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Paper Electrophoretic Separation of Some Long-Lived Fission Products

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ABSTRACT

High voltage paper-electrophoresis of fission products from 24 hour neutron-irradiated and 150 days-decayed 90% highly enriched uranyl nitrate solution has been carried out by using the specially designed migration apparatus. The separation of Zr-95 and Nb-95 from the other fission products is possible under the migration condition of 0.1 M-HClO₄ (pH=0.85), 0.05 M-HCl+0.09M-KCl (pH=0.9), 0.1M-HCl (pH=1.1) and 0.01 M-HCl (pH=2.0). Zr-95 and Nb-95 are separated out at +1cm from the fiducial point. The separation of Zr-95 and Nb-95 from each other is possible under the migration condition of 0.1 M-HClO₄, 0.05 M-HCl+0.09 M-KCl, 0.1 M-HCl and 0.1 M-HAc+0.1 M-NaAc (pH=4.68) together with 2% ammonium oxalate. Nb-95 is separated out at -6~-7cm from the fiducial point and Zr-95 at +1~-1cm. The separation of Ru-103 from the other fission products is possible under the migration condition of 0.025 M-Na₂CO₃+0.025 M-NaHCO₃ (pH=10.0), 0.01M-Na₃PO₄ (pH=11.7) and 0.1 M-NaOH (pH=13.2). Ru-103 migrates towards the anode -6cm, -4cm and -3cm, respectively.

INTRODUCTION

The accumulating quantities of radioactive wastes generated by the increasing scale of nuclear power generation has stimulated active research and development work on the management and control. For UO₂ samples which are analyzed a long time after discharge, ¹⁴⁴Ce-¹⁴⁴Pr, ¹⁰⁶Ru, ⁹⁵Zr-⁹⁵Nb, ¹³⁷Cs and ⁹⁰Sr are measured after chemical separations. The presence of ruthenium, zirconium and niobium in nuclear spent fuel is undesirable because these metals interfere seriously with the fuel reprocessing steps due to their complex chemistry.

The separation techniques of fission products in

liquid state cover precipitation¹⁾, solvent extraction²⁾ and ion exchange³⁻⁶⁾. Precipitations from solutions have disadvantages of coprecipitation which results in contaminated products. Solvent extraction is widely used for isolation and purification of many radionuclides. The extracting agents are partly decomposed by radiation with unfavorable effects on the separation achieved. Ion exchange method is selective and does not permit the entire spent fuel to be fractionated. The ion exchange materials consist of organic compounds which are subjected to chemical and radiolytic attack by the process liquid.

Electrophoresis has the advantage of saving the carrier and provides of fractionating the material

of spent fuel. By using this technique, halogens, rare-earth, alkaline-earth and alkaline elements have been separated from the other fission products within 20 minutes⁷⁻¹¹). In paper electrophoretic separation, the migration distance L is directly proportional to the product of the potential gradient E (V/cm) and the migration time t (sec) as given by

$$L = u \cdot E \cdot t$$

where u is the mobility (cm/V/cm/sec). The potential gradient should be applied as high as possible. Under the high potential gradient, the temperature of the paper strip is increased due to Joule's heat. Therefore, the separation spots are broadened. To avoid such results, a forced removal of the Joule's heat is necessary to keep the temperature low enough and constant during the migration.

Object of the present work is to separate some long-lived elements from 24 hours-neutron-irradiated and 150 days-cooled 90% enriched uranyl nitrate solution by the method of high voltage paper electrophoresis.

EXPERIMENTAL

Materials

In order to produce long-lived fission nuclides, about 5mg of enriched (90%) uranyl nitrate, dissolved in water, was sealed in a silica ampoule and irradiated for 24 hours at a thermal neutron flux of 1.2×10^{13} n.cm⁻².sec⁻¹ in the rotary specimen-rack of TRIGA mark III reactor, followed by a cooling time of 150 days. A number of electrolyte of different pH values were prepared and the pH value of the solutions thus obtained was measured by a hydrogen electrode at 18°C. Composition and measured pH values of the electrolytes are given in Table 1.

A 2% ammonium oxalate solution was used as a stopping agent of rare earth ions. All other reagents used in the chemical procedure were of A.R. quality.

Migration Apparatus

Paper-electrophoresis apparatus specially designed for the separation consists of a pair of electrode cells connected with platinum electrodes and a mi-

Table 1. Composition and measured pH values of the electrolyte

No.	Electrolyte composition	pH
1	0.1 M-HClO ₄	0.85
2	0.05 M-HCl+0.09 M-KCl	0.9
3	0.1 M-HCl	1.1
4	0.01 M-HCl	2.0
5	5×10^{-3} M-NTA	1.9
6	0.01 M-HClO ₄	2.2
7	0.01 M-citric acid	2.6
8	0.1 M-acetic acid+	
	0.1 M-sodium acetate	4.68
9	0.01 M-acetic acid+	
	0.01 M-sodium acetate	4.70
10	0.01 M-KH ₂ PO ₄ +	
	0.01 M-Na ₂ HPO ₄	6.85
11	0.025 M-Na ₂ CO ₃ +	
	0.025 M-NaHCO ₃	10.0
12	0.01M-Na ₃ PO ₄	11.7
13	0.01M-NaOH	12.0
14	0.1M-NaOH	13.2

gration cell, 30×20×4cm, in which the migration plate is provided. The cell was made of copper sheet, and the migration plate was duplicated with teflon sheet (0.3mm in thickness). The cell was cooled with ice-water putting through a hole of 2-cm diameter. The electrode cells and the migration cell were placed into a Lucite container.

Procedure

A strip of Whatman No.1 filter paper, 40cm long and 1.5cm wide, was wetted with the supporting electrolyte solution, and the excess solution was soaked with filter paper. The strip was set on the migration plate and its both ends were dipped into the electrode cells containing 300cm³ each of electrolyte. One microlitre of the the sample solution was applied at the fiducial point of the paper strip by using a lambda pipette. The strip was covered with polyvinyl sheets, 31×5×0.02cm, and the electrodes were connected to the d.c. power supply, Toyo model III BA-8, Osaka, Japan. After a potential of 1,000 volt was applied for twenty minutes, the strip

was removed from the migration apparatus, dried and cut into pieces of one centimetre length. The radioactivity of each piece was measured by Nuclear Chicago model 3725 NaI(Tl) well-type gamma scintillation counter. The gamma rays from the cut paper strip were analyzed by ORTEC model 7044, 4000 channel pulse height analyzer connected with Ge(Li) detector of active volume 75cm³ having a FWHM of 1.9 KeV at 1332 KeV of Co-60 source.

RESULTS AND DISCUSSION

Identification of Fission Products

The oxidation numbers and the chemical forms of fission product elements are various in aqueous solution. Most of the chemical species of the fission products are ionic in a common aqueous solution and the half of them are cations. The oxidation numbers or the chemical forms of many cations are changeable as functions of the kind, the concentration and the pH value of the supporting electrolyte solution.

Fig. 1 indicates the gamma-ray spectrum of uranyl nitrate solution neutron irradiated for 24 hours and decayed for 150 days. In the spectrum, photopeaks from 64.0 days Zr-95, 34.97 days Nb-95, 39.35 days Ru-103, 114.43 days Ta-182, 32.50 days Ce-141, 284.8 days Ce-144, 10.98 days Nd-147, 2.62 years Pm-147, 4.96 years Eu-155 and 161.1 days Lu-177m are observed. There are only small rises corresponding to the photopeaks of 2.77 years Sb-125 at 380.4 and 427.9 KeV, 42.4 days Hf-181 at 482.0 KeV, 171 days Ir-194m at 328.5, 390.8 and 482.6 KeV and 1,200 years Ho-166 at 240.0, 711.7 and 1010.2 KeV. Although 17.3 minutes Pr-144 at 696.4 and 863.6 KeV is observed, its radioactivity is negligible.

For uranyl nitrate solution which is analyzed 150 days after discharge, Zr-95, Nb-95, Ru-103, Ta-182, Ce-141, Ce-144, Nd-147, Pm-147, Eu-155 and Lu-177m were determined by the paper-electrophoresis. Figs. 2-15 indicate typical paper-electrophoresis histogram of the 24-hours neutron-irradiated uranyl nitrate solution under different pH of the supporting electrolyte solutions. The solid line presents the his-

toqram without a stopping agent, and the dotted line with a stopping agent, 2% ammonium oxalate.

Fig. 2 indicates the paper-electrophoresis histograms of the neutron irradiated uranyl nitrate solution under 0.1 M-HClO₄ electrolyte without and with 2% ammonium oxalate. The whole of the radioactivity appears in three peaks without a stopping agent and three peaks with a stopping agent. Species (1) remains almost at the starting point and is identified as mainly Zr-95 and Nb-95. Species (2) migrates 6cm from the origin towards the cathode and is identified as mainly Ru-103. Species (3) at +13cm from the origin is identified as mainly Ce-141, 144, and is partially contaminated with Ru-103 and other products. The stopping was carried out by spotting one microlitre of 2% ammonium oxalate at the starting point. Species (4) migrates 6cm from the origin towards the anode and is identified as mainly Nb-95.

A large part of the rare-earth nuclides remain almost at the starting point and the species (5) is partially contaminated with Zr-95, Nb-95 and Ru-103. Species (6) at +11cm from the origin is identified as mainly Ru-103.

Fig. 3 indicates the paper-electrophoresis histograms of the neutron irradiated uranyl nitrate solution under 0.05 M-HCl plus 0.09 M-KCl electrolyte. The whole of the radioactivity appears in three peaks without a stopping agent and four peaks with a stopping agent. Species (7) at +1cm from the origin is mainly Zr-95, Nb-95 and Ru-103. Species (8) at +4cm is Zr-95, Nb-95, Ru-103 and is contaminated with other fission products. Species (9) at +8cm is Ru-103 and other fission products. Species (10) at -7cm is Zr-95 and Nb-95. Species (11) at -1cm is Zr-95, Nb-95 and other fission products. Species (12) at +3cm is mainly Ru-103. Species (13) at +7cm is Ru-103 and is contaminated with other fission products.

Fig. 4 indicates the paper-electrophoresis histograms of the neutron irradiated uranyl nitrate solution under 0.1 M-HCl electrolyte. The whole of the radioactivity appears in four peaks without a stopping agent and three peaks with a stopping agent. Species (14) at +1cm is mainly Zr-95, Nb-95 and is partially contaminated with other products.

Both species (15) at +5cm and (16) at +8cm are Ru-103. Species (17) at +11cm is mainly Ce-141, Ce-144. Ru-103 and other products are also observed in species (17). Species (18) at -6cm is mainly Nb-95 and species (19) at +1cm is Zr-95, Nb-95 and other products. Species (20) at +7cm is mainly Ru-103.

Fig. 5 indicates the paper-electrophoresis histograms of the neutronirradiated uranyl nitrate solution under 0.01 M-HCl electrolyte. The whole of the radioactivity appears in two peaks without a stopping agent and one peak with a stopping agent. Species (21) at +1cm is mainly Zr-95 and Nb-95. Species (22) at +7cm is mainly Ru-103, Ce-141 and Ce-144.

Fig. 6 indicates the paper-electrophoresis histograms of the neutronirradiated uranyl nitrate solution under 5×10^{-3} M-NTA(Nitilotriacetic acid) electrolyte. The whole of the radioactivity appears in three peaks without a stopping agent and one peak with a stopping agent. Species (23) at -4cm is Nb-95. Species (24) at +2cm is Zr-95, Nb-95, Ru-103, Ce-141, Ce-144 and other products. Species (25) is mainly Ru-103.

Fig. 7 indicates the paper-electrophoresis histograms of the neutronirradiated uranyl nitrate solution under 0.01 M-HClO₄ electrolyte. The whole of the radioactivity appears in three peaks without a stopping agent and two peaks with a stopping agent. Species (26) at -1cm is Zr-95, Nb-95, Ru-103 and is partially contaminated with other products. Species (27) at +4cm and species (28) at +7cm are mainly Ru-103. Species (28) is contaminated with other products. Species (29) at -7cm is mainly Nb-95. Species (30) at -1cm is Ce-141 and other products.

Fig. 8 indicates the paper-electrophoresis histograms of the neutronirradiated uranyl nitrate solution under 0.01 M-citric acid electrolyte. The whole of the radioactivity appears in three peaks without a stopping agent and one peak with a stopping agent. Species (31) at -3cm is mainly Nb-95. Species (32) at +2cm is Zr-95, Nb-103 and other products. Species (33) at +9cm is Ta-182 and other products.

Fig. 9 indicates the paper-electrophoresis histograms of the neutronirradiated uranyl nitrate solution under 0.1 M-acetic acid plus 0.1 M-sodium acetate electrolyte. The whole of the radioactivity appears in two peaks both. Species (34) at +2cm is Zr-95, Nb-95, Ru-103 and other products. Species (35) at +9cm is Ta-182 and other products. Species (36) at -6cm is mainly Nb-95. Species (37) at -1cm is Zr-95, Ru-103 and other products.

Fig. 10 indicates the paper-electrophoresis histograms of the neutronirradiated uranyl nitrate solution under 0.01M-acetic acid plus 0.01 M-sodium acetate electrolyte. The whole of the radioactivity appears in two peaks without a stopping agent and one peak with a stopping agent. Species (38) at +2cm is Zr-95, Nb-95, Ru-103 and other products. Species (39) at +9cm is Ta-182 and other products.

Fig. 11 indicates the paper-electrophoresis histograms of the neutronirradiated uranyl nitrate solution under 0.01 M-KH₂PO₄ plus 0.01 M-Na₂HPO₄ electrolyte. The whole of the radioactivity appears in two peaks without a stopping agent and one peak with a stopping agent. Species (40) at -6cm is mainly Ru-103. Species (41) at +1cm is Zr-95, Nb-95, Ru-103 and other products.

Fig. 12 indicates the paper-electrophoresis histograms of the neutronirradiated uranyl nitrate solution under 0.025 M-Na₂CO₃ plus 0.025 M-NaHCO₃ electrolyte. The whole of the radioactivity appears in two peaks without a stopping agent and one peak with a stopping agent. Species (42) at -6cm is mainly Ru-103. Species (43) at -1cm is Zr-95, Nb-95 and other products.

Fig. 13 indicates the paper-electrophoresis histograms of the neutronirradiated uranyl nitrate solution under 0.01 M-Na₃PO₄ electrolyte. The whole of the radioactivity appears in two peaks without a stopping agent and one peak with a stopping agent. Species (44) at -4cm is mainly Ru-103. Species (45) at +1cm is Zr-95, Nb-95, Ru-103 and other products.

Fig. 14 indicates the paper-electrophoresis histograms of the neutronirradiated uranyl nitrate solution under 0.01 M-NaOH electrolyte. The whole of the radioactivity appears in two peaks without a

stopping agent and one peak with a stopping agent. Species (46) at +1cm is Zr-95, Nb-95, Ru-103 and other products. Species (47) at +3cm is Ta-182 and other rare-earth products.

Fig. 15 indicates the paper-electrophoresis histograms of the neutronirradiated uranyl nitrate solution under 0.1 M-NaOH electrolyte. The whole of the radioactivity appears in two peaks without a stopping agent and one peak with a stopping agent. Species (48) at -3cm is mainly Ru-103. Species (49) at +1cm is Zr-95, Nb-95, Ru-103 and other products.

Separation of Zirconium, Niobium and Ruthenium

The ratios of fission products in the uranyl nitrate solution neutron-irradiated for 24 hours and decayed for 150 days are shown in Figs. 2-15 as the ratio of activity of each migrated nuclide against the total activity of each nuclide on the paper-electrophoresis histogram.

The separation of Zr-95 and Nb-95 from the other fission products in the uranyl nitrate solution neutron-irradiated for 24 hours and decayed for 150 days is possible under the migration condition of 0.1M-HClO₄ (pH=0.85), 0.05 M-HCl+0.09 M-KCl (pH=0.9), 0.1M-HCl (pH=1.1) and 0.01M-HCl (pH=2.0). In the 0.1M-HClO₄ electrolyte, 96% Zr-95 and 96% Nb-95 appear in the +1cm peak and are separable from the other fission products. In the 0.05 M-HCl+0.09M-KCl electrolyte, 52% Zr-95 and 64% Nb-95 appear in the +1cm peak and are separable from the other fission products, though they are contaminated by Ru-103. In the 0.1 M-HCl and 0.01 M-HCl electrolytes, 100% Zr-95 and 100% Nb-95 appear in the +1cm peak and are separable from the other fission products. The separation of Zr-95 and Nb-95 from each other is possible by the addition of 2% ammonium oxalate as a complexing agent. In the system of 0.1 M-HClO₄ -2% ammonium oxalate, 70% Nb-95 appears in the -6cm peak and 70% Zr-95 in the +1cm peak, and therefore Zr-95 and Nb-95 are separable from each other, though they are contaminated by the other fission products. In the system of 0.05 M-HCl+0.09 M-KCl -2% ammonium oxalate, 41% Nb-95 appears in the -7cm peak and 77% Zr-95 in the -1cm

peak, and therefore Zr-95 and Nb-95 are separable from each other. In the system of 0.1M-HCl -2% ammonium oxalate, 47% Nb-95 appears in the -6 cm peak and 80% Zr-95 in the +1cm peak, and therefore Zr-95 and Nb-95 are separable from each other. In the system of 0.1 M-acetic acid +0.1 M-sodium acetate -2% ammonium oxalate, 62% Nb-95 appears in the -6cm peak and 72% Zr-95 in the -1cm peak, and therefore Zr-95 and Nb-95 are separable from each other.

The separation of Ru-103 from the other fission products is possible under the migration condition of 0.025 M-Na₂CO₃+0.025 M-NaHCO₃ (pH=10.0), 0.01 M-Na₃PO₄ (pH=11.7) and 0.1 M-NaOH (pH=13.2). In the 0.025 M-Na₂CO₃+0.025 M-NaHCO₃ electrolyte, 61% Ru-103 appears in the -6cm peak and is separable from the other fission products, though Ru-103 is contaminated by the other fission products. In 0.01 M-Na₃PO₄ electrolyte, 39% Ru-103 appears in the -4cm peak and therefore is separable from the other fission products. In the 0.1 M-NaOH electrolyte, 53% Ru-103 appears in the -3cm peak and therefore is separable from the other fission products.

In summary, the fractionation of fission products, in particular, Zr-95, Nb-95 and Ru-103, has been developed by the method of high voltage paper-electrophoresis. Although the nuclides obtained have been contaminated with other fission products, Zr-95 and Nb-95 from the other fission products, and from each other, and Ru-103 from the other fission products are separated with some significant yields. We are presently working to further decrease the contaminant.

ACKNOWLEDGEMENT

Partial support of this work by the Korean Traders Scholarship Foundation is gratefully acknowledged.

REFERENCES

1. V. Kourim and O. Vojtech, Atomic Energy Review, 12, 215(1974).

2. A.A. Siczek and M.J. Steidler, Atomic Energy Review, 164(1978).	7. Von E.W. Gunther and K. Starke, Radiochim. Acta, 11, 131(1969).
3. A.K. Jain, S. Agrawal and R.P. Singh, J. Radioanal. Chem., 54, 171 (1979).	8. T. Hashimoto, T. Tamai, et al., J. Nucl. Sci. Technol., 7, 92(1970).
4. B.T. Kenna and K.D. Murphy, J. Inorg. Nucl. Chem., 41, 1535 (1979).	9. E. Jercan and G.R. Popa, J. Chromatog., 42, 89(1969).
5. J.D. Baker, R.J. Gehrke, R.C. Greenwood, et al., Radiochim. Acta, 28, 51(1981).	10. A. Ohyoshi, E. Ohyoshi, T. Tamai et al., J. Inorg. Nucl. Chem., 34, 3293(1972).
6. B.H. Lee and J.G. Bang, J. Kor. Assoc. Rad. Prot., 8(1), 15(1983).	11. T. Tamai, J. Takada, et al., Ann. Rep. Res. Reactor Inst. Kyoto Univ., 11, 48(1978).

여과지전기영동법에 의한 장수명 핵분열 생성물분리

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요 약

특별히 제작한 영동장치를 써서 고전압 전기영동법에 의하여 24시간 중성자 조사하고 150일 냉각한 90% 농축질산우라닐 수용액의 핵분열 생성물을 분리하였다.

핵분열생성물부터 Zr-95, Nb-95의 분리는 0.1M-HClO₄(pH=0.85), 0.05M-HCl+0.09M-KCl(pH=0.9), 0.1M-HCl(pH=1.1), 0.01M-HCl(pH=2.0)의 이동조건에서 가능하며 Zr-95, Nb-95는 원점부터 +1cm의 거리에서 분리된다.

Zr-95와 Nb-95의 상호분리는 2% 수산암모늄을 첨가하는 경우 가능하다. 즉 0.1M-HClO₄, 0.05M-HCl+0.09M-KCl, 0.1M-HCl, 0.1M-식초산+0.1M-식초산나트륨(pH=4.68)의 이동조건에서 원점부터 -6~-7cm 거리에서 Nb-95, +1~-1cm 거리에서 Zr-95가 각각 분리된다.

핵분열생성물부터 Ru-103의 분리는 0.025M-Na₂CO₃+0.025M-NaHCO₃(pH=10.0), 0.01M-Na₃PO₄(pH=11.7), 0.1M-NaOH(pH=13.2)의 이동조건에서 가능하며 Ru-103는 각각 원점부터 -6cm, -4cm, -3cm거리 이동한다.

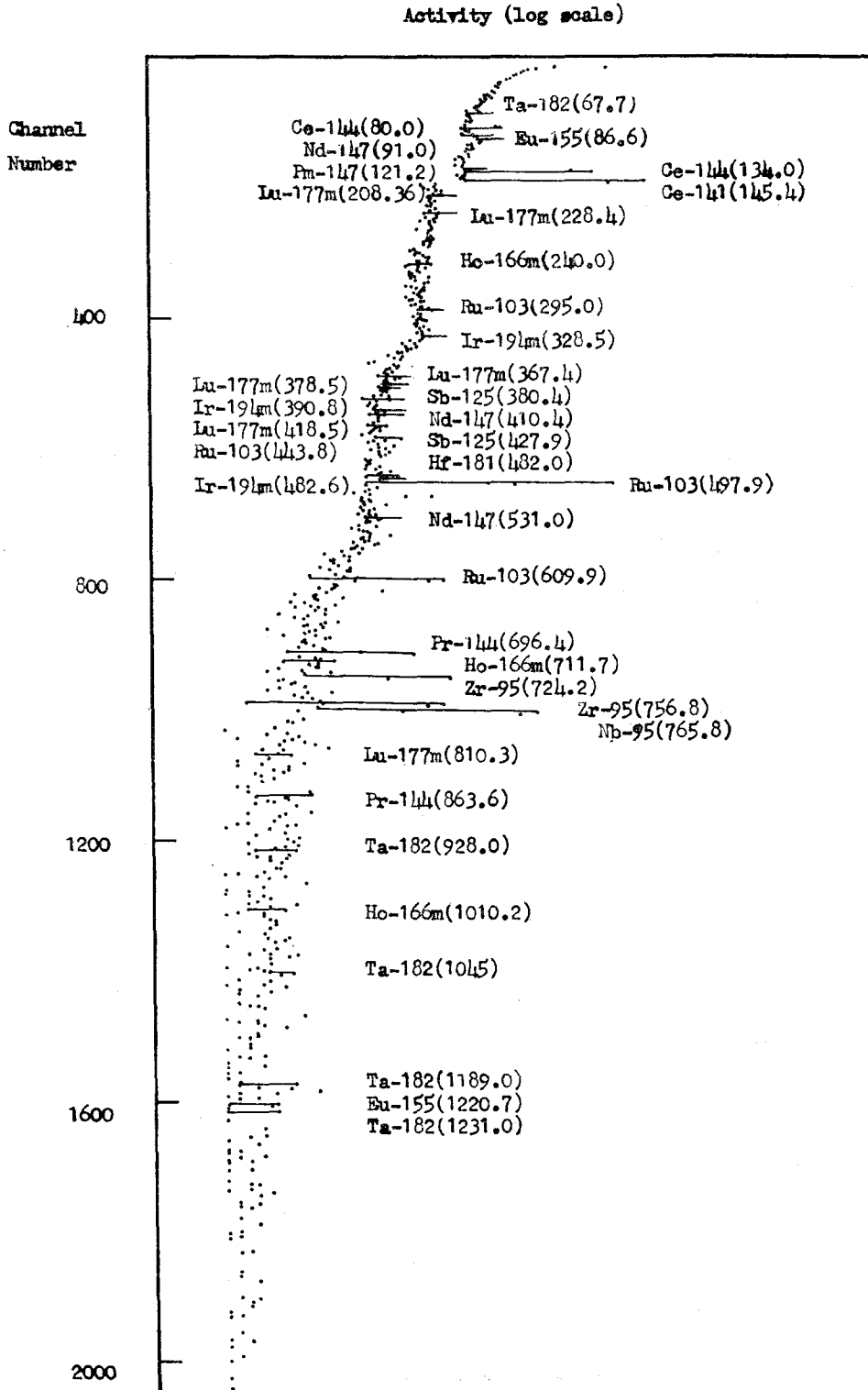


Fig. 1. Gamma-ray spectrum of uranyl nitrate solution at 150 days after the end of 24 hours irradiation. The gamma-ray energy in KeV is given in parentheses.

