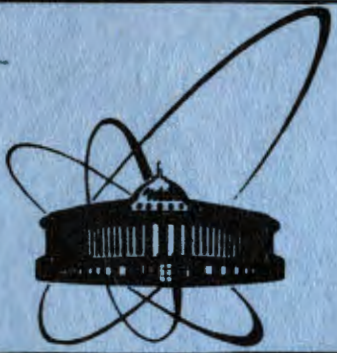

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# DETERMINATION OF RARE-EARTH ELEMENTS BY THE SIMULTANEOUS GAMMA-NEUTRON ACTIVATION ANALYSIS USING A MICROTRON

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## INTRODUCTION

Instrumental and radiochemically supported neutron activation analysis (NAA) has been used to determine various rare-earth elements (REE) in rocks and ores for several years [1-4]. On the other hand, photon activation analysis (PAA) can be considered as an effective analytical method for these elements, too [7]. But for some of them the sensitivities of PAA are rather poor in comparison with thermal NAA, while for others the situation is different. Separate irradiation with either photons or neutrons seems to be laborious and time-consuming. So it is worthwhile to investigate the simultaneous analysis of REE by irradiation in a mixed neutron-gamma field. The latter is easily available at electron accelerators [8].

## EXPERIMENTAL

For irradiations the cycle electron accelerator - microtron was used. Its parameters were listed in refs. [9,11]. In order to obtain a mixed gamma-neutron field a cubic lucite block 30x30x30 $cm^3$ in size with a central hole was used. A lead $\gamma \rightarrow n$ converter with a thickness of 20 mm situated in the cube centre served as a fast neutron source (fig.1). In preliminary experiments the thermal neutron flux and the bremsstrahlung intensity were measured with Au-foils via the registration of gamma lines at 411.8 keV ($^{198}$Au) and at 356.6 keV ($^{196}$Au) from the reactions (n,$\gamma$) and ($\gamma$,n) on the stable isotope $^{197}$Au, respectively. In Fig.2 are shown the neutron and photon fluxes as a function of the distance r from the tungsten target along the bremsstrahlung beam axis. The absolute thermal neutron flux in the cube centre, determined using Au foils is $2 \times 10^8$ n/$cm^2 \cdot s$.

The samples as well as the standards weighting about 5 g each suitably packed in polyethylene capsules 25 mm in diameter and 10 mm in height were placed between the target and the $\gamma \rightarrow n$ converter. The irradiation was performed by a bremsstrahlung beam generated from the tungsten target and by thermal neutrons obtained with the above-mentioned device. The maximum electron energy was 20.5 MeV, mean current - 12 μA, irradiation time - 3 hours. Corrections for space flux variation were made by placing Au-foil flux monitors between the capsules. Gamma-ray



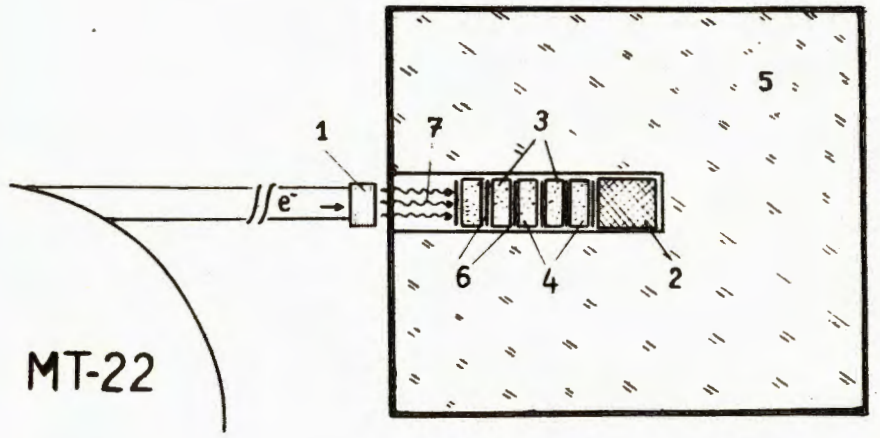


Fig.1. Schematic view of the device for obtaining a mixed gamma-neutron field. 1 - Bremsstrahlung target, 2 - lead converter, 3 - samples, 4 - standards, 5 - plexiglass cube, 6 - Au - foils, 7 - photon beam.

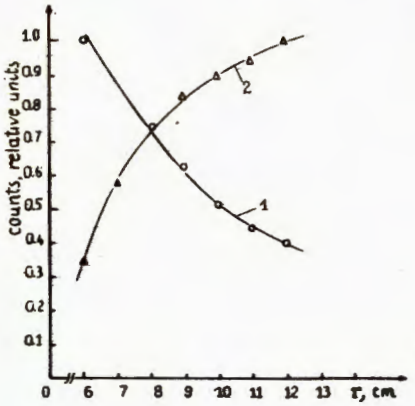


Fig.2. The dependence of photon (1) and neutron (2) flux densities on the distance from the bremsstrahlung target.

spectra were accumulated by a spectroscopic system including a 25 $cm^3$ Ge(Li) detector coupled with a LP-4900 pulse-height analyzer (NOKIA ELECTRONICS). Each spectrum was measured during 20 min at all decay times, with the subsequent treatment using the computer program PROBA designed to calculate the energy area, FWHM and error for each peak found [10]. Standards were prepared by micropipetting a standard stock solution of the REE into the capsule used for samples and by diluting to a known volume with distilled water. The total amount of standards and samples that can be irradiated is chosen with precaution against the effect of neutron self-shielding [5]. Fig.3 illustrates the gamma-ray spectra obtained from a REE sample irradiated in graphite cube of the same microtron MT-22 during 6 hours after 4-day decay (1) and from the same sample irradiated in a mixed gamma-neutron field for 3 hours after 5-day decay (2).

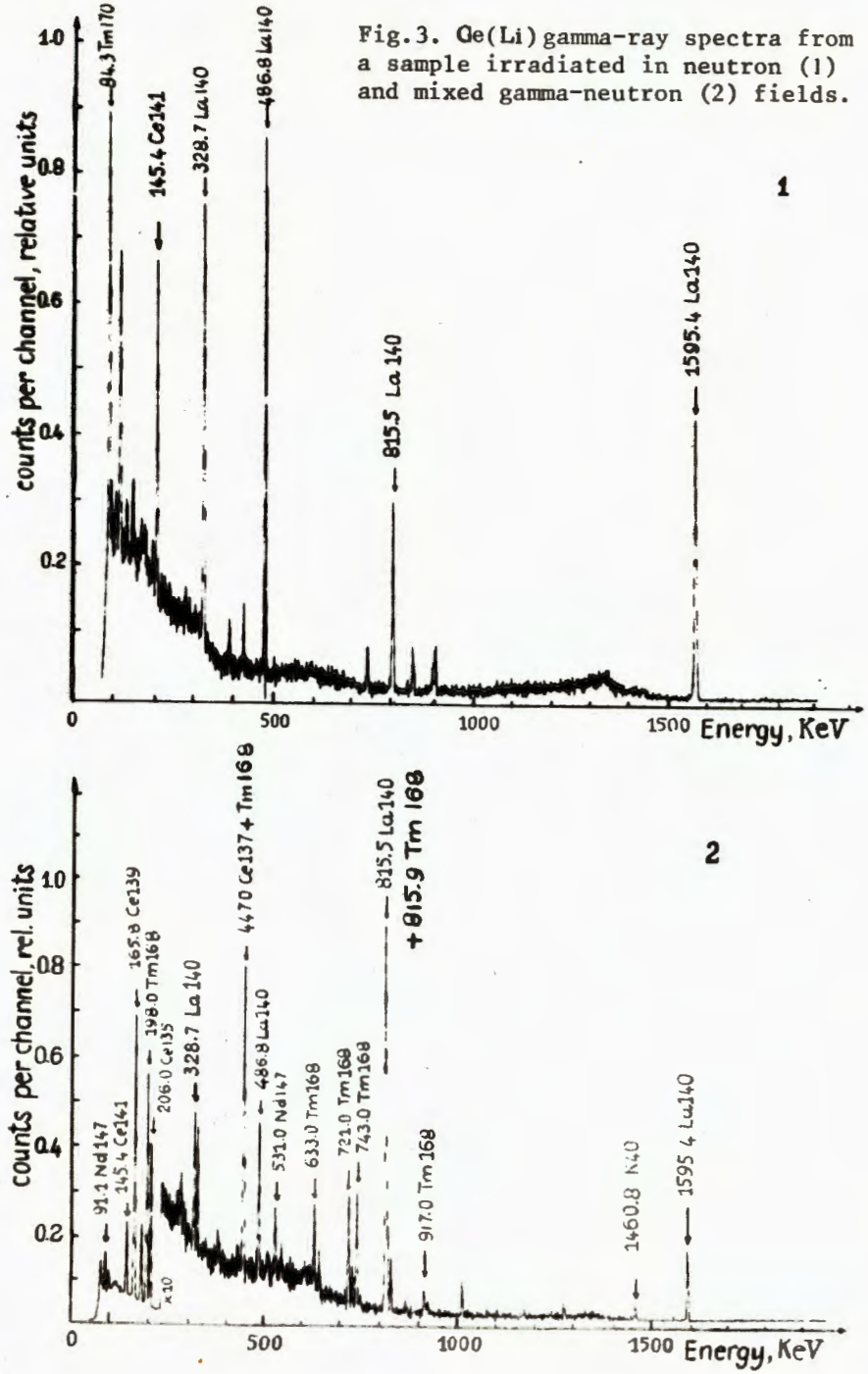


Fig.3. Ge(Li) gamma-ray spectra from a sample irradiated in neutron (1) and mixed gamma-neutron (2) fields.



## RESULTS AND DISCUSSION

In table 1 there are listed the sensitivities covering essentially all the radioactive products of REE. The sensitivities have been extrapolated to the end of a 3-hour irradiation in a neutron field only and in a mixed gamma-neutron one and expressed in counts per second per 1 mg of the element. They were also normalized to a standard doze rate. The neutron activation was carried out in the graphite moderator surrounding the uranium bremsstrahlung target /11/. The maximal thermal neutron flux in its centre is $4 \times 10^8$ n/cm$^2$·c. The data presented in table 1 were obtained for 5 ml of water solution containing 0.4mg/ml of each REE. Two runs of gamma-ray measurements were carried out after a one-day decay for Dy, Er, Eu, Gd, Pr and after 2 days for the remainder. The contents of La, Tb, Ho, Lu were determined only via $(n,\gamma-)$ reactions for both graphite and lucite moderators. In those cases the sensitivities obtained in the graphite moderator were a factor of 1.4-6 better than in the lucite moderator. For Y, Ce, Nd and Dy irradiation a mixed flux is preferable due to the $(\gamma,n)$ reactions. In the cases where radionuclides ($^{141}$Ce, $^{153}$Sm, $^{152m}$Eu, $^{159}$Gd and $^{175}$Yb) were produced via both $(n,\gamma)$-and $(\gamma,n)$ reactions the detection sensitivity for neutron irradiation was comparable to or lower than that for irradiation with a mixed flux. It is difficult to evaluate the differences in sensitivity for elements, obtained in neutron and mixed gamma-neutron irradiations for it depends on many factors such as neutron flux density, neutron spectra, isotope abundance, the value of resonance integrals, the shape of the excitation function for the $(\gamma,n)$ reaction, etc. In many cases the interferences can be neglected or easily be accounted for by other gamma-ray lines due to the radionuclides. Some data on the interfering and reference peaks are summarized in table 1. The radionuclides are listed in the order of gamma-ray energies. The calculations are carried out using the well-known data tabulated in /12/. When the same nuclide arises from both $(\gamma,n)$ and $(n,\gamma)$ reactions simultaneously, the mixed gamma-neutron flux is difficult to correct for by using just few standards and of monitor foils as shown in Fig.1. In this case it is convenient to use the new standardization method proposed in /13/. The REE content of rock samples was determined by irradiation with a mixed flux and, for checking, also in a thermal neutron field, too (table 2). The results show a fairly high degree of consistency. With the application of the method of REE analysis described in this paper only one irradiation is needed for the determination of all REE. A smaller number of $\gamma$-spectrum measurements are required due to the $(\gamma,n)$ reactions used. Besides REE, several elements such as Nb, Zr, etc., that are not convenient for determination by thermal neutron irradiation can be

Table 1

Sensitivities of the mixed neutron-gamma and neutron activation; Interfering photopeaks and reference peaks

| Element | Nuclide (half-life) | Reaction pathway | Principal gamma-ray peak, keV | Sensitivity Count./mg.s NEUTRON | Sensitivity Count./mg.s MIXED | Interfering isotopes (half-life) | Energy, keV Interfering | Energy, keV Reference | Correction ratio** |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| $_{39}Y$ | $^{88}Y$(108D) | $^{89}Y(\gamma,n)^{88}Y$ | 898 | | 0.23 | | | | |
| | | | 1836 | | 0.11 | | | | |
| $_{57}La$ | $^{140}La$(40.2H) | $^{139}La(n,\gamma)^{140}La$ | 328.7 | 3.81 | 2.00 | $^{151}Gd$(120D) | 328.2 | 153.6 | 0.01 |
| | | | 486.8 | 3.43 | 1.88 | $^{160}Tb$(72.1D) | 486.8 | 879.0 | 0.01 |
| | | | | | | $^{47}Ca$(4.55D) | 489.2 | 297.0 | 0.02 |
| | | | 815.5 | 1.11 | 0.56 | $^{168}Tm$(93D) | 815.9 | 198.2 | 0.15 |
| | | | 1595.4 | 1.78 | 0.93 | | | | |
| $_{58}Ce$ | $^{135}Ce$(17.2H) | $^{136}Ce(\gamma,n)^{135}Ce$ | 265.5 | | 0.95 | | | | |
| | $^{137}Ce$(9H) | $^{138}Ce(\gamma,n)^{137}Ce$ | 447 | | 0.20 | | | | |
| | $^{139}Ce$(140D) | $^{140}Ce(\gamma,n)^{139}Ce$ | 165.8 | | 4.29 | | | | |
| | $^{141}Ce$(32.4D) | $^{142}Ce(\gamma,n)^{141}Ce$ | 145.4 | 0.08 | 1.15 | $^{175}Yb$(101H) | 144.8 | 282.0 | 0.22 |
| | | $^{140}Ce(n,\gamma)^{141}Ce$ | | | | $^{59}Fe$(44.6D) | 142.5 | 1099.0 | 0.18 |
| $_{59}Pr$ | $^{142}Pr$(19.2H) | $^{141}Pr(n,\gamma)^{142}Pr$ | 1575.4 | 0.20 | (*) | | | | |
| $_{60}Nd$ | $^{147}Nd$(11.6D) | $^{148}Nd(\gamma,n)^{147}Nd$ | 91.1 | (*) | 1.32 | $^{169}Yb$(32.0D) | 93.6 | 63.0 | 0.06 |
| | | $^{146}Nd(n,\gamma)^{147}Nd$ | 531.0 | (*) | 0.12 | | | | |

Table 1 (continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| $_{62}Sm$ | $^{153}Sm$(1.9D) | $^{154}Sm(\gamma,n)^{153}Sm$ | 69.4 | 0.54 | (*) | $^{153}Gd$(241D) | 69,7 | 97.5 | 0.08 |
| | | $^{152}Sm(n,\gamma)^{153}Sm$ | 103.2 | 2.45E1 | 2.41E1 | $^{153}Gd$(241D) | 103.2 | 97.5 | 0.70 |
| $_{63}Eu$ | $^{152}Eu$(9.3H) | $^{153}Eu(\gamma,n)^{152m}Eu$ | 121.8 | 1.01E1 | 1.12E1 | $^{131}Ba$(11.7D) | 123.8 | 496.0 | 2.33 |
| | | $^{151}Eu(n,\gamma)^{152m}Eu$ | 344.0 | 1.84 | 2.13 | | | | |
| | | | 841.6 | 2.80 | 3.11 | | | | |
| | | | 963.6 | 2.21 | 2.42 | | | | |
| | | | 1315.0 | 0.01 | (*) | | | | |
| $_{64}Gd$ | $^{159}Gd$(18H) | $^{160}Gd(\gamma,n)^{159}Gd$ | 363.5 | 1.85 | 9.40 | $^{171}Er$(7.5H) | 363.0 | 882.0 | 1.86 |
| | | $^{158}Gd(n,\gamma)^{159}Gd$ | | | | | | | |
| $_{65}Tb$ | $^{160}Tb$(72.1D) | $^{159}Tb(n,\gamma)^{160}Tb$ | 86.8 | 5.50 | 0.90 | $^{191}Pt$(3.0D) | 85.1 | 539.0 | 0.02 |
| | | | 298.6 | 1.33 | 0.23 | $^{186}Re$(88.9H) | 296.9 | 768.0 | 0.01 |
| | | | 879.4 | 0.38 | 0.05 | $^{143}Ce$(33H ) | 880.0 | 293.0 | 0.005 |
| | | | 1177.9 | 0.15 | 0,04 | | | | |
| $_{66}Dy$ | $^{155}Dy$(10.2H) | $^{156}Dy(\gamma,n)^{155}Dy$ | 227.0 | | 0.25 | | | | |
| $_{67}Ho$ | $^{166}Ho$(1.1D) | $^{165}Ho(n,\gamma)^{166}Ho$ | 80.6 | 1.90E1 | 1.01E1 | $^{191}Pt$(3 D) | 82.4 | 539.0 | 1.50 |
| $_{68}Er$ | $^{171}Er$(7.5H) | $^{170}Er(n,\gamma)^{171}Er$ | 308.1 | 0.01 | (*) | $^{169}Yb$(31.8D) | 307.0 | 198.0 | 0.17 |
| | | | | | | $^{160}Tb$(72.1D) | 309.5 | 879.0 | 0.13 |

Table 1 (continued)

| * | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|
| $^{69}Tm$ | $^{168}Tm$(85D) | $^{169}Tm(\gamma,n)^{168}Tm$ | 185 | | 1.23 | | | | |
| | | | 198 | | 3.65 | | | | |
| | | | 448 | | 0.48 | | | | |
| | | | 547 | | 0.03 | | | | |
| | | | 633 | | 0.10 | | | | |
| | | | 646 | | 0.05 | | | | |
| | | | 721 | | 0.16 | | | | |
| | | | 732 | | 0.05 | | | | |
| | | | 743 | | 0.16 | | | | |
| | | | 917 | | 0.02 | | | | |
| | $^{170}Tm$(128.6D) | $^{169}Tm(n,\gamma)^{170}Tm$ | 84.3 | 0.65 | (*) | $^{160}Tb$(72.1D) | 86.8 | 879.0 | 3.57 |
| $^{70}Yb$ | $^{169}Yb$(31.8D) | $^{168}Yb(n,\gamma)^{169}Yb$ | 63.1 | 0.10 | (*) | $^{188}W$ (60 D) | 63.5 | 291.0 | 0.54 |
| | | $^{170}Yb(\gamma,n)$ $^{169}Yb$ | 177.0 | 1.76 | 0.31 | $^{182}Ta$(115 D) | 179.0 | 198.0 | 0.88 |
| | | | 307.5 | 0.60 | (*) | | | | |
| | $^{175}Yb$(4.2D) | $^{174}Yb(n,\gamma)^{175}Yb$ | 113.0 | 1.03 | 2.10 | $^{177}Lu$(6.7D) | 112.9 | 320.0 | 83.33 |
| | | $^{176}Yb(\gamma,n)^{175}Yb$ | 282.9 | 0.68 | 1.40 | | | | |
| | | | 396.1 | 1.01 | 1.83 | | | | |
| $^{71}Lu$ | $^{177}Lu$(6.7D) | $^{176}Lu(n,\gamma)^{177}Lu$ | 113.0 | 7.00 | 4.60 | | | | |
| | | | 208.4 | 7.02 | 4.85 | $^{188}W$ (60D) | 207.8 | 291.0 | 0.03 |

* The gamma-peak areas are below the $3\sqrt{Nb}$ level, Nb -background counts within peak boundaries.
** Correction ratio: interfering-peak area/reference-peak area ; $EN=10^{N}$.



Table 2

Concentrations of some REE found in ores by neutron and mixed neutron-gamma activation

| Samples | Elements | Contents of elements, ppm | |
|---|---|---|---|
| | | neutron | mixed |
| KT-779 | Ce | 2760 ±80 | 2820±85 |
| | La | 2400± 90 | 2500±100 |
| | Sm | 830± 40 | 850 ±50 |
| | Yb | 540 ± 30 | 500 ± 50 |
| | Tb | 104 ± 10 | 100 ± 10 |
| | Ho | 85 ± 20 | 90 ± 22 |
| | Lu | 60 ± 7 | 55 ± 8 |
| KT-818 | Ce | 22000 ± 600 | 21000 ± 800 |
| | La | 18000 ± 500 | 19000 ± 400 |
| | Nd | 6200 ± 250 | 6400 ± 200 |
| | Sm | 560 ± 50 | 630 ± 60 |
| | Eu | 410 ± 40 | 480 ± 35 |
| | Tb | 120 ± 10 | 140 ± 15 |
| KT-819 | Ce | 53000 ± 900 | 53000 ± 1000 |
| | La | 47000 ± 1000 | 46000 ± 1100 |
| | Sm | 3500 ± 300 | 3700 ± 250 |
| | Eu | 590 ± 50 | 610 ± 40 |
| | Ho | 350 ± 30 | 380 ± 40 |

easily analysed simultaneously. The sensitivity depends mainly on the accelerator beam power. As for the microtron, it can be successfully applied for the analysis of REE ores by the described method.

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REFERENCES


1. Mosen A.W., Schmitt R.A., Wasilevskis J. Anal.Chim.Acta, 1961, 25, p. 10.
2. Cobb J.C. Anal.Chem., 1967, 39, p. 127.
3. Tomura K. et al. Anal.Chim.Acta, 1968, 41, p. 217.
4. Graber F.M., Lukens N.R., MacKenzie J.K. J.Radioanal.Chem., 1970, 4, p. 229.
5. Van den Bergh F., Adams F., Hoste J. J.Radioanal.Chem., 1970, 4, p. 347.
6. Henderson P., Williams C.T. J.Radioanal.Chem., 1981, 2, p. 445.
7. Kato T., Voigt A.F. J.Radioanal.Chem., 1970, 4, p. 325.
8. Kapitza S.P., Tchipenjuk Iu.M. Proc. of the 4th USSR Conference on Application of New Nuclear Method in National Economy, JINR, P18-82-117, Dubna, 1981, p. 29.
9. Vo Dac Bang, Tran Dai Nghiep. Radiochem. Radioanal.Letters, 1983, 55(5-6), p. 321-330.
10. Phillippot J. Ck.IEEE Trans. NS-17, 1970, 3, p. 446.
11. Belov A.G. et al. JINR, P9-82-301, Dubna, 1982.
12. Bowman W.W., MacMurdo W. Atomic Data and Nuclear Data Tables, 1974, 13, p. 89-292.
13. Vo Dac Bang, USSR Author's Certificate No. 973249, Bull. OIPOTZ, 1982, 41, p. 196.



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Определение редкоземельных элементов /РЗЭ/ гамма-нейтронным активационным анализом с использованием микротрона


Применение одновременно активации гамма-квантами и нейтронами является одним из эффективных методов анализа редкоземельных /РЗЭ/ и других элементов. Смешанное поле гамма-квантов и нейтронов получено в кубовом замедлителе из оргстекла с комбинированными конверторами: электрон-гамма ($e \to \gamma$) и гамма-нейтрон ($\gamma \to n$) на пучке микротрона. Чувствительность данного метода сравнивается с чувствительностью метода нейтронно-активационного анализа, проведенного на кубовом замедлителе из графита того же микротрона. Обсуждаются преимущества и недостатки предложенного метода.



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Vo Dac Bang et al. E18-84-99

Determination of Rare-Earth Elements by the Simultaneous Gamma-Neutron Activation Analysis Using a Microtron


The combination of photon and neutron activation provides an effective method of analysis of rare earths and other elements. A mixed gamma-neutron field is obtained with electron-to-gamma ($e \to \gamma$) and gamma-to-neutron ($\gamma \to n$) converters combined with a lucite moderator. The samples are activated simultaneously. The sensitivities of this method have been compared with neutron activation in a graphite moderator cube using the same microtron. The advantages and shortcomings of the method are discussed.



The investigation has been performed at the Laboratory of Nuclear Reactions, JINR.

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