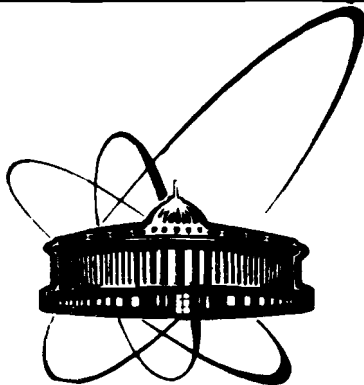


89-725



ОБЪЕДИНЕННЫЙ
ИНСТИТУТ
ЯДЕРНЫХ
ИССЛЕДОВАНИЙ
ДУБНА

G 52

E6-89-725

B. Gleisberg, B.M. Ly, B. Gorski

INVESTIGATIONS OF THE SEPARATION
OF Np, Pa, U, Th AND REE
IN GEOLOGICAL SAMPLES

Submitted to Actinides-89 International Conference,
Tashkent, USSR, September 24-29, 1989

1989

Introduction

The quantitative determination of trace amounts of Th, U and REE in very depleted rocks is necessary to get information about genetic processes in the investigated area. U, Th and REE are used as geochemical indicators. On the other hand, the knowledge of the contents of these elements in natural materials is of importance when they are rich enough for their use as raw materials. We treated two types of geological samples which differ considerably in their origin and in the U, Th and REE contents.

Table 1. REE, U and Th contents in geological samples

Material Element	I		II	
	Peridotitic rocks /1,2/	Bastnaesites /3,4/	Monazites	
Σ REE	3-15 ppm	73-76%	56-75%	
U	0.04-0.8 ppm	0.02-0.1%	0.02-0.35%	
Th	0.15-0.7 ppm	0.1-1%	0.5-10%	

It is clear that the analytical methods and chemical separation procedures should be very different for these two types of materials.

PART I

Radiochemical Neutron Activation Analysis (RNAA)

of Microamounts of REE, U and Th in Peridotitic Rocks

Trace amounts of REE, U and Th can be analysed by RNAA. Only effective isolation of the REE-group, of NP-239 and Pa-233 from the interfering isotopes resulting from large amounts of Fe, Cr, Ni and Sc-microamounts allows precise determination of U-, Th- and REE-contents.

With regard to above-mentioned demands two different schemes of separation were tested and compared:

A) Cation exchange and solvent extraction

B) Extraction Chromatography

To estimate the suitability of the described separation schemes for the determination of REE in such types of samples being rich in U or Th but poor in REE and thus demanding separation from U or Th before irradiation, the behaviour of U and Th is presented in this paper as well.

I. Experimental

Determination of Distribution Coefficients

Distribution coefficients in different systems of examination were obtained under stationary conditions by shaking the reagents for 15 minutes at room temperature. The behaviour of Sc, REE, Np and Pa as well as of U and Th was controlled by radioactive tracers.

1. 100 mg of cation exchange resin Wofatit KPS were shaken with 8 ml of HCl/H₂C₂O₄-solution containing Ce-139, Y-88 and Lu-173. After centrifugation aliquots of initial and equilibrium solution were measured using a Ge(Li)-detector, and K_d calculated.

2. Extraction experiments with 1.5% TOPO/cyclohexane were carried out by shaking each 1.5 ml of organic and of aqueous phase containing Np-239, Pa-233 or Sc-44/46 in HNO₃. For Np-extraction 0.1 ml of H₂O₂ (30%) was added. The λ -activity was measured in aliquots of two phases.

3. Distribution coefficients for the investigation of the extraction-chromatographic method were determined by using following procedure: A 0.07 M solution of diethylenetriamine-pentaacetic acid (DTPA) in 1 M lactic acid, containing some quantity of HNO₃ and a salting out reagent (Cu²⁺) was added to the nitrate of the element studied, labelled by the corresponding radioactive tracer (Np-239, Pa-233, Sc-44/46, Y-88, Tm-170, U-237, and Th-231). After complete dissolution the aqueous phase was shaken with an equal volume of TOPO in benzene (0.06-0.1M).

Investigation of Separation Schemes

The separation schemes were tested in the presence of GDR Standard Rock ZGI-Serpentinit SW after sample decomposition with a mixture of HF/HNO₃/HClO₄ and adding Np-239, Pa-233, Sc-44/46, Y-88, Tb-160 and Lu-173. Some chromatographic experiments for sorption and desorption of U and Th were carried out using U-237 and Th-231 without any rock matrix.

A) Cation Exchange and Solvent Extraction

The first step - sorption, purification and desorption of REE - was realized in a cation exchange column: Wofatit KPS (length=80 mm, diameter = 8.5 mm, particle size = 0.2-0.4 mm). The decomposed sample was fully dissolved in a small amount of 0.5 M HCl and injected in the column. After washing with 0.1 M H₂C₂O₄/0.5 M HCl and 2M HCl the REE-group was eluted with 6 M HNO₃.

B) Extraction Chromatography

TOPO was used as a fixed phase, 20% on supporting agent Wofatit EP-60 (column: length = 40 mm, diameter = 3 mm, particle size of EP-60 = 0.1-0.2 mm /5/).

120 mg of decomposed rock sample were dissolved in 0.3 ml 5.5 M HNO₃ and a mixture of 0.07 M DTPA, 1 M lactic acid and a salting-out agent (0.5 M Cu²⁺ or 0.2 M Fe²⁺) was added. This solution was injected in the extraction chromatographic column. The extractant was washed with 3 ml of a pure Cu-DTPA/lactic acid mixture. After removing the salting-out reagent with 3 M NH₄NO₃ separation of REE group, Sc and Pa was realized.

RNAA of Peridotitic Rocks and Meteorites by Cation Exchange
and Solvent Extraction

The detailed procedure is described in /1,2/.

Sample and standard materials were irradiated in the Rossendorf Research Reactor for 10-15 hrs at $3-5 \cdot 10^{13}$ n/cm²s. After allowing sample activity to decay for 24-36 hrs sample dissolution and separation on Wofatit KPS were carried out. To control the chemical yield Y-88, Ce-144 and Np-238 were used. The evaporated REE fraction was counted using a Ge(Li)-detector.

The Np and Pa containing fraction of the geological sample was evaporated. After destruction of oxalic acid Pa and Np were extracted from HNO₃-solution (10 ml) with 1.5% TOPO/cyclohexane (10 ml) in the presence of H₂O₂.

I. Results and Discussion

A. Cation Exchange and Solvent Extraction

The distribution coefficients of some REE in 0.1 M oxalic acid as a function of HCl-concentration on Wofatit KPS are represented in fig. 1. The K_d-values are high enough for quantitative sorption of all REE from 0.1 M H₂C₂O₄/0.5 M HCl. Low HCl concentrations increase the sorption of REE.

The cation exchange separation scheme is presented in fig. 2. Most of the interfering elements pass the resin immediately. Washing with 2 M HCl affects the good purification of REE from Co, Cr and other isotopes. The radiochemically almost pure REE-fraction is eluted from resin with 6 M HNO₃. The immediate passage of Np and Pa demands, as a second step, their selective separation from nearly complete matrix. This is achieved by extraction with TOPO/cyclohexane

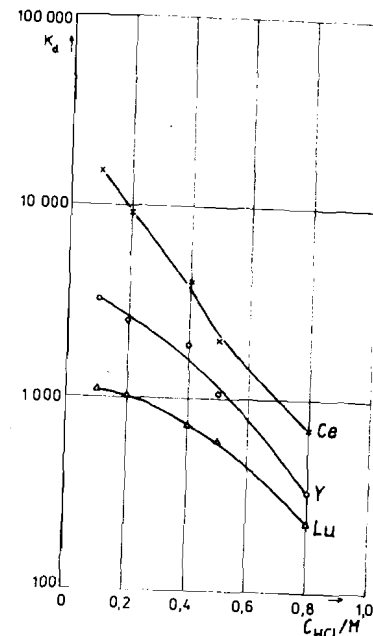


Fig. 1. Distribution coefficients of Ce, Y and Lu on Wofatit KPS in H₂C₂O₄/HCl as a function of HCl - concentration.

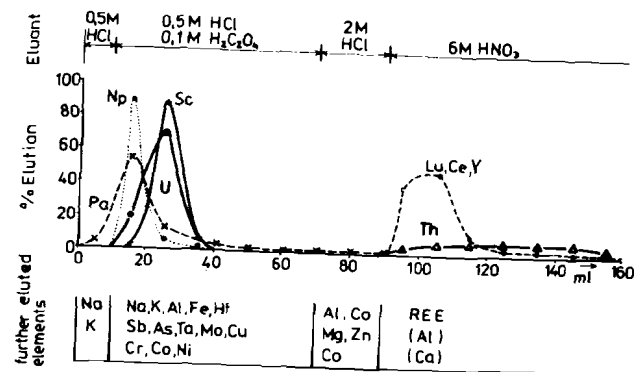


Fig. 2. Behaviour of REE, Np, Pa, Sc, U, Th and other elements during separation on Wofatit KPS.

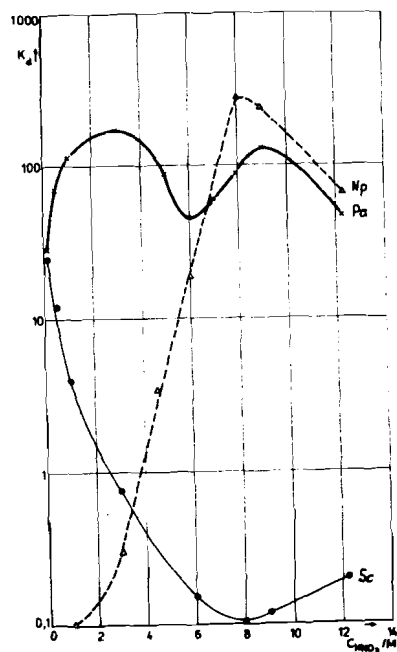


Fig. 3. Influence of HNO_3 -concentration on the distribution coefficients of Np (IV, V, VI), Pa and Sc
Organic phase: 1.5% TOPO in cyclohexane.

from 6-8 M HNO_3 in the presence of H_2O_2 /6/. The organic phase contains, in addition to the radionuclides Np and Pa, small Sc-46 -activities.

Detailed investigations of the extraction behaviour of Np, Pa and Sc as functions of the concentration of nitric acid have shown that optimal conditions for separation of Np and Pa from Sc are obtained using 8 M HNO_3 (fig. 3). It must be mentioned that the K_d -value of Np is a total K_d of Np (IV, V, VI). When the relation between the different valencies of Np is another one than in this experiments, other values of distribution coefficients are obtained. By reextraction of the organic phase with 6-8 M HNO_3 Np-distribution

coefficients >300 were observed. This underlines that there are no losses of Np by washing the organic phase with 6-8 M nitric acid for its purification from interfering matrix isotopes.

With regard to the applicability of the cation exchange method for preliminary U- and Th-separation from REE-microamounts the following conclusions can be drawn:

- U immediately passes the resin from $H_2C_2O_4/HCl$ -solution and the REE-fraction contains no U.
- Th is slowly eluted with 6 M HNO_3 , thus partially accompanying the REE-fraction.
- If a quantitative REE-Th separation is necessary, Th can be removed from the resin by washing with 40 ml of 4 M H_3PO_4 before REE desorption.

B. Extraction Chromatography

Distribution coefficients of Np (IV, V, VI), Pa, Sc as well as REE, U and Th as functions of the concentration of $Cu(NO_3)_2$ can be taken from fig. 4. For Cu concentrations from 0.1-1 M $Cu(NO_3)_2$ nearly all K_d -values increase with increasing Cu^{2+} -concentration. The K_d of Pa does not vary at concentrations from 0.5-1 M Cu^{2+} . If the Cu-concentration is more than 1 M, the distribution coefficients of Sc and Np continue to grow while the K_d values of REE, U, Th and Pa begin to decrease. The total K_d -value of Np (IV, V, VI) reaches its maximum when the concentration of the salting-out agent reaches 2 M. All K_d -values are high enough for the quantitative sorption of elements on the chromatographic column using 0.5 M $Cu(NO_3)_2$. The extraction chromatographic experiments, however, indicated that Np is only partially sorbed on the column. This can be connected with different valences of Np as confirmed by reextraction results, and also by a second - step extraction of the aqueous phase.

Table 2. Distribution coefficients of Np on 0.1 M TOPO/benzene

Conditions	K_d
first extraction (2.5 M Cu-DTPA, lact.ac.)	5.33
second extraction of aqueous phase (2.5 M Cu-DTPA, lact.acid)	0.07
reextraction with 0.5 M Cu-DTPA, lact.ac.)	> 200

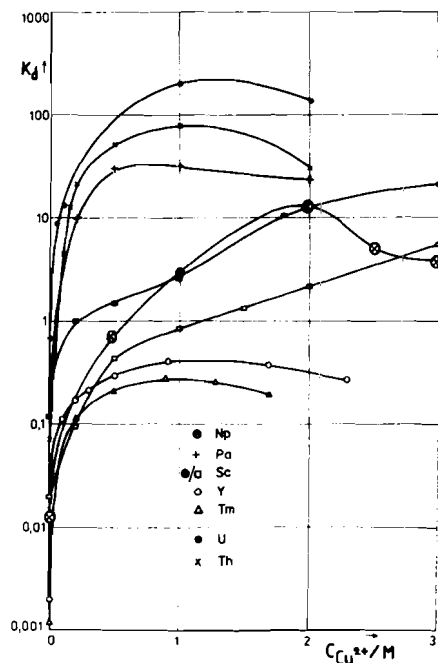


Fig. 4. Dependence of the salting-out agent concentration on the distribution coefficients of Y, Tm, Sc, Pa, Np (IV, V, VI), U and Th

organic phase: 0.1 M TOPO in benzene for Sc, Np, Y, Tm
 0.06 M TOPO in benzene for Th, Pa
 0.01 M TOPO in benzene for U
 aqueous phase: Cu, DTPA, lact.acid,
 0.3 M HNO_3 ($C_{\text{Th}}=7.7 \cdot 10^{-4}$ M,
 $C_{\text{U}}=8 \cdot 10^{-4}$ M $C_{\text{Sc}}=3.4 \cdot 10^{-2}$ M,
 ■ Sc without carrier)

However, it must be taken into account that such a complex matrix as a geological sample may have a great influence on the behaviour of trace elements.

Fig. 5 represents the extraction chromatographic separation of REE, Pa and Sc and the behaviour of other elements using a complexing agent and 0.5 M $\text{Cu}(\text{NO}_3)_2$ as a salting-out reagent. A very good separation is achieved. Partially extracted Np is eluted together with Sc with 6 M H_3PO_4 .

The results published in /5/ allow the conclusion that a number of most abundant macroamounts present in peridotitic rocks, such as Co, Ni, Cr, Fe, Al, and Mn, can automatically serve as salting-out agents for REE- and Sc-extraction.

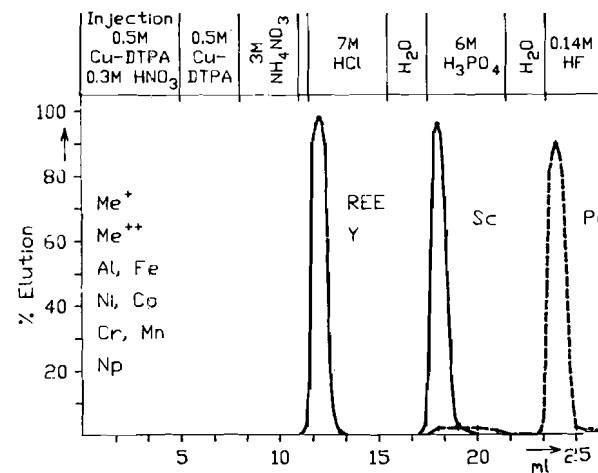


Fig. 5. Extraction chromatographic separation of REE, Pa, Sc and other elements on TOPO from 0.5 M $\text{Cu}(\text{NO}_3)_2$, 0.07 M DTPA, 1 M lact. acid - 100 mg Serpentin SW

If 0.2 M Fe²⁺ was used as a salting-out reagent (instead of 0.5 M Cu), the results of extraction chromatography were not as good. The partial coextraction of Fe causes great losses of REE and Sc (no losses of Pa) by injection of the sample Serpentin SW.

The Fe-amounts of this rock (5.18% = $1.7 \cdot 10^{-2}$ mol/l) do not interfere with the sorption of Sc, REE and Pa if Cu is added as a salting-out agent.

Concerning the applicability of the extraction chromatography with TOPO in the presence of complexing agents for the separation of REE from U and Th it can be estimated that this method allows the separation of U and Th from REE. It should be noted that great amounts of U and Th compete with the sorption of REE when column capacity is not sufficient. The capacity is $2.5 \cdot 10^{-5}$ Mol Th and $3.5 \cdot 10^{-5}$ Mol U for the column used ($1.1 \cdot 10^{-4}$ Mol TOPO). The presence of each 0.5 mg Th and 0.5 mg U does not interfere with the REE-sorption on the chromatographic column, while the presence of each 1.0 mg Th and 1.0 mg U results in losses of 12-18% of light (Ce) and heavy (Lu) REE.

U and Th are washed out from the column completely by 4-6 M phosphoric acid together with Sc (fig. 5), or by 2 M (NH₄)₂CO₃.

I. Conclusions

The separation scheme A has already been successfully used for the determination of ppm- and ppb-contents of REE, U and Th. The second step (solvent extraction) is very effective for the isolation of Np and Pa from matrix constituents and can be carried out quickly.

The separation scheme B is expected to be applicable to determine the REE- and Th-contents in depleted rocks. Its advantage is the efficient purification of the REE-fraction from Sc and Pa in a

one-cycle process with immediate removal of interfering matrix components.

For RNAA of samples with unknown matrix the chemical yield should always be controlled using radioindicators not interfering with the analysis of the elements being investigated.

PART II

Separation of Th, U and REE in Monazites

Instrumental nuclear analytical methods allow one to determine some light REE (LREE) and Y in Bastnaesites and Monazites. Complete analysis including heavy REE (HREE) requires their separation from matrix components and from large amounts of LREE. Preconcentration of HREE by extraction chromatography with HDEHP demands preliminary separation of Th, U and other elements.

II. Experimental

The behaviour of U and Th during the separation steps was observed using x-ray fluorescence analysis with a ¹⁰⁹Cd-source. Particular investigations aimed at studying the sorption and desorption of U and Th, were controlled by ²³¹Th and ²³⁷U produced by γ -irradiation using the microtron MT-25 in the reactions $^{238}\text{U}(\gamma, n)^{237}\text{U}$ and $^{232}\text{Th}(\gamma, n)^{231}\text{Th}$. Fig. 6 describes the separation scheme of Monazite samples. After the sample decomposition (100-200 mg) with a mixture of conc. acids HF, HNO₃, HClO₄ (1:1:1.5) and evaporation to dryness the residue was dissolved in 11 M HCl (25-40 ml).

The sample solution passed an anion exchange resin Dowex 1x8 (50-100 mesh) and Fe, Zr and U were retained. The REE and Th contain-

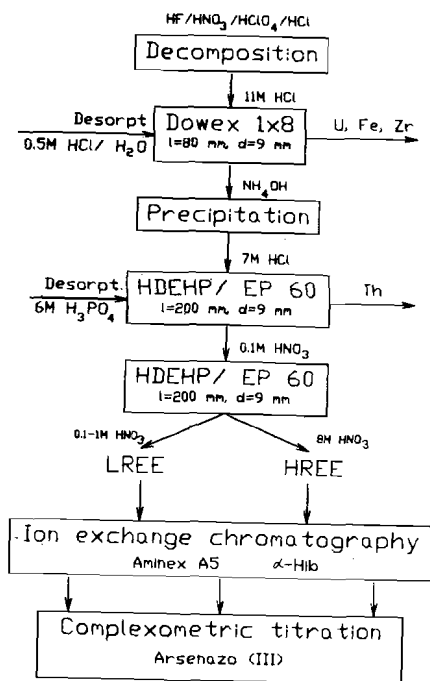


Fig. 6. Separation scheme for the analysis of Th and all REE in Monazites.

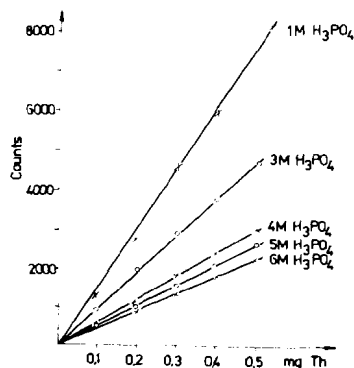


Fig. 7. The influence of H_3PO_4 -concentration on Th measuring effectivity using x-ray fluorescence spectroscopy.

ing the effluent were precipitated with NH_4OH .

After dissolution of the precipitate in 7-9 M HCl (10 ml) Th-sorption was accomplished on a column where HDEHP was used as a fixed phase (20% HDEHP on the supporting agent Wofatit EP-60, particle size of EP-60 = 0.1-0.2 mm). When the sample has passed the column, 60 ml 7-9 M HCl were still necessary to guarantee that no REE are retained on the column.

The REE-solution was evaporated and dissolved in 0.1-0.4 M HNO_3 to pass a second HDEHP / EP-60 - column for separation LREE from HREE using a gradient of HNO_3 -concentration.

The determination of individual REE contents was realized after separation of aliquots of each fraction (HREE, LREE) by ion exchange chromatography on Aminex A5 with α -Hib at pH=4.55 (column: length = 110 mm, diameter = 3 mm, particle size = 13-14 μm). The REE contents were determined by titration of the Arsenazo (III)-REE-complex with EDTA. This method is described in detail in [7]. After sorption of Th on the first HDEHP-column Th was desorbed with 6 M H_3PO_4 (50 ml). The Th contents of Monazites could be determined using x-ray fluorescence spectroscopy (^{109}Cd -source, Si(Li)-detector 30 mm^2) in an aliquot of the phosphoric acid solution (1.5 ml) in polyethylene vials. The influence of the H_3PO_4 -concentration on the Th measuring effectivity is shown in fig. 7.

After sample decomposition and dissolution with 11 M HCl an insignificant residue remained. X-ray analysis has shown that the residue did not contain any U, Th and LREE, however, it contained Ba, Zr and Ti. Particular investigations after fusion the residue with Na_2O_2 have proved that it contains no REE.

II. Results and Discussion

In table 3 the REE contents found in three Monazite samples in comparison with literature values are listed.

Table 3. Relative REE contents in investigated Monazite samples compared with literature values

REE oxides	/4/	Contents, % average of 3 samples
La ₂ O ₃	23	24.3
Ce ₂ O ₃	45	42.8
Pr ₂ O ₃	5.0	5.5
Nd ₂ O ₃	18.4	17.1
Sm ₂ O ₃	2.3	2.3
Eu ₂ O ₃	0.07	0.16
Gd ₂ O ₃	1.7	1.6
Tb ₂ O ₃	0.16	>0.16
Dy ₂ O ₃	0.52	-
Y ₂ O ₃	2.0	-
Ho ₂ O ₃	0.09	0.08
Er ₂ O ₃	0.13	0.19
Tm ₂ O ₃	0.013	0.33
Yb ₂ O ₃	0.061	0.053
Lu ₂ O ₃	0.06	0.036

The results are in good agreement with the literature values. The experiments have shown that the Th sorption on the HDEHP column depends on kinetic factors. The determination of the capacity of different sorption rates shows the kinetic influence (Table 4).

Table 4. The influence of the flow rate of Th-sorption on the capacity of the sorbent

Rate ml/cm ² s	Capacity Mol Th/Mol HDEHP
55	0.068
10	0.072
6	0.089
3	0.119
0.06	0.230

These results show that at very low sorption rates the theoretical capacity of the sorbent can almost be achieved. For a quantitative Th sorption on the HDEHP/EP-60 column low flow rates are necessary.

The Th contents obtained in three Monazite samples are listed in Table 5 compared with measurements of natural radioactivity /8/. Table 5. Comparison of results of Th contents in Monazites using different analytical methods

Sample	Th content, %	
	RFA after chemical separation	Meas. of natural radioactivity /8/
1	5.36	5.55
2	3.60	3.66
3	5.00	5.36

The Th contents obtained by x-ray fluorescence analysis after radiochemical separation are in good agreement with those measured by natural radioactivity of the samples.

II. Conclusions

The method described allows a quick separation of large amounts of Th, U and LREE from small amounts of HREE. A simultaneous determination of Th contents using x-ray fluorescence analysis after desorption of Th from the extractant HDEHP/EP-60 by phosphoric acid solution is possible. The x-ray spectrums of the H₃PO₄ fractions show no other lines but Th.

In combination with ion exchange chromatography and complexometric titration the contents of all individual REE can be determined.

Acknowledgements

The authors are thankful to Prof. I.Zvara for his support of this work, to A.G.Byelov for irradiations on the microtron, to E.Troger and A.Milek for their help in carrying out many experiments.

References

1. B.Gleisberg, S.Niese, W.Kramer. Chem. Erde 47 (1987), pp.231-242.
2. B.Gleisberg, S.Niese. 4th Meeting on Nuclear Analytical Methods, Dresden 1987, May 4-8, Proceedings, Vol. 1, pp. 205-211.
3. D.I.Ryabchikov, V.A.Ryabukhin. "Analytical chemistry of REE and Yttrium" (in Russian), Nauka, Moscow, 1966.
4. M.Helgorski, M.Levague. Science et techniques 1978, 32, pp. 19-27.
5. B.Gorski, Yu.S.Korotkin, V.N.Kosyakov. Journ. of Radioanal. Nucl. Chem., (Articles, 121, 1/1988), pp. 73-81.
6. B.Gleisberg, S.Niese. 4th Working Meeting "Isotopes in Nature", Leipzig 1986, Proceedings pp. 281-287.
7. B.Gleisberg, B.M.Ly (in prepeare)
8. B.Gleisberg, B.M.Ly, W.Helbig, ZfK Report, KB 1989.

Received by Publishing Department
on October 20, 1989.

Глайсберг Б., Ли Б.М., Горски Б.

E6-89-725

Исследования по выделению Np, Pa, U, Th
и PЗЭ в геологических образцах

В первой части исследовались две методики радиохимического нейтронно-активационного анализа для определения содержания Th, U и PЗЭ в геологических образцах (а) катионный обмен и экстракция, (б) экстракционная хроматография. Изучалось поведение U и Th с целью оценки использованной методики для образцов с большими содержаниями U и Th, но с микроколичествами PЗЭ. Предлагается метод селективного извлечения U и Th. Во второй части описывается эффективная методика выделения и определения PЗЭ и Th в монацитах.

Работа выполнена в Лаборатории ядерных реакций ОИЯИ.

Препринт Объединенного института ядерных исследований. Дубна 1989

Gleisberg B., Ly B.M., Gorski B.

E6-89-725

Investigations of the Separation
of Np, Pa, U, Th and REE in Geological Samples

In the first part two some methods of the radiochemical neutron activation analysis of U, Th and REE trace amounts in geological samples have been studied. They are: (i) cation exchange and extraction, and (ii) extraction chromatography. The behaviour of U and Th was also observed and conclusions were made regarding the applicability of the methods for the rocks which are rich in U and Th but depleted of REE. The method is recommended for the selective separation of U and Th. The second part represents an effective separation method for the determination of all REE and Th contents in monazites.

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

Preprint of the Joint Institute for Nuclear Research. Dubna 1989