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The Determination of Plutonium in the Fall-out Samples at Kanazawa

Yoshikazu INOUE

Institute of Radiological science,
Anagawa, Chiba 280

and Masanobu SAKANOUÉ

Radiochemical Laboratory, Department of Chemistry,
Faculty of Science, Kanazawa University,
Kanazawa 920

Abstract--- The tracer studies of the radiochemical procedure for the separation and the determination of plutonium in the fallout sample were made by using the methods of ion exchange, electro-deposition and alpha-spectrometry.

The developed procedure for the determination of plutonium isotopes was applied to the fallout samples at Kanazawa due to the third and the fifth nuclear test explosion of China. The contents of uranium and neptunium isotopes were also determined in addition to the examinations of γ decay curves and spectra for these samples. And, based on these data, some discussions were made as to the source material of the nuclear bomb used in the Chinese fifth test explosion.

1. Introduction

The observation of fall-out radionuclides at Kanazawa from 1963 to 1965 were reported previously for the four cases of the nuclear test explosion¹⁾. Especially, for the fall-out from the first Chinese nuclear test explosion, the determination of uranium isotopes (^{234}U , ^{235}U , ^{238}U and ^{237}U) were carried out and the existence of ^{239}Pu was suggested in the alpha spectrum. But its determination could not be made definitely, because the analytical separation method was not specially designed for plutonium. In 1966, the third and the fifth nuclear test explosion of China were done and their fall-out samples were collected at Kanazawa. In these cases,

separation of plutonium from other radioactive nuclides was made and its amounts could be determined. And some discussions were made as to the source material of these nuclear bomb. Furthermore, in the first part of this report, the development of the chemical procedure for the determination of plutonium is shown.

2. Apparatus

- 1) Electric centrifuge : Model-FT9S, Kubota Seisakusho Co., Ltd.
- 2) Gamma-scintillation detector : well type NaI (TI) crystal, $1 \frac{3}{4} \times 2$ ''.
- 3) GM counter : End-window type GM tube with 50 mm diameter, Aloka, Model GM-5006, (window thickness 2.4~2.6 mg/cm², (B.G.) 30 cpm.
- 4) Alpha scintillation detector : ZnS (Ag) crystal with 2'' diameter.
scaler : Aloka, Model TDC-1, Nihon Musen Co., Ltd.
- 5) Double gridded ionization chamber : Osaka Dempa Co., Ltd. (Resolution power) : 2~3 % (FWHM) for Pu-238. (B.G.) : 0.015~0.025 cpm/100 KeV for 4~6 MeV Region. (Counting efficiency) : $49.3 \pm 1.5\%$, estimated by an aliquot of the standard solution of Pu-239 (total 0.1332 μ Ci ; Radiochemical Center, UKAEA).
- 6) 100 channel pulse height analyser : Model AN-100, Kobe Kogyo Co., Ltd.

3. Chemicals

All chemicals are the guaranteed reagent except for the organic reagent Di-isobutyl keton (DIBK).

Acid : HCl, HNO₃, HClO₄, HF, H₂SO₄, H₂C₂O₄ and their mixtures.

Salt solution : 2 M HCOONH₄, 4 M NaCl, 10 mg/ml Fe³⁺ carrier solution, and AlCl₃ solution in 8 M HCl.

Organic reagent for solvent extraction : DIBK pre-equilibrated with 8 M HCl.

Radioactive tracers : Plutonium-238²³⁾ and uranium-232²³⁾ used in this work were prepared in our laboratory. Neptunium-237 was obtained from RCC in England. Uranium-237 and neptunium-239 were prepared from neutron irradiated uranium-238, using anion exchange resin (Dowex-IX8) and extraction techniques⁴⁾.

Ion exchange resin : Dowex-IX8 (200~400 mesh). The resin obtained commercially was washed with HCl and distilled water, repeatedly. After washing with sufficient HCl, resin was stored in 1 M HCl.

Ion exchange column : The ion exchange column shown in Fig. 1 was made of polyethylene tube in order to avoid corrosive effect of hydrofluoric acid on the glass column. In any case, flow rate was not controlled, but it had nearly constant rate (0.1~0.4 ml/min.) of gravitational flow.

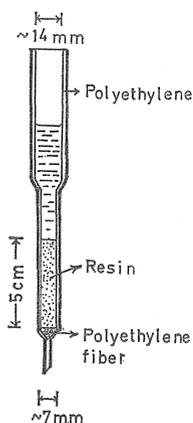


Fig. 1. Ion exchange column

4. Tracer studies of analysis for plutonium

4-1. Sample decomposition and the concentration of plutonium with hydroxide of iron by coprecipitation*

The sample, 5~10 g of soil or other material, was first treated with conc. HNO_3 to decompose organic materials and then digested on a hot plate with conc. HClO_4 and conc. HF in a Pt dish repeatedly till the residue turned to semi-transparent silica gel. Although the fallout samples may be decomposed almost in this step, remaining residue was treated furthermore by fusion with flux of sodium and potassium carbonate and the cake was taken up with conc. HCl , and then a large amount of hot distilled water.

From the sample solution obtained by the above method of decomposition, plutonium was collected by the coprecipitation with ferric hydroxide.

4-2. Tracer studies for the chemical separation of plutonium.

4-2-1. The method (A).

The analytical method for the separation of plutonium from other elements coprecipitated with ferric hydroxide, especially from uranium, was examined by employing uranium-232 (containing small amount of its daughter, thorium-228) and plutonium-238 as tracers. Three different sample solutions, one containing only plutonium-238 (sample A), the second only uranium-232 (sample B), and the third both plutonium-238 and uranium-232 (sample C), were prepared.

One tenth milliliters of 0.2 M $\text{Fe}(\text{NH}_4\text{SO}_4)$ was added to the sample solution containing hydrochloric acid in order to adjust the valency state of plutonium to Pu(III). After warming, the sample solution was made to 8 M HCl -0.5M HF solution and passed through the Dowex-IX 8 anion exchange resin column (resin volume, 3 ml). In this process uranium and iron were retained on the column and Ra, Ac, Th, Pa, Np Pu, alkali and alkaline-earth metals passed through the column⁵⁾. After washing the column with 6~7 times column volumes of 8M HCl -0.5M HF , uranium was eluted by passing 10 times column volumes of 6 M HCl -0.1M HClO_4 , iron remained on the column even after this elution process. To the effluent of 8 M HCl -0.5M HF , 2 M AlCl_3 solution was added enough to mask fluoride ion, then this solution was passed through the Dowex-1 \times 8 resin preconditioned by 5.5M HCl and the column was washed 5.5M HCl . In this process, Pu(III) was separated into 5.5M HCl effluent from neptunium which would be retained on the resin. The effluent of 5.5M HCl was evaporated and its residue was taken up by 8 M HCl . In order to oxidize Pu(III) to Pu(IV), 0.3 ml of 3 M NaNO_2 solution was added to this solution. By passing this solution through the Dowex-IX 8 resin preconditioned with 8 M HCl ,

Pu(IV) was retained and other several elements passed through. After washing the column with 8 M HCl, Pu(IV) was eluted with 5 M HCl.

The conditions of these ion exchange separations were based on our preliminary experimental results shown in Fig. 2, which was obtained by using the tracer solution containing both Pu(III) and Pu(IV).

This shows the adsorption curve of Pu(IV) on the Dowex-1×8 resin. The original tracer solution was consisted of about 8% of Pu(III) and 92% of Pu(IV), because no adsorption of Pu(III) on the Dowex-1X8 had been confirmed in any concentration of HCl.

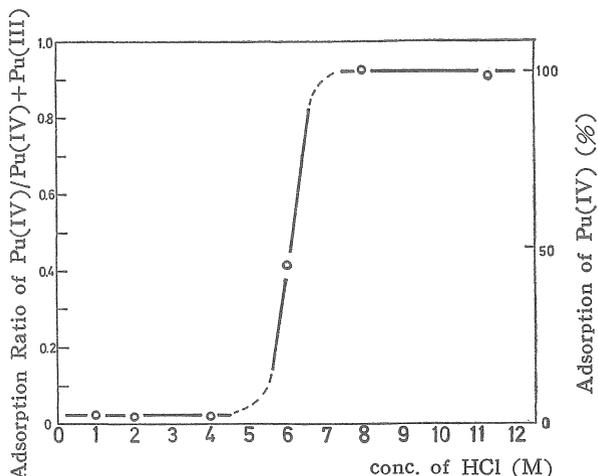


Fig. 2. Adsorption curve of Pu(IV) on the Dowex-1×8 anion exchange resin

The uranium fraction in anion exchange method was evaporated to nearly dryness and the residue was taken up with 2 ml of 2 M HClO₄ under heating. Then, 2 ml of HCOONH₄ and 10 ml of distilled water were added to make up the electrolytic solution⁶⁾. The solution was transferred into an electrodeposition cell and uranium was electrodeposited on a stainless steel plate for about 2 hours at a constant current 0.5 A.

The plutonium fraction was evaporated to nearly dryness and taken up with 1 ml of 0.1M HCl under heating. Then, 5 ml of 4 M NaCl, 1 ml of 0.5M H₂C₂O₄, 0.75 ml of 2 M HCOONH₄ and distilled water were added to make up the total volume 10.0 ml of the electrolytic solution. From this solution, plutonium was electrodeposited on a stainless steel plate for about 2 hours at a constant current 0.5 A.

The overall analytical scheme is shown in Fig. 3. The alpha spectrometric results (Fig. 4) of these electrodeposited plates show that uranium and plutonium could be separated from each other by the procedure mentioned above.

4-2-2. The other method (B).

Another separation method was examined for uranium, neptunium and plutonium, using H₂C₂O₄-conversion method⁶⁾ of anion exchange resin.

(procedure)

A solution of U-232, Np-239 and Pu-239 was nearly dried up together with conc. HNO₃ on a hot plate several times. The residue was treated with 20 ml of dil. HCl and 10 mg of Fe³⁺ was added and then NH₃ gas was passed through the solution until its pH became to about 8. Ferric hydroxide formed was gathered by centrifugation and washed with hot dil. NH₄OH, and dissolved in 0.5M H₂C₂O₄ solution of small

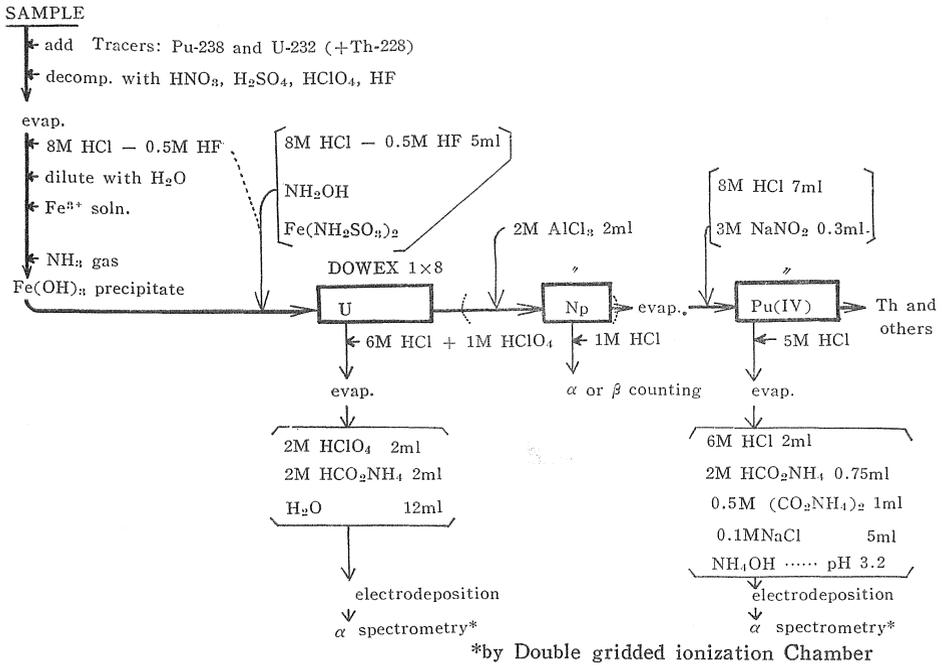


Fig. 3. The analytical scheme for plutonium used in tracers study

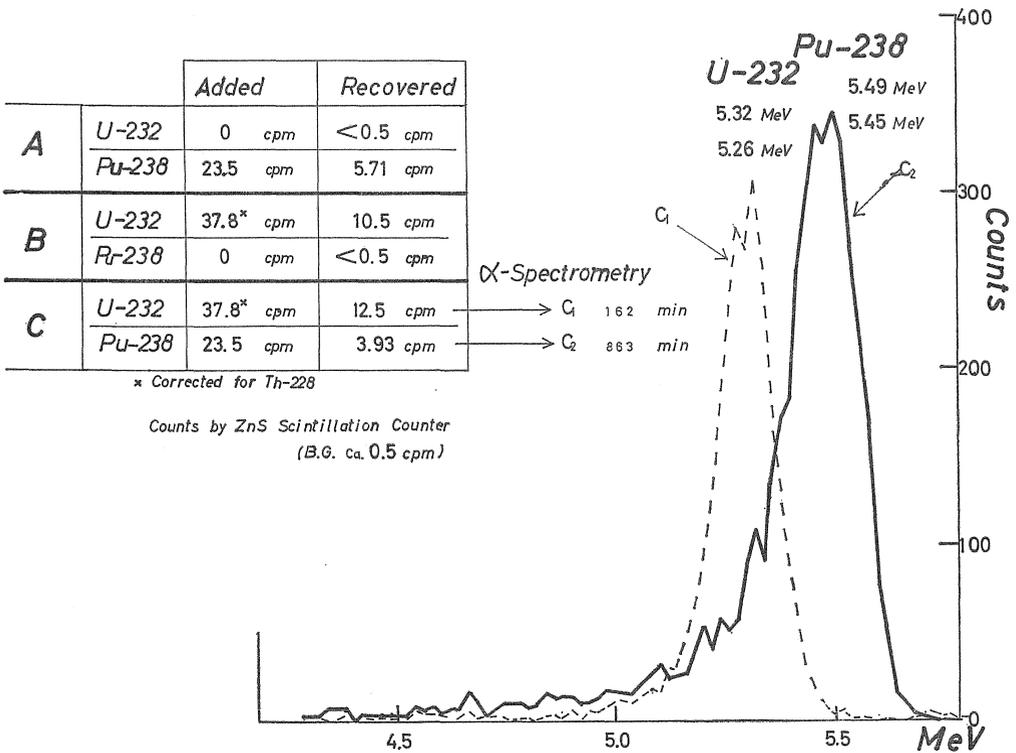
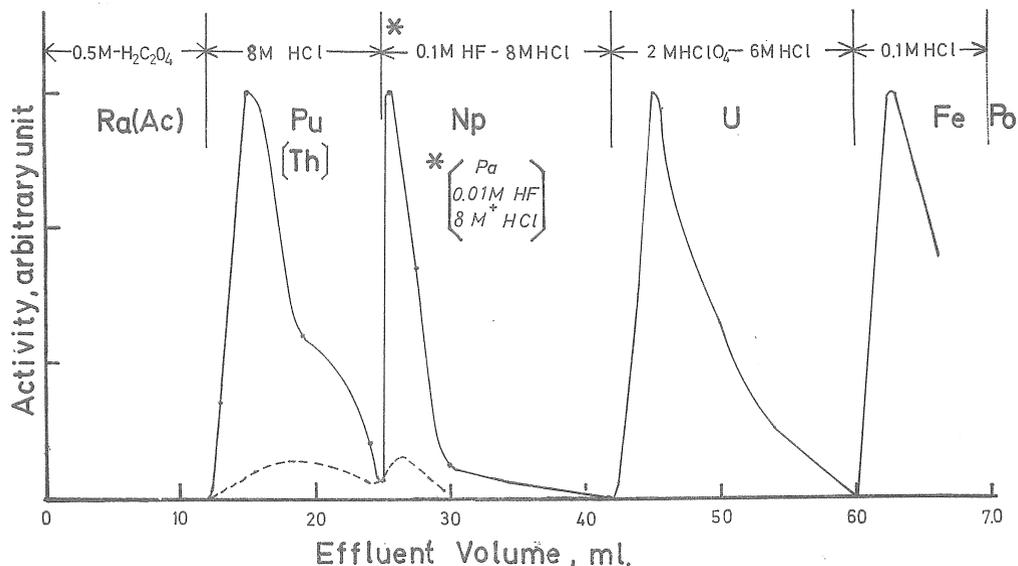


Fig. 4. The results of tracers study

quantity as possible. Then this solution was passed through an oxalate form Dowex-1×8 resin (resin volume 2.5 ml). In this process, uranium, thorium, protactinium and iron were retained on the column, but alkali and alkaline earth metals passed through. After washing the column with several column volumes of 0.5M $H_2C_2O_4$, the eluants were changed stepwisely in the order of 8M. HCl, 8M HCl-0.1M HF, 6M HCl-2M $HClO_4$ and final distilled water.

The elution diagram of uranium, neptunium, plutonium and iron is shown in Fig.



Dowex 1×8 (200~400 mesh) [oxalate form] Column ϕ : 0.8 cm, L: 5 cm, Flow rate ~ 0.4 ml/min.cm²

Fig. 5. Elution curve of Pu, Np, U and Fe from anion exchange resin

5. The result shows that plutonium is eluted in 8M HCl effluent along with thorium, neptunium eluted in 8M HCl-0.1M HF along with protactinium, and uranium eluted in 6M HCl-2M $HClO_4$, respectively.

This method is useful for the fallout sample, containing little amount of thorium and protactinium isotopes which will interfere the alpha spectra of Pu-238 and Pu-239 and Np-237 (a yield tracer for Np-239 determination). A residual part of Pu-239 appeared in the 8M HCl-0.1M HF fraction, because the foregoing elution with 8M HCl might not be sufficient. Another cause of low recovery of Pu-239 from 8M HCl fraction may be attributed to the incomplete quantitative electrodeposition of plutonium. Recovery of neptunium in 8M HCl-0.1M HF fraction exceeded over 90%, but a part of it (several percent) was eluted in 8M HCl fraction, owing to the fact some species of neptunium was not adsorbed on the resin.

4 - 3 The electrodeposition of plutonium

In the preliminary study mentioned above, the electrodeposition of plutonium was made under the similar conditions as had been used for the electrodeposition of

thorium or neptunium. Optimum conditions for plutonium was investigated from the stand points of the initial pH, the concentration of ammonium formate, sodium chloride, and oxalic acid and electrolytic time. Other factors such as voltage, current, temperature, volume of electrolyte and area of cathode plate which would have influence on the yield were kept nearly constant.

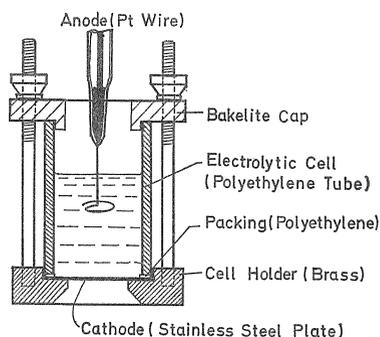
The conditions of each electrolytic experiment is shown in Table 1, respectively.

Table 1. The tracer experiments of the electrodeposition of plutonium

No. of experimental series	Initial pH	2M HCOONH ₄ (ml)	4M NaCl (ml)	0.5M H ₂ C ₂ O ₄ (ml)	Time (hrs.)
1	varried	0.75	5	1	2
2	3.2~4.1	varried	5	1	2
3	3.6~4.0	0.70	varried	0.6	2
4	3.1~4.0	0.70	5	varried	2
5	3 ~ 4	0.70	5	0.5	varried

To the solution in Table 1, dil. HCl or dil. NaOH was added to adjust pH and the total volume was made to 10 ml with distilled water. The electrolysis was done at a constant current density of about 70~80 mA/cm² with an applied voltage of about 5 V for each cell, except for the experiment No. 3 series in which an applied voltage was changed according to the amount of 4 M NaCl solution in order to maintain the constant current.

As shown in Fig. 6, the anode was a spiral platinum wire and the cathode was a stainless steel plate (3.4 cm diameter). A cell was a polyethylene tube with 5 cm height and 2.8 cm of inner diameter. The yield of electrodeposition was estimated from the ratio of the recovered alpha activity of plutonium on the cathode plate to that on the gold coated copper plate on which the same amount of plutonium as that used for the electrolysis was mounted and evaporated carefully to dryness. Great care had to be taken to spread the material on the dish



0 1 2 3 4 cm

Fig. 6. Electrodeposition cell

evenly and thinly, to reduce the self-absorption of alpha particles to a minimum. As the satisfactory mounting could not be secured by successive addition and evaporation of dil. HCl solution of plutonium, some errors may be introduced into the estimation of absolute yield owing to the fact that small quantity of salt residue remained on the gold coated plate and self-absorption of alpha ray may occur. But the results obtained seem to be correct relatively.

Results.

- 1) As shown in Fig. 7, the yield of plutonium did not depend largely upon the initial pH of the electrolyte. Even above initial pH value below 3, the yield exceeded over about 70%.

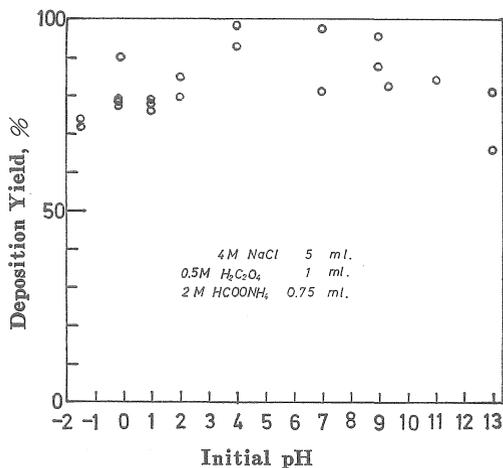


Fig. 7. Effect of initial pH on Electrodeposition (Pu)

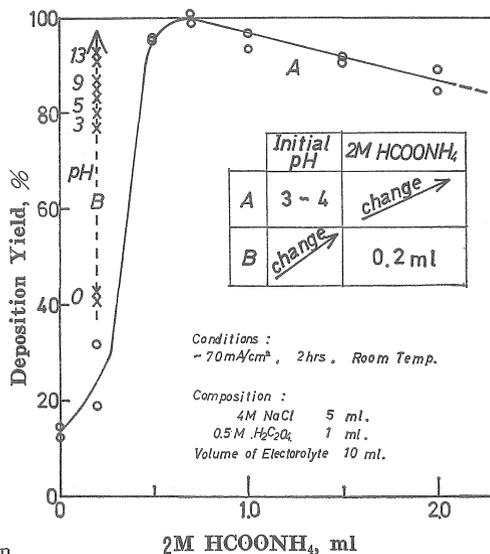


Fig. 8. Effect of HCOONH₄ on electrodeposition of Pu

- 2) On the other hand, the yield depended sensitively on the concentration of ammonium formate. As shown in Fig. 8, the addition of 0.7~0.75 ml of 2 M HCOONH₄ solution to 10 ml of electrolyte is most preferable. The decomposition of ammonium formate raised the pH of the electrolyte during the electrolysis and increases the yield of the electrodeposition of plutonium⁷⁾.
- 3) Oxalic acid seems to play a role of masking some metallic element such as iron⁸⁾ and of controlling the evolution of hydrogen at the cathode. As slight decrease in the yield was observed when more than 1.5 ml of 0.5M H₂C₂O₄ was added and in the absence of oxalic acid. As seen from Fig. 9(a) the addition of 0.5 ml of 0.5M H₂C₂O₄ solution will be favorable.

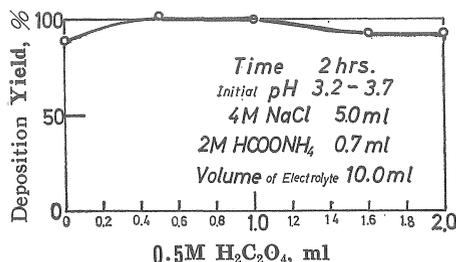
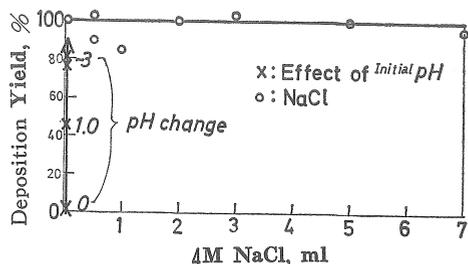


Fig. 9. a) Effect of H₂C₂O₄ on electrodeposition (Pu)



b) Effect of NaCl on electrodeposition (Pu)

- 4) The amount of sodium chloride did scarcely influence on the yield as shown in Fig. 9(b) but play a role of reducing the resistance of the electrolyte. In practice, 3 ~ 5 ml of 4 M NaCl solution was favorable.
- 5) As for the electrolytic time, the yield began to rise abruptly after about 20 minutes and reached at the plateau in about 50 minutes and then continued to rise slowly. This phenomenon was parallel with the pH change of the electrolyte. The electrolysis of 2 hours was necessary for the quantitative electrodeposition of plutonium.

From these results, the best conditions were as follows. The electrolyte is the mixture of the weak acidic solution of sample, 0.75 ml of 2 M HCOONH₄, 0.5 ml of 0.5M H₂C₂O₄ and 5 ml of 4 M NaCl solution and the pH is adjusted 3 ~ 4 with dil. NaOH or dil. HCl and is made up total volume to 10 ml with H₂O.

5. Fallout samples and their analysis

5-1. Determination of plutonium in the fallout samples due to the third nuclear explosion of China.

The third nuclear explosion of China was done on May 9, 1966. By surveying with a radiation detector, all of the sample containing hot particles, dust and soil was collected on the roof of the faculty building of the Kanazawa University on 11, May. Their γ decay curves and spectra were shown in Fig. 10.

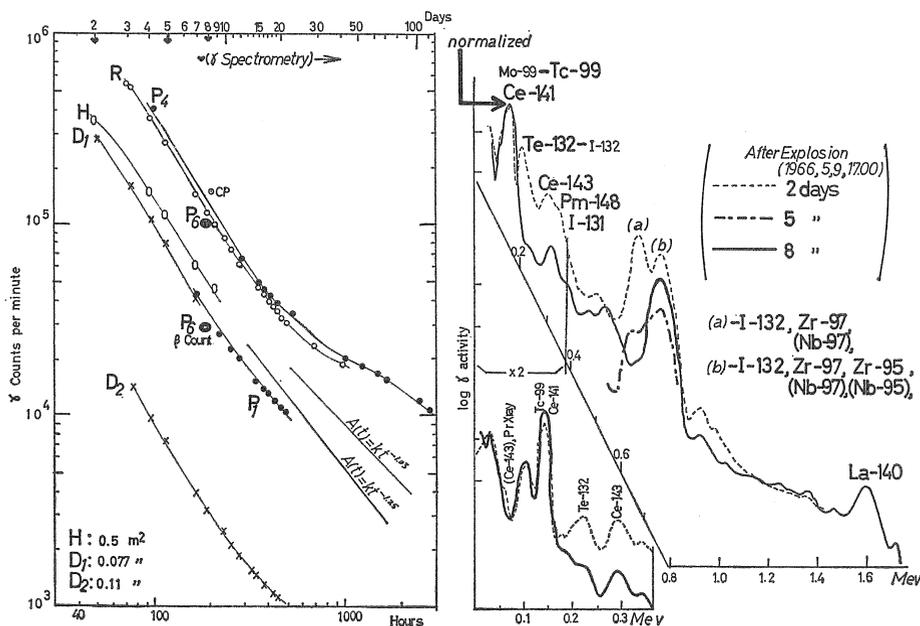


Fig. 10. The γ spectra and decay curve of the fallout from the third nuclear explosion of China

The sand (1.5 g) containing the fallout dust ("R") was analysed by the scheme shown in Fig. 3 (Method A mentioned above in 4-2-1.). In Fig. 11, the amount of Pu-239, U-234 and U-238 in the sample "R" was shown with the recovered tracers of Pu-238 and U-232, respectively.

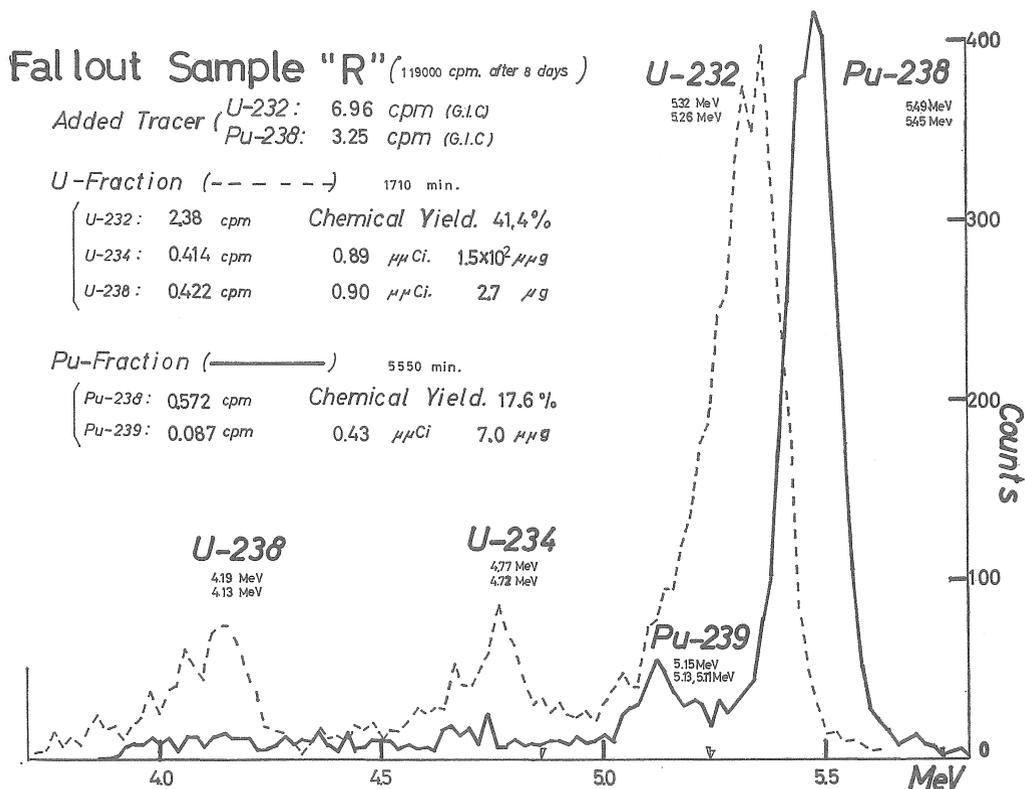


Fig. 11. The analytical results of fallout sample from the third nuclear test of China

5-2. Separation of plutonium-239 and others in the fallout samples due to the fifth nuclear explosion of China.

The fifth nuclear explosion of China was done on December 28, 1966. The snow as water of 12 l/m^2 was sampled on the rooftop of the Faculty building of Science of Kanazawa University on January 1, 1967. Other samples were also collected for measuring the γ decay and the γ spectra (Fig. 12). This fallout samples were treated by the oxalic acid conversion method which was already mentioned above in the tracer study (4-2-2, Method B), followed by the step of radiochemical separation with γ counting and γ spectra.

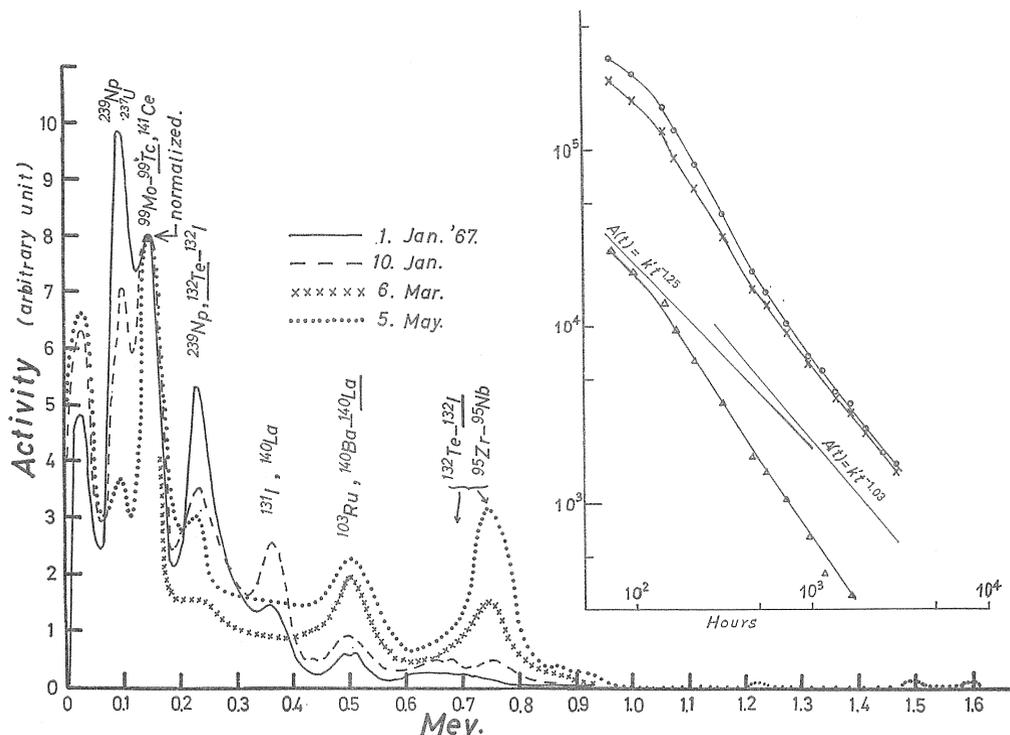


Fig. 12. The γ spectra and decay curve of the fallout from the fifth nuclear explosion of China

(Procedure)

The sample volume was reduced to about 20 ml by evaporation and the resulting liquor was centrifugated for 4 minutes at 5000 r.p.m.. The supernate (S_1) and the precipitate (P_1) were separated. The ratio of γ activity of each fraction (P_1/S_1) was nearly equal to 10 at 13 days after explosion. Neptunium-239 was predominant in γ spectra of both fractions. The precipitate, having 6×10^5 cpm at 14 days after the explosion, was decomposed in a glass beaker with conc. HNO_3 , conc. H_2SO_4 and conc. $HClO_4$ by warming on a hot plate. Then, the tracers 6.0 dpm of plutonium-238, 13.2 dpm of neptunium-237 and 11.1 dpm of uranium were added in this solution.

This solution was transferred into a platinum dish and dried up with conc. HF and conc. $HClO_4$ on a hot plate repeatedly. The degree of decomposition was checked by the γ counting of the undissolved residue. Then, the dried up sample was taken up in 5 ml of conc. HCl and the total volume was made to about 20 ml with H_2O , 5 mg of Fe^{3+} being put into in this course. Dil. NH_4OH was added drop by drop under warming of the solution on a water bath, until the pH of the solution became to about 10. After centrifugation, ferric hydroxide precipitate was washed by hot. 0.01M NH_4OH . This coprecipitation process was done twice. The hydroxide precipitate thus obtained was dissolved in 5 ml of 0.5M $H_2C_2O_4$ under warming and the resulting solution of yellowish green color was feeded on an oxalate form anion exchange resin Dowex-1 \times 8 column (resin volume 2.5 ml).

Each element was stepwisely eluted with the eluants of 0.5M $\text{H}_2\text{C}_2\text{O}_4$, 8 M HCl, 8 M HCl-0.1M HF, 6 M HCl-1M HClO_4 and 0.1M HCl, succesively. Several fractions of each eluant were examined by γ activity and the elution was continued until its γ activity lowered nearly to its back ground activity. According to the γ spectra of each fraction, it was confirmed that there were mainly Te-132-I-132, Be-140-La-140, and Ce-141 in the 0.5M $\text{H}_2\text{C}_2\text{O}_4$ fraction, Np-239, Zr-95-Nb-95 in the 8 M HCl fraction, and Mo-99-Tc-99 and U-237 in the 6 M HClO_4 fraction.

The electrodeposition of neptunium was carried out as follows. Since the first fraction of 6 ml of 8 M HCl-0.1M HF effluent contained dominantly Np-239 from its γ spectrum, it was dried on a hot plate with conc. HNO_3 and the residue was taken up with 2 ml of 1M HCl by heating calmly. Then, 5 ml of 4 M NaCl, 0.75 ml of 2 M HCOONH_4 , 1 ml of 0.5M $\text{H}_2\text{C}_2\text{O}_4$ and distilled water (1.25 ml) were added. The solution thus prepared was transfered into a polyethylene electrodeposition cell and neptunium was electrodeposited on a stainless steel cathode plate at a constant current 0.5 A for 2 hours.

The electrodeposition of uranium was carried out as follows. The first three fractions (about 20 ml) of 6 M HCl- 1M HClO_4 effluent contained only U-237 from their γ spectra. They were gathered and dried up and the residue was taken up with 1M HClO_4 (2 ml) under heating. After addition of 2.5 ml of 2 M HCOONH_4 , and 10 ml of distilled water, the electrodeposition of uranium was done on a stainless steel plate for 2 hours at a constant current of 0.5 A.

The purification and the electrodeposition of plutonium was carried out as follows: About 18 ml of 8 M HCl fraction was dried up with conc. HNO_3 and conc. H_2SO_4 . There were considerable amount of white residue which might be composed of alminium, rare earth metal salts and others. As this residue might interfere the electrodeposition of plutonium and the contamination with neptunium was also found in this fraction by γ spectrum, purification of plutonium was done furthermore. After dissolving the residue in dil. HCl by warming on a hot plate, 0.5 ml of 3 M NaNO_2 was added to adjust the valency of plutonium to tetravalent. After putting 10 mg of Fe^{3+} into the solution, distilled water was added to make the total volume to 180 ml and dil. NaOH was added drop by drop to about pH 8. Ferric hydroxide precipitate was separated by centrifugation and washed with distilled water. The 8 M HCl solution of this precipitate was feeded on the column of the chloride form Dowex-1 \times 8 anion exchange resin. Plutonium (IV) adsorbed on the resin was eluted by 0.1 M HCl. The second purification was carried out in order to remove neptunium in 0.1M HCl. The residue obtained by drying up this solution was dissolved in 0.5M $\text{H}_2\text{C}_2\text{O}_4$. After feeding the solution on the oxalate form Dowex-1 \times 8 resin column, the elution with 8 M HCl was performed in the similar process as the initial separation. The effluent of 8M HCl obtained was dried up with conc. HClO_4 and the resultant was dissolved in 8M HCl. After removing a small quantity of iron with DIBK extraction from 8M HCl solution, the aqueous phase was treated with conc. HClO_4 and conc. HNO_3 to

decompose the organics. The residue was taken up with a mixture of 0.5M $\text{H}_2\text{C}_2\text{O}_4$ (0.5 ml), 2 M HCOONH_4 (0.75 ml), 4 M NaCl (5 ml) and distilled water (3.75 ml) and the electrodeposition was carried out at a constant current of 0.5 A for 2 hours.

6. Estimation of uranium, neptunium and plutonium isotopes by β counting and alpha spectrometry in the fallout samples (5-2)

(1) Uranium isotopes.

For the determination of U-234 and U-238, the electrodeposited uranium was subjected to the alpha spectrometry by a double gridded ionization chamber with a 100 channel pulse height analyser. In order to estimate the amount of U-237 in the sample, β activity was measured for 30 days by an end window type G.M. counter with 50 mm diameter. From alpha ray spectrum, the uranium content and the activity ratio of U-234/U-238 were determined, by taking account of the chemical yield (30.4%) from U-232 peak area in the same spectrum and by assuming the counting efficiency (50 %) of alpha spectrometry. As the β decay curve obtained showed the existence of U-237, the initial activity of U-237 at the explosion was estimated by extrapolating its decay curve. The correction factors applied in this estimation were the chemical yield and the counting efficiency (12 %) of G.M. counter which was calculated from the counting efficiency (16 %) measured by U_3O_8 (UX_2) standard source being covered with aluminium foil, taking account of β ray absorption of U-237.

(2) Neptunium isotope.

After alpha spectrometry was made for electrodeposited neptunium in order to know the chemical yield (43.5 %) from Np-237 peak area, β activity of it was measured by G.M. counter for more than 30 days. Its decay curve was almost equal to that of Np-239 at the beginning, but finally it showed there a little contamination with U-237. When initial activity of neptunium-239 was estimated by extrapolating the decay to the explosion time taking into account of the chemical yield and the counting efficiency (15 %) of G.M. counter, this activity of uranium-237 was subtracted from total activity together with back ground activity.

(3) Plutonium isotope.

The amount of plutonium-239 was also estimated by alpha spectrometry of electrodeposited plutonium source in the assumption that the peak of 5.15 MeV was only due to plutonium-239, not to plutonium-240⁹⁹. The overall chemical yield of plutonium was proved to be 8.1 % by the 5.50 MeV peak area of plutonium-238 in Fig. 13.

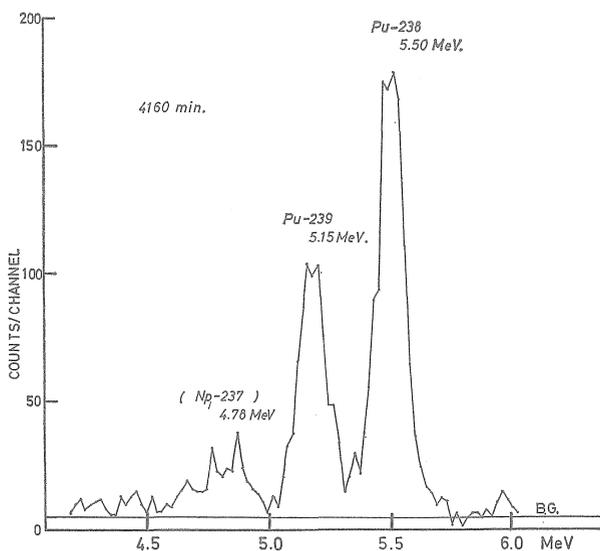


Fig. 13. α ray spectrum of the snow sample from the fifth nuclear explosion of China (Dec. 28, 1966)

7. Results and discussions

1) The chemical separation methods of plutonium from other actinides, especially uranium and thorium isotopes were developed as Method A (4-2-1) and (4-2-2) and they were applied to the fallout samples of the third and fifth nuclear explosion of China, respectively, and the estimation of their contents were made as shown below with that of some other nuclides. The Method B (4-2-2) of the oxalate form anion exchange was considered to be useful to the chemical separation of actinides, such as thorium, protactinium, uranium, neptunium and others. Plutonium (IV) was eluted from chloride or nitrate form Dowex-IX8 anion exchange resin by 0.5M $H_2C_2O_4$. The chemical species of oxalate complex of plutonium formed in this step was not known enough, but the authors consider that Pu (IV) is reduced to Pu (III) by 0.5M $H_2C_2O_4$ on the resin under the presence of H^+ ion.

2) As shown in Table 2, the cumulative amount of plutonium-239, about $1.5\mu Ci/Km^2$ was brought in our kanazawa district by the fallout in three days after the fifth nuclear explosion of China. The initial atomic ratio of Pu-239/U-238 seems to have some relation to the neutron density in nuclear explosion. Its ratio was about 2.3×10^{-5} which agreed well with the other author's data of 1.2×10^{-5} ¹⁰⁾ for hot particles brought by the same nuclear explosion of China.

The initial atomic ratio of Np-239/U-237 in the fallout particles is considered to have some relation to the abundance ratio of slow neutrons to fast. The ratio of Np-239/U-237 was about 18 which agreed well with the other same author's data of 24 for both the combined sample of about 90 hot particles and rain sample collected soon after the same explosion.

Table 2. The results of the analysis of the snow sample from the fifth nuclear explosion of China (Dec. 28, 1966)

[Snow sample (12 l as water); Sampling area: 1m²
Total γ counts ca. 6×10^5 cpm after 14 days of the explosion.]

nuclide	counting time and its ray	cpm. (at Jan. 19, 1967)	initial activity (at Dec. 28, 1966)	atom number
Pu-239*	4160 min	0.147 \pm 0.007	1.48 $\mu\mu$ Ci	6.1 $\times 10^{10}$
Np-239	5 min	3082 \pm 30	10.4 μ Ci	1.13 $\times 10^{11}$
U-237	6 min	1691 \pm 17	0.193 μ Ci	6.00 $\times 10^9$
U-234	1640 min	0.159 \pm 0.012	0.44 $\mu\mu$ Ci	
U-238	1640 min	0.116 \pm 0.011	0.34 $\mu\mu$ Ci	2.6 $\times 10^{15}$

$$\text{atom number ratio } \frac{\text{Pu-239}}{\text{U-238}} = 2.3 \times 10 \quad \frac{\text{Np-239}}{\text{U-237}} = 18$$

$$\text{activity ratio } \frac{\text{U-234}}{\text{U-238}} = 1.37 \pm 0.14$$

* Obtained on the assumption that the α activity at about 5.15 MeV is due to Pu-239 only.

The activity ratio of U-234/U-238 in this snow sample containing fallout particles had the value of 1.37 which would be apparently greater than unity, even though the tailing of the large peak of uranium-232 (5.32 MeV) which had been added previously as a tracer, might contribute to the small peak of uranium-234 (4.77 MeV) in their spectrum. Its ratio of 1.13 \pm 0.04 is also reported for the rain sample of above mentioned author's¹⁰⁾. But its ratio in the combined sample of 230 hot particles was reported to be 1.20 \pm 0.03. The discussion of these ratio of uranium will remain, as different kinds of samples were used.

The estimated value of plutonium-239 was 1.48 $\mu\mu$ Ci and this was about 55% of the equivalent value of plutonium-239 activity calculated from the β decay of neptunium-239. This value may become one of the proof to deny the supposition that the bomb was plutonium origin, though the lower value of plutonium-239 may be caused by the fractionation of these two elements.

In the sample for the third nuclear explosion of China, the activity ratio of U-234/U-238 and the atomic ratio of Pu-239/U-238 were 1.00 and 2.6 $\times 10^{-6}$, respectively. But as this sample contained a lot of soil together with dust and hot particles, these two values may be affected considerably by the amount of uranium isotopes in the soil and could not be compared with the data of the fifth nuclear explosion of China.

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