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Paper Electrophoretic Separation of Fission Products

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여과지 전기영동에 의한 핵분열 생성물 분리

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Abstract

Paper electrophoretic separation of fission products has been carried out by using the specially designed migration apparatus. In general, the isolation of rubidium, strontium, zirconium, ruthenium, cesium, cerium, molybdenum, and some short-lived fission products is more efficient under 0.1M HCl electrolyte as compared with 0.1M NaOH electrolyte. In addition to Np-239, I-131~135 were, in particular, observed with different iodine chemical species obtained by the paper-electrophoretic separation of short, neutron-irradiated uranyl nitrate solution.

요 약

특별히 제작한 영동장치를 써서 여과지 전기영동법에 의한 핵분열 생성물의 분리를 하였다. 일반적으로 루비듐, 스트론튬, 지르코늄, 루테튬, 세슘, 세륨, 모리브덴 그리고 몇가지 단수명 핵분열 생성물의 분리는 0.1몰 가성소오다 전해질보다 0.1몰 염산 전해질 경우 더욱 효과적이다. 넵투늄-239에 대하여 특히 요오드 131~135등이 단시간 중성자 조사한 질산 우라닐 용액의 여과지 전기영동법 분리에서 얻은 요오드 화학종 등에서 관찰되었다.

Introduction

The binary fission of uranium-235 by thermal neutron yields nuclides of 37 elements; that is, from zinc to dysprosium or in atomic numbers from 30 to 66, and their atomic masses are distributed between 72 and 161. The separation technique of fission products in liquid state covers precipitation, solvent extraction, ion exchange and electrophoresis. Rapid separation of short-lived tin and antimony nuclides from fission products was performed using sulfide method by Wahl et al.¹⁾ Fast, continuous method for the separation of Zr, Nb, Tc, Br and I from fission product mixtures was described by Broden et al.²⁾ In the method, continuous multistage chemical separation of liquid-liquid phases was carried out by H-centrifuges. Iodine isotopes produced by fission of uranium were isolated rapidly from the other elements by ion exchange in a silver chloride layer by Denschlag et al.³⁾ Electrophoresis has the advantage of saving the carrier which is necessary to use in an ordinary chemical procedure. In addition, the method is suitable for studies on chemical forms of carrier-free ions in fission products. By using this technique, halogens, rare-earth, alkaline-earth and alkaline elements have been separated from the other fission products within 20 minutes⁴⁻⁸⁾.

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. Jokl⁹⁾ derived a relation between zone mobilities of migrating species on paper strips and their molecular weights. The equation is

$$\frac{u}{Z} = a \sqrt{\frac{1}{m}} + b$$

where u is the zone mobility, Z the charge number, m the molecular weight of the migrating species, a is a constant for the ionic species with the given dissociation number, and b is a constant depending on the migrating conditions used.

The aim of the present work is to separate some elements from fission product mixtures and to study the chemical species formed, by using a high voltage paper electrophoresis.

Experimental

Material

The production of Rb-86 ($t_{1/2}=18.7$ d), Rb-88 ($t_{1/2}=17.8$ m) Sr-87m ($t_{1/2}=2.8$ h) and Zr-97 ($t_{1/2}=16.8$ h) was carried out by irradiating rubidium carbonate, strontium nitrate and zirconium nitrate respectively without purification on account of guaranteed reagents. The salts were irradiated for 10 or 20 minutes at a thermal neutron flux of $1.5 \times 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$ in a pneumatic tube of TRIGA mark III reactor. Ru-103 ($t_{1/2}=39.35$ d) in ruthenium chloride, Cs-137 ($t_{1/2}=30.1$ y) in cesium chloride, and Ce-144 ($t_{1/2}=284.8$ d) in cerous chloride were obtained from the Radiochemical Centre, Amersham, England.

Mo-99($t_{1/2}=66\text{h}$) in molybdenum oxide was obtained from the Korea Advanced Energy Research Institute. In order to produce fission nuclides, a small amount of 8×10^{-3} M uranyl nitrate solution was taken into a polythene vial and irradiated for ten minutes at a thermal neutron flux of $1.5\times 10^{13}\text{ n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$ using a pneumatic tube, and another small amount was taken into a silica ampoule and irradiated for one week at a thermal neutron flux of $1.2\times 10^{13}\text{ n}\cdot\text{cm}^{-2}\cdot\text{sec}^{-1}$ using a rotary specimen rack of TRIGA mark III reactor. The uranyl nitrate solution was prepared from the depleted UO_2 powder, obtained from the International Atomic Energy Agency Laboratory, Vienna, Austria. 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 migration cell in which the migration plate is provided. The migration cell, $30\times 20\times 4\text{cm}$, and the cell cover, $30\times 17\times 6\text{cm}$, were made of copper sheet, and the migration plate and the cover plate were duplicated with teflon sheet(0.3mm in thickness). The migration cell and the cell cover were cooled with ice-water putting through a hole of 2-cm diameter. The electrode cells, migration cell, and cell cover 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, 0.1M HCl or 0.1M NaOH, 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 300cm^3 each of electrolyte. A few microlitre of the radioactive solution was applied at the fiducial point of the paper strip by using a lambda pipette. The strip was covered with polyvinyl sheets, $31\times 5\times 0.02\text{cm}$, and the cell cover was placed onto the migration cell. The electrodes were connected to the d.c. power supply, Toyo model III BA-8, Osaka, Japan, and a potential of 1500V was applied for ten minutes. After the electrophoresis run was over, 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 Fujitsu model EA-14 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 75cm^3 having a FWHM of 1.9keV at 1332 keV of Co-60 source.

Results and Discussion

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 complete separation of a desired species of cation from many others is very difficult within short migration time. The mobilities of oxo-acid anions can not be estimated completely because there are few informations. The chemical behaviours in carrier-free state is not always same as in ordinary

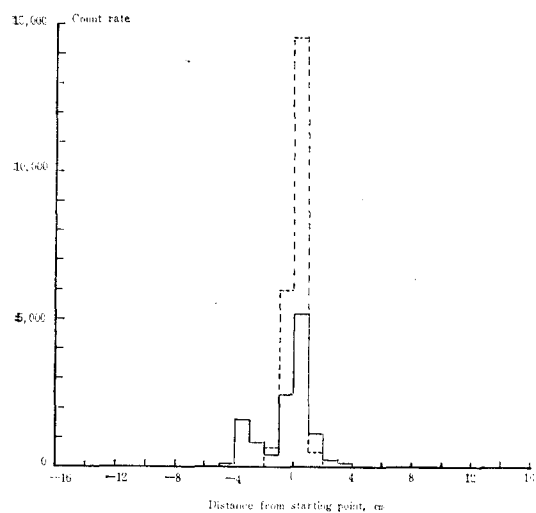


Fig. 1. Paper-electrophoresis Histogram of Ruthenium-103 in Ruthenium Chloride
 — 0.1M HCl electrolyte
 ... 0.1M NaOH electrolyte.

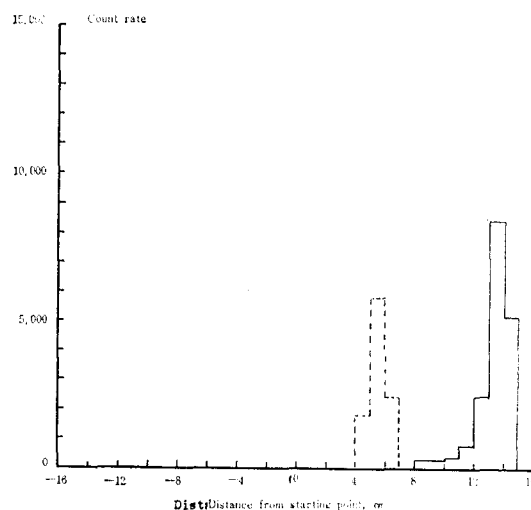


Fig. 2. Paper-electrophoresis Histogram of Cesium-137 in Cesium Chloride
 — 0.1M HCl electrolyte
 ... 0.1M NaOH electrolyte.

concentration of solution. The location of migration band of a desirable element must be decided by a side experiment of carrier-free ions.

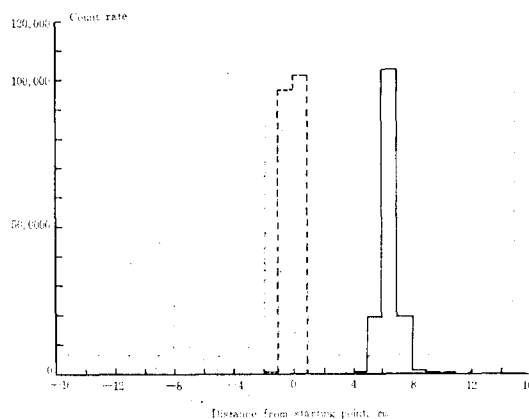


Fig. 3. Paper-electrophoresis Histogram of Cerium-144 in Cerous Chloride
 — 0.1M HCl electrolyte
 ... 0.1M NaOH electrolyte.

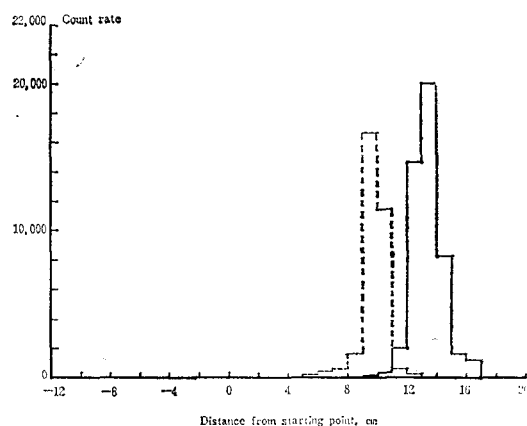


Fig. 4. Paper-electrophoresis Histogram of Neutronirradiated Rubidium Carbonate
 — 0.1M HCl electrolyte
 ... 0.1M NaOH electrolyte.

Figures 1-10 indicate typical paper-electrophoresis histogram of the separated patterns of ruthenium-103, cesium-137, cerium-144, neutronirradiated rubidium carbonate, strontium nitrate and zirconium nitrate, molybdenum-99, a mixture of Ru-103, Cs-137 and Ce-144, 10min. irradiated uranyl nitrate and one week irradiated

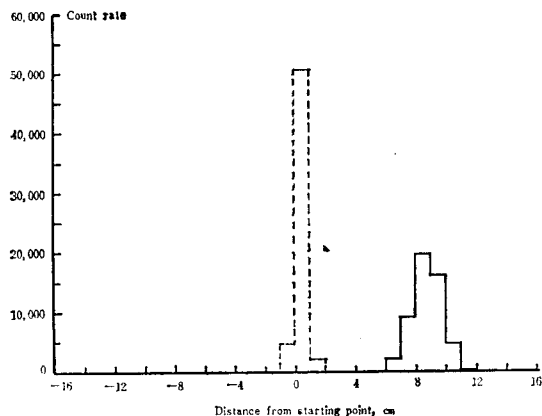


Fig. 5. Paper-electrophoresis Histogram of Neutronirradiated Strontium Nitrate
 — 0.1M HCl electrolyte
 ... 0.1M NaOH electrolyte.

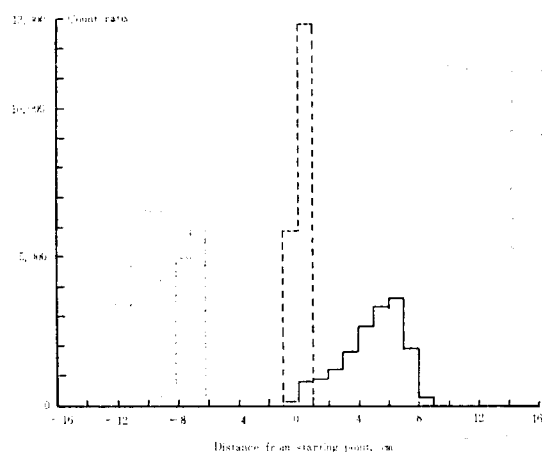


Fig. 6. Paper-electrophoresis Histogram of Neutronirradiated Zirconium Nitrate.
 — 0.1M HCl electrolyte
 ... 0.1M NaOH electrolyte

uranyl nitrate, under different pH of supporting electrolyte solutions, 0.1M HCl (pH=1.1) and 0.1M NaOH (pH=13.0). The solid line presents the histogram with 0.1 M HCl and the dotted line with 0.1M NaOH.

Separation of Ruthenium Ion

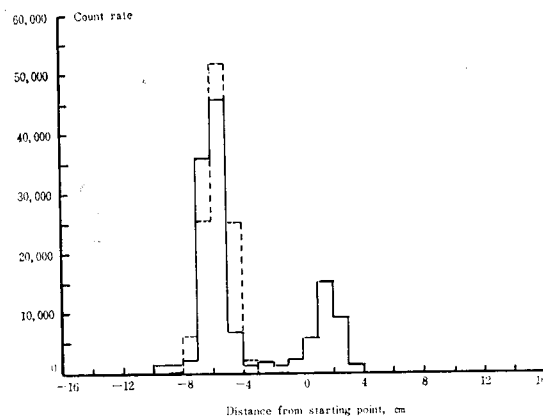


Fig. 7. Paper-electrophoresis Histogram of Molybdenum-99 in Molybdenum Oxide
 — 0.1M HCl electrolyte
 ... 0.1M NaOH electrolyte.

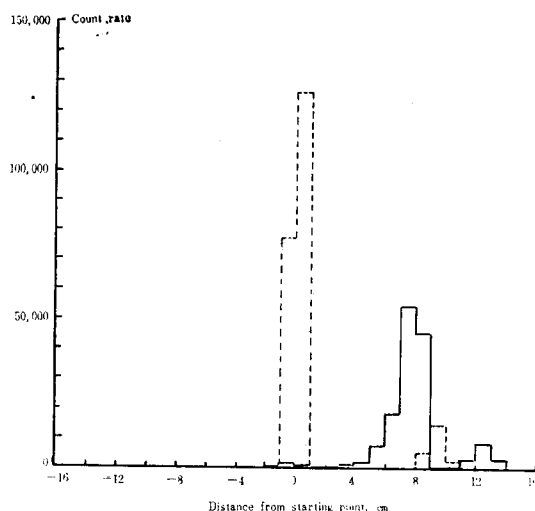


Fig. 8. Paper-electrophoresis Histogram of Mixture of Ru-103, Cs-137 and Ce-144
 — 0.1M HCl electrolyte
 ... 0.1M NaOH electrolyte

In the acidic solution, the Ru-103 radioactivity appears in two peaks; the major part of activity migrates towards the cathode +1cm, due to ruthenium chloride, and the small part of the activity migrates towards the anode -4cm, probably forming $(\text{RuCl}_5 \cdot \text{H}_2\text{O})^{2-}$ or $(\text{RuCl}_6)^{3-}$. In the alkali solution, the whole of radioactivity migra-

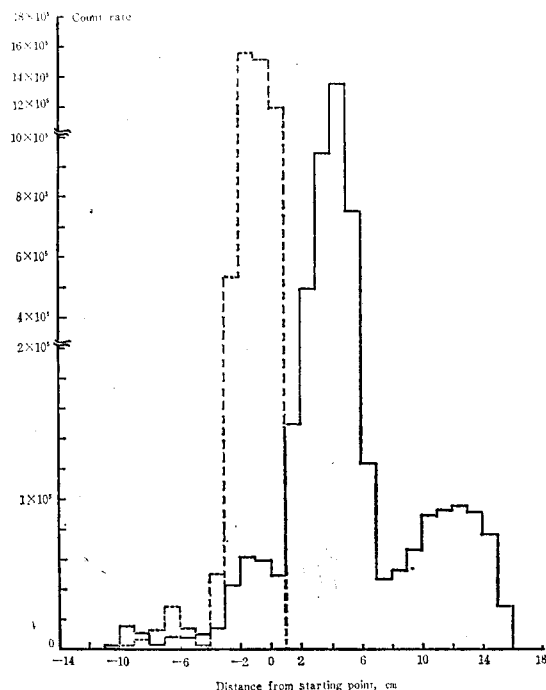


Fig. 9. Paper-electrophoresis Histogram of Neutron-irradiated Uranyl Nitrate Solution for 10min
 — 0.1M HCl electrolyte
 ... 0.1M NaOH electrolyte

tes towards the cathode +1cm, probably forming $(\text{RuCl}(\text{H}_2\text{O})_5)^{2+}$.

Separation of Cesium Ion

In the acidic solution, the whole of Cs-137 radioactivity migrates towards the cathode, i.e. +14cm from the origin due to Cs(I)Cl . In the alkali solution, the Cs-137 radioactivity migrates towards the cathode, i.e. +6cm from the origin, probably due to the formation of cesium hydroxide, CsOH .

Separation of Cerium Ion

In the acidic solution, the whole of Ce-144 radioactivity migrates towards the cathode, i.e. +7cm from the origin due to Ce(III)Cl_3 . In the alkali solution, the Ce-144 radioactivity remains at the starting

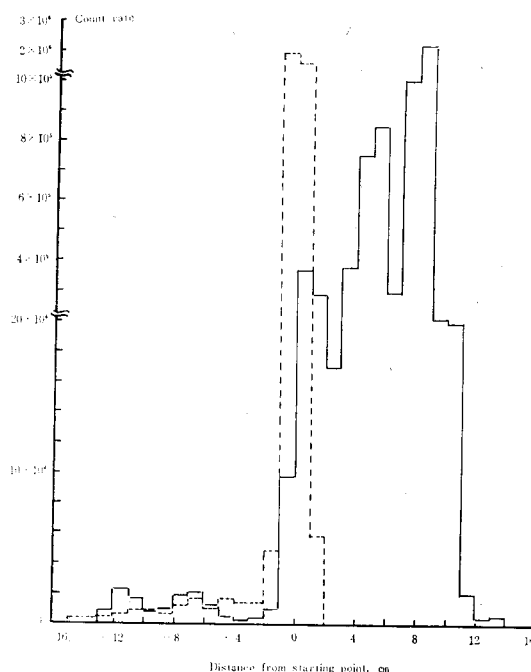


Fig. 10. Paper-electrophoresis Histogram of Neutron-irradiated Uranyl Nitrate Solution for 1week
 — 0.1M HCl electrolyte
 ... 0.1M NaOH electrolyte

point, probably due to the formation of cerium hydroxide, $\text{CeO}_2 \cdot \text{H}_2\text{O}$, insoluble in water.

Separation of Rubidium Ion

In the acidic solution, the whole of rubidium radioactivity migrates towards the cathode, i.e. +14cm from the origin due to Rb(II)Cl_2 . In the alkali solution, the rubidium radioactivity migrates towards the cathode, i.e. +10cm from the origin, probably due to the formation of rubidium hydroxide, Rb(OH)_2 .

Separation of Strontium Ion

In the acidic solution, the whole of Sr-87m radioactivity appears in one peak at

+9cm, due to strontium nitrate, $\text{Sr}(\text{NO}_3)_2$. In the alkali solution, the Sr-87m radioactivity migrates towards the cathode +1cm, probably forming $\text{Sr}(\text{OH})_2$.

Separation of Zirconium Ion

In the acidic solution, the whole of Zr-97 radioactivity migrates towards the cathode, i.e. +7cm from the origin due to $\text{Zr}(\text{IV}) (\text{NO}_3)_4$. In the alkali solution, the Zr-97 radioactivity remains almost at the starting point, probably forming zirconium hydroxide, $\text{Zr}(\text{OH})_4$ and $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$.

Separation of Molybdenum and Technetium

In the acidic solution, the radioactivity appears in two peaks; one migrates towards the cathode +2cm, due to the formation of molybdenum chloride, $\text{Mo}(\text{IV}) \text{Cl}_4$, and the other migrates towards the anode -6cm, Tc-99m formed by the decay of Mo-99, forming $\text{Tc}(\text{VII})\text{O}_4^-$. In the alkali solution, the radioactivity appears in one peak at -6cm, probably the mixture of MoO_4^{2-} and TcO_4^- , decay and growth of ^{99}Mo - ^{99m}Tc system.

Separation of Ruthenium, Cesium and Cerium

In the acidic solution, the radioactivity appears in three peaks; two of which migrate towards the cathode and one remains at the starting point.⁸ The peak at +13 cm is identified as the Cs(I), +8cm as the Ce(III), and zero line as the Ru(III), because its rate of migration is identical with that of paper-electrophoresis histogram of each nuclides. In the alkali solution, the radioactivity appears in two peaks; one of which migrates towards the cathode and the other remains almost at the starting point. The peak at +10cm is identified as the Cs(I). The peak at the starting point

is the mixture of Ce(III) and Ru(III), probably forming cerium hydroxide, $\text{CeO}_2 \cdot \text{H}_2\text{O}$ and ruthenium aqo-complex, $(\text{RuCl}(\text{H}_2\text{O})_5)^{2+}$.

Separation of Short-lived Fission Products

The paper-electrophoresis histogram of uranyl nitrate solution neutron-irradiated for ten minutes is as follows: In the acidic solution, the radioactivity appears in five peaks; three of which migrate towards the cathode, and two of which migrate towards the anode. The major part of the activity migrates +9cm from the origin towards the cathode-species(I). A large part of the activity migrates +6cm from the origin towards the cathode-species(II). A considerable amount of the activity remains almost at the starting point-species(III). A small amount of the activity migrates -7 cm and -12cm from the origin towards the anode-species(IV) and (V). Species (I) is identified as Np-239 by the observed gamma-ray spectrum and the half life determined, and is probably the mixture of UO_2^{2+} and NpO_2^{2+} , decay and growth of ^{239}U - ^{239}Np system. The majorities of species (II) and (III) are also Np-239 according to the observed gamma-ray spectra and are probably NpO_2^+ and NpO_2OH^+ respectively¹⁰. Species (IV) and (V) are identified as a mixture of I-131, 132, 133, 134 and 135 by the observed gamma-ray spectra, probably with IO_3^- and I^- respectively¹¹. In the alkali solution, the radioactivity appears in four peaks; the whole of radioactivity migrates towards the anode. The major part of the activity migrates -1cm from the origin towards the anode, probably forming NpO_5^{3-} -species (I). A small amount of the activity migrates -5cm, -7 cm and -10cm respectively, from the origin towards the anode-species (II), (III)

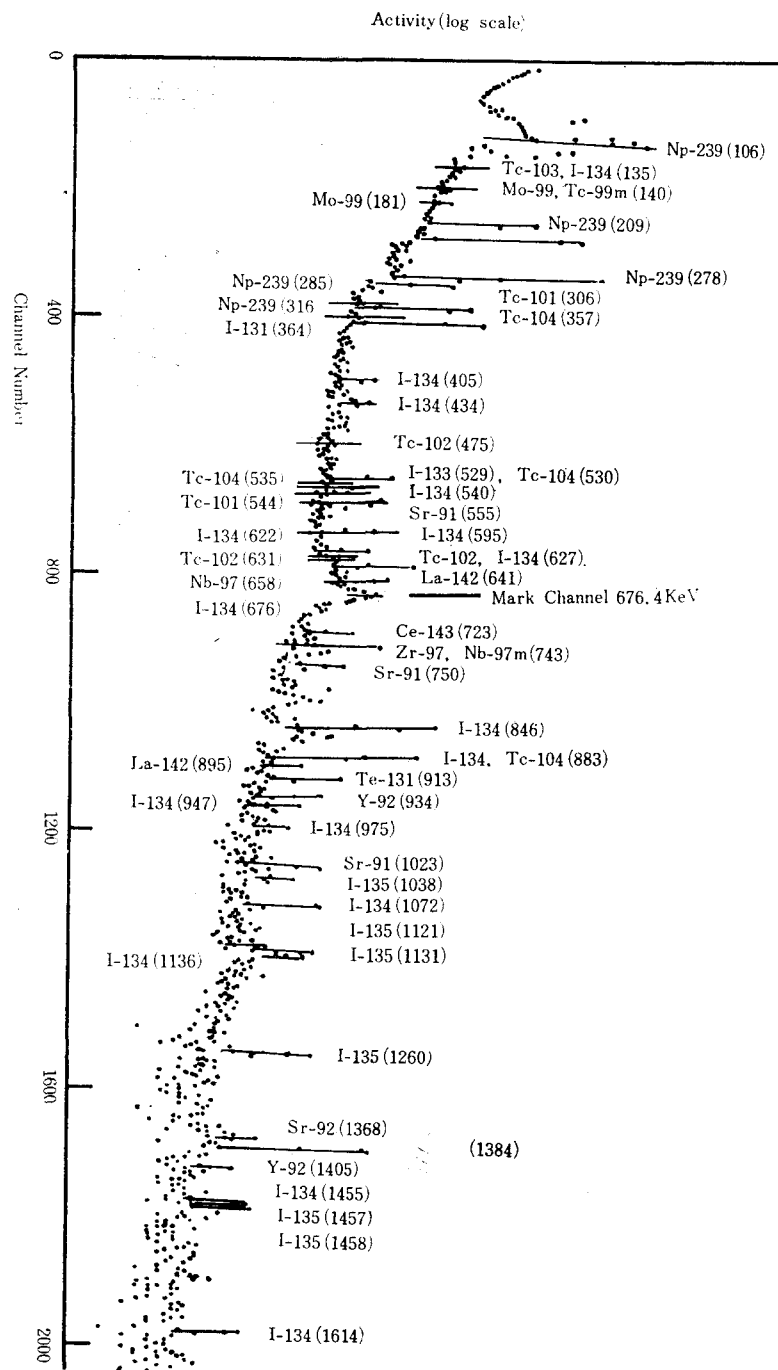


Fig. 11. Gamma-ray Spectrum of Uranyl Nitrate Solution at 3hrs. 30min. after the End of 10min. Irradiation. The gamma-ray energy in keV is given in parentheses.

and (IV). Species (II), (III) and (IV) are a mixture of I-133, 134 and 135, probably with IO_4^- , IO_3^- and I^- respectively, applicable to the Jokl's equation⁹. In the gamma-ray spectra, Mo-90, Tc-99m, 101, 102, 103, 104 and Te-131 are also found in the species (II), and Tc-99m, 101 in the species (III).

Fig. 11 indicates the gamma-ray spectrum of uranyl nitrate solution neutron-irradiated for ten minutes. In the spectrum, many photopeaks from 2.355 days Np-239, 52 minutes I-134 and 6.59 hours I-135 together with those of many nuclides are observed. Some photopeaks overlap each other on account of the limitation in gamma spectrometric resolution. The observed nuclides in the original solution are also found in the gamma-ray spectra of migrating species on the paper-electrophoresis strip.

The paper-electrophoresis histogram of uranyl nitrate solution neutron-irradiated for one week is as follows: In the acidic solution, the radioactivity appears in four peaks; two of which migrate towards the cathode, and two of which migrate towards the anode. The major part of the activity migrates +5cm from the origin towards the cathode-species (I). A large part of the activity migrates +13cm from the origin towards the cathode-species(II). A considerable amount of the activity migrates -2cm from the origin towards the anode-species(III). A small amount of the activity migrates -10cm from the origin towards the anode-species(IV). Species(I) is identified as Np-239 by the observed gamma-ray spectrum at 106, 278 and 228keV. and is probably due to the formation of NpO_2^+ . Ba-140 and La-140 are found from the species(II) by the observed gamma-ray spectrum at 537keV for Ba-140

and at 1596, 487 and 329 keV for La-140, probably with a mixture of Ba(II) and La(III). Te-131 is found from the species (III) by the observed gamma-ray spectrum at 852, 774 and 150keV, probably with TeO_3^{2-} . I-131 is found from the species(IV) by the observed gamma-ray spectrum at 637, 364 and 284keV, probably with I^- . In the alkali solution, the radioactivity appears in two peaks; the whole of radioactivity migrates towards the anode. The major part of the activity migrates -1cm to -2cm from the origin towards the anode, probably forming NpO_5^{3-} -species (I). A small amount of the activity migrates -7cm from the origin towards the anode, probably due to IO_3^- -species(II).

In general, the isolation of rubidium, strontium, zirconium, ruthenium, cesium, cerium, molybdenum and some short-lived fission products is more efficient under 0.1M HCl electrolyte, compared with 0.1M NaOH. Although the studies have made the separation of some known nuclides in fission products and some short-lived nuclides produced by thermal fission process of uranium-235 by paper-electrophoresis, the method of separation can be applied to the study of the other fission products. The separation of desired species from many other fission products can be performed under different pH of supporting electrolyte solution.

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