluminum Can Third Aluminum Can

Sample Name
KTS-1
KTS-2
SOIL-5
SOIL-7
S-16

Sample Name
KTS-3
KTS-4
SOIL-5
SOIL-7
S-16
BLANK

Sample Name
Dolamitte-2
Dolamitte-4
SOIL-5
SOIL-7
S-16

Table 2.4. Content of the Second Run; Irradiation at January 11, 1988

First Aluminum Can

Second Aluminum Can

Sample Name
Küçükhöyük- tepe
Kocadeve- bagirtantepe
SOIL-5
SOIL-7
S-16

Sample Name
MTA'S SAMPLES
SAMPLE-1
SAMPLE-2
SOIL-5
SOIL-7
BLANK
S-16

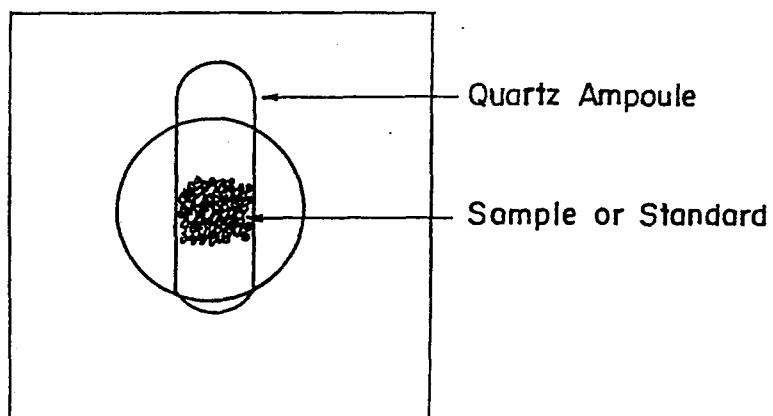


Figure 2.3. Card Board Used in Counting.

2.4. Counting

2.4.1. Counting System

The flow-diagram of the counting system used is shown in Figure 2.4.

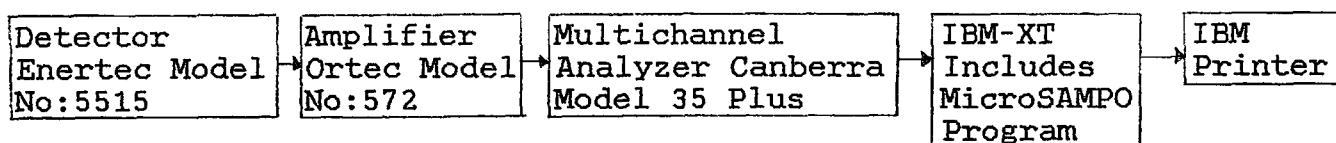


Figure 2.4. The flow-diagram of the Counting System

A high purity germanium (HPGe) γ -ray detector, Enertec Model which has 85 cm^3 volume was used for counting. Samples were placed in the counting positions above the detector, in a cave which is made of lead bricks in order to reduce the background activity. Power to the detector was supplied by an Ortec power supply. Signals

from intrinsic Ge-detector was amplified by an Ortec amplifier. Spectra obtained in a Canberra Model 35 MCA were transferred to the IBM -XT computer and were analyzed by using MicroSAMPO program described previously.

2.4.2. Calibration of the System and MicroSAMPO Program

Peak shapes and peak widths were calibrated with shaping time during the counting and full width at half maximum (FWHM) was calculated at 1332.5 keV peak energy of Co-60 for resolution of the peak. The FWHM of the peak was 1.97 keV and the peak to Compton ratio was 43:1.

The microSAMPO program has four calibration files and a library file. These are as follows:

- The energy calibration for identification of γ -ray energies which were obtained by using point sources Co-60, Cs-137, Na-22, Ba-133 and Eu-152. Energy, a function of channel number is calculated as [23].

$$E = A * C + B$$

where;

E: Energy of the peak centroid in keV.

C: Peak centroid channel.

A and B are coefficients determined from a least square fitting (A is the slope and B accounts for any system non-linearity). The energy region considered in the gamma spectra of MCA was regulated to 60-2000 keV region ($A \approx 0.5$ keV/channel). As seen in Figure 2.5, Energy

calibration curve is linear.

- Shape calibration for good fitting is one of the essential features of the microSAMPO program which improves the accuracy, consistency and speed of fitting. The peak shape function consists of a gaussian center, exponential upper and lower tails which are joined smoothly to the gaussian curve . The maximum number of peaks for fitting is hundred. The fitting parameters are determined by the micrSAMPO program automatically, but these parameters can be changed by the user with the interactive modes. The aim of the peak fitting is to resolve the overlapping peaks, to obtain the accurate area of the peak, to reduce the error in the peak determination and background. After storing the point sources data to the program, the shape of the peaks were calibrated by gaussian fitting.
- The full energy (photo peak) detection efficiency of coaxial high purity germanium (HPGe) detector was calibrated at different distances from the detector (at 8cm , 18.5 cm and 32.5 cm distances). The log-log plot of detector efficiency versus γ -ray energy is shown at these distances in Figure 2.6.

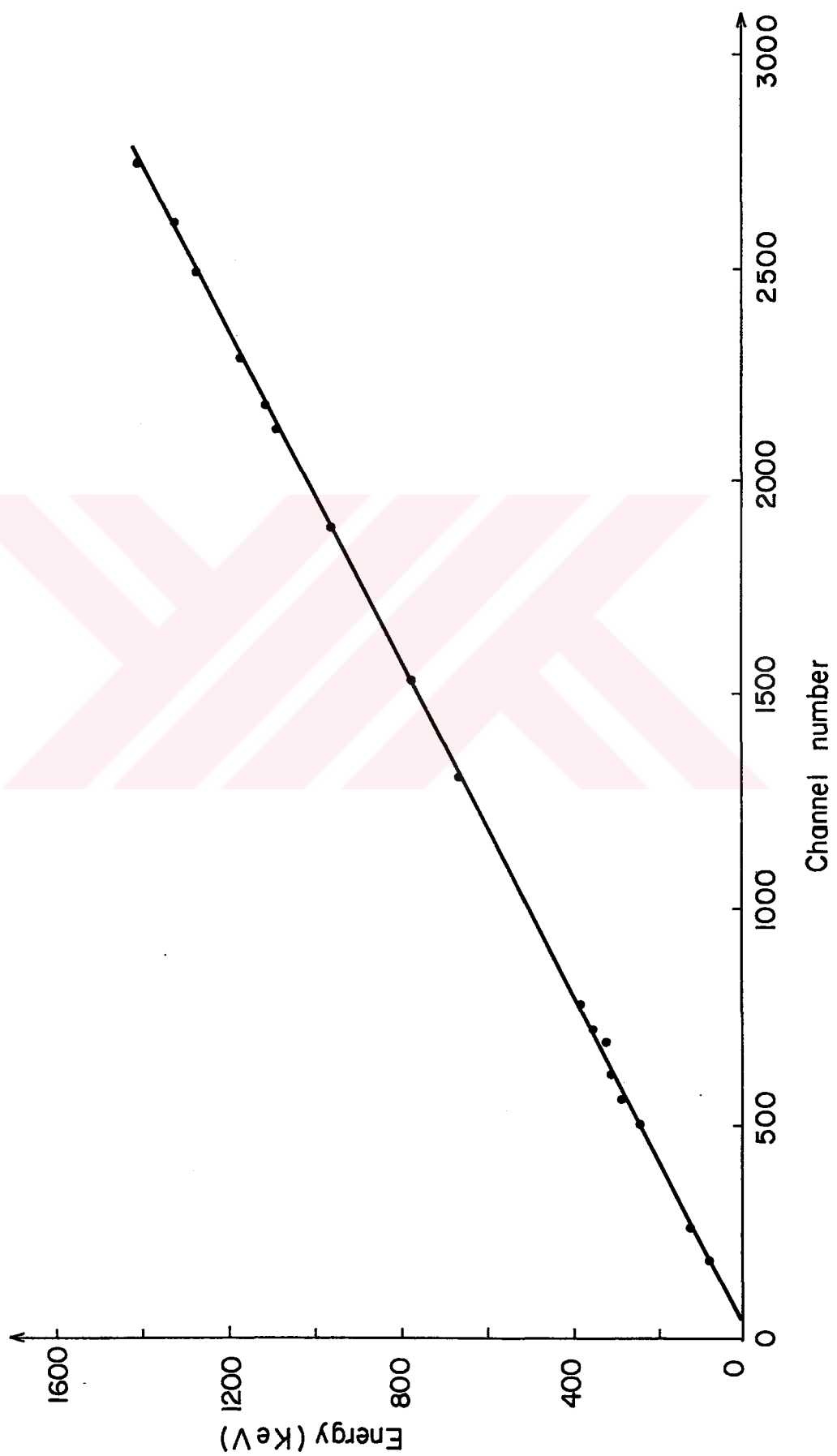


Figure 2.5 Energy Calibration Curve

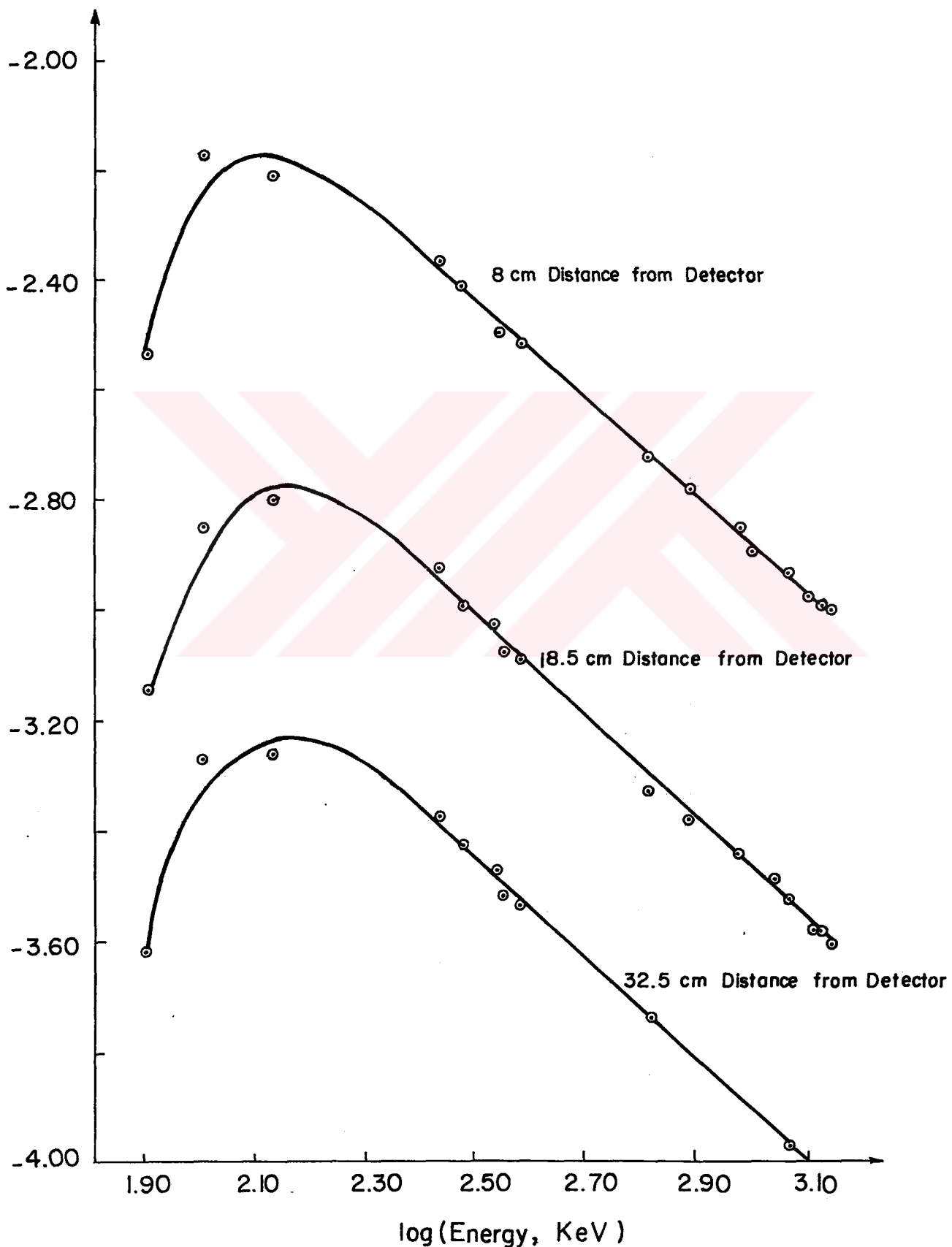


Figure 2.6 Log-Log Efficiency Curve of the Detector

After optimization of counting system, samples, standards reference materials and blanks were counted in three consecutive counting positions on high Purity Germanium (HPGe) detector for 4 hours after 5-15 days cooling, for 6 hours after 22-35 days cooling and for 6 hours after 90-140 days cooling [Fig. 2.7]. Thus, with two or three counting intervals, about thirteen REE's can be measured. The blanks were clean and their contributions to the samples and standards were negligible.

After identification of nuclides, following data were obtained for each peak present in the spectrum.

- Energy in keV and the net area (in counts) of the peak.
- Percent standard deviation of the net area.
- Names of possible nuclides for each peak in the nuclide identification file and the net activity (pCi/g) for that nuclide.
- Relative standard deviation of the net activity.

The distance of samples and standard reference materials from detector were adjusted to minimize the pulse pile-up. The dead time was kept below 10 % throughout the present experiments.

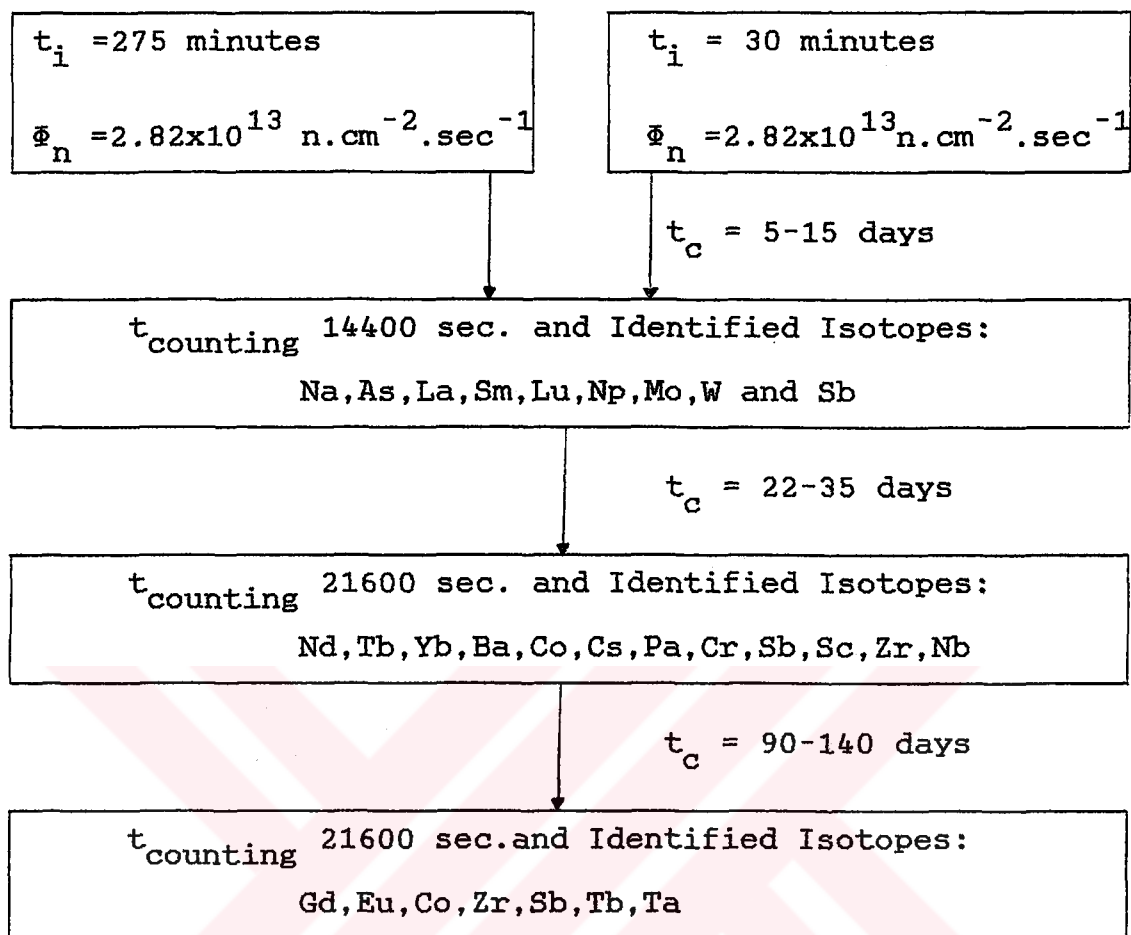


Figure 2.7. Irradiation and Counting Scheme of Long Lived Isotopes

2.5. Concentration Calculations

MicroSAMPO program gives an output which includes energy, peak area, percent error of area and pCi/g activity of the elements present in the sample. There is only one file for the spectrum analysis. The concentrations of elements in the sample can be calculated by a subprogram prepared for that purpose. Standard's

Sample's and Blank's activities were used in calculations as follows:

$$B = \frac{(A_0 \pm EA_0)_{\text{samp}} - (A_0 \pm EA_0)_b}{(A_0 \pm EA_0)_{\text{std}} - (A_0 \pm EA_0)_b} \quad (2.1)$$

$$(C \pm EC)_{\text{samp}} = \frac{M(\text{std}) * (C \pm EC)_{\text{std}}}{M(\text{samp})} * B \quad (2.2)$$

In which;

B: Activity ratio of sample to standard corrected by blank's activity.

C(samp): Concentration of element of interest in the sample

EC(samp): Error in the concentration

A_0 (samp): Decay corrected activity of the sample

EA_0 (samp): Error in decay corrected activity

A_0 (b) : Decay corrected activity of the blank

EA_0 (b) : Error in decay corrected activity of the blank

A_0 (std) : Decay corrected activity of the standard

EA_0 (std) : Error in decay corrected activity of the standard

M(std) : Mass of the standard (mg)

M(samp) : Mass of the sample (mg)

C(std) : Concentration of standard

EC(std) : Error in the concentration of standard.

A computer program in basic language was written (Appendix B and C) and transferred into the Lotus 1-2-3 Package Program in order to simplify the calculations. Then, all calculations were done by using this program.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Determination of Elements Using Long Half-lives Isotopes

The gamma-ray spectra of the irradiated samples were studied after suitable cooling times which will give interference free photo-peaks of the desired elements. The cooling times along with relevant nuclear data of the isotopes are given in Table 3.1. The gamma-ray spectra of samples obtained after 275 minutes irradiation are shown in Figures 3.1 and 3.2. The energies of the gamma-lines used for the determination of all induced radionuclides with relevant nuclear data are given in Appendix D. The selection of photo-peak for analysis and some interferences from other radionuclides are briefly discussed for each element as follows:

Scandium: Scandium-46 has two photo-peak energies at 889.3 keV and at 1120.5 keV. Both of these energies can be used to calculate the concentration of scandium after 2-4 weeks cooling [14], but 889.3 keV photo-peak is the one which is mostly used.

Table 3.1. The List of Gamma Lines, Radionuclide Energies and Experimental Parameters for the Ore Samples (Dolamitte-2).

Energy(KeV)	Radionuclide	Half Life	Exp.Parameter
103.2	Sm-153	46.5 h	A
103.2	Gd-153	241.6 d	B
106.4	Np-239	2.4 d	A
110.0	Yb-169	32.0 d	B
113.0	Lu-177	161.0 h	A&B
121.8	Eu-152	4818.0 d	B
133.0	Hf-181	42.5 d	B
140.5	Mo-99	66.0 h	A
145.4	Ce-141	32.5 d	B
177.2	Yb-169	32.0 d	B
181.1	Mo-99	66.0 h	A
198.0	Yb-169	32.0 d	B
208.4	Lu-177	161.0 h	A&B
216.1	Ba-131	11.7 d	B
228.2	Np-239	2.4 d	A
244.7	Eu-152	4818.0 d	B
276.4	Ba-133	10.5 y	B
277.6	Np-239	2.4 d	A
298.6	Tb-160	72.1 d	B
312.0	Pa-233	27.0 d	B
320.1	Cr-51	27.7 d	B
328.8	La-140	40.2 h	A
340.6	Pa-233	27.0 d	B

Energy(KeV)	Radionuclide	Half Life	Exp.Parameter
344.3	Eu-152	4818.0 d	B
373.2	Ba-131	11.7 d	B
396.3	Yb-175	100.6 h	A
415.9	Pa-233	27.0 d	B
479.5	W-187	23.9 h	A
482.0	Hf-181	42.5 d	B
487.0	La-140	40.2 h	A
496.2	Ba-131	11.7 d	B
551.0	Annihilation		
531.4	Nd-147	11.0 d	B
559.5	As-76	23.3 h	A
569.3	Cs-134	387.6 d	B
602.7	Sb-124	60.2 d	B
685.7	W-187	23.9 h	A
724.2	Zr-95	65.5 d	B
756.7	Zr-95	65.5 d	B
765.8	Nb-95	35.1 d	B
778.8	Eu-152	4818.0 d	B
795.8	Cs-134	387.6 d	B
815.8	La-140	40.2 h	A
834.8	Mn-54	312.7 d	B
867.4	Eu-152	4818.0 d	B
873.2	Eu-154	8.5 d	B
879.4	Tb-160	72.1 d	B
889.3	Sc-46	42.5 d	B

Energy(KeV)	Radionuclide	Half Life	Exp.Parameter
898.0	Y-88	106.6 d	B
964.0	Eu-152	4818.0 d	B
996.3	Eu-154	8.5 y	B
1004.8	Eu-154	8.5 y	B
1078.8	Rb-86	18.6 d	B
1085.8	Eu-152	4818.0 d	B
1099.2	Fe-59	44.6 d	B
1115.5	Zn-65	244.0 d	B
1120.5	Sc-46	83.8 d	B
1173.2	Co-60	1920.0 d	B
1177.9	Tb-160	72.1 d	B
1189.0	Ta-182	114.5 d	B
1221.4	Ta-182	114.5 d	B
1230.0	Ta-182	114.5 d	B
1271.9	Tb-160	72.1 d	B
1274.5	Na-22	2.6 y	B
1291.6	Fe-59	44.6 d	B
1332.5	Co-60	1920.0 d	B
1408.0	Eu-152	4818.0 d	B
1460.0	K-40	1.25×10^9 y	B
1596.2	La-140	40.2 h	A
1691.0	Sb-124	60.2 d	B
2091.0	Sb-124	60.2 d	B

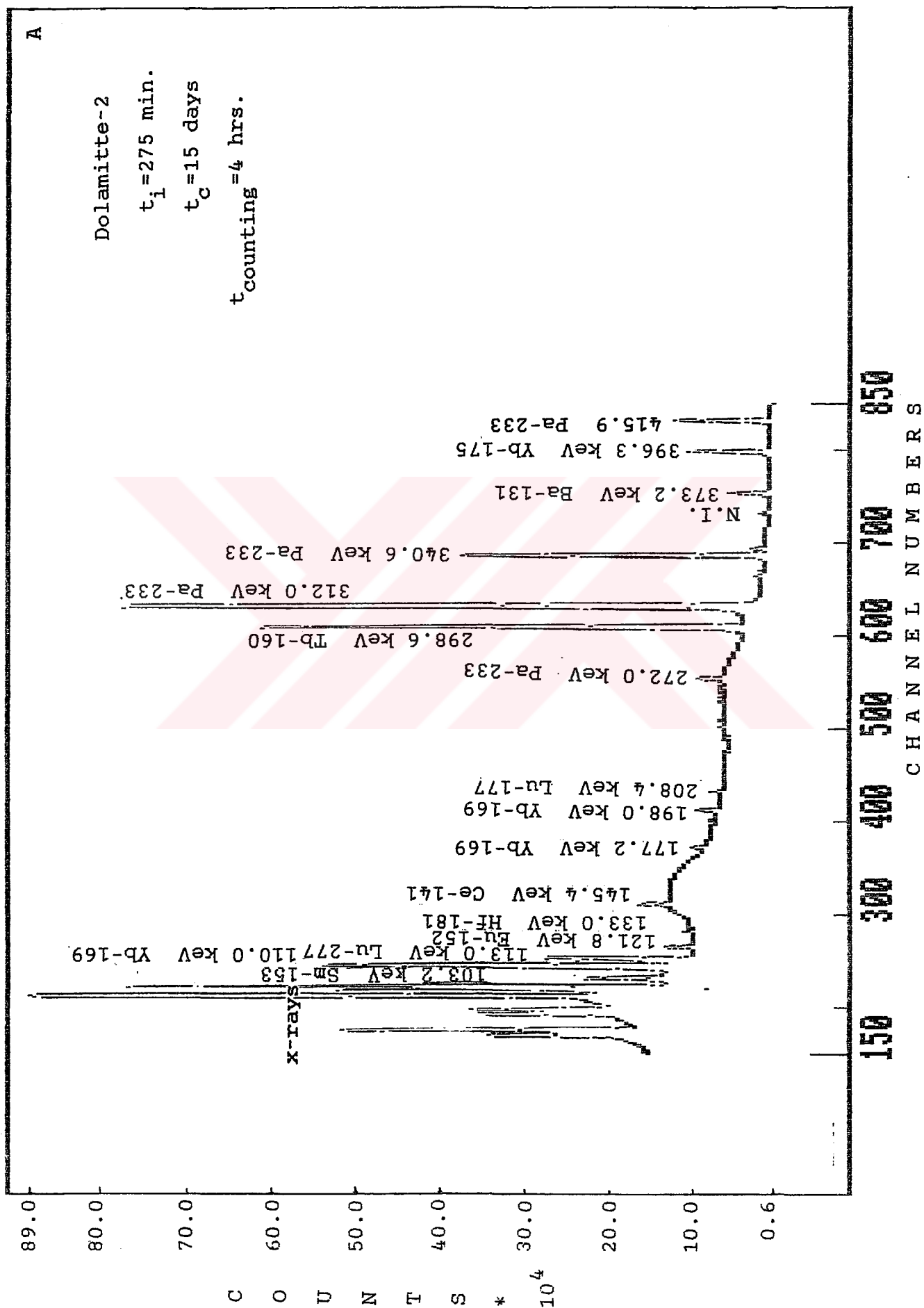
A : Best identified after fifteen days of cooling

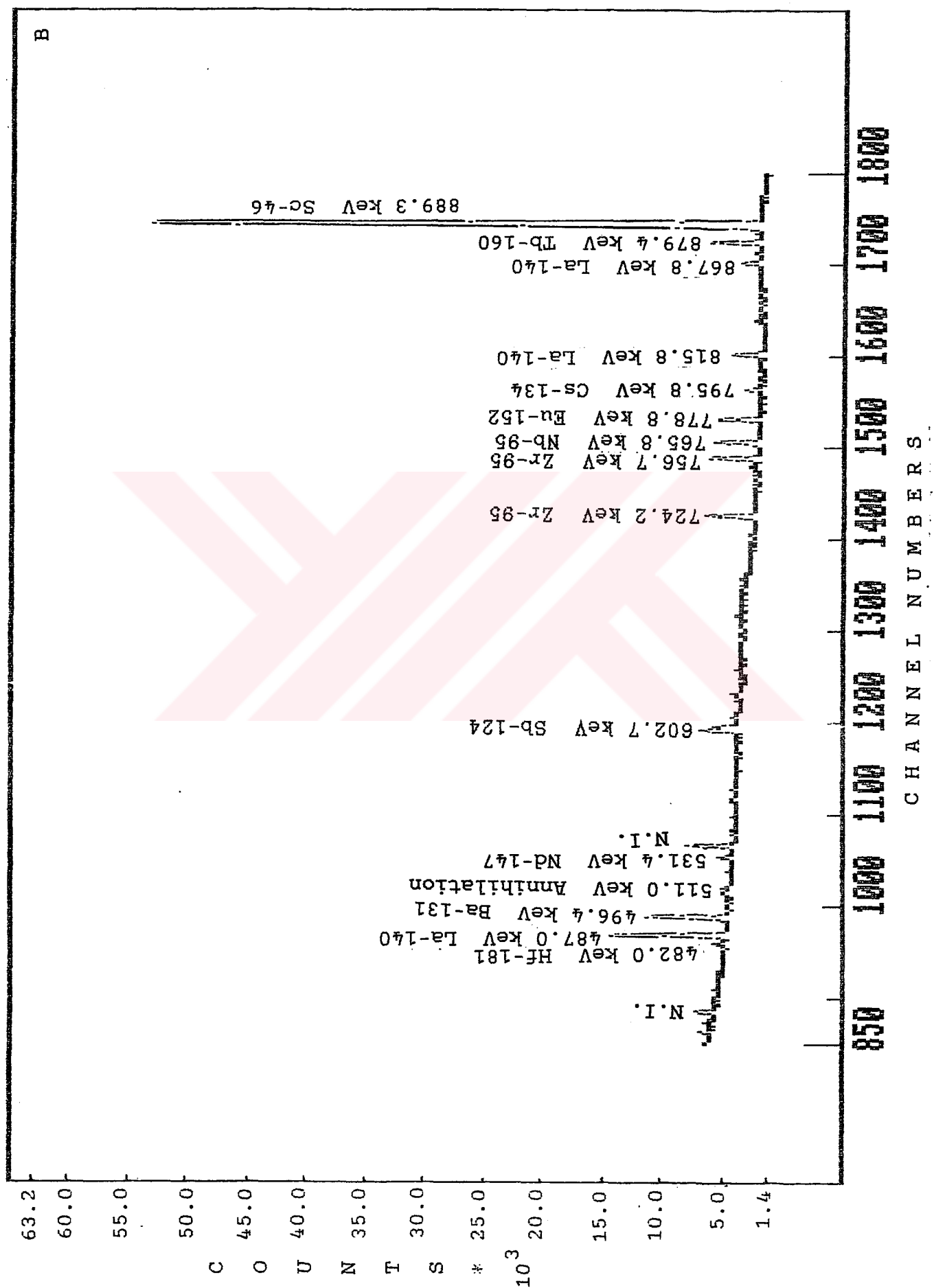
B : Best identified after thirty Days of cooling

d : day h : hour y : year

Figure 3.1. Gamma-Ray Spectrum of Activated
Dolamitte-2 Ore Sample ($t_i=275$ min.,
 $t_c=15$ days, $t_{\text{counting}}=4\text{hrs}$).

- a) Expanded Spectrum Between Channels 150-850
- b) Expanded Spectrum Between Channels 850-1800
- c) Expanded Spectrum Between Channels 1800-3400





CHANNEL NUMBERS

1800 2000 2500 3000 3400

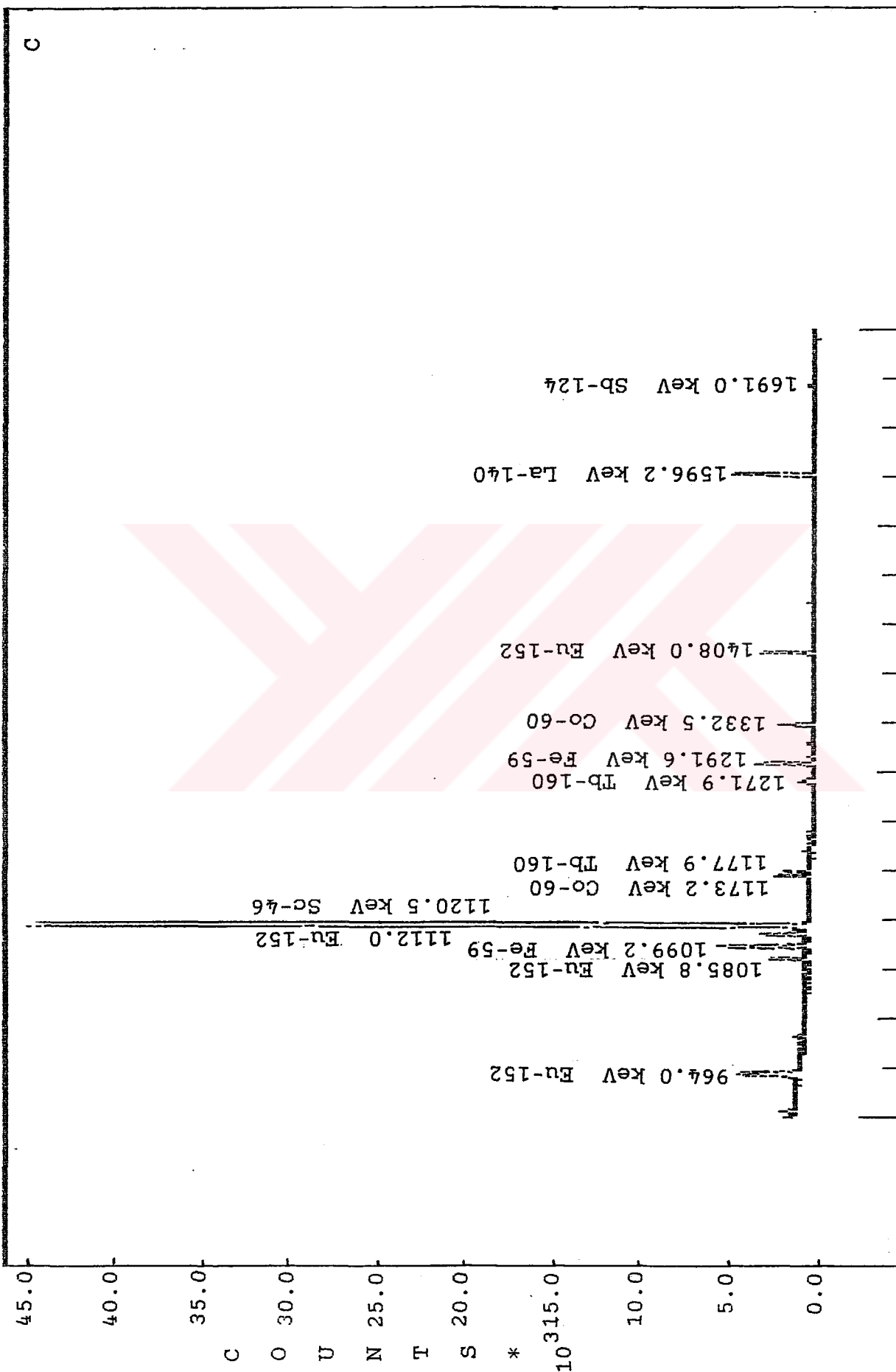
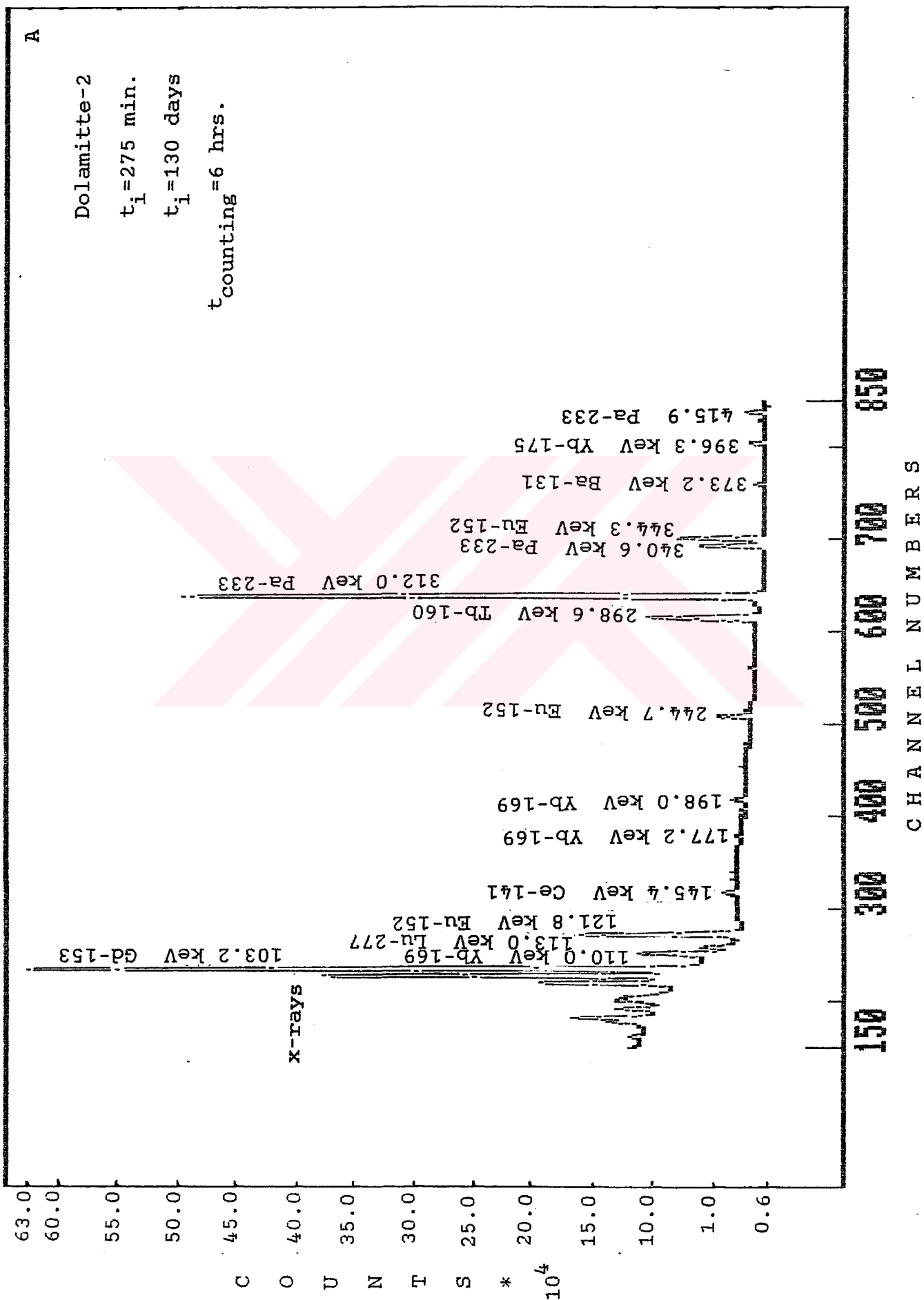


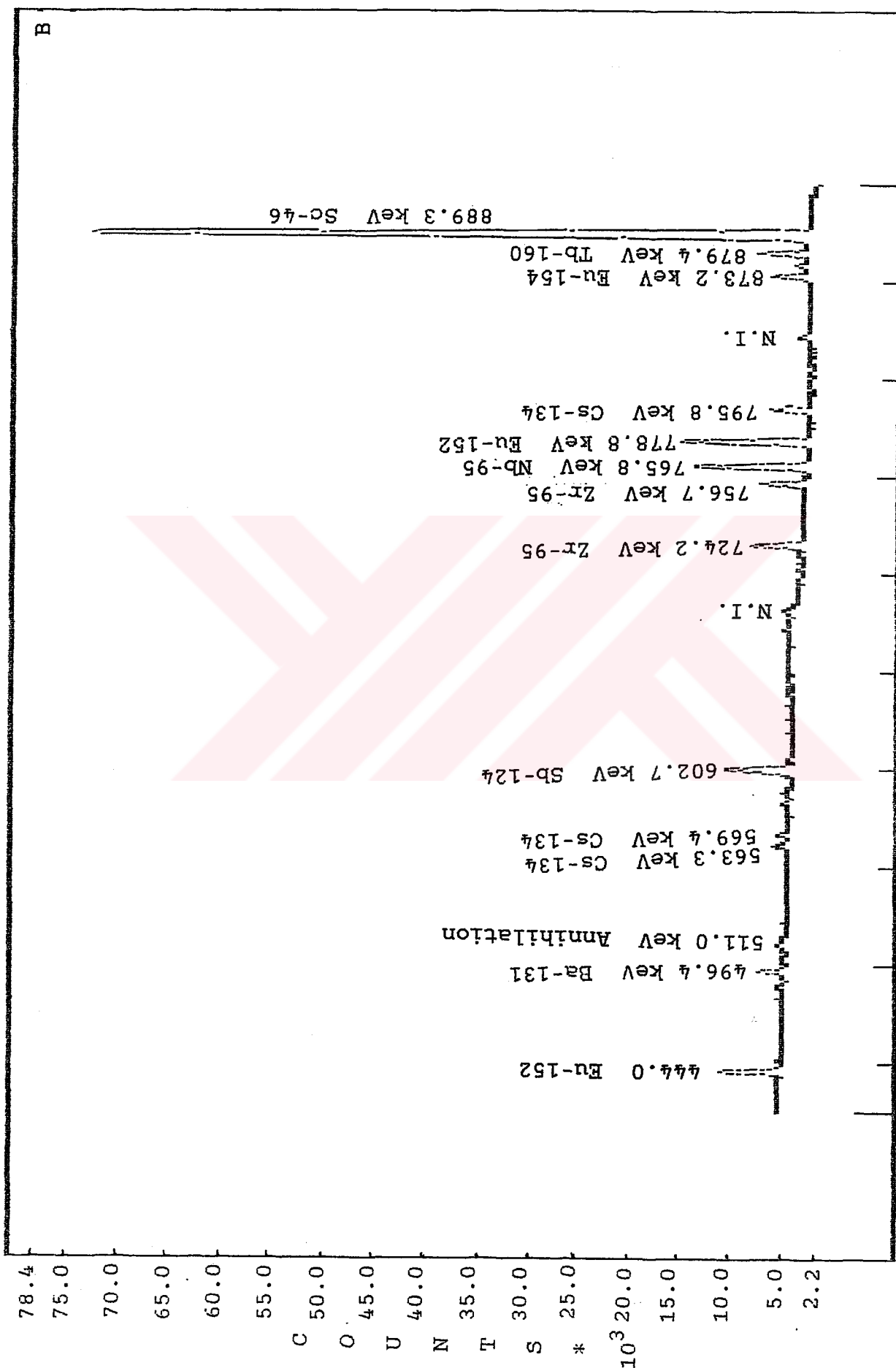
Figure 3.2. Gamma-Ray Spectrum of Activated
Dolamitte-2 Ore Sample ($t_i=275$ min.,
 $t_c=130$ days, $t_{\text{counting}}=6$ hrs).

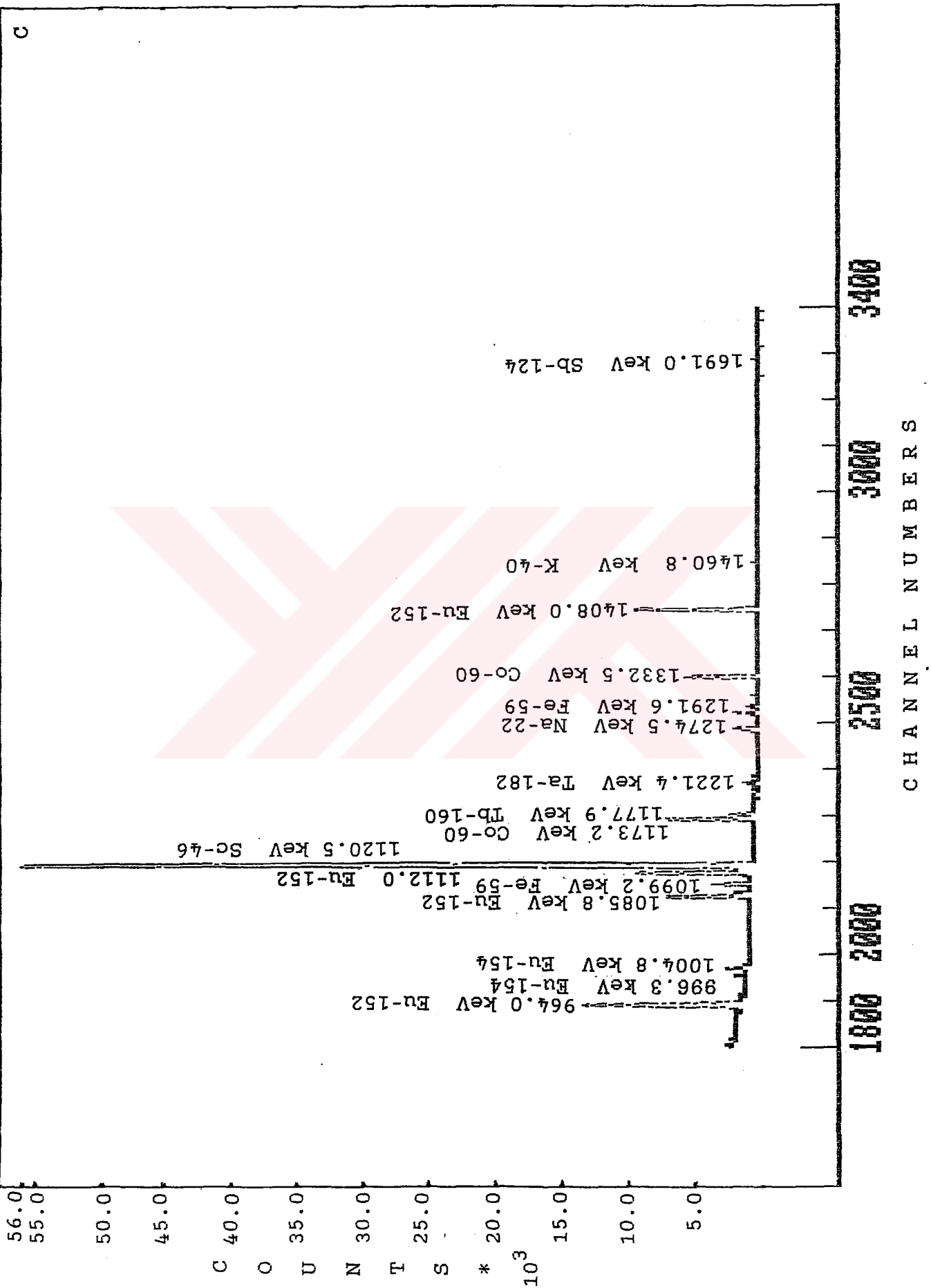
- a) Expanded Spectrum Between Channels 150-850
- b) Expanded Spectrum Between Channels 850-1800
- c) Expanded Spectrum Between Channels 1800-3400



CHANNEL NUMBERS

850 1000 1100 1200 1300 1400 1500 1600 1700 1800





Chromium: The 320.1 keV photo-peak of Cr-51 was used to calculate the concentration of chromium which is free from any interferences.

Iron: The photo-peak of Fe-59 at 1099.2 keV and 1291.5 keV are free from interference after two weeks cooling time. The 192 keV peak of Fe-59 is not used because it suffers from interference of the 192 keV peak of Tb-160.

Cobalt: Cobalt-60 has two photo-peak energies at 1173.2 keV and at 1332.5 keV. No interferences were encountered in the measurement of Co-60 after 2-4 weeks cooling.

Zinc: Zn-65 can be measured after a cooling period of a few weeks at 1115.5 keV gamma-ray [24].

Zirconium: After four weeks of cooling, the long-lived Zr-95 was used. The 756.9 keV gamma-ray is free from interference, whereas the 724.2 keV peak is subject to interference from the 722.7 keV peak of Sb-124. The contribution from the fission of U-235 will be discussed in 3.5.1 [25].

Molybdenum: The associated photo-peak energies for Mo-99 are 140.5 keV and 739.4 keV. These energies are free from interferences and they were used to calculate the concentration of molybdenum.

Antimony: The concentration of antimony was determined by using the 1691.0 keV peak of Sb-124.

Cesium: Among the many photo-peaks of Cs-134, the peaks at 795.8, 801.0 and 1007 keV are the best choices.

Barium: The photo-peaks of Ba-131 at 496.2 keV and at 373.2 keV are used after long irradiation and 2-4 weeks of cooling time. The 123.7 keV photo-peak can not be used because it has interference from the 121.7 keV peak of Eu-152.

Lanthanum: The La-140 is easily determined after irradiation using one of its several photo-peaks. The high abundance photo-peak of La-140 at 1596.2 keV which is free from interferences was used for the determination of Lanthanum. The contribution of La-140 from U-235 (n,f) reaction is negligible [25,26].

Cerium: The three isotopes of cerium produced by irradiation, Ce-139 is not useful for analytical purposes, its use resulted in consequently high and erroneous results. Using 145.5 keV peak of Ce-141 gave mutually agreeable results.

Neodymium: The photo-peak of Nd-147 at 531.4 keV which is free from interferences was used for determination of Nd. The high abundance peak at 91.0 keV is surrounded by the other peaks which can not be resolved. Also the 319.4 keV peak can not be resolved from the peak of Lu-177M. The short-lived Nd-147 can not be used due to interferences.

Samarium: The both peaks of Sm-153 have interferences from various isotopes. Within 3-4 days of cooling 103.2 keV peak due to Sm-153 can be used. However with increasing time, the contributions from other isotopes starts mounting resulting in erroneously higher results.

Europium: Eu-152 has numerous photo-peaks. The high abundance peaks at 1408.0 keV and 778.8 keV are free from interferences. Both of these were used for the determination of this element [26]. The other peak at 121.7 keV can not be resolved from 123.2 keV of Eu-154.

Gadolinium: The high abundance of Gd-153 at 103.2 keV was used as the 97.0 keV peak has serious interferences. The peaks of Sm-153 and Np-239 at 104.0 and 103.7 keV, respectively interfere with the 103.2 keV peak of Gd-153. This interference can be avoided by counting the sample after three weeks cooling during which interfering isotopes decay out. In case of thorium containing samples a correction has to be made for the contribution of 103.0 keV peak of Pa-233. However, this energy was not used for the determination of Pa-233.

Terbium: The photo-peak of Tb-160 at 1178.0 keV was used as other high abundance peaks have no interferences [27].

Ytterbium: The Yb-175 and Yb-169 can be used for Yb determination. The 282.6 keV line of former and 308.0 keV of later are interference free. Both gave nearly the same values in the ore samples that we analyzed.

Lutetium: The Lu-177 is determined through its interference free 208.4 keV line about two weeks after irradiation [26].

Hafnium: The photo-peak of Hf-181 at 482.0 keV was found to be free from interference after four weeks of cooling time and was used for the determination of Hafnium.

Tantalum: Tantalum has two interference free photo-peaks at 1189.0 keV and at 1221.5 keV. These photo-peak energies can be used to calculate the concentration of tantalum after 2-4 weeks cooling.

Thorium(Pa-233): The Th-232 was converted to Pa-233 after irradiation and β -decay. The associated photo-peak energy for Pa-233 is 311.9 keV which was used for thorium determination.

Uranium(Np-239): U-238 was converted to Np-239 after irradiation and β -decay. This 106.4 keV photo-peak energy of Np-239 was used for the determination of Uranium.

3.2. Standards

Three different standards were used to calculate concentrations of elements in ore samples. These are IAEA (Soil-5), IAEA (Soil-7) and S-16 [22]. All standards were irradiated at the same conditions and the concentrations of elements in Soil-5 were calculated by using Soil-7 as standard. Also, Soil-7 were checked by using Soil-5 as standard. It was found that a highly accurate and precise multielement determination can be achieved by using these standards. There are fourteen elements certified in Soil-5 and fifteen elements certified in Soil-7. Thirteen elements are certified in S-16. Others are the recommended values in both Soil-5 and Soil-7. These recommended values were checked in five different aluminum cans (Tables 2.3 and 2.4) and they were found to have the same with recorded values in the standards. Some of these recommended values were also checked with S-16 standard (Tables 2.3 and 2.4). After discussion of these recommended values, the recommended concentrations of elements in standards were used in the calculations. By using these three standard reference materials, one can determine upto 25 elements in irradiated samples.

3.3. Quality Assessment

The amount of interested elements in Soil-5 standard can be compared with other two standards Soil-7 and S-16 in order to minimize the statistical errors in countings and in calculation of concentrations for the elements. After selecting of interference free peaks, the concentration of element for this peak can be used according to its statistical error. The comparison of standard concentrations are shown in Tables 3.2 and 3.3. Generally, our results are in good agreement with those of the certified and recommended values of standards (Appendix A) and with literature values [28].

Also these standards contain many elements with long lived isotopes. After 90-140 days of cooling, upto 12 certified elements can be determined in the standards.

Table 3.2. Concentrations of Elements in IAEA(Soil-5)
Determined by INAA Using IAEA(Soil-7) as a Standard.

Element(mg/kg)	IAEA(Soil-5)	Range	This Work	[28]
Sc	14.8	14.1-15.5	14.9±0.2	
Cr	28.9	26.1-31.7	29.5±1.6	31.3±3.3
Fe(%)	4.45	4.26-4.67	4.54±0.07	
Co	14.8	14.0-15.6	14.8±0.2	16.1±0.6
Zn	368	360-376	366±6	374±14
Zr	221	-	222±2	224±10
Nb	9	-	9.5±0.7	11.3±1.2
Mo	1.7	-	1.3±0.1	
Sb	14.3	12.1-16.5	15.4±0.8	
Cs	56.7	53.4-60.0	58.2±0.5	60.0±3.0
Ba	562	509-615	575±31	515±27
La	28.1	26.6-29.6	27.9±1.6	
Ce	59.7	56.7-62.7	58.0±1.2	61.6±2.4
Nd	29.9	28.3-31.5	30.0±1.9	
Sm	5.42	5.03-5.81	5.40±0.40	
Eu	1.18	1.10-1.26	1.17±0.07	
Tb	0.67	0.61-0.74	0.78±0.10	
Yb	2.24	2.04-2.44	2.50±0.40	
Lu	0.34	0.29-0.38	0.34±0.02	
Hf	6.30	6.00-6.60	6.52±0.30	
Ta	0.76	0.71-0.82	0.76±0.04	
Th	11.3	10.6-12.0	11.6±0.3	
U	3.15	2.70-3.60	3.17±0.17	

Table 3.3. Concentrations of Elements in IAEA(Soil-7)

Determined by INAA Using IAEA(Soil-5) as a Standard.

Element(mg/kg)	IAEA(Soil-7)	Range	This Work	[28]
Sc	8.30	6.90-9.00	8.52±0.22	
Cr	60	49-74	60.7±4.5	71.7±5.8
Fe(g/kg)	25.7	25.2-26.3	25.5±0.9	
Co	8.9	8.4-10.1	8.8±0.3	9.4±0.5
Zn	104	101-113	109±8	98±7
Zr	185	180-201	188±3	172±5
Nb	12	7-17	8.7±0.1	10.2±0.3
Mo	2.5	0.9-5.1	2.3±0.2	
Sb	1.7	1.4-1.8	1.6±0.1	
Cs	5.4	4.9-6.4	5.3±0.2	5.3±0.1
Ba	159	131-196	155±9	130±9
La	28	27-29	26±2	
Ce	61	50-63	63±2	61±2
Nd	30	22-34	28±2	
Sm	5.10	4.48-5.50	5.40±0.32	
Eu	1.0	0.9-1.3	1.1±0.1	
Gd	-	-	21.8±1.5	
Tb	0.6	0.5-0.9	0.6±0.1	
Yb	2.4	1.9-2.6	2.5±0.2	
Lu	0.3	0.1-0.4	0.39±0.02	
Hf	5.1	4.8-5.5	5.3±0.2	
Ta	0.8	0.6-1.0	0.81±0.05	
Th	8.2	6.5-8.7	7.3±0.4	
U	2.6	2.2-3.3	2.4±0.1	

3.4. Long Irradiation Results

The results of first , second ,and third counting for KTS-1 , KTS-2 , KTS-3 and KTS-4 ore samples are given in Tables 3.4 , 3.5 , 3.6. Also , the first , second and third counting results of ore samples of Dolamitte-2 , Dolamitte-4 , Küçükhöyüklütepe and Kocadevebagirtantepe are given in Tables 3.7 , 3.8 and 3.9.

In the first counting , the concentrations of As , Mo and Na were not calculated in some ore samples (Tables 3.4 and 3.7) because of high activity of ore samples. The best results of these ore samples were selected from first , second and third countings according to their statistical errors and agreeability of concentrations with in each other. Some second counting results were selected for best results according to their statistical errors. Also , in some cases , average of three countings were taken for the best results. The best results of these ore samples are given in Tables 3.10 and 3.11. The concentrations of elements in second counting are in good agreement with MTA's and GÜlovali's results [29]. The MTA Institute's results were obtained by X-ray Fluorescence method. The GÜlovali worked on KTS-1 ore sample with Instrumental Neutron Activation Analysis.

Table 3.4. The Results of the First Counting (5-15 Days Cooling) for the Ore Samples.

Element	KTS-1	KTS-2	KTS-3	KTS-4
Na(g/kg)	-	7.2±0.8	7.8±0.9	8.3±1.0
Sc(mg/kg)	17.3±0.8	15.4±1.4	11.5±1.3	8.5±0.5
Cr(mg/kg)	498±35	-	31.3±2.9	162±14
Fe(g/kg)	25.3±1.4	84.1±1.4	23.1±5.3	18.4±1.7
Co(mg/kg)	25.3±2.4	1.9±0.7	1.3±0.1	1.2±0.4
Zn(mg/kg)	-	-	360±40	210±20
As(mg/kg)	200±30	-	160±20	-
Sr(g/kg)	-	2.5±0.1	1.3±0.1	3.1±0.2
Zr(mg/kg)	143±11	77±9	96±7	107±10
Nb(mg/kg)	4.0±0.4	1.4±0.2	1.8±0.6	7.0±0.9
Sb(mg/kg)	4.8±0.7	2.8±0.3	3.9±0.5	7.3±0.6
Cs(mg/kg)	12.4±1.5	0.8±0.1	1.9±0.4	5.4±0.5
Ba(g/kg)	105±10	122±14	32±6	142±24
La(g/kg)	3.8±0.1	9.4±0.4	4.4±0.3	12.5±0.7
Ce(g/kg)	17.6±2.9	13.4±2.2	4.8±0.4	12.3±0.9
Nd(g/kg)	14.5±0.7	3.3±0.3	1.4±0.3	-
Sm(g/kg)	3.00±0.33	0.63±0.07	0.15±0.03	0.35±0.06
Eu(mg/kg)	355±32	71±5	25±2	41±3
Gd(mg/kg)	560±90	430±40	610±60	150±20
Tb(mg/kg)	55.2±4.8	11.4±1.2	7.4±1.3	11.6±1.2
Yb(mg/kg)	41.6±7.2	-	19.4±0.2	36.9±4.5
Lu(mg/kg)	-	-	36.2±5.4	-
Hf(mg/kg)	5.6±1.4	10.7±1.2	31.3±0.3	4.1±0.4
Th(g/kg)	5.4±1.2	2.4±0.2	2.7±0.3	1.3±0.3
U(mg/kg)	9.4±1.3	181±10	8.0±0.4	8.6±0.4

Table 3.5. The Results of the Second Counting (22-35 Days Cooling) for the Ore Samples.

Element	KTS-1	KTS-2	KTS-3	KTS-4
Sc(mg/kg)	18.0±0.2	14.6±0.3	10.4±0.3	8.6±0.3
Cr(mg/kg)	500±32	39.1±2.6	30.1±1.7	168±13
Fe(g/kg)	26.7±1.1	96.5±1.3	26±6	18.1±0.7
Co(mg/kg)	25.9±1.0	1.8±0.1	1.4±0.1	1.0±0.1
Zn(mg/kg)	-	-	360±30	210±20
Sr(g/kg)	-	2.5±0.1	1.3±0.2	3.1±0.2
Y(g/kg)	-	-	-	42.3±5.6
Zr(mg/kg)	146±9	87±3	89±3	104±9
Nb(mg/kg)	3.0±0.1	1.2±0.1	1.6±0.1	7.0±0.5
Sb(mg/kg)	5.6±0.3	3.0±0.3	3.8±0.2	10.7±0.5
Cs(mg/kg)	10.3±0.4	1.0±0.1	1.8±0.1	5.0±0.3
Ba(g/kg)	115±12	132±8	36±4	145±11
Ce(g/kg)	15.3±1.3	13.2±1.0	4.7±0.4	12.0±0.7
Nd(g/kg)	14.8±0.4	3.4±0.2	1.3±0.2	2.5±0.1
Eu(mg/kg)	383±30	71±6	28±3	42±4
Gd(mg/kg)	540±100	420±50	520±100	150±20
Tb(mg/kg)	54.0±5.3	12.5±0.9	8.0±1.5	10.9±0.6
Yb(mg/kg)	62.6±4.2	28.4±1.2	22.7±2.1	37.5±4.4
Lu(mg/kg)	-	-	36.2±4.3	-
Hf(mg/kg)	4.2±0.2	10.6±1.0	30.1±1.2	4.5±0.3
Th(g/kg)	5.3±0.2	2.9±0.2	2.9±0.2	1.5±0.2

Table 3.6. The Results of the Third Counting (90-140 Days Cooling) for the Ore Samples

Element	KTS-1	KTS-2	KTS-3	KTS-4
Sc(mg/kg)	18.0±0.9	14.7±0.5	10.8±0.4	8.4±0.4
Cr(mg/kg)	496±34	38.5±4.4	32.3±4.3	167±27
Fe(g/kg)	26.6±1.4	76.1±6.4	25.0±6.1	19.5±0.8
Co(mg/kg)	26.1±0.9	1.8±0.2	1.4±0.1	1.3±0.2
Zn(mg/kg)	-	-	350±40	240±40
Sr(g/kg)	-	-	1.4±0.6	3.4±0.5
Zr(mg/kg)	140±10	78±4	97±5	101±6
Nb(mg/kg)	5.0±0.4	1.6±0.2	1.7±0.4	7.4±1.2
Sb(mg/kg)	5.6±0.6	2.7±0.2	3.0±0.4	9.2±0.7
Cs(mg/kg)	14.2±1.6	1.1±0.1	1.7±0.2	5.5±0.6
Ba(g/kg)	116±12	136±18	34±8	113±21
Ce(g/kg)	15.8±2.7	14.1±1.9	3.6±0.2	13.0±0.9
Nd(g/kg)	14.9±0.7	3.2±0.4	1.1±0.1	2.3±0.6
Eu(mg/kg)	371±13	71.8±4.0	28.7±1.9	40.8±3.2
Gd(mg/kg)	540±80	420±50	510±60	160±20
Tb(mg/kg)	54.0±5.6	13.4±1.4	9.1±0.6	11.5±1.2
Yb(mg/kg)	62.6±6.2	24.0±2.1	21.0±1.1	37.3±3.7
Hf(mg/kg)	4.5±0.9	10.5±0.9	33.4±0.4	4.6±0.7
Th(g/kg)	5.1±0.5	2.3±0.3	2.8±0.4	1.3±0.4

Table 3.7. The Results of the First Counting(5-15 Days Cooling) for the Ore Samples

Element	Dolamitte-2	Dolamitte-4	K.Höyükü	K.Devebagirtan
Na(g/kg)	-	16.0±0.2	-	-
Sc(mg/kg)	36.7±1.3	32.9±0.4	14.6±1.0	42.8±2.4
Cr(mg/kg)	26.9±2.9	84.6±9.3	73.2±4.6	66.4±3.2
Fe(g/kg)	42.3±0.6	52.1±1.2	26.6±9.2	31.9±1.7
Co(mg/kg)	29.2±3.1	24.2±0.9	5.5±0.5	4.4±0.2
Zn(mg/kg)	-	-	280±30	340±40
As(mg/kg)	-	-	-	6.7±0.6
Y(mg/kg)	-	-	650±50	-
Zr(mg/kg)	147±13	163±9	98±4	-
Nb(mg/kg)	6.0±0.2	4.7±0.4	1.1±0.1	1.4±0.1
Mo(mg/kg)	-	-	46.7±4.9	-
Sb(mg/kg)	23.4±2.8	26.2±3.2	13.4±0.2	4.1±0.5
Cs(mg/kg)	11.9±0.3	4.4±0.5	8.6±1.2	6.8±1.1
Ba(g/kg)	-	0.4±0.1	114±9	76.0±6.2
La(g/kg)	5.0±0.2	-	10.3±1.3	12.4±1.4
Ce(g/kg)	7.0±1.0	6.0±1.0	21.4±2.2	20.2±2.2
Eu(mg/kg)	21.2±0.6	11.2±0.2	45.7±1.5	57.4±2.4
Gd(g/kg)	1.1±0.1	0.4±0.1	-	-
Tb(mg/kg)	17.3±1.8	7.2±0.9	7.5±0.8	21.4±1.5
Yb(mg/kg)	74.6±7.4	56.6±6.1	16.4±2.4	25.3±2.1
Hf(mg/kg)	3.1±0.9	3.2±0.1	1.4±0.2	6.5±0.9
Th(g/kg)	11.2±0.9	3.9±1.1	2.6±0.3	3.1±0.3
U(mg/kg)	-	996±40	24±2	45±4

Table 3.8. The Results of the Second Counting (22-35 Days Cooling) for the Ore Samples

Element	Dolamitte-2	Dolamitte-4	K.Höyüklü	K.Devebagirtan
Sc(mg/kg)	34.4±0.6	31.9±0.4	13.9±0.4	42.6±1.3
Cr(mg/kg)	27.0±3.2	82.8±9.3	74.6±7.9	66.4±9.7
Fe(g/kg)	43.1±0.8	51.9±0.7	26.8±0.4	32.0±0.7
Co(mg/kg)	25.3±1.7	20.8±0.9	5.2±0.4	4.6±0.3
Zn(mg/kg)	210±20	-	200±10	320±20
Sr(g/kg)	-	1.6±0.1	2.3±0.2	-
Y(mg/kg)	-	-	830±90	-
Zr(mg/kg)	143±5	165±6	96±2	98±3
Nb(mg/kg)	6.1±0.4	4.2±0.2	1.0±0.1	1.3±0.1
Sb(mg/kg)	20.5±1.3	23.8±1.6	10.7±1.4	4.0±0.2
Cs(mg/kg)	11.2±1.2	4.8±0.3	9.2±1.1	8.0±0.3
Ba(g/kg)	0.4±0.1	0.5±0.1	109±1	72.0±4.7
Ce(g/kg)	6.2±0.2	5.0±0.2	21.2±1.8	22.7±2.3
Nd(g/kg)	-	-	3.9±0.4	-
Eu(mg/kg)	20.0±1.2	12.5±0.5	46.6±2.3	67.6±1.2
Gd(g/kg)	1.13±0.25	0.40±0.03	0.19±0.02	0.40±0.02
Tb(mg/kg)	16.5±1.6	7.0±0.7	8.0±0.5	17.6±1.8
Yb(mg/kg)	69.0±4.3	52.9±5.1	19.1±1.3	28.9±1.6
Lu(mg/kg)	-	-	2.2±0.2	-
Hf(mg/kg)	4.2±0.3	3.4±0.2	1.4±0.1	9.7±0.9
Th(g/kg)	11.5±0.03	4.0±0.1	2.4±0.2	2.8±0.2

Table 3.9. The Results of the Third Counting (90-140 Days Cooling) for the Ore Samples

Element	Dolamitte-2	Dolamitte-4	K.Höyüklü	K.Devebagirtan
Sc(mg/kg)	34.6±3.3	31.8±3.2	13.5±0.5	42.2±1.7
Cr(mg/kg)	29.1±1.7	86.5±6.3	75.3±4.6	67.1±4.0
Fe(g/kg)	43.4±9.0	51.7±0.7	27.0±1.1	31.8±1.3
Co(mg/kg)	27.2±1.4	21.6±2.7	5.3±0.2	4.7±0.3
Zn(mg/kg)	240±20	-	240±20	330±50
Sr(g/kg)	-	1.82±0.12	2.37±0.24	-
Y(mg/kg)	-	-	840±100	-
Zr(mg/kg)	142±4	166±12	97±3	92±7
Nb(mg/kg)	5.6±0.4	4.6±0.4	1.2±0.1	1.2±0.2
Sb(mg/kg)	24.2±2.6	24.2±2.4	12.0±0.9	4.7±0.4
Cs(mg/kg)	11.3±0.8	4.9±0.3	9.4±2.1	8.8±1.6
Ba(g/kg)	0.5±0.1	0.5±0.1	111±9	73.2±5.4
Ce(g/kg)	6.4±0.6	6.4±0.7	21.3±1.8	23.1±2.3
Nd(g/kg)	-	-	4.2±0.6	-
Eu(mg/kg)	18.8±0.7	11.6±0.4	45.7±3.1	67.9±3.4
Gd(g/kg)	1.12±0.16	0.42±0.05	0.21±0.02	0.42±0.05
Tb(mg/kg)	18.5±1.5	6.1±0.7	8.4±0.7	19.4±3.7
Yb(mg/kg)	66.5±0.7	48.2±5.4	19.3±0.7	28.5±2.0
Lu(mg/kg)	-	-	2.2±0.2	-
Hf(mg/kg)	3.4±0.3	3.7±0.2	14.0±1.7	12.0±1.4
Ta(mg/kg)	1.0±0.1	1.0±0.1	-	1.5±0.1
Th(g/kg)	11.7±0.6	4.2±0.9	2.2±0.3	3.0±0.4

Table 3.10. Elemental Concentrations of Ore Samples:
Best Results Obtained From All Three Countings.

Element	KTS-1	KTS-2	KTS-3	KTS-4
Na(g/kg)	-	7.2±0.8	7.8±0.9	8.3±1.0
Sc(mg/kg)	18.0±0.2	14.6±0.3	10.6±0.3	8.4±0.2
Cr(mg/kg)	500±32	39.1±2.6	30.1±1.7	168±13
Fe(g/kg)	26.7±1.1	96.5±1.3	26.0±5.8	18.8±0.5
Co(mg/kg)	25.8±1.0	1.8±0.2	1.4±0.2	1.0±0.1
Zn(mg/kg)	-	-	360±30	210±20
As(mg/kg)	200±30	-	160±20	-
Sr(g/kg)	-	2.5±0.1	1.3±0.1	3.1±0.2
Y(g/kg)	-	-	-	42.3±5.6
Zr(mg/kg)	143±6	87±3	94±3	104±5
Nb(mg/kg)	3.0±0.1	1.2±0.1	1.6±0.1	7.0±0.5
Sb(mg/kg)	5.6±0.3	2.9±0.2	3.8±0.2	10.7±0.5
Cs(mg/kg)	10.3±0.4	1.0±0.1	1.8±0.1	5.0±0.3
Ba(g/kg)	111±7	132±8	36±4	145±11
La(g/kg)	3.8±0.1	9.4±0.4	4.4±0.3	12.5±0.7
Ce(g/kg)	15.3±1.3	13.6±1.0	4.8±0.3	12.0±0.7
Nd(g/kg)	14.8±0.4	3.4±0.2	1.3±0.1	2.5±0.1
Sm(g/kg)	3.00±0.33	0.63±0.07	0.15±0.03	0.35±0.06
Eu(mg/kg)	370±15	71.1±2.9	27.4±2.9	41.3±1.9
Gd(mg/kg)	540±80	420±50	520±100	150±20
Tb(mg/kg)	54±5	12.5±0.9	8.2±0.8	11.3±0.7
Yb(mg/kg)	62.6±4.2	28.4±1.2	21.9±1.2	37.4±2.9
Lu(mg/kg)	-	-	36.2±4.3	-
Hf(mg/kg)	4.2±0.2	10.6±0.7	30.1±1.7	4.4±0.3
Th(g/kg)	5.3±0.2	2.9±0.2	2.9±0.2	1.5±0.2
U(mg/kg)	9.4±1.3	181±10	8.0±0.4	8.6±0.4

Table 3.11. Elemental Concentrations of Ore Samples :
Best Results Obtained From All Three Countings.

Element	Dolamitte-2	Dolamitte-4	K.Höyüklü	K.Devebagirtan
Na(g/kg)	-	16.0±0.2	-	-
Sc(mg/kg)	35.2±1.2	32.2±1.1	14.0±0.4	42.5±1.1
Cr(mg/kg)	27.7±1.6	82.8±9.3	74.4±3.4	66.6±3.7
Fe(g/kg)	4.3±0.3	5.2±0.1	2.7±0.1	3.2±0.1
Co(mg/kg)	27.2±1.3	22.2±1.0	5.3±0.2	4.6±0.3
Zn(mg/kg)	210±20	-	200±10	320±20
As(mg/kg)	-	-	-	6.66±0.55
Sr(g/kg)	-	1.6±0.1	2.3±0.2	-
Y(mg/kg)	-	-	840±70	-
Zr(mg/kg)	144±5	165±5	97±2	95±4
Nb(mg/kg)	6.1±0.4	4.2±0.2	1.1±0.1	1.3±0.1
Mo(mg/kg)	-	-	46.7±4.9	-
Sb(mg/kg)	20.5±1.3	23.8±1.6	11.4±0.8	4.0±0.2
Cs(mg/kg)	11.5±0.4	4.8±0.3	9.2±1.1	8.4±0.8
Ba(g/kg)	0.5±0.1	0.5±0.1	109±7	72.6±2.4
La(g/kg)	5.0±0.2	-	10.3±1.4	12.4±1.4
Ce(g/kg)	6.2±0.2	5.0±0.2	21.3±1.1	22.0±1.3
Nd(g/kg)	-	-	3.9±0.3	-
Eu(mg/kg)	20.6±0.7	11.8±0.2	46.0±1.4	67.8±1.8
Gd(g/kg)	1.13±0.12	0.41±0.03	0.19±0.02	0.41±0.03
Tb(mg/kg)	17.4±1.1	6.6±0.5	8.0±0.5	18.5±2.1
Yb(mg/kg)	69.0±4.3	50.6±3.7	19.2±0.8	28.7±0.9
Lu(mg/kg)	-	-	2.2±0.2	-
Hf(mg/kg)	4.2±0.3	3.4±0.2	1.4±0.1	9.7±0.4
Ta(mg/kg)	1.0±0.1	1.0±0.0	-	1.5±0.1
Th(g/kg)	11.5±0.3	4.0±0.5	2.4±0.2	3.0±0.2
U(mg/kg)	-	996±40	24±2	45±4

3.5. Comparison of Results With Other Works

The concentrations of elements in Tables 3.10 and 3.11 are compared with MTA Institute's and Gülovalı's results [29]. They are shown in Tables 3.12 , 3.13 , 3.14 and 3.15. Although their lists are not complete to compare with ours , in general the agreement with available elements are very good.

Table 3.12. Comparison of Concentrations in KTS-1 with Other Works.

Element	KTS-1(This Work)	KTS-1(MTA)	KTS-1 [29]
Sc(mg/kg)	18.0±0.2	-	15±2
Fe(g/kg)	26.7±1.1	40.3	26.4±6.2
Co(mg/kg)	25.8±1.0	-	21±3
As(mg/kg)	200±30	-	190±20
Sb(mg/kg)	5.6±0.3	-	6.0±1.0
Cs(mg/kg)	10.3±0.4	-	8.0±1.0
Ba(g/kg)	111±7	145	118±14
La(g/kg)	3.8±0.1	4.0	3.6±0.4
Ce(g/kg)	15.3±1.3	14.5	15.6±1.9
Nd(g/kg)	14.8±0.4	15.0	15.0
Sm(g/kg)	3.0±0.3	3.0	-
Eu(mg/kg)	370±15	700	320±30
Tb(mg/kg)	54.0±5.3	-	70±10
Yb(mg/kg)	62.6±4.2	40.0	30±10
Th(g/kg)	5.3±0.2	5.7	5.3±0.6

Table 3.13 Comparison of Concentrations in KTS-2 and KTS-3
with MTA's Results

Element	KTS-2 (This Work)	KTS-2 (MTA)	KTS-3 (This Work)	KTS-3 (MTA)
Na(g/kg)	7.2±0.8	8.45	7.8±0.9	7.5
Fe(g/kg)	96.5±1.3	91.6	26.0±5.8	28.0
Sr(g/kg)	2.5±0.1	3.0	1.3±0.1	2.0
Ba(g/kg)	132±8	148	36±4	52
La(g/kg)	9.4±0.4	9.0	4.4±0.3	4.0
Ce(g/kg)	13.6±1.0	11.0	4.8±0.3	-
Nd(g/kg)	3.4±0.2	3.5	1.3±0.1	0.15
Sm(g/kg)	0.63±0.07	0.70	0.15±0.03	0.20
Eu(mg/kg)	71.1±2.9	70.0	27.4±2.9	-
Yb(mg/kg)	28.4±1.2	30.0	21.9±1.2	-
Th(g/kg)	2.9±0.2	2.9	2.9±0.2	2.8
U(mg/kg)	181±10	170	8.0±0.4	8.5

Table 3.14. Comparison of Concentrations in KTS-4 with MTA's Results.

Element	KTS-4(This Work)	KTS-4(MTA)
Na(g/kg)	8.3±1.0	8.4
Fe(g/kg)	18.8±0.5	19.4
Sr(g/kg)	3.1±0.2	4.0
Ba(g/kg)	145±11	141
La(g/kg)	12.5±0.7	13.0
Ce(g/kg)	12.0±0.7	12.5
Nd(g/kg)	2.5±0.1	3.0
Sm(g/kg)	0.4±0.1	0.4
Eu(mg/kg)	41.3±1.9	40.0
Yb(mg/kg)	37.4±2.9	40.0
Th(g/kg)	1.5±0.2	2.0
U(mg/kg)	8.6±0.4	8.5

Table 3.15. Comparison of Concentrations in Dolamitte-2 and Dolamitte-4 with MTA's Results.

Element	Dolamitte-2 (This Work)	Dolamitte-2 (MTA)	Dolamitte-4 (This Work)	Dolamitte-4 (MTA)
Na(g/kg)	-	-	16.0±0.2	10.0
Sc(mg/kg)	35.2±1.2	30.0	32.2±1.1	30.0
Cr(mg/kg)	27.7±1.6	40.0	82.8±9.3	100.0
Fe(g/kg)	43.0±3.1	40.0	51.8±0.5	40.0
Sr(g/kg)	-	-	1.6±0.1	1.5
Zr(mg/kg)	144±5	150	165±5	150
Ba(g/kg)	0.4±0.9	0.4	0.5±0.1	0.4
Th(g/kg)	11.5±0.3	11.4	4.0±0.5	3.5
U(g/kg)	-	-	1.0±0.1	1.1

3.5.1. Spectral Interferences From Thermal Neutron

Fission of U-235

Since geological samples contain certain amount of uranium. The spectral interferences of uranium fission are important to determine concentration elements such as Ba, Cr, Ce, Mo, Nd and Zr in thermal neutron activation analysis [25]. The degree of interference is given in terms of apparent concentration of the element of interest per concentration of uranium. The uranium fission corrections for elements are given in Table 3.16.

Table 3.16. Uranium Fission correction (Apparent ppm element/ppm Uranium, γ -ray) [25]

Isotope	(keV)	Correction Factor
Ba-131	496.2	$3.6 \pm 0.3 [\exp(0.0402t_d)]$
Ce-141	145.4	0.27 ± 0.02
Cr-51	320.0	0.006 ± 0.002
Mo-99	140.5	1.7 ± 0.1
Nd-147	91.1	0.20 ± 0.01
Zr-95	756.7	10.9 ± 0.9

t_d : Delay time measured in days.

As seen, the interferences on especially Zr concentration might be very important, if the uranium concentration is high. In our measurement, the correction on Ba, Ce, Cr, Mo, and Nd concentration are negligible. On the other hand, in some cases we did not observe 10 times of the uranium concentrations on Zr concentration. This discrepancy was not understood very well.

3.6. Estimation of Rare Earth Elements in Eskişehir-Beylikahır Deposits

Eskişehir-Beylikahır thorium deposits are located at the Eskişehir-Sivrihisar-Beylikahır-Kızılcaören Village region. This region is 40 km north-west of the town of Sivrihisar and the its area is about 15 km². Thorium deposits in this region naturally include metamorfits, metasilicate stones , metaofiolits and young volcanic groups. Also,they have different minerals such as fluorite, barite and the name of these deposits is called complex thorium deposit [5].

MTA Institute is working on this complex to determine whole amount of deposit and the concentration of fluorite , barite and rare earth oxides such as La_2O_3 , CeO_2 and Nd_2O_3 since 1970. As results of these works 0.9 million tons of rare earth oxides were estimated from approximately 30.4 million tons of estimated deposits and the average concentration of rare earth oxides was about 3.1 % [5]. Total amount of thorium ore is about 1.61×10^8 tons and total amount of ThO_2 in whole complex deposits is about 3.84×10^5 tons with a weighted average concentration of 0.21% [6]. The thorium deposits occur at different places. The name of these places and the average concentrations (in %) of rare earth oxides are shown in Table 3.17; as estimated by MTA.

Table 3.17. Kızılcaören Village(Eskişehir-Sivrihisar-Beylikahır) Complex Thorium Deposit [20].

	Deposit Vol.	Deposit Wt.	R.E.Oxides (Ce+La+Nd)	Wt.of R.E.E in Deposit
Name	(m ³ x10 ⁶)	(tonsx10 ⁶)	Aver.Conc.(%)	(tonsx10 ⁵)
Devebağirtantepe	1.80	6.55	3.67	2.40
Küçükhöyükütepe	3.80	14.0	3.27	4.57
Canavarinisirti	1.33	4.93	2.65	1.30
Kocadevebağirtantepe	0.80	2.53	2.55	0.64
Köyyeritepe	0.24	0.95	2.06	0.20
Yaylabasitepe	0.21	0.74	4.46	0.33
Kocayaylatepe	0.18	0.69	1.25	0.09
Total	8.35	30.40	3.14	9.53

In this work , we determined the concentration of REE's in Küçükhöyükütepe and Kocadevebağirtantepe deposits by INAA method. The individual and total concentrations of some REE's in these deposits are shown in Table 3.18. The concentrations of rare earth elements were taken from Table 3.11. Using the REE percentages given in Table 3.18. for both Küçükhöyükütepe and Kocadevebağirtantepe deposits, total and individual amounts of some REE were estimated. The weight of deposits were taken from Table 3.17. They are shown in Tables 3.19 and 3.20.

Total weight of REE elements in Küçükhöyükütepe and Kocadevebağirtantepe deposits together in Table 3.19 are in good agreement with total weight of REE elements for these deposits shown in Table 3.17.

Table 3.18. Individual and Total Concentration of REE in Küçükhöyüklütepe and Kocadevebağirtantepe Deposits.

Element	Küçükhöyüklütepe	Kocadevebağirtantepe
Sc(mg/kg)	14.0±0.4	42.5±1.1
Y(mg/kg)	840±70	-
La(g/kg)	10.3±1.3	12.4±1.4
Ce(g/kg)	21.3±1.1	22.0±1.3
Nd(g/kg)	3.9±0.3	-
Eu(mg/kg)	46.0±1.4	67.8±1.8
Gd(mg/kg)	190±20	410±30
Tb(mg/kg)	8.0±0.5	18.5±2.1
Yb(mg/kg)	19.2±0.8	28.7±0.9
Lu(mg/kg)	2.2±0.2	-
Total REE(%)	3.66±0.17	3.50±0.19
Th(%)	0.24±0.02	0.30±0.02

The concentrations of Y, Nd and Lu in Kocadevebağirtantepe deposit were not determined.

Table 3.19. Total Amounts of REE in Küçükhöyüklü and Kocadevebağirtantepe Deposits.

Weight of Deposit		Rare Earth Elements (Sc+Y+La+Nd+Eu+Gd+Tb+Yb+Lu)	REE Wt.in Deposits
Name	(tonsx10 ⁶)	Average Concentration(%)	(tonsx10 ⁶)
Küçükhöyüklütepe	14.0	3.66	0.51
Kocadevebağirtantepe	2.53	3.50	0.09
Total	16.53	3.64*	0.60

* : Weighted Average Concantration.

Table 3.20. Amounts of Some REE in Küçükhöyüktepe and Kocadevebağirtantepe Deposits.

Element	Küçükhöyüktepe (tonsx10 ³)	Kocadevebağirtantepe (tonsx10 ³)
Sc	0.20	0.11
Y	11.7	-
La	144	31.6
Ce	298	56
Nd	54.5	-
Eu	0.64	0.17
Gd	2.66	1.04
Tb	0.12	0.47
Yb	0.27	0.07
Lu	0.03	-
Total	510	90.0

3.6.1 Estimation of Thorium in Eskişehir Beylikahır Deposits

The biggest thorium deposits are in Kocadevebağirtantepe and Küçükhöyüktepe deposits. The MTA's estimation covers all thorium deposits, but weighted average percentages of thorium and REE's in other deposits are smaller than the Kocadevebağirtantepe and Küçükhöyüktepe deposits. Therefore, Kocadevebağirtantepe and Küçükhöyüktepe deposits were estimated for thorium content.

The estimated ThO₂ content for Kocadevebağirtantepe

is 2.86×10^5 tons and for Küçükhöyüktepe 0.98×10^5 tons. Weighted average concentration of thorium for these deposits is about 0.21 % [6]. Therefore , total amount of ThO_2 is 3.84×10^5 tons from 1.83×10^8 tons of ThO_2 ores and the content of thorium ore is calculated as 1.61×10^8 tons. We determined the concentrations of thorium in Kocadevebağirtantepe and Küçükhöyüktepe deposits by INAA as 0.30 ± 0.02 % for Kocadevebağirtantepe and 0.24 ± 0.02 % for Küçükhöyüktepe (Table 3.18). From the content of thorium ore, 1.61×10^8 tons, total amount of thorium was calculated as 4.0×10^5 tons with a weighted average concentration is 0.25 %. Therefore, total ThO_2 was estimated as 4.6×10^5 tons in both Kocadevebağirtantepe and Küçükhöyüktepe deposits. In comparison, our determined value, 4.6×10^5 tons of ThO_2 is in good agreement with MTA's value 3.84×10^5 tons of ThO_2 .

3.6.2 Thorium Deposits in the World

The biggest thorium deposits are in China , U.S.A and India have largest thorium deposits. Also, Brazil has large amount of thorium deposits. Thorium deposits in the World are shown in Table 3.21.

Reasonable assured thorium deposits are in India , Brazil and U.S.A and estimated additional thorium deposits are in Canada , Egypt and U.S.A.

Table 3.21. Thorium Deposits in the World [6]

Country	Reasonably Assured Deposit (tonsx10 ³)	Estimated Additional Deposit (tonsx10 ³)
Australia	21.0	0
Brazil	58.2	3
Canada	0	340
Denmark	15.0	0
Egypt	14.7	280
India	320	0
Liberia	0.5	0
South Africa	11.0	0
Turkey	0	460
U.S.A	102.4	250
Total	542.8	1333

Reasonably assured thorium deposits of Turkey are in Eskişehir-Beylikahır thorium deposit. Total amount of ThO₂ in reasonable+estimated sections of the deposit is about 4.6×10^5 tons. Total thorium deposits in Eskişehir-Beylikahır region occupy 34 % of estimated thorium deposits in the World [6].

3.6.3 Rare Earth Element Deposits in The World

Total amount of REE deposits in the world are about 47 million tons with Reasonable+Estimated potentials. The biggest REE deposits are in U.S.A and second largest potential of REE deposits are in India. The REE deposits in the world are shown in Table 3.22.

Table 3.22. The REE Deposits in the World[6].

Country	Reasonably Assured Deposit(tonsx10 ⁶)	Estimated Additional Deposit(tonsx10 ⁶)	Total (tonsx10 ⁶)
U.S.A(Bastnasite)	5.0	26	31
India(monazite)	1.0	2.0	3.0
U.S.S.R	0.5	9.5	10.0
Australia	0.4	0.3	0.7
Brazil	0.4	0.2	0.6
Canada	0.3	1.1	1.4
Turkey	0	0.6	0.6
Total REE in World	7.73	40.0	47.7

Eskişehir-Beylikahır thorium deposits in Turkey contain rare earth minerals. The weighted average concentration of REE in Küçükhöyüktepe and Kocadevebağırtepe deposits were estimated about 3.64 %. Total amounts of REE in these deposits are about 6.0×10^5 tons. Therefore, these thorium deposits could be very important in terms of their REE content.

CHAPTER 4

4. CONCLUSIONS

In this study , the Rare Earth Elements and Thorium contents of Eskişehir-Beylikahır thorium deposits were determined. We were able to determine up to 25 elements including 10 REE , Th and U by instrumental neutron activation analysis. We showed that INAA is a precise and reliable method for the determination of REE and other elements in Eskişehir-Beylikahır thorium deposits. The calculation resulted that total REE and Th percentages are 3.66 ± 0.17 % and 0.24 ± 0.02 % for Küçükhöyüktepe and 3.50 ± 0.19 % and 0.30 ± 0.02 for Kocadevebağirtantepe respectively. From The MTA's estimation [20] of 14.0×10^6 and 2.5×10^6 tons of ores at Küçükhöyüktepe and Kocadevebağirtantepe respectively , we calculated total REE deposits as 51.0×10^4 and 9.0×10^4 tons. Also, from the MTA's estimation [6] of 1.83×10^8 tons of ThO_2 ores at Küçükhöyüktepe and Kocadevebağirtantepe together , we calculated total ThO_2 as 4.6×10^5 tons and thorium content is about 4.0×10^5 tons with a weighted average thorium concentration 0.25 %. By adding of REE contents from other thorium deposits, the amount of REE will somewhat be increase. Since the importance and usage of REE are everincreasing, more research should be done for both REE and thorium estimations in Turkey.

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APPENDIX A

Reference Concentrations of Standard Soil-5, Soil-7
and S-16.

Element	Soil-5	Soil-7	S-16
Na(g/kg)	19.2±1.1	2.4	-
K(g/kg)	18.6±1.5	12.1	3.3±0.6
Sc(mg/kg)	14.8±0.66	8.3	-
Cr(mg/kg)	28.9±2.8	60	154±8
Mn(mg/kg)	852±37	631	3100±500
Fe(g/kg)	44.5±1.9	25.7	24.5±12
Co(mg/kg)	14.8±0.76	8.9	-
Ni(mg/kg)	(13.0)	26	-
Zn(g/kg)	368±8.2	104	239.5±16.3
Ga(mg/kg)	18.4±1.6	10	-
As(mg/kg)	93.9±7.5	13.4	-
Se(mg/kg)	(1.3)	0.4	-
Br(mg/kg)	5.4±1.0	7	-
Rb(mg/kg)	138±7.40	51	-
Sr(g/kg)	(0.33)	0.18	1.1±0.1
Y(g/kg)	(0.02)	0.02	1.16±0.50
Zr(mg/kg)	(221)	185	-
Nb(mg/kg)	(9.0)	12	-
Mo(mg/kg)	(1.7)	2.5	-
Cd(mg/kg)	(1.5)	1.3	-
Sb(mg/kg)	14.3±2.2	1.7	-
Cs(mg/kg)	56.7±3.3	5.4	-
Ba(g/kg)	0.56±0.05	0.16	166±0.2

Reference Concentrations of Standarts Soil-5, Soil-7
and S-16.

Element	Soil-5	Soil-7	S-16
La(mg/kg)	28.1±1.5	28	7300±100
Ce(mg/kg)	59.7±3.0	61	1.27±0.01(%)
Nd(mg/kg)	29.9±1.6	30	-
Sm(mg/kg)	5.42±0.39	5.1	-
Eu(mg/kg)	1.18±0.08	1.0	-
Gd(mg/kg)	(35.0)	-	-
Tb(mg/kg)	0.67±0.08	0.8	-
Yb(mg/kg)	2.24±0.2	2.4	-
Lu(mg/kg)	0.34±0.04	0.3	-
Hf(mg/kg)	6.3±0.3	5.1	-
Ta(mg/kg)	0.76±0.06	8.3	-
Pb(mg/kg)	129±26	60	403.5±12.0
Th(mg/kg)	11.3±0.73	8.2	1.55±0.12(%)
U(mg/kg)	3.15±0.45	2.6	192±78

():Recommended Value

APPENDIX B

BASIC PROGRAM FOR CALCULATING THE CONCENTRATION OF ELEMENT IN THE SAMPLE WITH STATISTICAL ERROR

```
10 PRINT "ENTER ENERGY OF THE PEAK"
11 INPUT A$
12 PRINT "AREA OF STANDRAT"
13 INPUT A
14 PRINT "AREA OF SAMPLE"
15 INPUT B
16 PRINT "AREA OF BLANK"
17 INPUT C
18 PRINT "HALF LIFE OF ELEMENT"
19 INPUT E1
20 PRINT "DECAY MIDTIME OF STANDARD"
21 INPUT F
22 PRINT "DECAY MIDTIME OF SAMPLE"
23 INPUT G
24 PRINT "DECAY MIDTIME OF BLANK"
25 INPUT H
26 PRINT "MASS OF STANDARD"
27 INPUT K
28 PRINT "MASS OF SAMPLE"
29 INPUT L
30 PRINT "CONCENTRATION OF STANDART"
31 INPUT M
32 PRINT "ERROR IN STANDARD"
33 INPUT EA
34 PRINT "ERROR IN SAMPLE"
35 INPUT EB
36 PRINT "ERROR IN BLANK"
37 INPUT EC
38 PRINT "ERROR IN BACKGROUND"
39 INPUT ED
40 PRINT "ERROR IN CONCENTRATION"
41 INPUT EF
42 X=A*EXP((0.693/E1)*F)
43 Y=B*EXP((0.693/E1)*G)
44 Z=C*EXP((0.693/E1)*H)
45 N=Y-Z
46 R=X-Z
47 O=K/L
48 S=O*M*(N/R)
49 EX=(X/100)*EA
50 EY=(Y/100)*EB
51 EZ=(Z/100)*EC
52 EG=((EY)^2+(EZ)^2+(EF)^2)^0.5
53 EH=((EX)^2+(EZ)^2+(EF)^2)^0.5
54 EI=(N/R)*((EG/N)^2+(EH*R/N)^2)^0.5
55 EM=M*(N/R)*((EF/M)^2+(EI*R/N)^2)^0.5
56 ES=O*EM
57 PRINT "MASS OF ELEMENT IN SAMPLE AT";A$;"keV IS:";S
58 PRINT "ERROR OF ELEMENT IN SAMPLE AT";A$;"keV IS:";ES
```

APPEDIX C

ERROR ANALYSIS

Experimental errors in analytical results depend on random and systematic contribution. The random part is conveniently characterized by a standard deviation and referred to by the term "Precision" while the "Accuracy" refers to the systematic part.

Elemental concentrations with uncertainties are determined by INAA in the individual samples are a combination of statistical errors associated with the areas under peaks in the gamma ray spectra of samples, standards, blanks and backgrounds. The errors of blanks and background to be subtracted from samples and standards [30].

The statistical uncertainties for gamma-ray counting are governed by poisson statistics so the expected standard deviation of the summation of counts in a photopeak, $p = \sqrt{p}$.

The statistical theory is the best or most probable value for the absolute standard deviation S of a summation is given as,

$$S^2 = S^2_{\text{sample}} + S^2_{\text{blank}} + S^2_{\text{background}}$$

For multiplication and division, the relative standard deviations are combined in a similar way to obtain the standard deviation of sample with a sample concentrations [31].

$$Wt(sample) = Wt(standard) * \frac{A_{sample}}{A_{standard}}$$

The uncertainty associated with measured of $Wt(sample)$ is :

$$\left(\frac{S(Wt(sample))}{Wt(sample)}\right)^2 = \left(\frac{S(Wt(stand))}{Wt(stand)}\right)^2 + \left(\frac{S(A_{sample})}{A_{sample}}\right)^2 + \left(\frac{S(A_{stand})}{A_{stand}}\right)^2$$

The uncertainties for each measured quantity changes from one sample to another. Respectively the overall error will be around 15 %.

APPENDIX D

Physical Constants and the Representative Gamma-Rays
for Each Product Nuclide

Target Nuclide	Natural Abund. (%)	Product Nuclide	Half Life	Thermal Cross-Sec. (b)	Representative Gamma-Ray (KeV)
Na-23	100	Na-24	15.1 h	0.529±0.007	1368.5
Sc-45	100	Sc-46	83.9 d	28.3±0.7	889.4, 1120.5
Cr-50	4.3	Cr-51	27.8 d	15.9±0.7	320.1
Fe-58	0.3	Fe-59	45.0 d	1.14±0.02	1099.3, 1291.2
Co-59	100	Co-60	5.4 d	37.7±0.4	1173.2, 1332.5
Zn-64	49.9	Zn-65	245 d	0.77±0.03	1115.5
As-75	100	As-76	26.5 h	4.48±0.11	559.1
Rb-85	72.1	Rb-86	18.7 d	0.40±0.005	1077.0
Zr-94	17.4	Zr-95	65.0 d	0.07±0.008	724.2, 756.7
Mo-98	23.8	Mo-99	67.0 h	0.136±0.003	140.5, 739.7
Sb-121	57.3	Sb-122	2.8 d	6.21±0.1	563.9, 692.8
Sb-123	42.8	Sb-124	60.0 d	4.44±0.9	602.7, 1691.6
Cs-133	100	Cs-134	2.1 y	30.4±1.7	604.6, 795.8
Ba-130	0.101	Ba-131	12.0 d	8.8±0.9	123.7, 496.3
La-139	99.91	La-140	40.0 h	9.0±0.33	487.0, 1596.2
Ce-140	88.48	Ce-141	33.0 d	0.54±0.04	145.4
Nd-146	17.22	Nd-147	11.0 d	2.0	91.0, 531.0
Sm-152	26.73	Sm-153	47.0 h	212±12	69.68, 103.2
Eu-151	47.82	Eu-152	12.7 y	4410±66	344.3, 1407.9
Tb-159	100	Tb-160	72.1 d	450±50	879.3, 1178.1
Yb-168	0.14	Yb-169	32.0 d	3470±50	177.0, 198.0

Target Nuclide	Natural Abund. (%)	Product Nuclide	Half Life	Thermal Cross-Sec. (b)	Representative Gamma-Ray (KeV)
Yb-174	31.84	Yb-175	42.0 d	141±2	282.6, 396.1
Lu-176	2.59	Lu-177	6.7 d	3375±130	113.0, 208.4
Hf-180	35.24	Hf-181	42.5 d	12.6±0.7	133.0, 482.0
Ta-181	100	Ta-182	115 d	21.1±0.8	1188.9, 1221.3
W-186	38.4	W-187	24 h	35.4±0.8	479.5, 685.7
Th-232	100	Pa-233	27 d	7.4±0.1	300.2, 311.9
U-238	99.3	Np-239	2.4 d	2.74±0.06	106.1, 277.6

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