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DETERMINATION OF ELEMENTS IN LEACH SOLUTIONS AND RESIDUES BY INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

Elements in leach solutions and residues of thorium bearing ores have been determined by instrumental neutron activation analysis. This technique has been applied to determine Sc, Fe, Co, As, Sb, Ba, La, Ce, Eu, Tb, Yb and Th. Instrumental neutron activation analysis has advantages to the other techniques because it is an accurate, precise, specific and nondestructive method.

ÖZET

Toryum içeren cevherlerin özütleme çözeltileri ve kalıntılarındaki elementler aletli nötron aktivasyon analiz yöntemi uygulanarak tayin edilmiştir. Yöntemin uygulanmasıyla tayin edilen elementler Sc, Fe, Co, As, Sb, Ba, La, Ce, Eu, Tb, Yb ve Th'dur. Yöntem, kesin, doğru, hassas olması, tahripkar olmaması, matriks etkilerinin varsa bile çok az olması nedenleriyle diğer yöntemlere tercih edilmiştir.

INTRODUCTION

Thorium has been found in quantities from traces to major amounts in more than 100 minerals in the world /1/. It is also often associated with rare earths. Thorium concentration of thorium-bearing ores in Turkey is quite low, generally not above 0.3 percent /2/. Therefore, to recover thorium alone is ordinarily not feasible. It is, then, required to investigate the ore, leach solutions and residues in a variety of elements. The present study is aimed to determine the elements in leach solutions and residues with a

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sufficient sensitivity.

Instrumental neutron activation analysis was selected as being one of the most sensitive and highly specific analytical method for identification and measurement of elements in a variety of complex sample matrices. One of the advantages of this method is the possibility of identification of many isotopes that are produced under the irradiation conditions and thus possibility of multi element determinations in a small amount of sample. Usually only one irradiation and several measurements after different decay times, provide determination of many elements /3/. For quantitative determinations sample and standard comparison method was applied.

Th and La have been determined in leach solutions of thorium-bearing ores in Turkey /4/. Determination of cerium and other rare earths is very important, since the ore have not been found to be of economic value for thorium alone. On the other hand, to know the elemental composition of leach solutions is necessary, because any impurity present will seriously affect the subsequent thorium purification steps. Therefore the importance of analysis of leach solutions and residues comes from both purification of thorium and recovery of rare elements.

EXPERIMENTAL

1. Sample and Standard Preparation

0.2 ml. of leach solutions were pipetted dropwise on Whatman 42 filter papers, which were folded, dried and pressed into pellets of 1 cm in diameter and a few mm. thick. They were sealed individually in polybags.

Spent residues were dried at 110°C and they were grounded, mixed throughly and then weighed into polyethylene bags and were sealed.

National Bureau of Standards fly ash standard reference material (SRM 1633) was used as standard /5/. One weighed standard was placed in each set of samples which were stacked up in a polyethylene tube together, and the tubes were sealed.

2. Irradiation and Counting

The samples and standards were irradiated for one hour at Istanbul Technical University, Nuclear Energy Institute, TRIGA Reactor with a neutron flux of about 10^{12} n. cm^{-2} sec^{-1}.

The samples and standards were counted with a Ge(Li) detector of 40 cm^3 active volume coupled to 4096-channel pulse height analyzer. The resolution of the system (FWHM) was 2.2 keV for the 1332 keV gamma-ray of ^{60}Co.

The analyzer was calibrated with standard sources each time before the counting. Counting and cooling times were arranged considering the nuclear properties of the radioisotopes. Due to transportation difficulties of the irradiated samples, the first counts were taken after 3 days of decay, and only As and La were determined. For long-lived isotopes (Sc, Fe, Co, Sb, Ba, Ce, Eu, Tb, Yb and Th), samples were counted after about 30 days of cooling. Counting times were about 1000 seconds and 4-7 hours for short-lived and long - lived isotopes, respectively.

3. Calculations

The gamma ray spectra were taken by a multichannel analyzer, and peak areas were calculated by the built-in microprocessor, which employes linear background subtraction. Necessary corrections for decay times and counting times, then were made for each isotope.

The amount of an element in a sample was calculated from the ratio of the corresponding peak areas in the sample and standard.

RESULTS AND DISSUCCION

The gamma-ray spectrum of a leach solution for the observed long-lived isotopes is given in Fig.1. The radioisotopes used in the determinations, and their nuclear decay properties are listed in Table-1.

Although many of the nuclides have more than one gamma rays, in order to obtain correct result, peaks which were free of serious interferences were selected. As it is seen from Fig.1., there is no serious spectral interference, which may cause identification or çalculation error. Since all of the short-lived isotopes have decayed in three days prior to measurement, it was not possible to observe any isotope with a half-life less than one day.

Irradiation of solutions at the Triga Mark II reactor of Institute for Nuclear Energy was not possible and since precipitation may occur in leach solutions by time, in addition to the difficulty of transporting large number of liquid samples of high

acidity, it was necessary to adopt the technique described previously. Since fresh leach solutions were pipetted without delay and filter papers were dried under low temperature, the resultant tablets represent the actual leaching conditions. On the other hand, it is possible to conserve the leach solutions by means of dried tablets without any change in composition for further analysis for a long time.

TABLE-1. Production and properties of radionuclei observed

Element	Nuclear Reactions	Target Abundance %	Product Half-life	γ-ray used keV
Sc	$^{45}Sc(n,\gamma)^{46}Sc$	100	84 d.	889; 1120
Fe	$^{58}Fe(n,\gamma)^{59}Fe$	0.33	44.6 d.	1099; 1291
Co	$^{59}Co(n,\gamma)^{60}Co$	100	5.27 y.	1173; 1332
As	$^{75}As(n,\gamma)^{76}As$	100	1.1 d.	559; 657
Sb	$^{123}Sb(n,\gamma)^{124}Sb$	42.75	60.0 d.	1691
Ba	$^{130}Ba(n,\gamma)^{131}Ba$	0.10	11.6 d.	216; 496
La	$^{139}La(n,\gamma)^{140}La$	99.91	1.68 d.	487; 1596
Ce	$^{140}Ce(n,\gamma)^{141}Ce$	88.48	33 d.	145
Eu	$^{151}Eu(n,\gamma)^{152}Eu$	47.82	12.5 y.	344; 964; 1408
Tb	$^{159}Tb(n,\gamma)^{160}Tb$	100	72.3 d.	879; 1178
Yb	$^{168}Yb(n,\gamma)^{169}Yb$	0.14	30.7 d.	177
	$^{232}Th(n,\gamma)^{233}Th$	100		
Th	$^{233}Th \xrightarrow{\beta} {}^{233}Pa$		27.4 d.	300; 312

Analysis of the residues resulting from leaching processes, provide a double check of analysis of tablets along with that of ore samples. Conventional methods of analysis for solutions present problems like high acidity and matrix effects, while dissolution of solid samples like residues cause additional practical problems, such methods were not possible to apply both to solutions and residues.

Instrumental neutron activation analysis was the only method available for application to all kinds of samples under investigation. Since irradiation and counting conditions were identical for all the samples and comparative method of analysis was applied, any type of error that might arise otherwise was overcome.

In Table-2, elemental analysis of a diluted leach solution and a residue is given as an example. Some of the elements were not detected in leach solutions. It is worth noting that elements can be determined in a wide range of concentration limits. A better understanding is achieved if the minimum detectable amount of an element for the experimental conditions is given.

In this study, limits of detection have been estimated from the experimental data for the following elements: Na, Sc, Cr, Fe, Co, As, Br, Sb, Ba, La, Ce, Eu, Tb, Yb, W and Th. In the determinations, a multi-element standard was used to minimize matrix effects /5/.

In order to determine the limits of detection under the mentioned irradiation and counting conditions, the product yields were first estimated. The yield is defined as the count rate available per gram of element, in cpm/g. Detection limit, on the other hand, is defined as the minimum amount of an element detectable by this technique under the experimental conditions, in micrograms. More detailed information is given in several literature /6,7/.

TABLE-2. Analyses of a leach solution and residue.

Element	Leach Solution, ppm	Residue, %
Sc	0.1	0.00116
Fe	-	3
Co	-	0.0025
As	-	0.02
Sb	-	0.0008
Ba	146	12.4
La	55	0.072
Ce	160	0.287
Eu	5	0.0044
Tb	1	0.0012
Yb	0.4	0.0018
Th	90	0.3

Table-3 gives calculated product yields and limits of detection of elements in three fly ash standard (SRM 1633) samples. The differences in values are due to following reasons. Each sample was irradiated at different times, possibly at different position in the reactor, expectedly at different neutron flux. Since

yields and detection limits were calculated from the experimental data, absence of accurate flux values have not caused any error. However, increase in flux, increases the yield, thus results in better detection limit. Another factor effecting the results was the counting conditions, such as counting geometry, fractional dead time of the analyzer system besides conventional errors.

As a result, instrumental neutron activation analysis is successfully applied for multielement samples, both for solids and solutions, as the other spectrographic analysis.

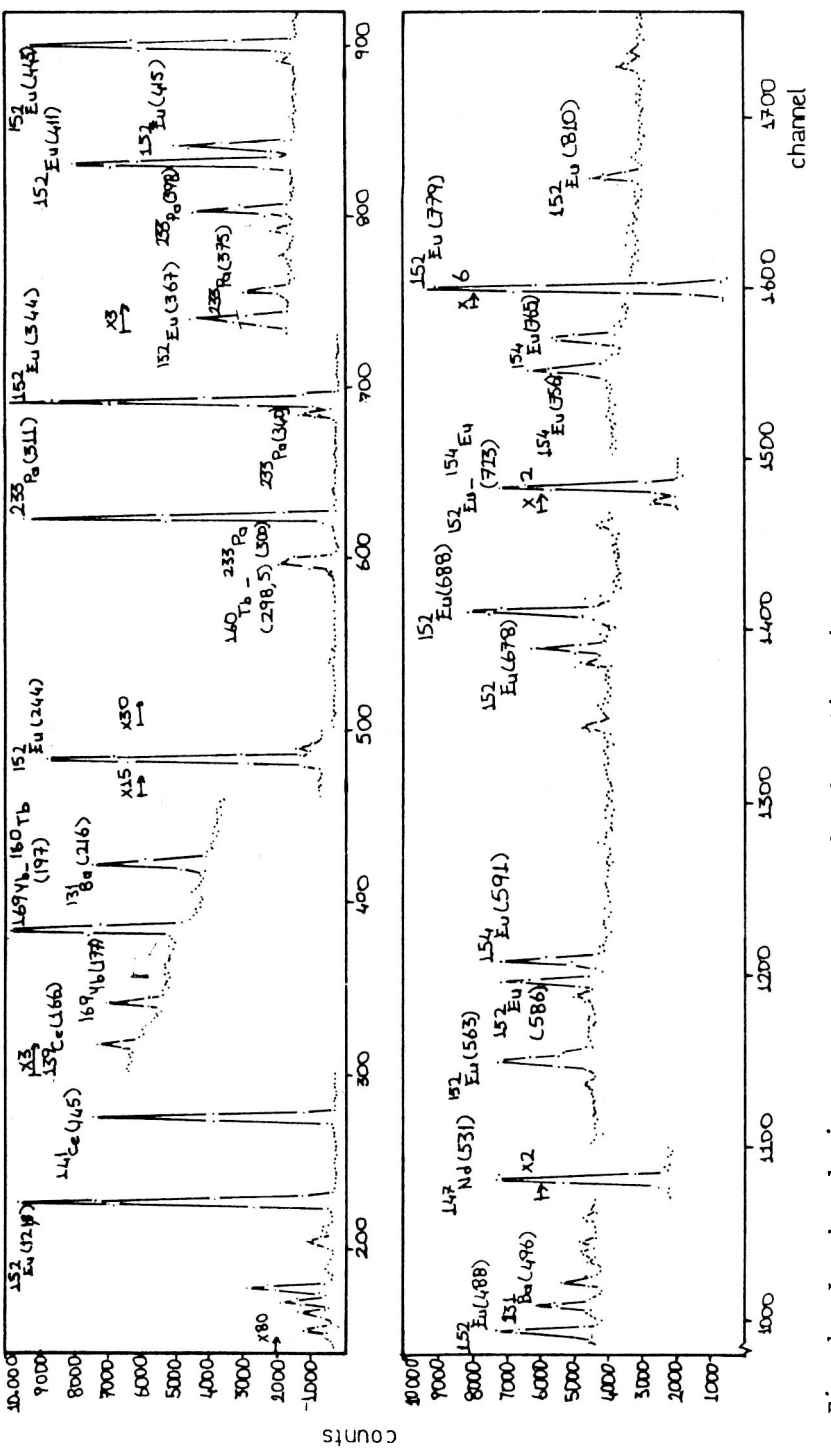

Fig. 1. Leach solution γ-ray spectrum for long-lived isotopes.

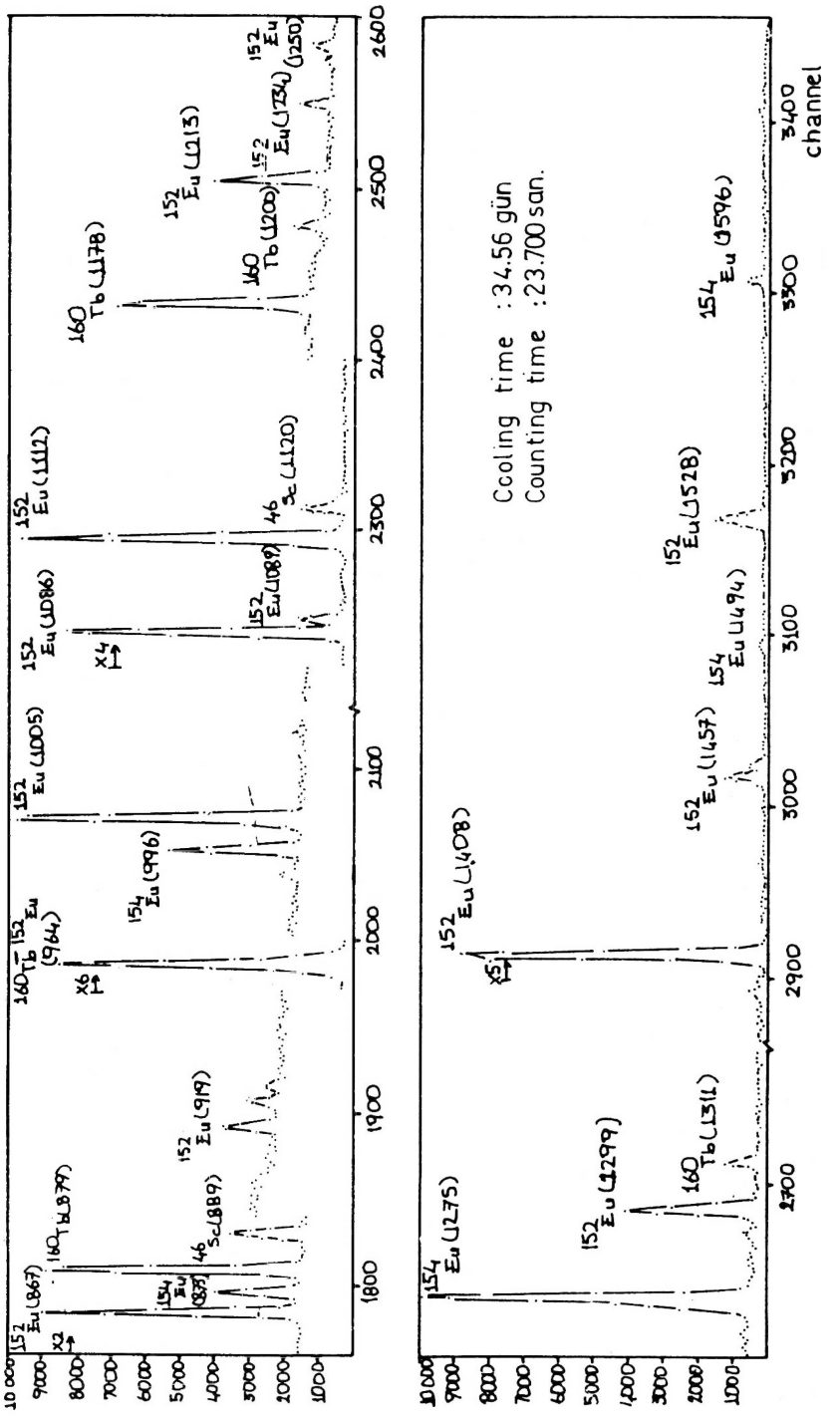

Fig.1. Leach solution γ-ray spectrum for long-lived isotopes (cont'd)

TABLE-3. Experimental INAA Product Yields and Limits of Detection.

Element	Isotopes	Gamma-ray Energy (keV)	Yield (cpm/g. element)			Limit of detection (µg)		
			1	2	3	1	2	3
Na	^{24}Na	1368	1.10×10^{8}	1.07×10^{8}	0.75×10^{8}	0.09	0.09	0.13
Sc	^{46}Sc	889	4.74×10^{8}	4.96×10^{8}	3.24×10^{8}	0.02	0.02	0.03
Cr	^{51}Cr	320	8.72×10^{6}	8.36×10^{6}	6.01×10^{6}	1.15	1.19	1.66
Fe	^{59}Fe	1099	2.47×10^{5}	3.68×10^{5}	2.50×10^{5}	40.49	27.12	40.00
Co	^{60}Co	1173	1.90×10^{7}	1.84×10^{7}	1.27×10^{7}	0.53	0.54	0.79
As	^{76}As	559	3.16×10^{8}	2.72×10^{8}	2.05×10^{8}	0.03	0.04	0.05
Br	^{82}Br	554	7.58×10^{7}	9.32×10^{7}	6.87×10^{7}	0.13	0.11	0.15
Sb	^{124}Sb	1691	1.13×10^{7}	1.18×10^{7}	8.07×10^{6}	0.88	0.85	1.24
Ba	^{131}Ba	496	6.37×10^{5}	6.36×10^{5}	4.60×10^{5}	15.70	15.70	21.80
La	^{140}La	487	1.61×10^{8}	1.40×10^{8}	1.16×10^{8}	0.06	0.07	0.09
Ce	^{141}Ce	145	2.17×10^{7}	2.02×10^{7}	1.54×10^{7}	0.46	0.49	0.65
Eu	^{152}Eu	779	3.82×10^{7}	3.91×10^{7}	2.80×10^{7}	0.26	0.25	0.36
Tb	^{160}Tb	879	8.47×10^{7}	8.41×10^{7}	5.70×10^{7}	0.12	0.12	0.18
Yb	^{169}Yb	177	5.00×10^{7}	6.70×10^{7}	5.07×10^{7}	0.20	0.15	0.20
W	^{187}W	479	2.57×10^{8}	3.00×10^{8}	2.05×10^{8}	0.04	0.03	0.05
Th	^{233}Pa	311.9	1.50×10^{8}	1.44×10^{8}	1.03×10^{8}	0.07	0.07	0.10

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