

## THE CONCENTRATION OF SHORT-LIVED SPONTANEOUSLY FISSIONING NUCLIDES FROM IRON-MANGANESE NODULES

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The paper reports on the observation of the spontaneously fissioning nuclides as a result of hydrochemical and high-temperature processing of iron-manganese nodules. The spontaneous fission in the samples obtained was measured by the track method using electrochemical etching, and nuclides with  $T_{1/2} = 15$  d,  $T_{1/2} = 25$  d (similar in chemical properties to Os) and  $T_{1/2} = 62$  d (similar in chemical properties to Pb and Ra) were detected.

The content of the parent nuclide in iron-manganese nodules corresponds to  $4 \cdot 10^{-14} - 8 \cdot 10^{-14}$  g/g.

Сообщается о наблюдении короткоживущих спонтанно делящихся нуклидов в результате гидрохимической и высокотемпературной переработки железо-марганцевых конкреций. В полученных образцах определялось спонтанное деление трековым методом с применением электрохимического травления и были обнаружены нуклиды с  $T_{1/2} = 15$  сут,  $T_{1/2} = 25$  сут (близкий по химическим свойствам Os) и  $T_{1/2} = 62$  сут (близкий по химическим свойствам Pb и Ra).

Содержание материнского нуклида в железо-марганцевых конкрециях соответствует  $4 \cdot 10^{-14} - 8 \cdot 10^{-14}$  г/г.

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### INTRODUCTION

Academician A. P. Vinogradov [1] drew attention to the possibility of using the iron-manganese nodules as the objects of search for superheavy elements (SHE) in nature. The nodules concentrate from ocean water mercury, thallium, lead, bismuth and other elements with a factor of enrichment  $10^5 - 10^7$  [2] and, possibly, nuclides with  $Z = 108 - 126$ .

Search of the SHE in the Atlantic iron-manganese nodules was carried out by E. Cheifetz et al. [3]. Limit to the concentration of the SHE was obtained at the level of  $10^{-14}$  g/g. A similar result was obtained by A. Stoughton et al. [4] for the Pacific nodules. G. N. Flerov et al. conducted work on search of the SHE in the iron-manganese nodules [5], products of their chemical processing using the high-temperature sublimation and water chemistry. Limit values were obtained equal to  $4 \cdot 10^{-14}$  g/g and for heavy homologues of mercury and thallium —  $2 \cdot 10^{-15}$  g/g, lead —  $5 \cdot 10^{-16}$  g/g, bismuth —  $3 \cdot 10^{-16}$  g/g.

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In this work, new methods of the chemical enrichment were used for concentration of the heavy elements. The samples of low mass were obtained for registration of spontaneous fission using the solid-state detectors (SSD) [6–9].

### EXPERIMENTAL

The acid leaching, the extraction concentration and the distillation of organic solutions were used for chemical concentration of spontaneously fissioning nuclides from iron-manganese nodules. Uranium and transuranium elements have low volatility. Thus, sublimation products do not contain known spontaneously fissioning nuclides.

The scheme of hydrochemical processing for the 13 kg nodules from the 6298-52 station is shown in Fig. 1.

Samples of nodules were crushed to 150–200 mesh size and then dissolved in the solution of the concentrated nitric acid at room temperature for two days. The ratio of phases was (liquid : solid)  $L : S = 1 : 1$ . For a more complete leaching of the acid solution, hot water was added and then filtering of the precipitate was held. Iron hydroxide was precipitated at pH 8 from the nitric acid solution and, after separation from the solution by filtration, was dissolved in the hydrochloric acid. Then from hydrochloric solution with a volume of 30 litres the elements were extracted by solutions of Zn-salt 2-ethylhexylisobutyldithiophosphoric acid (Zn-2-EHBDTPH) in mineral oil (50%) [10] and oil sulfide (OS) [11] with a boiling point of about 200 °C. The extractants in the amount of 100 ml Zn-2-EHBDTPH and 20 ml OS were dissolved in 1 litre of acetone, and the mixture was added to 70 °C 0.3 M HCl solution of nodules. After mixing of the solutions and cooling to room temperature the extractants were removed by carbon tetrachloride at the ratio of phases (solution : organic)  $S : O = 30 : 0.5$ . The organic fraction was then separated from water solution. Carbon tetrachloride was

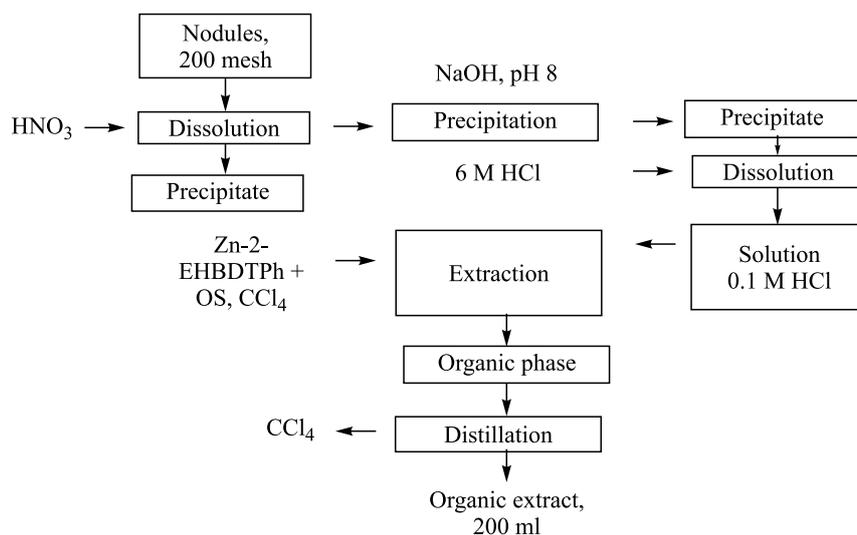


Fig. 1. The scheme of hydrochemical processing of 13 kg iron-manganese nodules from the 6298-52 station

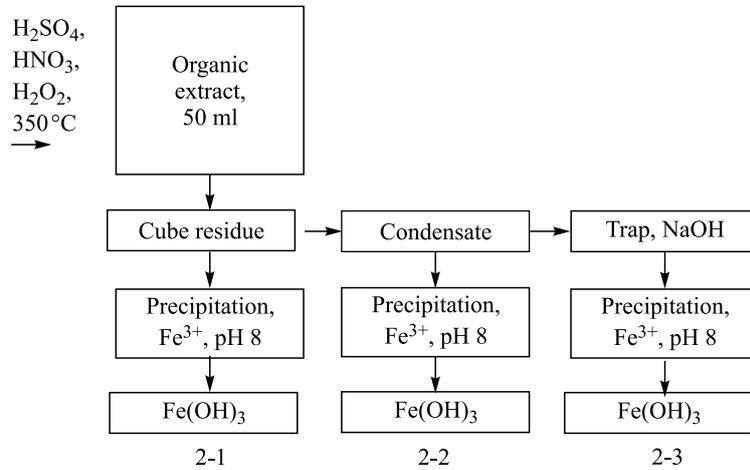


Fig. 2. The scheme of the processing of the extract

vapourised away on a water bath. The organic extract of volume 200 ml at rest was obtained, 50 ml of which was processed according to the scheme presented in Fig. 2.

The scheme of the processing of the extract is shown in Fig. 2.

The organic fraction of volume 50 ml was processed with sulfuric acid in the presence of hydrogen peroxide and nitric acid at 300–350°C. Volatile products were captured by a system of traps. The first trap collected distillate, the next two with a 6 M NaOH solution condensed the volatile products. 25 mg iron chloride were added as a carrier in the condensate and the alkaline solutions, and precipitated as iron hydroxides at pH 8.

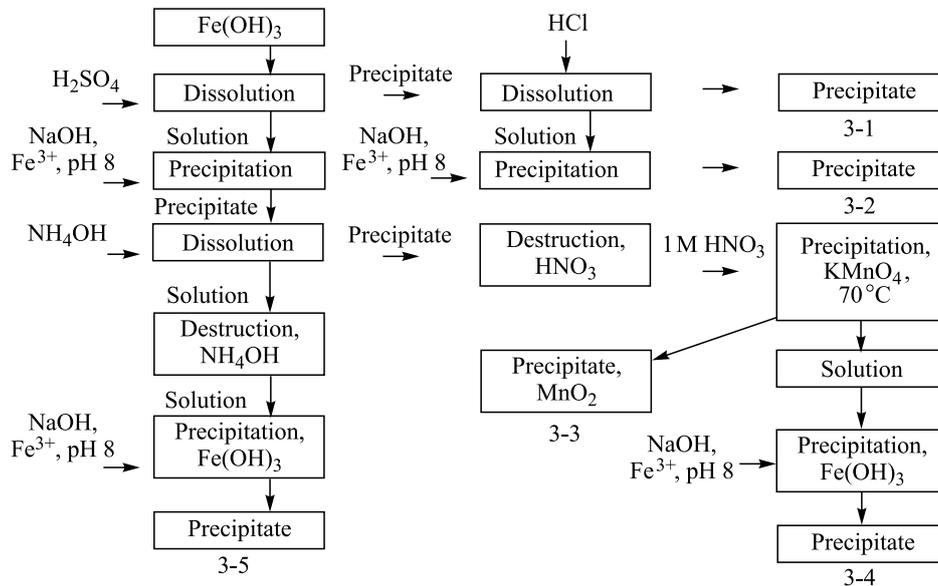


Fig. 3. The scheme of iron hydroxides processing from the cube residue (2-1)

Activities of spontaneous fissioning nuclides were determined in iron hydroxides by the track method. Iron hydroxides from a cube residue (2-1) after the measurements were processed.

Iron hydroxide from the cube residue was dissolved in the solution of sulfuric acid. As a result, the solution and the insoluble residue were obtained. The precipitate of sulphate after separation was treated with HCl solution, the insoluble precipitate (3-1) separated. Iron hydroxides were precipitated from the solution and selected (3-2). Iron hydroxide was precipitated from the sulfuric acid solution by NaOH at pH 8, the resulting precipitate separated and treated with the solution of  $\text{NH}_4\text{OH}$ . The solution was heated to destruction of  $\text{NH}_4\text{OH}$  and precipitation was carried out of metal hydroxides with NaOH solution at pH 8 (3-5). The residue after treatment with  $\text{NH}_4\text{OH}$  was dissolved in the solution of 1 M  $\text{HNO}_3$ . The solution was heated up to  $70^\circ\text{C}$  and  $\text{KMnO}_4$  was added to precipitate manganese dioxide.  $\text{MnO}_2$  was separated from the solution (3-3). Iron hydroxide was precipitated from the solution with NaOH at pH 8 (3-4).

Figure 3 shows the scheme of iron hydroxides processing from the cube residue (2-1).

**X-Ray Fluorescence Analysis of Samples.** Determination of stable elements was carried out on spectrometer with the Si(Li) detector with 200 eV resolution on the  $\text{FeK}\alpha_{1,2}$  line (6.4 keV). Radioisotopic sources of  $^{109}\text{Cd}$  and  $^{241}\text{Am}$  were used for excitation of X-ray radiation [12].

**Determination of Uranium.** The uranium content was determined by the track method. The accuracy of determination of uranium was 10%. The detection limit of uranium corresponded to  $10^{-9}$  g/g [7].

**Radioactive Nuclides Used in the Work.** The study of the element distribution during processing of samples was done with the help of their radioactive nuclides.  $^{74}\text{As}$  ( $T_{1/2} = 17.77$  d,  $E_\gamma = 595.9$  keV),  $^{126}\text{I}$  ( $T_{1/2} = 13$  d,  $E_\gamma = 388.5$  keV),  $^{185}\text{Os}$  ( $T_{1/2} = 94$  d,  $E_\gamma = 646$  keV),  $^{203}\text{Hg}$  ( $T_{1/2} = 46.59$  d,  $E_\gamma = 279$  keV), and  $^{203}\text{Pb}$  ( $T_{1/2} = 52.1$  h,  $E_\gamma = 279.18$  keV) were used as tracers and obtained by irradiation of the elements or their compounds on the MT-22, 25 microtrons of FLNR [13].

**Measurement of Gamma Spectra.** Gamma spectra of samples were measured using ultrapure Ge and thin coaxial Ge(Li) detectors. Energy resolution was 0.6 keV at the line with energy 122 keV for the ultrapure Ge detector and 3 keV at the line of  $^{60}\text{Co}$  with energy 1332 keV for the coaxial Ge(Li) detector.

**Detection of Spontaneous Fission.** Registration of spontaneously fissioning nuclides in the samples was done using lavsan solid-state detectors (SSD) with areas of 16 and 150  $\text{cm}^2$  and 175  $\mu\text{m}$  thickness [6, 7, 9]. The sample by layer about 1  $\text{mg}/\text{cm}^2$  was placed between two detectors. After a multi-day exposure, the detectors were separated, purified from the substance, and washed, and traces from spontaneous fission were manifested by electrochemical etching with the 6 M NaOH solution at a voltage of 10 kV/cm and a frequency of 5 kHz [6].

Identification of the tracks as fragments of nuclide fission was conducted on two detectors. If the coordinates of the tracks coincided, they were determined as traces of nuclide fission. The registration efficiency was 76% for one of the detector and 48% for coincidence tracks.

In addition, the detectors were subject to chemical etching in the 6 M NaOH solution at  $60^\circ\text{C}$  for 1 h. Search for tracks was carried out using a microscope with  $320\times$  magnification [6, 7]. The content of uranium in the lavsan was at the level of  $10^{-10}$ – $10^{-11}$  g/g [7].

### RESULTS AND DISCUSSION

The distribution of elements in the extract processing (Fig. 2) is given in Table 1.

The results of measurement of total track number from spontaneously fissioning nuclides in samples obtained at the processing of organic fraction are given in Table 2.

Table 1. The distribution of elements in the extract processing (%)

Element	Cube residue	Condensate	Trap, NaOH
Ti	46	23	37
Ni	50	50	—
Cu	98	1	1
Zn	92	4	4
Ga	—	100	—
Ge	—	100	—
As	—	34	66
Se	100	—	—
Mo	92	8	—
Ag	40	60	—
Cd	100	—	—
Sb	100	—	—
Te	100	—	—
I	—	—	Traces
Os	—	—	100
Ir	100	—	—
Pt	100	—	—
Au	100	—	—
Hg	—	100	Traces
Tl	100	—	—
Pb	100	—	—
Bi	100	—	—
At	—	—	Traces

Table 2. The results of measurement of total track number from spontaneously fissioning nuclides in samples obtained at the processing of organic fraction (Fig. 2)

No.	Sample	Mass, g	Content of U, g/g [13, 14]	The number of tracks, d		
				50	62	33
2-1	Cube residue	0.180	$10^{-7}$	13	8	3
2-2	Condensate	0.050	$2 \cdot 10^{-7}$	0	0	0
2-3	Trap	0.020	$2 \cdot 10^{-7}$	22	2/26	—

Figure 4 presents the dependence of the total track number on the exposure time of the samples presented in Table 2.

The spontaneously fissioning nuclide in the cube residue has  $T_{1/2} = 62$  d. The cube residue contains elements with a valence of 1+ to 6+.

The spontaneous fission is not observed in the condensate. The elements Ni, Ga, Ge, Ag, and Hg are concentrated in the condensate.

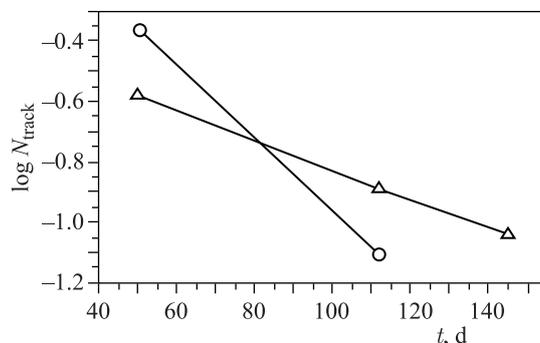


Fig. 4. The dependence of the total track number on the exposure time of samples:  $\Delta$  — cube residue,  $T_{1/2} = 62$  d;  $\circ$  — trap, NaOH,  $T_{1/2} = 25$  d

The nuclide with  $T_{1/2} = 25$  d is observed in the iron hydroxides from alkaline traps. Os (100%) and traces of I, At are concentrated in this sample. Perhaps osmium is the homologue of the nuclide observed.

Uranium and transuranium elements have low volatility. Thus, sublimation products do not contain known spontaneously fissioning nuclides.

Monitoring of contamination in samples by isotopes of transuranic elements was carried out by observing of an  $\alpha$  radiation. Spectra of the  $\alpha$  radiation of samples obtained in the processing of iron-manganese nodules were observed using a cylindrical ionization chamber with a measuring area of  $4200 \text{ cm}^2$ . The energy resolution of  $\alpha$ -spectrum lines in the region of 5–6 MeV was 150 keV. The measuring results show that the background related to possible contamination from Pu, Cm and Cf targets or of the products of nuclear explosions in iron-manganese nodules is 100 times less than the activity observed [15].

The cube residue was processed according to the scheme presented in Fig. 3 to identify the closest homologues of the nuclide observed. Table 3 shows the results of measurements of spontaneously fissioning activity in samples on the processing of cube residue (Fig. 3). The uranium content in these samples did not exceed  $2 \cdot 10^{-7} \text{ g/g}$  which leads to one spontaneous fission in 100 mg of the sample for  $10^5$  days of the exposure.

The dependence of the total track number on the exposure time of the sample insoluble in  $\text{H}_2\text{SO}_4$  and HCl is given in Fig. 5.

In the experiment, the mercury was concentrated in the condensate, so it can be removed from consideration. Therefore, the nuclide insoluble in  $\text{H}_2\text{SO}_4$  and HCl is similar in chemical

Table 3. The results of measurements of spontaneously fissioning activity in samples on the processing of cube residue (Fig. 3)

No.	Sample	Mass, g	Track number, d		
			46	33	76
3-1	Precipitate $(\text{SO}_4)^{-2}, \text{Cl}^-$	0.028	2	1	1
3-2	$\text{Fe}(\text{OH})_3$	0.006	0	—	—
3-3	$\text{MnO}_2$	0.006	6	1	—
3-4	$\text{Fe}(\text{OH})_3 (\text{MnO}_{2 \text{ sol}})$	0.010	6	0	—
3-5	$\text{Fe}(\text{OH})_3 (\text{NH}_4\text{OH})$	0.010	0	—	—

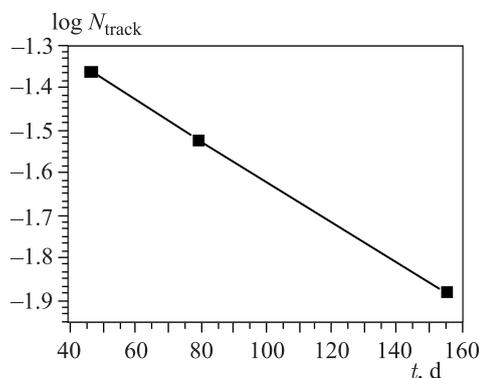


Fig. 5. The dependence of the total track number on the exposure time of the sample insoluble in  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ ,  $T_{1/2} = 63$  d

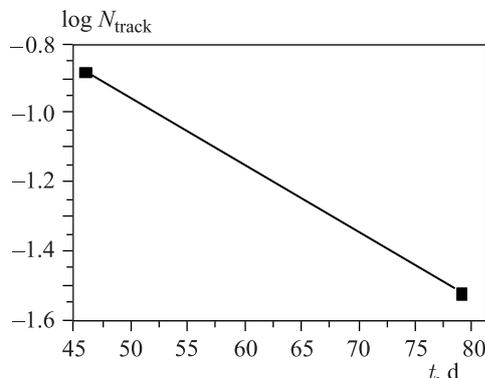


Fig. 6. The dependence of the total track number on the exposure time of the  $\text{MnO}_2$  sample,  $T_{1/2} = 15$  d

properties to Pb and Ra. Insoluble precipitates of Ba, Hg, Pb and Ra are formed in sulfuric acid. The spontaneously fissioning nuclide is the homologue of these elements and has a valence of 2+. The difference between the two results  $T_{1/2} = 62$  and 63 d is the deviation in the experiences. The dependence of the total track number on the exposure time of the  $\text{MnO}_2$  sample is shown in Fig. 6 (3-4).

Six tracks were recorded for 46 days of exposure in manganese dioxide (3-3) and iron hydroxide (3-4). The spontaneous fissioning nuclide in  $\text{MnO}_2$  has  $T_{1/2} = 15$  d. Zr (45%) and Ir (50%) are also sorbed [16] on manganese dioxide; probably the nuclide has chemical properties similar to those of these elements.

Spontaneously fissioning nuclide is not precipitated with  $\text{MnO}_2$ , but precipitated with iron hydroxides, decays completely for 46 days; perhaps its chemical properties are similar to those of elements with the valence 1+, 2+, 3+ and the platinoids.

Twenty-two tracks were observed for 50 days in iron hydroxide from the alkaline trap at processing of the extract of volume up to 50 ml. This is concerned with the nuclide with  $T_{1/2} = 25$  d. The efficiency of the track registration from spontaneous fission is 48%, then 46 nuclides decay for 50 days. There were 61 nuclides in the initial sample at the time of extraction. The total number of nuclides in 200 ml of the extract will be equal to 244.

Assuming that the nuclides were extracted at 100% and are in secular equilibrium with the parent nuclide of  $T_{1/2} = 10^9$  y, we can determine the initial number of the parent nuclei by the equation  $\lambda_1 N_1 = \lambda_2 N_2$ , which corresponds to  $N_2 = 3.6 \cdot 10^{12}$  nuclei. Hence the content of the parent nuclide on the assumption of  $Z > 114$  is equal to  $8 \cdot 10^{-14}$  g/g (based on the mass of the nodules equal to 13 kg).

Calculations for nuclides with  $T_{1/2} = 62$  d, which remains in the cube residue in the processing of Zn-2-EHBDTPH + OS,  $\text{CCl}_4$ , correspond to the content of the parent nuclide in iron-manganese nodules equal to  $4 \cdot 10^{-14}$  g/g.

The results of observation of the content of the spontaneously fissioning nuclide in iron-manganese nodules are in the same range of concentrations ( $8 \cdot 10^{-13}$ – $6 \cdot 10^{-14}$  g/g) as in [3–5].

The chemical properties of the nuclides observed and their half-lives are different and they belong to the decay chain of the more long-lived nuclide.

## CONCLUSIONS

1. Spontaneously fissioning nuclides with different chemical properties and different half-lives are observed in the products at processing of iron-manganese nodules. The nuclides are dissolved in  $\text{HNO}_3$  and extracted by solutions of Zn-salt 2-ethylhexylisobutyldithiophosphoric acid in mineral oil and oil sulfides.

2. The cube residue contains nuclide with  $T_{1/2} = 62$  d; it is not soluble in  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ , and the chemical properties are similar to those of Pb, Ra.

3. The nuclide with  $T_{1/2} = 25$  d is concentrated in the alkaline trap; the chemical properties are similar to those of Os.

4. The nuclide with  $T_{1/2} = 15$  d is not dissolved in  $\text{NH}_4\text{OH}$  and sorbed on  $\text{MnO}_2$ . The nuclide probably has chemical properties similar to those of Zr and Ir.

5. The nuclide decays completely for 46 days and is not precipitated on  $\text{MnO}_2$ , but precipitated with iron hydroxides; perhaps its chemical properties are similar to those of elements with the valence 1+, 2+, 3+ and platinumoids.

6. The content of the parent nuclide in iron-manganese nodules corresponds to  $4 \cdot 10^{-14}$ – $8 \cdot 10^{-14}$  g/g.

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