SYMPOSIUM
ON
RADIO-CHEMISTRY

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SYMPOSIUM ON RADIO-CHEMISTRY

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1. The Solvent Extraction Behavior of Ions in TBP-Hydrochloric Acid System

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This is a comprehensive study on the solvent extraction behavior of more than fifty chemical elements (Na - Cm) in the undiluted TBP - hydrochloric acid system. The variation of the distribution ratio was studied for each element under various acidities of the aqueous solution. The distribution ratio was determined radiometrically using a radioactive indicators. Some of the indicators were imported and others prepared by the neutron irradiation in JRR-1 with subsequent chemical treatments. The radiochemical purities were checked by gamma-spectrometry, decay and/or beta-absorption with aluminum foils. The specific activity of these indicators varies from carrier-free to 10^4 cpm/100 microg.

Although in some cases the chemical species of the elements to be studied could not be defined unambiguously, the most common species were chosen as far as possible.

Distribution ratio values thus obtained show a regularity to a certain extent against the Z value, atomic number, at 2, 4, 6, 9 or 12 M acidity.

The comparison of the acid dependence of distribution ratios between two given elements gives the convenient acidity for the mutual separation of the elements. In a similar way, many group separations could be discussed by comparing distribution ratios.

Some examples are given for the separation of a few couples of elements.

2. The Solvent Extraction Behavior of Irons in HDEHP-Hydrochloric Acid System

Kan Kimura
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Bis (2-ethyl hexyl) orthophosphoric acid, HDEHP, is one of the dialkyl phosphoric acids and has been used as a solvent extraction reagent for many elements, particularly in the uranium recovery system.

In this paper, the distribution ratios of nearly fifty chemical elements are determined in HDEHP (50% vol. toluene solution) - hydrochloric acid system, in order to find out the fundamental data for the solvent extraction separations.

The HDEHP used was imported from the U.S.A. and was purified according to the ANL method.

The distribution ratio was determined radiometrically using a radionuclide. Namely, activities in the aliquots of each phase were directly measured with a γ -ray scintillation counter, after hydrochloric acid solution containing the radionuclide were contacted with 50% HDEHP-toluene. When a given radionuclide is not a γ -emitter, the aliquots were evaporated on dishes, and β -activities were measured with G.M. counter.

Some of the nuclides were imported and the others were prepared by the neutron irradiation in JRR-1 followed by chemical treatments. The radiochemical purities of these nuclides were checked by the ceday, γ and/or β -ray energy.

The radioactive nuclides were taken in a high specific activity as far as possible, in order to keep the concentration of the elements low. The maximum concentration was about 100 microg./ml. in the initial hydrochloric solution and the minimum specific activity was about 10^4 cpm/100 microg. In some cases, the radioactive nuclide could be used carrier-free. The ratios were studied in acidities ranged form 10^{-2} to 1N.

Generally speaking, the distribution ratio increases as the valence of cation becomes higher, and the acid dependence is inverse power of the valence.

Possible many group separations will be discussed.

3. The Radiochemical Separation between ^{95}Zr and ^{95}Nb by Tri-n-butyl Phosphine Oxide

by Hirokazu Umezawa and Reinosuke Hara
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During the course of study on the extraction of ^{95}Zr - ^{95}Nb by organophosphorus compounds, it was observed that ^{95}Zr and its daughter ^{95}Nb showed a similar behavior in the extraction by n-alkyl phosphates, whereas the extraction by phosphinate or phosphine oxide resulted in the different Kd values between these two species. The present study was initiated to follow the behavior of ^{95}Zr and ^{95}Nb in the extraction by tri-n-butyl phosphine oxide (TBPO) with carbon tetrachloride diluent, and the possibility for the mutual separation was investigated.

The stock solution of 2 M HNO_3 containing ^{95}Zr and ^{95}Nb at the radiochemical equilibrium was shaken with 0.01 M TBPO to extract the species. The organic phase was repeatedly washed by 2 M HNO_3 pre-equilibrated with 0.01 M TBPO, and the aqueous phase was also washed by 0.01 M TBPO pre-equilibrated with 2 M HNO_3. The organic phase concentrated the species whose Kd value was determined to be $\sim$ 100, whereas in the aqueous phase the species with the Kd value of $\sim$ 0.1 was collected. The determination of β ray absorption as well as half lives identified the species to be ^{95}Zr in the organic phase and ^{95}Nb in the aqueous phase.

The distribution coefficients of ^{95}Zr and ^{95}Nb in 1 - 13 M HNO_3 by the extraction with 0.01 M TBPO are listed in Table 1.

<u>Table 1</u>

HNO_3	^{95}Zr	^{95}Nb
1	1 10^2	5 10^{-2}
2	1 10^2	7 10^{-2}
4	1.1 10^2	1.3 10^{-1}
6	1.2 10^2	2.4 10^{-1}
8	9.5 10	3.5 10^{-1}

Table 1 (Cont'd)

HNO_3	^{95}Zr	^{95}Nb
10	5.5 10	4.7 10^{-1}
13	1.3 10	9 10^{-1}

The solvent dependences of Kd values at 2 M HNO_3 are also shown in Table 2.

Table 2

TBPO (M)	^{95}Zr	^{95}Nb	^{95}Zr - ^{95}Nb
0.001	2.2 10^{-1}		
0.002	5.0		3.8 10^{-1}
0.005	5.8 10	1.0 10^{-2}	5.0 10^{-1}
0.01	1.3 10^{2}	7.9 10^{-2}	7.5 10^{-1}
0.02	1.9 10^{2}	5.1 10^{-1}	6.5
0.05		2.6	
0.1		4.0	

The complete separation between ^{95}Zr and ^{95}Nb at the radiochemical equilibrium should give the activity ratio of 1 : 2, from which the optimum solvent concentration was determined to be 0.005 M TBPO. The figures in Table 2 indicate the Kd value of 0.5 at 0.005 M TBPO. Below 2 M HNO_3 concentration, the hydrolysis of zirconium must have been encountered, thus the extraction below 2 M HNO_3 was avoided.

The operational procedure is outlined below:

Equal volumes of both ^{95}Zr - ^{95}Nb solution in 2 M HNO_3 and 0.005 M TBPO - Cl^4 were shaken in the thermostat, and two layers, the aqueous and the organic, were separated. Zirconium was extracted into the organic phase, while niobium remained in the aqueous phase.

The organic phase was washed by the equal volume of 2 M HNO_3 pre-equilibrated with 0.005 M TBPO, diluted with CCl_4, then the scrubbing of zirconium was made by concentrated HNO_3. The same back-extraction was repeated, and the scrubbed solutions were combined. The yield of 95% was obtained. The scrubbed solution was then washed with CCl_4 to remove any remaining TBPO. The aqueous phase containing niobium was first washed with 0.005 M TBPO pre-equilibrated with 2 M HNO_3, then with CCl_4 to remove TBPO. The purities of ^{95}Zr and ^{95}Nb thus obtained were confirmed by the comparison of Kd values with the reference Kd values obtained on pure ^{95}Zr and ^{95}Nb, as well as by the determination of both β ray absorption and half lives.

As the solvent TBPO was quite soluble in water as compared with other solvent such as TBP, the scrubbing solution must have been pre-equilibrated with the organic phase. The extraction from HCl solution was tried, but both ^{95}Zr and ^{95}Nb showed a similar Kd values as indicated in Table 3, thus the mutual separation could not be achieved.

Table 3

HCl (M)	^{95}Zr	^{95}Nb
1	0.2	0.18
4	1.1	1.4
8	11	11
12	19	14

4. Separation of Thorium and Rate Earths Tracers by Azines

By Kakuzo Tada, Noboru Oi and Yasuko Tsuge
(Matsuda Research Laboratory, Tokyo Shibaura Electric Co.)

1. The excellent extraction separation of thorium and rare earths tracers in ammonium nitrate salting-outed aqueous medium can be accomplished by the use of azines (RR'C-N=CRR')

Azine, the condensation product of ketones and hydrazine, was used as the additive to metylisobutylketone (hexone).

2. From several azines, metylisobutylketazine, isophoroneketazine and dibenzalhydrazine were selected. The organic phase was prepared by mixing the desired amount of azine with hexone. The aqueous phase which contains thorium (0 - 0.5M) and ammonium nitrate, was extracted by this mixed solvent, and distribution ratio of thorium and rare earths tracers (^{144}Ce-^{144}Pr, $^{152-4}$Fu, ^{153}Sm, ^{170}Tm) were determined.

3. Although the addition of azines causes the increase of rare earth distribution ratios significantly, its degree is considerably small compared to the enhancement of thorium extraction. Accordingly, large separation factor (100-1,000 fold larger than TBP) was obtained.

The concentration of azine in hexone should be less than 20% to retain the extraction of rare earths below 2%. But even in this case the extraction of thorium was fairly good. For example, the distribution ratio of thorium between aqueous solution, 0.2 M $Th(NO_3)_4$ - 7.5M NH_4NO_3, and hexone was 0.02. In the presence of 20% (Vol) metylisobutylketazine this increased to 180.

4. The order of extractability of rare earths tracer was Ce > Eu > Sm. Fission products was more extractable.

The distribution ratio of rare earths decreased with increasing feed thorium concentration and were practically independent of the mixed rare earths concentration in the aqueous phase.

5. The example of the distribution ratios of thorium and rare earth with several solvents were given below.

It seems to be evident that ketone-azine type solvent is effective, especially in single contact analytical extraction, for the separation of thorium and rare earths.

Table

○ Th $(NO_3)_4$ 0.1M-NH_4NO_3 7.5M	D_{Th}	D_{Eu}	Separation Factor (D_{Th}/D_{Eu})
TBP (20%) CCl_4 (80%)	8.5	0.38	23
Hexone	0.02	*—	—
Mesityl Dxide	0.40	0.003	130
Hexone-Methylisobutyl-ketazine (20%) (80%)	1,000	0.012	90,000
Hexone(76 wt%)-Isophorone-ketazine (24 wt%)	200	0.027	7,400
○ Th $(NO_3)_4$ 0.45M-Ca $(NO_3)_2$ 4M-HNO_3 3M			
TBP (20%) CCl_4 (80%)	0.99	**—	—
Hexone	1.29	0.015	84
Hexone (80%)-Methylisobutyl-ketazine (20%)	10.9	0.0085	1,300

* Extraction is almost zero

** Third layer formation

5. Studies on Extraction of Ce-144 with Acetylacetone

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Tohoku University, Sendai)

The solvent extraction with acetylacetone as a method of a simple and rapid separation of Ce-144 from fission products was studied.

To 5 ml. of Ce-144 solution (carrier-free), 1 ml. of 1 M sodium bromate is added, followed by 3 ml. of 20% acetylacetone carbon tetrachloride solution. The mixture is shaken for 3 minutes. By this method the extraction of Ce-144 is complete over the pH range of 4-9. Over 90% extraction is obtained without sodium bromate, but it takes much more time to extract completely.

As extraction solvents, carbon tetrachloride, benzene, chloroform, xylene, isoamyl acetate, methyl isobutyl ketone, and isopropyl ether are examined, and carbon tetrachloride, benzene, and chloroform are preferable. The optimum pH range of these solvents is almost the same as that of carbon tetrachloride.

Ce-144 extracted in the organic phase is able to be stripped completely with mineral acids of 0.1 N or over.

Decontamination of fission products and rare-earth nuclides was investigated. Each pure nuclide, Sr-90 (Y-90), Zr-95 (Nb-95), Ru-106, Cs-137, and Eu-152-154, is extracted individually by the standard procedure, and the organic phase obtained is washed with 6 ml. of an aqueous solution containing 1 ml. of 1 M sodium bromate and pre-saturated with 20% acetylacetone carbon tetrachloride, and then stripped into an equal volume of 1 N nitric acid. In this procedure, Ce-144 is recovered more than 99%, on the other hand, all the nuclides except Zr-95 (Nb-95) are extracted not more than 0.1%. Zr-95 (Nb-95) is extracted considerably, but it is possible to prevent this by adjusting the condition of the aqueous phase.

This method is simple and rapid, and the application to fission products make it possible to separate Ce-144 with high purity.

Generally, it is difficult to separate the daughter Pr-144 from the parent Ce-144 on account of the short half life of the former. But in the acetylacetone method, the mutual separation of Ce-144 and Pr-144 is easy because Pr-144 is not extractable. After the period of time for the radioactive equilibrium of Ce-144 with Pr-144 in the organic phase, the aliquot (6 ml.) of the organic phase is shaken with 3 ml. of the washing solution used in the above procedure. The radiochemical purity of Pr-144 obtained was more than 99.5%, and it took only 3 minutes for this separation.

6. Solvent Extraction of Radioruthenium as the Ocinate

Toyoaki Kato and Yoshinaga Oka
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Tohoku University, Sendai)

Because of the need for a simple and effective method for the separation and the determination of radioruthenium in fission products, its extraction behavior with oxine was studied.

The radioactive ruthenium nitrate solution, used in this work, was prepared by distillation of ruthenium tetroxide formed by oxidation of radioactive ruthenium trichloride (Ru-Rh-106) with lead peroxide in sulfuric acid. The ruthenium tetroxide was absorbed in 1 N nitric acid solution containing 3% hydrogen peroxide. The carrier solution of ruthenium nitrate was also prepared from ruthenium trichloride as described above.

Oxine solution in n-propanol or acetic acid and buffer solution of suitable pH were mixed in a small test tube and its volume was adjusted to 6 ml. with water. Then to it 0.1 ml. of Ru-106 solution (ca. 0.05 c.) and, if desired, 0.1 ml. of carrier solution of ruthenium nitrate (Ru, 10 g.) were added and the content was heated in a constant temperature bath.

After the formation of the oxinate, the content was transferred to a separatory funnel and extraction was carried out by shaking for 1 minute with 2 ml. of organic solvent. The phases were separated and their gamma radioactivities were counted in a well-type scintillation counter.

When 2 ml. portion of 0.05 M oxine in n-propanol was used, ruthenium was completely extracted in a single extraction with n-butanol after heating for 1 hour at 60°C at pH of 4 - 6.

The formation of the oxinate was complete in the aqueous phase containing acetate or biphthalate as the buffer but not sufficient in the citrate, phosphate or ammonium buffer solution.

Chloride, nitrate, sulfate and borate ions did not interfere.

When 1 ml. of 1 M oxine in 10 N acetic acid solution was used and pH was adjusted with 1 ml. of 2 N sodium acetate solution, complete extraction of ruthenium with benzene was attained by 30 minutes heating at 60°C (or 10 minutes at 80°) followed by 1 minute shaking.

Reextraction of ruthenium from benzene phase was carried out by two successive 10 minutes shaking with equal volume of 18 N sulfuric acid solution.

In the procedure of benzene extraction, no Cs-137, Sr-90 and Y-90 but 2% of Ce-144 and 87% of Zr-95 (Nb-95) were extracted.

The latter elements, however, were easily stripped from benzene phase by shaking with dilute mineral acid (i.e. 1 N nitric acid) whereby causing negligible loss of ruthenium.

These method was applicable to the separation of radioruthenium from fission products.

7. Isolation of Zirconium and Niobium from Fission Products by Solvent Extraction with Dilute TBP

Tomitaro Ishimori, Kenju Watanabe and Hirokazu Umezawa
(JAPAN ATOMIC ENERGY RESEARCH INSTITUTE)

During the solvent extraction studies on zirconium and niobium in the system of TBP - hydrochloric acid solution, it was found that both elements are extracted with very diluted TBP in toluene from 8 - 10 N hydrochloric acid. Pure toluene does not work for the extraction.

Distribution ratios for zirconium and niobium are shown in the following table.

Conc. of TBP in Toluene (%)	Distribution Ratio Zirconium		Niobium	
	8N-HCl	10N-HCl	8N-HCl	10N-HCl
100	7.0×10^2	3.6×10^3	2.3×10^3	9.9×10^2
50	7.1×10^2	-	2.0×10^3	-
20	5.8×10^2	2.3×10^3	-	-
10	3.3×10^2	6.7×10^2	6.1×10^2	1.0×10^3
5	1.8×10^2	-	1.8×10^2	1.7×10^2

(Table Cont'd)

Conc. of TBP in Toluene (%)	Distribution Ratio Zirconium		Niobium	
	8N-HCl	10N-HCl	8N-HCl	10N-HCl
2	3.0×10	1.5×10^2	-	-
1	8.8	5.9×10	8.1	2.8×10
0.5	2.3	1.6×10	-	-
0.2	4.0×10^{-1}	3.6	4.2×10^{-1}	1.2

In these conditions, most of other chemical elements is not extracted, remaining in the aqueous phase. Thus, extraction with 1% TBP in toluene from 8 - 10N hydrochloric acid provides a nice method for the separation of zirconium and niobium from the slow neutron fission products of uranium.

(1) A synthetic mixture was prepared by additing Zr-95 - Nb-95 into an old fission product solution. From the mixture, Zr-95 - Nb-95 was recovered by the 1% TBP extraction from 10N hydrochloric acid.

(2) A finely powdered mixture of uranium dioxide and oxalic acid was irradiated in JRR-1 for two hours. After standing for one day, the fission products were collected in oxalic acid solution by dissolving the irradiated mixture in 1 - 0.5 N hydrochloric acid. The oxalic acid solution was dried up and the residue was heated in order to remove oxalic acid by

sublimation. The remaining fission products were dissolved in 8N hydrochloric acid.

The resultant solution was shaken with 1% TBP. The zirconium and niobium extracted were stripped from the organic phase with 0.5N hydrochloric acid. The final product contains Zr-97 - Nb-97 (about 99%), Zr-95 - Nb-95 (about 1%) and a very small amount of Np-239. The extraction from 10N hydrochloric acid is not preferable because of the high contamination of Np-239.

(3) Starting from a mixture of Zr-95-Nb-95, Ce-144 and small amounts of other fission products, Zr-95-Nb-95 is isolated by a similar extraction from 10N acid in the absence of Np-239.

This method is supposed to be a handy way for the cleaning up of Zr-95-Nb-95 tracer.

8. Studies on the Solvent Extraction of Metalo- β diketone Chelates.

-Solvent extraction of uranium as dibenzoylmethane chelate-

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Solvent extraction of uranium as a chelate with dibenzoylmethane, was investigated. Dibenzoylmethane reacts with uranium to form a stable chelate, which was used for a colorimetric determination of the metal by Yoe et. al.. And Pribil et. al. developed a method for the extraction of uranium, where dibenzoylmethane solution in ethyl acetate was used as an extracting solvent.

In the present investigation, dibenzoylmethane was added to an aqueous sample solution as acetone solution, in order to make reaction rapid. Best procedure was designed as follows.

To a sample solution, add 2 ml. of 10% EDTA solution and $CaCl_2$ solution equivalent to EDTA, adjust pH to 6 ~ 7, add 0.5 ~ 1 ml. of 5% dibenzoylmethane solution in acetone, and dilute to about 50 ml.. Warm the solution at 60 ~ 70°C for 10 ~ 15 minutes, cool, transfer into a 100 ml. separating funnel.

Add butyl acetate and shake for about 5 minutes.

Extraction recovery of uranium was determined colorimetrically by use of the absorption of uranium-dibenzoylmethane chelate which had an absorption maximum at 400 mu.. In this case, as the standard, crystal of the chelate whose composition was estimated as UO_2 $(DBM)_2$, was dissolved in butyl acetate.

Uranium could be almost quantitatively extracted with butyl acetate from an aqueous solution at a pH between 4.5 ~ 9 in the absence of EDTA, and between 6 ~ 8 in the presence of EDTA and $CaCl_2$, respectively, when the concentration of dibenzoylmethane was larger than 0.2%.

The procedure, above described, was successfully applied to the separation of uranium from mixed fission products, and the decontamination factor 1 ~ 2 x 10^4 was given for a single extraction.

9. Study on the Liquid-Liquid Uranium Extraction by the Onium Compounds

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(Faculty of Science, Hiroshima University)

Many analytical applications has been studied on the onium compounds in our laboratory. In this investigation, the fundamental problems for the extraction of uranium from atomic reactor fuel and from ores were studied.

Tetraphenylphoshonium chloride (TPPC) was mainly used. The uranyl ion should be changed to the anionic complex if TPPC was applied as the extracting reagent. Therefore the buffer solution which contain the benzoic acid and the sodium benzoate was used to form the anionic complex. Treatment of the solution containing the anionic complex with TPPC solution produce white precipitate which is readily extracted in chloroform.

In order to find the best condition for the extraction of the uranium, the relations between percentage extraction and TPPC concentration (or pH) were studied. The results showed that the optimum pH was 5. The extracted uranium in the solution 0.5 M H_2SO_4 containing 0.003% Tween-80 was determined by the polarographic method.

The ratio of the [UO_2^{++}] to [TPPC] in the extractable precipitate was 1. Under the best condition above mentioned (at pH 5), 9% of fission products with carrier and 2% of carrier free fission products were extracted respectively. The maximum percentage extraction of the uranium was about 98% at 25 ± 0.1° C.

10. The Separation of Uranium and Protactinium from Thorium by Liquid Anion Exchanger.

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The extraction of U, Pa and Th from HCl, HNO_3 or H_2SO_4 solution of various concentration with oil soluble secondary amine is studied. Amberlite LA-1 in kerosene diluent is used as an extractant.

Data of extraction ratio is compared with acid dependency of Kd value of these elements by anion exchange resin.

Amberlite LA-1 has a selectivity to uranium extraction.

This fact is applied to the separation of uranium from protactinium and thorium in HCl.

The separation of uranium and protactinium from 8 N HCl solution of thorium is studied. Both uranium and protactinium are extracted from 8 N NCl and protactinium is stripped with 3N NCl.

Uranium is stripped with 0.1 N $NaNO_3$ and about 60% of added uranium is recovered.

From 3N HCl solution of U, Pa and Th, only uranium is extracted and stripped with 0.1 N $NaNO_3$. One hundred % of added uranium is recovered in this process. Radiation damage of Amberlite LA-1 is studied. Degree of damage is measured by non aqueous titration method and by extraction method.

At a dose rate of 8×10^5 r/h and under the total dose of 5×10^6r, radiation damage of Amberlite LA-1 is negligible.

11. Separation of Radioactive Elements Using Ion Exchange Membrane

Application to Fission Products.

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and Other Metals, Tohoku University)

Studies on the separation of carrier-free radioisotopes from fission products were carried out by the use of ion exchange membrane. For an example, the following conditions were used in this experiments:

Ion exchange membrane: Amberlite IR 102 x C and
IR 101 x A.

pH of the sample solution: 10.0 with NH_4OH-NH_4Cl buffer solution.

The type and number of electrolytic vessels: The same 9 (A, B, C .... 1) vessels as the first report (A ~ E were connected with anion exchange membrane. E ~ I were connected with cation exchange membrane and original fission product sample was contained in E vessel.)

Electrolytic condition: 12.0 V, 1.5 mA for 69 hrs.

After electrolyzing, the separation of each nuclide in vessels was carried out by using cation exchange resin and was counted the radioactivity of each fraction. And then it was found that Sr-Y, rare earth elements and Cs were concentrated in G, H and I vessels, respectively.

12. Decontamination of ^{106}Ru in the solution of ^{99}Tc by the use of ion exchange membranes.

by

Tatsuro KAWASHIMA and Yoshio KODA

(Government Industrial Research Institute of Nagoya)

According to the specification, the tracer of ^{99}Tc used of which it was separated from the fission products at Oak Ridge National Laboratory is contaminated by ^{106}Ru of specific activity - 6×10^{-4} mc/ml. It seemed that this value was small, the effects of ^{106}Ru would not be ignored in some case, because the energy of β -ray of ^{99}Tc was low, i.e., 0.293 MeV, whereas ^{106}Rh, daughter of ^{106}Ru, emitted β -ray of high energy 3.53

MeV and γ -ray. In this experiment, the original ^{99}Tc solution was counted with a G.M. counter of end window type at the 2 cm distance from window, then the ^{106}Ru fraction in the -ray absorption curve was extrapolated to the 0 mg/cm^2 thickness of Al absorber, and the activity due to ^{106}Ru in total counts was 1.26%.

Ruthenium belonged to the eighth group and it was obtained in various valence state. As it was so complicated chemical nature that it formed complex compounds with various charge at presence of other ligands, that is, Ru gave rise to anionic and cationic complexes in HNO$_3$ solution, it was known that the Ru showed one of the most complicated chemical property in the fission products disposal. It was measured the activity at several parts of membrane after electrolysis, that of ^{106}Ru in HNO$_3$ solution by using ion exchange membranes. In the experiments, Amberplex A-1 and Amberplex C-1 were used as the ion exchange membranes, and the measurement of radioactivity was made by the Tracerlab Ltd. autoscaler. The result showed that in the cationic membrane Ru was uniformly distributed, while in the anionic membrane most parts of Ru was found at one side of original solution and its concentration decreased with the increase of the depth from the surface in the membrane and was low at the opposite surface. The reason why Ru has above behavior was speculated that the anionic membrane showed the effects like a kind of moleculer sieve by the presence of long anionic complexes of Ru in HNO_3 solution.

In this experiment, the behavior of Ru in membrane described above was applied to the decontamination of ^{106}Ru in ^{99}Tc solution. The degree of decontamination which was obtained by this procedure was as follows:

When $^{99}TcO_4$ in HNO_3 solution was electrolysed and recovered about 90% of ^{99}Tc, the activity due to ^{106}Ru decreased to about 1/30 of the original solution by the use of a sheet of anionic membrane and to about 1/50 by two sheets.

14. Separation of Carrier Free Yttrium-90 and Lanthanum-140 with Anion Exchange Resin of Carbonate Form.

Seizo MISUMI and Tomitsugu TAKETATSU
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Kyushu University)

We studied the adsorbabilities of a tracer amount of strontium and barium in carbonate solution on an anion exchange resin by using strontium-90 in radioactive equilibrium with yttrium-90 and barium-140 with lanthanum-140. It was found possible to separate yttrium-90 from strontium-90 and lanthanum-140 from barium-140 since only yttrium-90 and lanthanum -140 were adsorbed on the resin.

Results obtained by the equilibrium method showed that radioactive materials adsorbed on the resin decreased with increasing concentration of ammonium carbonate, and that decay curves of these radioactive materials corresponded to curves of yttrium-90 with half-life of 64 hrs. or lanthanum-140 of 40.2 hrs.

The column method applied here was the following; strontium-90 or barium-140 in 0.08 mol. ammonium carbonate solution was passed through the resin bed and flowed out completely with 10 ml. of washing solution (0.01 mol. ammonium carbonate solution or water), whereas yttrium-90 or lanthanum-140 adsorbed firmly on the resin bed was eluted with 50 ml. of 1 N hydrochloric acid. At the beginning of the elution, the resin particles were disturbed by bubbles of carbon dioxide, but it was gradually settled down and became uniformly packed again. This disturbance did not affect the elution of the tracer since only yttrium-90 or lanthanum-140 was adsorbed on the resin bed. Since water was used as the washing solution, this method proved favourable to obtain the carrier free yttrium-90 or lanthanum-140 because other substances except hydrochloric acid were not present in the yttrium-90 or lanthanum-140 solution.

To determine the contamination of strontium-90 in the yttrium-90 solution obtained by this method, ferric chloride (Fe^{3+}, 8 mg.) and strontium chloride (Sr^{2+}, 9 mg.) were added to the solution. Yttrium-90 was co-precipitated with ferric hydroxide and filtered. The ferric hydroxide was dissolved in hydrochloric acid and after its solution was dried up with an infra red lamp, the radioactivity of the sample was measured. Strontium in the filtrate was precipitated as sulfate and its precipitate was filterd and ignited. Then, the radioactivity in strontium sulfate was measured. The result obtained showed that the radioactivity of strontium-90 was less than 0.5% of the total radioactivity. Similarly the contamination of barium-140 in lanthanum-140 was shown to be practically negligible.

The effluent obtained by this procedure was again passed through the resin bed after it was allowed to stand for about 30 days. The result obtained showed that the procedure was good enough to supply yttrium-90 continously.

Experiments were carried out by using 0.08 mol. solution of sodium or potassium carbonate in place of ammonium carbonate in the procedure. It was found that the cations of the carbonate salts had no effect on the separation of yttrium-90 from strontium-90.

15 Separation of Technetium by Distillation Methods

Takanobu SHIOKAWA and Masuo YAGI
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The separation of technetium from other fission products in aqueous solution is most commonly performed by the distillation method using perchloric acid or sulfuric acid. But these separation procedures are not so complete, therefore various kinds of oxidizing agent, such as potassium bichromate, potassium permanganate, perchloric acid, and sulfuric acid, were employed and technetium separations by them were discussed.

Radioactive technetium was technetium-99m growthed from molybdenum-99 and it was separated from molybdenum by an anion exchange method. The activity of fractionated solutions were measured in polyethylene tube with a well type sodium iodide scintillation counter.

The optinum conditions for the distillation using these oxidant were concluded as follows.

(A) $K_2Cr_2O_7$ method: Technetium is distilled with the best yield from 40 ml of the starting solution containing 1 g of the oxidant and 17.5 ml of concentrated sulfuric acid.

(B) $KMnO_4$ method: Technetium distilled also from 50 ml of the starting solution containing 0.5 g of the oxidant and 22 ml of concentrated sulfuric acid.

(C) $HClO_4$ method: Technetium is distilled also from 50 ml of the starting solution containing 40 ml of 60 percent perchloric acid.

(D) H_2SO_4 method: Technetium is distilled also from 50 ml of the starting solution containing 25 ml of concentrated sulfuric acid.

The yields of technetium-99m under the optinum condition and time required for the distillation procedure in each methods are shown in following table.

Distillation method	Yield (%)	Time required for dist. (min)
$K_2Cr_2O_7$	83	90
$KMnO_4$	79	90
$HClO_4$	95	90
H_2SO_4	55	240

16. Coprecipitation of Neptunium with Lathanum Trifluoride

Eiko Nakamura
(JAPAN ATOMIC ENERGY RESEARCH INSTITUTE)

It is well known that oxidized neptunium does not coprecipitate with lanthanum trifluoride whereas reduced neptunium is carried down almost quantitatively. Although this is often utilized for the practical separation of neptunium, what the oxidized or reduced state means is not clearly defined. Some believe that both neptunium (V) and (IV) are carried down by lanthanum trifluoride, whereas others believe that neptunium (V) is not. Sometimes the expression of "the lanthanum fluoride carriable state" is used in the place of the oxidation states.

In the present study, the different modes of coprecipitation behavior of neptunium (IV), (V) and (VI) are studied with aids of the tracers for neptunium (IV), (V) and (VI).

The tracers are prepared by solvent extraction with tributyl phosphate and/or thenoyl trifluoroacetone. The oxidation state of neptunium used is determined according to the solvent extraction behavior as well as the coprecipitation behavior.

The distribution of neptunium (IV), (V) and (VI) between tributyl phosphate and some mineral acids had been determined in a previous study. After measuring distribution ratio of neptunium used in this study, the oxidation states are assigned by the comparison between these two values. On the other hand, it is well known that zirconium phosphate carries down only neptunium (IV) leaving neptunium (V) and (VI) in the solution.

Results show that neptunium (IV) and (V) can not be separately identified according to the behavior in carrying down with lanthanum trifluoride, while they are identified by the behavior in the solvent extractions or in the coprecipitation with zirconium phosphate. Thus it is presumed that both neptunium (IV) and (V) are carried down almost completely with lanthanum trifluoride while neptunium (VI) remains in the supernatant solution.

17. Separation of Carrier-Free As-77 from Germanium Targets

Mariko Inarida

(Department of Mining, University of Tokyo;

The bombardment of germanium with neutrons gives A_s-77 by the reaction, $^{76}Ge\ (n, \gamma)\ ^{77}Ge \xrightarrow{\beta} \ ^{77}As$. The author studied the separation of As-77 from germanium targets in carrier-free form, with extraction method by TBP.

As-77 and Ge-77 are used as the tracer for study on solvent extraction behaviors of arsenic and germanium in the hydrochloric acid solution and TBP. As-77 (carrier-free) is easily extracted from 3N hydrochloric acid solution, Ge-77 (2×10^{-2} M) is not extracted from these conditions. The irradiated germanium was heated and dissolved with aqua regia, provided with a reflux condenser. The irradiated germanium dioxide was dissolved with water. The solution was made 10 ml of hydrochloric acid solutions of 3 N. It was shaken with 5 ml of 50% TBP-kerosine in a separatory funnel for a minute. Arsenic was back extracted to aqueous layer by the addition of sodium chloride solution of 1 N to organic layer and by shaking the layer for one minute. 50% ~ 60% extraction ratio was obtained at optimum condition. The measured half-life of the isolated activity was 38.7 hours.

18. Separation of Arsenic from Germanium Target Irradiated by Protons.

K. Saito, S. Ikeda and M. Saito
(Institute for Nuclear Study, University of Tokyo,
and The Research Institute for Iron, Steel
and other Metals, Tohoku University)

Distillation and extraction methods were examined in order to study the separation of radioactive arsenic including ^{74}As in almost carrier-free state from germanium and germanium dioxide irradiated by protons, the energy ranging from 8 to 15 MeV. Arsenic was distilled as arsenous chloride with the aid of hydrogen bromide, after the removal of germanium as tetrachloride, in a current of nitrogen. The distillation proceeds rapidly and radioactive arsenic was collected in a good yield. The extraction of arsenic diethyldithiocarbamate with carbon tetrachloride, which is used for the photometric micro-analysis of arsenic was satisfactorily applied to the separation of almost carrier-free arsenic, provided that the pH is duely adjusted and a sufficient amount of the reagent is present. By extracting back the arsenic with diluted aqueous ammonia, radioactive arsenic was collected radiochemically pure and used for the measurement of conversion electron spectrum of ^{74}As.

19. Extraction of Almost Carrier-Free Niobium Isotopes from Zirconium Irradiated by Protons

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and The Research Institute for Iron, Steel
and Other Metals, Tohoku University)

The Extraction of radiochemically pure radioactive niobium in almost carrier-free state was examined to be used for the source preparation for conversion electron spectrometry.

The nuclides were produced by the reaction, ^{92}Zr (p,n) ^{92}Nb and the niobium was separated by the following methods. Ellenberg's method (Anal. Chem., 26, 1045 (1954)) for the separation of niobium from tantalum with tribenzylamine was satisfactorily applied to the extraction of niobium from zirconium. Back-extraction of niobium could also be made with diluted aqueous ammonia, 3% hydrogen peroxide solution or 2 N hydrochloric acid and radiochemically pure niobium collected by the use of radio-colloid formation. By the utilisation of Milner's method (Analyst, 80, 380 (1955)), almost carrier-free niobium was obtained by the extraction with methyl-iso-butyl-ketone (hexone) from 10 M hydrofluoric acid solution containing 6 M sulphuric acid and 2 M ammonium fluoride, the efficiency being more than 95%; it appears as if considerable amounts of radioactive niobium remains in the aqueous phase, when zirconium fluoride is present in the aqueous phase.

20. Separation of Technetium

Masayoshi Ishibashi, Taitiro Fujinaga and Mutsuo Koyama
(Chemistry Institute, Faculty of Science,
University of Kyoto)

Carrier free separations of Tc from target Mo and from fission product have been investigated. Sample Tc was prepared by the (p,n) reaction on Mo using the cyclotron of the Institute for Nuclear Study, Univ. of Tokyo. After two months cooling, no other radioisotopes except ^{95m}Tc and ^{96}Tc were identified in the sample by the gamma ray spectrometer.

Distillation Method Tc was separated from others by distilling it from sulfuric acid solution as Tc_2O_7. In the present work, the presence of oxidizing agents such as perchloric acid or nitric acid was found very effective to promote Tc distillation. Ru and a part of sulfuric acid are distilled simultaneously with Tc.

Extraction Method It is well known that TcO_4^- in 4 N-KOH solution can be extracted into pyridine. Over 99% of Tc and a part of Ru, Mo, and W were found extracted by the method, however the Ru, Mo, and W could be removed from Tc by a reverse extraction. Sr-Y, Ce-Pr, Zr, sulfate and chloride do not interfere with the extraction of Tc.

The separated Tc was then passed through the H type cation-exchange resin to remove potassium ions.

21. Separation of Radioactive Rhodium from Ruthenium Target

Hikaru SHIMOJIMA
(Tokyo Institute of Technology)

Chemical separation was made from a Ruthenium target of natural isotopic ratio bombarded with a proton from 63 inch cyclotron at the Institute for Nuclear Study, University of Tokyo. Carrier free and salt free separation was needed to prepare sources for a β-spectrometer and for a γ - γ angular correlation measurement in the study on the decay of Rhodium-102.

The fundamental experiments were made on the each separation processes,

(1) Separation with precipitation process, ferric chloride was added to the solution as a collector of Rhodium.

(2) Ion exchange resin process.

(3) Solvent extraction process.

(4) Electrolytic reduction process.

Chemical separation and source mounting were undertaken in combining the processes mentioned above.

There found a great difference in chemical behaviours when or without carrier added.

The followings were discussed in detail.

(i) Alkaline fusion and bisulfate fusion.

A sample of target, potassium hydroxide, potassium nitrate, ferric chloride (collector) were mixed and put in a nickel crucible, and heated to 400°C for 20 min. Residue of rhodium oxide was put in bisulfate fusion, and was made completely soluble to an aqueous solution.

(ii) Extraction rhodium of lower valence with organic solvents as ether, ethyl acetate, etc. Even without carrier, over 80% of extractions were made.

(iii) Adsorption and desorption to ion exchange resin. Kd were determined with a batch method, in rhodium-chloride system with 0.1, 0.3, 1, 3, 6, 9, 12 N HCl, in cation and anion exchange resins as well. With cation exchange resin, Dowex 50W-X8, rhodium was not adsorbed, in any of these, neither with anion exchange resin in over 3N HCl, but adsorbed in less conc. range of HCl.

Without carrier, a part of rhodium was found adsorbed quite strongly, and very hardly recovered, unless heated for long hours in boiling HCl.

Separation of rhodium from ferric, ruthenium etc., are very easy and complete with a use of ion exchange resins.

22. The Diffusion of Gaseous Fission Products from Semi-Homogeneous Nuclear Fuel.

Seishi Yajima, Sumio Ichiba,
Yuichiro Kamemoto and Koreyuki Shiba
(Japan Atomic Energy Research Institute)

Semi-homogeneous nuclear fuel is consisted of graphite powder and uranium dioxide powder which is homogeneously dispersed in the graphite powder. In our previous study, it was shown that, when a mixture of uranium dioxide (the diameter of the uranium dioxide particle was about 0.5 microns) and graphite powder in the weight ratio of 1:20 was irradiated with JRR-1 neutrons, about 80% of fission products recoiled out of the uranium dioxide powder and was captured by the graphite powder.

The investigation of the behavior, at high temperature, of the gaseous fission products which are captured in graphite powder will be of importance in connection with the reactor technology of the semi-homogeneous reactor.

In our experiment, the diffusion, at 400°, 800° and 1200°C, of Xe-135 and I-133 which were captured in several kinds of graphite powder was studied. The mixture of 1 g of graphite and 50 mg of uranium dioxide was irradiated in an experimental hole of JRR-1 at a thermal neutron flux of approximately 5×10^{11} neutrons/cm^2. sec. for about one hour. The irradiated sample was washed with a hot 6N-nitric acid solution to dissolve uranium and neptinum, and dried at 70°C. It was evident in our previous study, that the fission products captured in graphite were not leached with a nitric acid solution if the treatment is done in a short duration.

The fission products captured in graphite were cooled for 25 hours or 50 hours after irradiation and used for the diffusion experiment. During such cooling period, the predecessor of Xe-135 and I-133 were predominantly built up respectively. Graphite sample was heated in a stream of argon at 400°, 800° and 1200°C, and Xe-135 and I-133 which were released from graphite were trapped respectively in a charcoal trap and copper trap at 400°C. At appropriate intervals these traps were replaced by new ones.

The amounts of Xe-135 and I-133 captured in each trap were determined with gamma-ray spectrometry and the relation between the diffusion amounts of these nuclides and diffusion time was obtained.

The results show that there are two mechanisms for diffusion in a graphite grain, that is a rapid diffusion observed within about one hour with the subsequent slow diffusion after about one hour.

The amounts of these nuclides for rapid diffusion are appreciably greater than those for slow diffusion and the amounts vary with the temperature and the kinds of the samples. The amounts of diffusion in the natural graphite samples are appreciably greater than those of artificial graphite or the amorphous carbon samples. It will be suggested that the dependency of diffusion amounts on the kinds of samples will be related to the pattern of dislocations in the graphite grains.

The activation energies of these nuclides were obtained from the inclination of the slow diffusion curve and the values of about 2,000 cal./mole and of about 4,000 cal./mole were shown for each nuclides respectively.

23. The Purification of Americium from Reactor Wastes

Keiji Naito
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Japan Atomic Energy Research Institute)

Around 50 mg amount of americium was purified from large amount of impurities. The source of americium for this separation was a 5.6 l of waste solution from Hanford Reactors. The rough separation of large amount of impurities such as aluminum, bismuth and plutonium from the solution was carried out by precipitation method.

As the purification method, the anion exchange method was used. The residual plutonium, iron and bismuth were removed by using 9 mol HCl elution, and lanthanum was separated by using 5 mol NH_4SCN elution. The last impurity, aluminum, was removed by additing 2 mol NaOH solution repeatedly on the cation exchange column on which americium solution was adsorbed. Finally 95 ml of spectrographically pure americium solution was obtained, and the recovery of americium was nearly 100%.

(This research was carried out at the Radiation Laboratory, University of California, Berkeley, California, U.S.A.)

24. Determination of Small Amounts of Radionuclides in JRR-1 Primary Cooling Water.

Kaoru Ueno

(Japan Atomic Energy Research Institute)

For the operation of a high neutron flux, water cooled reacter, the detection or determination of radionuclides in the coolant are extremely important.

A sample of primary cooling water, which was taken from the stainless steel loop facility of JRR-1 at May 9, 1959, showed gamma activities of about $10^{-4}\,\mu c/ml$.

The coolant usually contains many kinds of radionuclides of widely different half-lives. They comes from neutron activation of fission. Therefore, the characteristics of the gamma radiation found in the sample were studied gamma-spectrometrically.

The gamma spectrum showed many high peaks at 0.32, 0.51, 0.83, 1.1 and 1.3 MeV. In order to simplify the analysis of this complex spectrum, samples were treated as follows:

The sample solution was dried and then dissolved with 11.4 N hydrochloric acid. This solution was transfered on to a Dowex 1 (H type) anion exchange resin column bed (ϕ 1 cm h 10 cm 100 - 200 mesh). The nuclides adsorbed on the column were eluted successively with acid solutions of decreasing acidities (11.4, 6.0 and 3.0 N hydrochloric acid). Thus gross separations of nickel, manganese, cobalt, and iron were accomplished. Observing the gamma activities of fractions from the anion exchange column with the 256 channel pulse height analyzer, the nuclides were identified by gamma energy, chemical property and half life. These nuclides found are given in Table 1 as well as the probable ways of formation.

Table 1. Nuclides in Stainless Steel Loop Coolant.

Nuclide	Half Life	Relative Concentration %	Method of Formation
^{54}Mn	310 day	12	^{54}Fe (n,p) ^{54}Mn
^{58}Co	72 day	58	^{58}Ni (n,p) ^{58}Co
^{60}Co	5.3 y	13	^{59}Co (n,γ) ^{60}Co
^{65}Zn	245 day	9	^{64}Zn (n,γ) ^{65}Zn
Unknown		8	

The radionuclides in coolant are supposed to come from (1) activation of impurities in water, (2) activation of water itself, (3) corrosion and scale formation, (4) fuel and fission products escaped into water from the reacter fuel solution.

The present result shows that the radionuclides found in the sample were formed by activation of impurities and corroded material presented in the water.

25. Studies on the Treatment of Radioactive Liquid Wastes

--- Removal of Radioactive Calcium and Strontium ---

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The supernatant produced on the decontamination of the low-level liquid wastes, but in a large amount, by means of the coagulation with hydroxides, must be not only neutralized but also controlled of its quality before it is disposed, directly or after secreening, to any of public water areas. Therefore, as alkaline coagulant aids, NaOH, Ha_2CO_3, $NaHCO_3$ would be more recommendable than ammonia or lime, which is apt to produce, respectively, ammonium salts or fine lime precipitates, after the neutralization, in the supernatant.

In our experiment, ferric hydroxide was used as the coagulant for its merit that it can raise favourably the pH value of the waste for the absorption process.

By the ordinary absorption process for water treatment with ferric hydroxide, Y and Ce are removed well at a pH range from 7 to 8, while Sr and La are scarecely removed. On the other hand, a past study reported that Sr could be removed with a ratio of 99%, when ferric hydroxide was precipitated with NaOH, under the coexistence of ammonium salts. For such a decontamination of radioactive strontium, our study was carried out to obtain further data on the effect of pH value as well as on the optimum condition producing good ferric hydroxide precipitates.

A sample was prepared in a total volume of 100 ml, containing ^{45}Ca (p-2) or $^{89,90}Sr$ (c.f.) (approximately by 25,000 cpm/ml) in 1 ml, a carrier solution of Ca or Sr of 0.001 M/l in 0 - 30 ml, Fe^{+++} solution of 0.1564 M/l in 5 ml and a coagulant aid (NaOH, NH_4OH or Na_2CO_3). After settling the precipitates, the supernatant-activity was counted, then the removal ratio was calculated.

With every of the three coagulant aids, the removal ratio remained within 0 - 15% for both of Ca and Sr at a pH value 3 - 5.

After raising the pH value with NaOH, however, a removal ratio of 95% was obtained at a pH value of 10.5, and the carrier amount of both Ca and Sr did not change so much. Further high dose of NaOH unfavourably affected the formation of ferric hydroxide precipitates.

With Na_2CO_3, a removal ratio of 70% or 97% was obtained, respectively at the pH value of 7.0 or 9.2 - 9.6, without resulting any bad effect by the increased amount of carriers.

With NH_4OH, a removal ratio of 43% or 92% was obtained, respectively at a pH value of 7.5 or 8.2, but with significantly bad effects, lowering the removal ratio, caused by the more carrier amount.

On the removal of Ca and Sr with ferric hydroxide, any other coagulant aids than Na_2Co_3 did not result good removal at the neutral pH range.

With every of NaOH, Na_2CO_3 and NH_4OH, the higher pH value produced the more removal efficiency than 95%, while NH_4OH was not so preferable, because it lowered the ratio with the increased amount of carrier and also harmed the waste quality, other than radioactivity, for its disposal to public water bodies.

Excessively large amount of NaOH hindered precipitation action, while Na_2CO_3 often caused floating flocs, especially when the CO_2 gas produced by agitation was not adequately released.

26. Decontamination of Radioactive Waste Solution by Adsorption with Activated Carbon and Argine Mixture

Kichizo Tanaka and Yoshio Koda
(Government Industrial Research Institute of Nagoya)

A survey of adsorption methods for the removal of fission products from waste solution containing high salt contents was mainly made. Several adsorbents have been used for decontaminating water and radioactive waste solution with varying degrees of efficiency. The decontamination of fission products in the waste solution was studied by adsorption with activated carbon and argine mixture compared with activated carbon and ion exchange resins.

The mixture was prepared by the addition of aqueous sodium arginate as the droplets to the acid solution suspended with activated carbon, thus formed precipitate was washed with 1N H_2SO_4, dried at 70° C for 24 hrs, and then evacuated for 1 hr. Activated carbon was also evacuated for 1 hr. before use. Dowex 50 X-4 and Dowex 2 (50-100 mesh) were conditioned with 1N sulfuric acid solution.

The following radioactive materials were used as contaminants; ^{137}Cs, ^{90}Y were obtained as the chlorides and ^{106}Ru, ^{95}Zr-^{95}Nb were obtained as the nitrates. Stock waste solution was a mixed fission product contaminant consisting of 30% ^{144}Ce, 10% ^{147}Pm, 3.5% ^{90}Sr, 3.2% ^{106}Ru, 2.7% ^{137}Cs and residual percent traces of a large number of other radioisotopes. The pH of this solution was taken by test paper, but in a few case, using a HORIBA glass electrode pH meter.

Each 2 gr. of adsorbent and 20 ml. of aliquot were mixed and agitated mechanically in the glass stoppered bottle for 2 hrs at 20° C., and then centrifuged. Each 1 ml of dried samples of the supernatant solution and 1 ml of initial sample were taken, placed in a stainless steel dish respectively, dired and counted using a G.M. mica end window tube (1.43mg/cm thick). Difference between the initial and final count rate represented the removal. From the ratio between initial and final count rate, distribution ratio was also determined.

This adsorbent was packed in columns successfully adsorbed a variety of fission product cations. Overall percent removals were shown as;

$$\left(1 - \sum_{i=1}^{N} A_i \ v_i \ / \ A_0 V \right) \times 100\%$$

where N is the numbers of final fraction, A and A_0 are the count rate of stock solution and i-th fraction per ml. respectively, v is the volume of eluate at i-th fraction and V is the total volume of eluate from 1 to i-th or N-th fraction.

The removal and distribution ratio were obtained as a function of pH of waste solution, the effects of the addition of carrier and of impurities particularly other salt on removals were also studied.

75% of ^{90}Sr in 500 ml was removed from the solution containing 80 mg strontium chloride per 1 litre in the flow rate of 5 cc per minutes by passing through the column in which activated carbon argine mixture was packed 5 grs, while only 36% of ^{90}Sr was removed by activated carbon treatment.

27. Study on the Treatment of Radioactive Liquid Waste by Chemically Modified Pulps

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Morihisa Maruko, Mutsuaki Shinagawa
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This report discussed about the possibility of the treatment of radioactive liquid waste by modified pulps. Oxidized pulps and phosphorylated pulps were used. In this investigation, the decontamination of ^{90}Sr (^{90}Y) was discussed mainly.

One gram of modified pulps was inserted in the column and radioactive solution was passed through it. 20 ml of each fraction was collected from the passed solution. One milliliter of each fraction was dried and its activity was measured G.M. counter.

The percentage removal of contaminant was as good as over 95% for both substances. The capacities of oxidized pulps and phosphorylated pulps were about 2.5 meq/g and 3.2 meq/g respectively. These modified pulps showed the ion exchange properties similar to those of the ion exchange resins (Amberlite IR-120).

28. The removal of the contaminating nuclides in aquous solutions with bentonite and precipitants

Hisateru Okuno and Hirofumi Arino
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Many works have been done with regard to the decontaminating capacity of the bentonites and these clays were found to be useful for the removal of radioactive cations in aquous solutions.

However, as bentonites swell in water easily and form very stable suspensions, it is difficult to separate bentonites from aquous solutions. Therefore, we have studied the coagulating and precipitating power of the carbonates of Ba, Ca and Mg for the purpose of getting the bentonites in compact forms as far as possible. According to our experimintal results, fairly good separations of bentonites from aquous phases were obtained without any decrease of the decontaminating capacities of the bentonites.

Bentonite which occured in Gunma Prefecture in Japan were added to solutions containing $^{144}Ce\ (NO_3)_3$.

Then, known amounts of the precipitants were added to the solutions. The precipitating velocities of the suspensions were observed. After stirring, these solutions were let stood still for 24 hours. After 24 hours aliquots of the supernatant aquous solutions were taken and their radioactivities were measured with the use of the Baird Atomic scintillation counter.

Under our experimental conditions, $BaCl_2$ (4 meq. or more) was effective for coagulating the bentonite suspensions, while the coagulating power of $(NH_4)_2\ CO_3$ was very small. $CaCl_2$ was effective as well and $MgCl_2$ (2 meq. or more) was most effective.

When chlorides of Ba, Ca or Mg and $(NH_4)_2CO_3$ were used in equal equivalent, the precipitating action of the carbonates produced in situ, were not satisfactory. But when either one was in excess to the other, the precipitating power was increased.

Generally speaking, whether the coagulating salts are present or not, nearly the same efficiency of removal of the contaminating nuclides were obtained with the bentonites. And the addition of the carbonates of Ba, Ca or Mg was effective in separating the bentonites from the aquous phases.

29. Studies on the Decontamination of Radioactive Contaminants from Water. Part 3

Vermiculite as an Ion-exchanger.

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K.K. Josui Kogyosho)

Although the ion exchange process is one of the most efficient methods for removing radioactivity from water, the cost of the ion exchange resins may limit widespread use unless suitable regeneration techniques are developed.

The clay mineral vermiculite exhibits the exchange of lattice ions, and the removal efficiencies of vermiculite do not appear to be significantly different from the sulfonic acid type cation exchange resins. In order to determine the breakthough capacity of the vermiculite, a calcium chloride solution (10^{-3} M as Ca^{++}) was passed through a column filled with sodium form sample regenerated with 3% sodium chloride solution, and fractions of the effluent were analysed for the calcium ion.

The usable 10% breakthrough capacities of 17 samples of vermiculite (20 to 60 mesh) were 0.297 0.541 and 0.411 0.859 meq./ml for 40 and 100 gram sodium chloride regenerant per liter. Using a 0.1 M hydrochloric acid solution for the acid treatment of the vermiculite, Na-Ca ion exchange breakthrough capacities of the acid treated samples were 0.356 0.672 and 0.475 0.898 meq. per milliliter for 40 and 100 gram per liter regeneration level. When the concentration of hydrochloric acid for the acid treatment was varied from 0.01 to 6 M, the maximum Na-Ca ion exchange capacities with 40, 60, 100, and 250 g NaCl/l regeneration level were 0.560, 0.769, 0.870, and 0.947 meq. per milliliter.

For the most effective removal of cesium from salt solution containing about 0.3 ~ 1.5 per cent by weight of mixed sodium chloride - calcium chloride, vermiculite is recommended. The removal efficiency of 99% of higher is possible.

30. The Separation of ^{90}Sr and ^{90}Y by Paper Electrophoresis

Shoichi Kawamura and Masami Izawa
(National Institute of Radiological Sciences)

The separability of ^{90}Sr and ^{90}Y by paper electrophoresis has been investigated using various acids as electrolytes. pH of the electroyte solutions were adjusted by adding NH_4OH. About 0.005 cc solution containing ^{90}Sr and ^{90}Y was spotted at the point of 10 cm from one end of the filter paper (Toyo filter paper, No. 3, 2 x 40 cm). The paper was clamped between plastic plates and voltage (10 v/cm) was applied on the paper placed in conventional migration cell for 1/2 - 2 hours.

After drying the paper, the electropherogram was cut into 1.0 cm segments and counted the radioactivity of each section by end-window GM counter. In some cases paper chromatogram-scanner was used for recording the activity.

Results:

(1) 0.01 M hydrochloric acid and 0.05 M formic acid: Separation was very poor with or without Sr and Y carriers in the solution to be analyzed.

(2) 0.05 M oxalic acid: Separability was maximum at pH 2 and 4. At pH 4, ^{90}Sr moved 10 cm in 2 hours, while ^{90}Y remained at origin.

(3) 0.1 M tartaric acid: ^{90}Sr and ^{90}Y could be separated at 10 cm in 2 hours when no carriers were added. Separability became poor by adding NH_4OH to the electrolyte, or by adding Sr and Y carriers to the solution to be analyzed.

(4) 0.05 M citric acid: Distance between the spot of ^{90}Sr and ^{90}Y was 10 cm, and it was 13 cm, when the pH was adjusted to 2.5 by adding NH_4OH. The electropherogram was not changed appreciably by the addition of Sr and Y carriers.

(5) 0.1 M acetic acid: Separation was very rapid and complete when no carrier was added; 6 cm in 30 minutes and 17 cm in 90 minutes. They were not separated completely when carriers were added.

From these experiments, the most suitable electrolyte for simple and rapid separation of ^{90}Sr and ^{90}Y is 0.1 M acetic acid solution when the active solution is carrier-free, and it is 0.05 M citric acid solution (pH 2.5) when the active solution contains Sr and Y carriers.

31. Adsorption of Fission Products by Various Kinds of Soils.

Chuichiro Sakurai, Masuo Yagi and Takanobu Shiokawa
(Ikeshinden High School and Radiochemistry
Research Laboratory, Shizuoka University)

It has been well known that the soil is a good adsorbant for fission products or radioactive fall-out. Therefore, the peculiarity of the adsorption of fission products by various kinds of soils found in Shizuoka Prefecture was investigated fundamentally.

The soil samples were collected from rice fields or vegetable gardens.

The adsorption ratio was calculated as follows:

Adsorption ratio (%) = Activity of soil x 100/Activity of soil + Activity of supernatant

Procedure was as follows:

0.5 g of dried soil was added to the 50 ml of solution containing radioactive tracer in an erlemyer flask. The solution was shaken vigourously for one minute and centrifuged after 18 hours standing.

As the results, all kind of soil had high adsorption ratio for the fission products, especially for cesium-137. The adsorption ratios were increased by an addition of a small amount of calcium ion, but were decreased by the large amount of it and phosphate ion.

32. A rapid Method for Determining Sr-90 and Cs-137 in Radioactive Fall Out Using an Ion-exchange Resin

Hiroyuki Tsubota
(National Institute of Radiological Sciences)

A rapid method for determining Sr-90 and Cs-137 in radioactive fall out using an ion-exchange resin has been devised based on the following two fundamental experiments:

1) Fe^{3+}, Al^{3+}, and rare earth ions deposit in a resin because of their hydrolysis-properties at high pH-values. They are not eluted from a column when ammonium formate or ammonium

acetate aq. solution is used as elutriant, pH of which is about 7.

2) The separability between Ca and Sr increases by adding particular organic solvents such as methyl alcohol, ethyl alcohol, acetone, and cellosolves, etc.. By adding dioxane, however, the separability is not changed appreciably. From the facts, it is supposed that Ca and Sr form water soluble complex ions with these organic solvents. Here, the ammonium acetate-methyl alcohol system is employed from a practical point of view, and in the system the mixed ratio for the best separability between Ca and Sr is in the range of 40 - 60% alcohol in volume.

Column:

Amberlite CG - 120, 100 - 200 mesh, ∅ 2.0 x 15 cm, H^+ - saturated form.

Elutriants:

Elutriant I, 2M ammonium acetate aq. soln: methyl alcohol = 1 : 1 (in volume) mixed soln.

Elutriant II, 2M ammonium acetate aq. soln.

Procedure:

1) Add 5 - 10 ml of 3N HCl to the dried chloride sample, and dilute to 30 - 50 ml with distilled water.

2) Elute Na^+, K^+, Mg^{2+} and Ca^{2+} with 300 ml of Elutriant I at the flow rate of 3 ml/min.

3) Elute Cs^+ and Sr^{2+} with 220 ml of Elutriant II at the flow rate of 2 - 3 ml/min.

4) Finally, elute Ba^{2+}, Fe^{3+}, Al^{3+}, and rare earth elements with about 500 ml of 4N HCl.

5) Determine the natural strontium content in the effluent of step 4) by EDTA titration method. Then, add Sr- and Cs-carriers, decompose EDTA, and precipitate $SrCO_3$ by adding Na_2CO_3. Measure the radioactivity in the $SrCO_3$-ppt. with a suitable counter decided.

6) Add $HClO_4$ to the filtrate of step 5), and precipitate $CsClO_4$. Measure the radioactivity of Cs-137 in the precipitate.

This procedure can be applied when the weight of the sample as chlorides is less than 1.5 gr. When the weight of chloride sample (W gr) is larger than 1.5 gr the column length (L cm) and the volume of elutriants (V ml) can be determined by the following relations:

$$L \geqq 10 + 5W / 1.5$$

$$\text{and} \quad V = V_o + L / 15$$

where V_o is the volume of elutriants indicated in steps 2) and 3) above.

33. Method for Determination of Strontium-90 in Fallout

Yuji Yokoyama and Tetsuo Hiyama
(Department of Chemistry, Faculty of Science,
University of Tokyo)

A new method is proposed to separate strontium-90 from large amounts of iron, aluminum and calcium in fallout samples. The method is based on the difference in the formation constants of metal-EDTA complex compounds among these metals. We found that, in suitable condition, strontium remains as cation, while the major part of iron, aluminum and calcium exists in the form of complex anion with EDTA. Cation exchange resin is used to separate cation (Sr) from complex anion (Fe, Al, Ca).

The procedure of anlysis is as follows.

Rain water samples are collected during the period of one month on a collecting surface of 1.0 m^2 area. Then the water is evaporated to dryness. After evaporation, strontium is extracted with hydrochloric acid. Extraction is repeated sevel times and the combined extract is evaporated. The extract contains considerable amount of salts. Generaly, it consists of about 10 g of chloride. The usual composition of the extract is estimated as follows:

Fe (III) 540 mg, Al 270 mg, Ca 800 mg, Mg 330 mg, Na 1300 mg, K 330 mg.

In the following procedure, we can treat 10 g of chloride as evaporated extract. The extract is dissolved with hydrochloric acid and diluted to 0.1N. Acetic acid (3.6 ml) and EDTA (4H form) 16 g are added to the solution. The acidity of the solution is adjusted to pH=4.0 with ammonia water and volume of the solution is made 600 to 1000 ml with water. Then the solution is passed through the resin column which consists of Dowex 50-X8, NH_4 form, 40 ml. After passing the sample solution, the column is washed with 300 ml of EDTA solution, (0.1 M, pH 4.0) which contains acetic acid (0.1 M) as buffer. Iron, aluminum, calcium and rare earth fission products are completely removed, while strontium is entirely absorbed in the column. Then strontium is eluted with 150 ml of EDTA-solution (0.1 M, pH 6.0) containing acetic acid (0.1 M).

The method is verified with tracers of strontium-90 and calcium-45 for synthetic samples of chloride mixture.

Result shows that the separation is fairly complete, even though the method is so simple.

34. Strontium-90 Concentration in Human Diet

Kunio Seto and Masahiro Takebe
(Department of Chemistry, Faculty of Science,
Tohoku University, Sendai)

Food materials were collected according to the receipes for rural inhabitants from the agricultural district Daiwa-machi which lies about 20 kilometers north of Sendai during June-July, 1958 and the Sr-90 concentration was estimated from those in the three parts of the food materials, i.e., the staple food (brown rice and cereal, 35.0 kg.), the subsidiary articles of diet (vegetables, beans and fresh water fish, 41.6 kg.) and the water (filtered rain water, 140 l.). The procedure of chemical analysis was as follows. Each part of the food materials was reduced to ashes. The ashes were dissolved in dilute hydrochloric acid. Silica was eliminated in the usual manner and the basic acetate method was applied to eliminate phosphoric acid. The alkaline earths were precipitated as oxalates. The oxalates were converted to carbonates by heat treatment and dissolved in dilute nitric acid. Strontium was separated from calcium by repeating precipitation with fuming nitric acid, and precipitated as carbonate after barium chromate precipitation. The strontium carbonate was allowed to stand to establish radioactive equilibrium between Sr-90 and Y-90, and then dissolved in dilute acid. Yttrium-90 was collected in ferric hydroxide and β-activity was measured. The Sr-90 concentration in human diet for rural inhabitants collected from Daiwa-machi during June-July, 1958 was estimated at 5.59 $\mu\mu$c/day/person, 5.28 S.U., and the water part had the highest Sr-90 content of the three parts of the food materials.

35. Deposition of Strontium-90 and its Seasonal Variation in the Fallout Observed from April, 1958 to March, 1959 in Niigata City.

S. Koyama and T. Sotobayashi

(Faculty of Science, Niigata University, Niigata)

I. Procedure. A simple and rapid procedure has been developed for radiochemical determination of strontium-90 in fallout samples. In order to save many laborsome operations of precipitation and filtration the present procedure employs E.D.T.A. as a masking agent of interfering metal ions, especially ferric and aluminum ions in a fallout sample. The mixed calcium and strontium oxalates which were precipitated with ammonium oxalate from a solution of 2% E.D.T.A. made up to pH 4.0, are ashed and dissolved in 2 n hydrochloric acid. From this solution strontium-90 is singly separated by the ion exchange technique, as we reported previously. The use of E.D.T.A. makes possible a simpler procedure with a radiochemical yield greater than 98%. Such a high yield eliminates the need for measurement of recovery of strontium.

II. Deposition of strontium-90 and its seasonal variation in Niigata City (38°N, 139°E).

The fallout rate of strontium-90 in Niigata City is 13.6 mc./km^2y, from April, '58 to March, '59 and the value is two or three times as large as those in the Pacific side of Japan, for example, 5.3 mc/km^2y, in Tokyo. The reason why such a large value was observed is not only the fact that Niigata has the larger amount of precipitation in winter, but, also that there are many times of showery precipitations and their specific activities (dpm/mm) are several times larger, compared with those in the Pacific side.

Judging from the data observed from April, '57 to July, '59 the strontium-90 concentration in rain and snow has a seasonal variation with a maximum in spring and a minimum in late summer. On the other hand, meterologists have been already suggested that the atmospheric ozone shows a seasonal variation with a peak in spring and a valley in autumn. This analogy may be mainly due to the periodicity of the large scale sinking motions of air from the stratosphere to the troposphere, and provides a clue to the atomosheric processes which transport the radioactive debris back to the ground.

36. Sr-90 in Sea Water

Y. Miyake, K. Saruhashi and Y. Katsuragi
(Tokyo Kyoiku University and
Meteorological Research Institute)

It is a difficult task to determine a trace amount of radio-nuclides including Sr-90 dissolved in sea water, because of the interference of larger amount of sea salt.

As to the radiochemical analysis of radio-strontium in sea water which was collected near Bikini-Eniwetok area, Miyake and Sugiura (1955) used the oxalic acid to separate calcium and strontium from the larger amount of magnesium. Bowen and

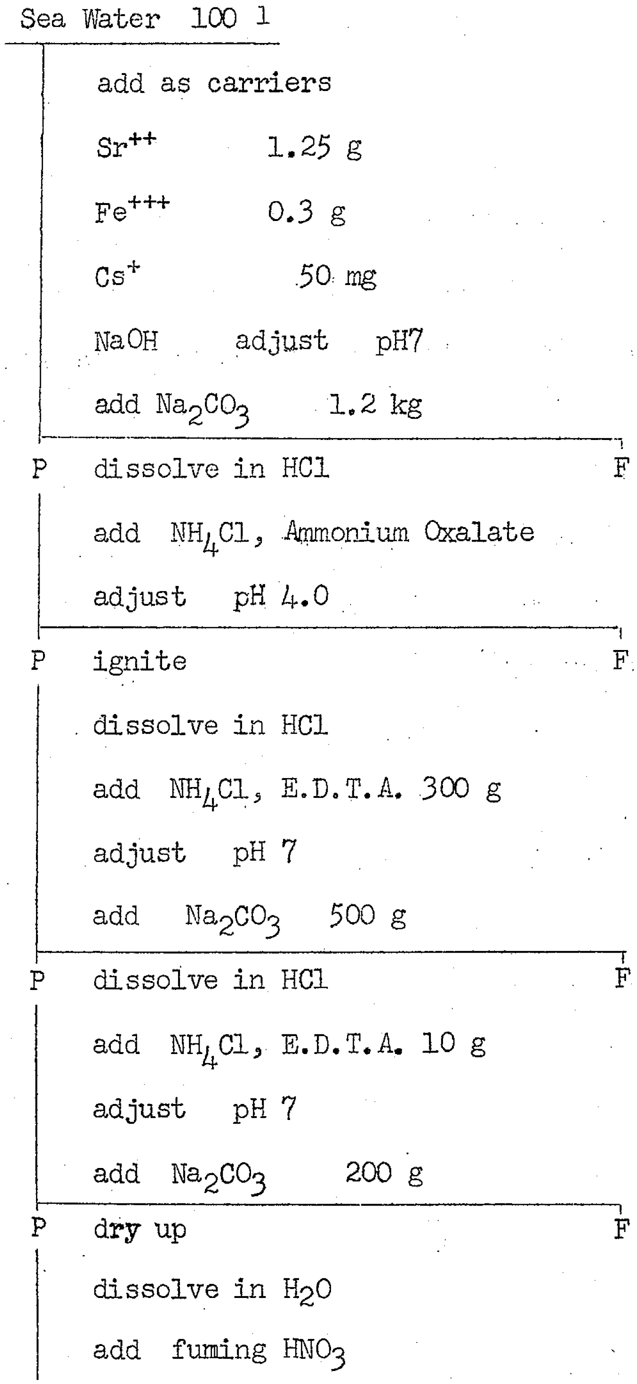
Sugihara (1959) made a determination of strontium-90 by using versene as a masking reagent for magnesium and calcium. Higano (1959) separated calcium and strontium as carbonate from sea water.

As a result of studies using Sr-90 as a tracer, the present authors arrived at the conclusion that the oxalate method is convenient to determine the Sr-90 from sea water. In this method, the yield of 80% of Sr-90 is obtained with a good reproducibility.

Before establishing the oxalate method, masking of magnesium and calcium with EDTA at different pH was tested. The result was unsatisfactory due to the poor reproducibility.

The activity of Sr-90 separated from sea water is measured with a thin wall counter surrounded by a steel shielding of 20 cm thick and anti-coincidence tubes. The scheme of the analytical procedure based on the oalic acid method is as follows.

The Scheme of Analytical Procedure



Sea Water 100 l

add as carriers

Sr^{++} 1.25 g

Fe^{+++} 0.3 g

Cs^{+} 50 mg

NaOH adjust pH7

add Na_2CO_3 1.2 kg

P dissolve in HCl F

add NH_4Cl, Ammonium Oxalate

adjust pH 4.0

P ignite F

dissolve in HCl

add NH_4Cl, E.D.T.A. 300 g

adjust pH 7

add Na_2CO_3 500 g

P dissolve in HCl F

add NH_4Cl, E.D.T.A. 10 g

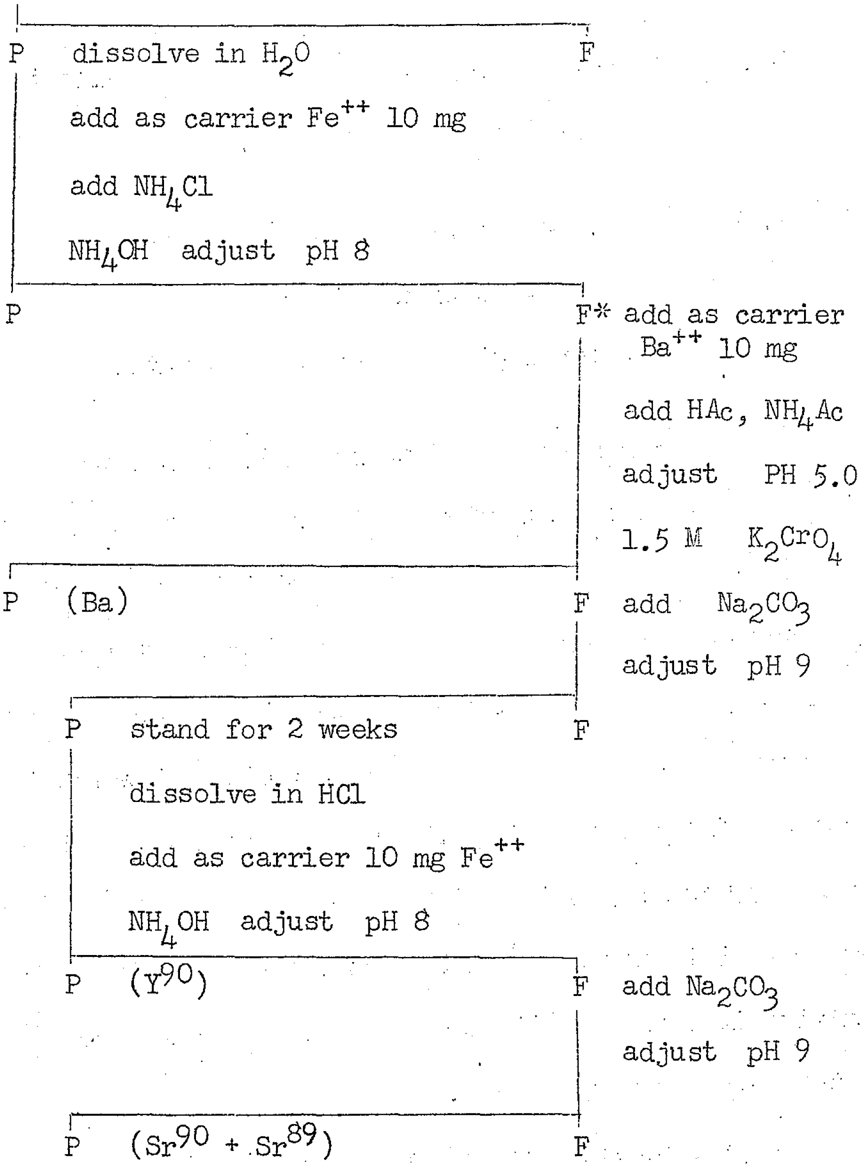
adjust pH 7

add Na_2CO_3 200 g

P dry up F

dissolve in H_2O

add fuming HNO_3


P
dissolve in H_2O
add as carrier Fe^{++} 10 mg
add NH_4Cl
NH_4OH adjust pH 8
F
P
F* add as carrier Ba^{++} 10 mg
add HAc, NH_4Ac
adjust PH 5.0
1.5 M K_2CrO_4
P (Ba)
F add Na_2CO_3
adjust pH 9
P stand for 2 weeks
dissolve in HCl
add as carrier 10 mg Fe^{++}
NH_4OH adjust pH 8
F
P (Y^{90})
F add Na_2CO_3
adjust pH 9
P (Sr^{90} + Sr^{89})
F

37. On the Relation Between Radioactive Fallout and Meteorological Conditions

Y. Miyake, K. Saruhashi, Y. Katsuragi and T. Kanazawa
(Tokyo Kyoiku University and
Meteorological Research Institute)

Miyake, Saruhashi and Katsuragi (1958) pointed out the effect of the local turbulence of the atmosphere as the possible mechanism of intrusion of the artificial radioactivity from the stratosphere into the troposphere. If there is such an effect, more radioactive material will be brought down to the earth by the rain caused by the cold front which is associated with a larger turbulence in the vertical direction. Koyama and Sotobayashi (1959) compared the activity of rain caused by both warm and cold fronts. They confirmed that the activity is larger in the rain of cold frontal type than that in the warm front type rain.

The present authors made the same kind of study concerning the radioactive rainfall in Tokyo of which results will be presented here.

Since we have a precipitation from 1400 to 2000 mm annually in Tokyo, to which 90% of the total radioactive fallout is attributed, the relation between the type of rain and activity was investigated. The comparison of the activity is done by converting it into the value of Sr-90. In order to eliminate the effect of rainfall amount, the concentration of the active material in the air column was calculated based on the method introduced by Miyake, Sugiura, Saruhashi and Kanazawa (1957). When the cyclone of the temperate zone passes north of 40°N on the north-east direction, the conspicuous cold front is generally associated with the cyclone. The rain along the cold front line is generally a scattered type with a smaller amount of precipitation. In this case, the larger turbulence occurs on the vertical direction in the air and the top of cloud often reaches 10 km above the ground. In such a type of rain, as the interval of rainfall is short and the rain drop is larger, the amount of radioactive fallout is smaller, but its specific activity (Sr-90 $\mu\mu$c/L) is the largest.

When the cyclone passed south of 40°N on the east or north-east direction, there are three types of rainfall as following:

1. by the effect of both, warm and cold fronts
2. by the effect of the warm front only
3. by the effect of the stagnant front along the southern coast of Honshu.

In these types of rainfall, the rain generally continues longer, and the rainfall amount is larger (20 mm - 30 mm on an average). In such a rain the total precipitation of Sr-90 is larger but the specific activity is smaller. The amount of rainfall which is associated with the cold front is less than 10% of the total, however, the amount of Sr-90 precipitated with such a type of rain reaches as high as 30% of the total which suggests the effectiveness of the cold front to bring the radioactive material on the earth.

38. Radiochemical Studies on "Bikini Ashes", Part IV.

On the Alpha Emitters.

Takanobu Shiokawa and Masuo Yagi

(Radiochemistry Research Laboratory, Shizuoka University)

The results of the radiochemical studies on the long lived fission products and induced radioactive nuclides found in "Bikini Ashes" were presented in the last annual symposium. However, the alpha emitting radioactive nuclides in the ashes were not yet investigated in detail, so that the analysis of the alpha emitters has been carried out now in addition to it, when it is five years after the fission on March 1st, 1954, and when the most of the short lived nuclides had decayed away.

In the present analysis, the separations of elements were carried out in usual manners by employing carriers or ion exchanger, and the identification of the nuclide was made by observing their characteristics in radioactivity by means of the proportional counter and the spectrum of alpha ray.

The helm-palms taken then off from the top of bambo-poles of the boat were ignited for the present analysis, and the ashes of them were used as the sample. The 10 grams of the ashes were treated with nitric acid by heating and the insoluble residues were fused with sodium carbonate, then dissolved also into nitric acid. Carriers were added to the combined solution and evaporated to dryness. At the first step ruthenium was distilled off with perchloric acid, and then silicates were removed by the dehydration process. Then, the sulfide group was separated in the acidity of 0.3 N hydrochloric acid by hydrogen sulfide and the next group was precipitated with ammonium hydroxide free from carbonate. The hydroxide precipitates were dissolved in the minimum of 6N nitric acid and was reprecipitated in the same manner. The last precipitates were centrifuged off and 5 drops of 5% hydroxylamine hydrochloride solution were then added into the precipitates to reduce plutonium to the trivalent state. The precipitates were then dissolved in the minimum of 8N hydrochloric acid and any of ferric chlorides were extracted three times the equal volumes of isopropyl ether saturated with 8N hydrochloric acid. The aqueous layer was then evaporated almost to dryness. The residue was dissolved in 10 ml of 9N hydrochloric acid containing 4 drops of concentrated nitric acid to oxidize neptunium and plutonium to the tetravalent state and the solution was run through the anion exchange column. When the level of the solution reached the top of the resin bed, 25 ml of 9N hydrochloric acid containing 5 drops concentrated nitric acid were run through the column, and the passed solutions were kept for the analysis of rare earths. Plutonium was eluted from the column with 9N hydrochloric acid containing ammonium iodide. Neptunium was then eluted from the column with 3N hydrochloric acid solution, followed and then uranium was eluted with 0.25N hydrochloric acid. The each fraction was evaporated to dryness to prepare the sample for alpha counting.

As the results, alpha activities of 7,380 cpm from plutonium fraction, of 80 cpm from neptunium fraction and of 5 cpm from uranium fraction were detected respectively. On the other hand, the long lived beta emitters in the same sample were also analysed.

The analytical results of the long lived nuclides in 10 grams of the helm palm ashes were summarized in following table.

Nuclide	Half-life	Amount detected(cpm)
^{60}Co	5.27 y	3,000
^{90}Sr	28 y	15,000
^{90}Y	64 h	15,000
$^{106}Ru(^{106}Rh)$	1.01 y	31,000
^{125}Sb	2.0 y	4,000
^{125m}Te	53 d	4,000
137Cs	29 y	2,500
$^{144}Ce(^{144}Pr)$	285 d	37,000
$^{147}Pm, ^{155}Eu$	2.6 y, 1.7 y	8,000
^{237}Np*	2.2 10^{6} y	80
^{239}Pu*	24360 y	7,380
U*	------	5

39. ^{7}Be in Meteoric Precipitations

Y. Miyake and T. Ohtsuka
(Tokyo Kyoiku University)

The radioactive isotope of beryllium ^{7}Be is produced in the atmosphere by cosmic rediation and it is dissolved in rain water and snow as beryllium hydroxide. The presence of ^{7}Be in meteoric precipitations was first reported by Arnold and Al-Salih (1955).(1) ^{7}Be decays with a half-life of 53 days and emits γ ray of 0.48 MeV. Up to now, several studies were published concerning ^{7}Be content in rain,(2), (3), (4) snow(5) and air.(6) On the other hand, the production rate of ^{7}Be on the earth has been calculated.(7), (8) According to the estimation by Lal et al. (1958), 7×10^{-2} ^{7}Be atoms per cm^2 column of atmosphere per second is produced in the atmosphere by cosmic rays.(8)

To a sample of rain water, Be^{++} and Fe^{+++} carriers are added. Supernatant solution is decanted and discarded after coprecipitating beryllium with ammonia. The precipitate is dissolved with hydrochloric acid, and the solution is filtered and made strongly basic to precipitate $Fe(OH)_3$ and other hydroxides. The supernatant solution is scavenged with Sb_2S_3

and $Fe(OH)_3$ successively to decontaminate fission product. The solution is then passed through an acetate-chloroform cycle to remove aluminum. Then beryllium is converted into $Be(NO_3)_2$ with concentrated nitric acid. The nitrate is ignited and weighed as BeO. The activity of ^7Be is measured by a single channel scintillation spectrometer which is equipped with a NaI(Tl) crystal of 1.5 inches dia. Radiochemical purity is tested by counting the activity with a low-level counter.

A sample of melted snow of 365 litres, collected on a polyvinyl chloride roof of 12 m^2 surface area, showed the activity of ^7Be of 4.1 ± 1.5 cpm. The chemical yield was 14% and no activity was found by β counting.

The another procedure of analysis is also being tested. After pH of rain water is adjusted to 3, Be^{++} carrier is added. The solution is passed through a column of cation-exchanging resin (Dowex 50, X-8). The beryllium is eluted with hydrochloric acid. The extraction and decontamination of beryllium from the elutant is done successively by adsorption of contaminants on anion-exchanging resin (Dowex 2, X-10) in HCl solution followed by scavenging with $Fe(OH)_3$ and finally by acetylacetonate-benzene cycle. The meteorological consideration on ^7Be in the atmosphere will be also discussed.

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40. The Change of ^{14}C Content of Atmosphere During Recent 50 Years

K. Kigoshi and Y. Tomikura

(Gakushuin University)

The recent change of ^{14}C content of atmosphere shows decrease by so called Suess effect during 1900 and 1945, and increase after 1950 by A-bomb tests. This change had been measured by several workers. But the exact knowledge on the figure of this change, and possible variation of the figure by local effects are useful data for geochemical problems and radiation hazard problems.

We measured ^{14}C content on the series of samples which was taken from a tree trunk cutting along at intervals of one or five years annual rings. The determinations of ^{14}C content of these samples are carried by β -proportional counting with acetylene gas. We have studied on the conditions of preparation of acetylene and on the characteristics of acetylene gas proportional counter.

The results on two trees (suburb of Osaka and Akita) show predicted smooth change of year-to-year. The measured increase after 1955 is nearly 2% per year. This agree well with the reported values obtained at New Zealand by Rafter and Fergusson.

41. Summary of the Deposition Potential of ^{99}Tc from Alkaline Solution and its Application to Standard Pure β Source on Thin Metallic Foil

N. Matsuura and H. Yumoto
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The University of Tokyo)

In this experiment Joliot's cell was adopted to deposit the technetium electro-chemically on the cathode of a thin metallic foil from pertechnetate solution. The rate of electrolysis and its completion was observed by measuring the radiation of the deposit with GM counter placed just behind the cathode. This method is recomendable to those nuclides which have soft β and no γ radiation, such as ^{99}Tc.

From the plots of Tc deposition rate against varying cathode potentials a well defined critical deposition potential of Tc from 2 N NaOH was obtained to be near 0.75 volt vs. S.C.E.

There are two possible processes for the deposition schema.

1) $TcO_4^- + 4H^+ + 3e = TcO_2 + 2\,H_2O$

2) $TcO_4^- + 8\,H^+ + 7e = Tc + 4\,H_2O$

Simple calculation of electrode potential for both according to Nernst's equation gave the value of 0.74 V (N.H.E.) and 0.50 V (N.H.E.) respectively. Otherwise the calculation from the result by Flagg et al. gave 0.77 V and 0.61 V respectively, the former of which is near to ours. Partly for this coincidence and partly for another related observations, present authors prefer the equation (1) in alkaline medium.

Other metals as well as silver were also found to be available as cathode metals for deposition of Tc. The foil with ^{99}Tc deposited turns out to be an excellent β standard source in the point of self scattering and self absorption.

42. Standard Sample of Surface Area Monitor

O. Yura and K. Maeda

(Electrotechnical Laboratory)

It is prescribed for surface area monitor that the standard sample of the monitor must be made of uranium oxide U_3O_8 (its activity below 3000 dpm) uniformly spread over the metal surface (its area above 50 cm^2) or of RaD + E + F which is used as the supplementary standard (See JIS Z 4303 $\sim$ 6).

In this report, both standards were made by means of the electrolytic method, and measured absolutely by the 2 π gas flow α proportional counting apparatus.

In preparing the uranium sample, the oxide was deposited at room temperature on the metal plate from the electrolyte consisting of uranyl nitrate dissolved in 0.2 N ammonium oxalate. The pH of the electrolyte was initially adjusted to 8 ~ 8.5 with ammonium hydroxide, and the current density set at 20 ~ 30 mA/cm^2. As the metal plate, the following were chosen; Ag, Pt, Cu, Pd and Al. The results obtained were good, especially in the cases of Ag and Pt, The disintegration rates of these samples were about 30 ~ 100 dpm, which are available enough to use as the standard.

In the case of RaD, the standard was deposited as lead dioxide on the palladium foil from lead nitrate solution acidified with nitric acid. The current density was set at 2 mA/cm^2, which was the best value of the current to obtain the good result of the electrodeposition. Very wide range of the activity of the RaD standard can be obtained by the electrolytic method, and owing to this, the standard may be superior to the uranyl sample at very low activity.

43. Measurement of α-ray Energy by Absorption Method

Takanobu Shiokawa, Itsuhachiro Hataye,
and Kunihiko Hasegawa

(Radiochemistry Research Laboratory,
Shizuoka University)

An accurate measurement of an energy of a charged particle depends on the deflections of its path in magnetic and electric fields. The absorption method using thin films is not so accurate as the method based on the deflections in magnetic and electric fields. But it needs not a large equipment and, therefore, the measurement is carried out comparatively easier. This method is poorer theoretically, but as it is a concise, we applied it to the measurement of α-ray energy.

As the alpha sources were used ^{210}Po which was mounted on a disque silver coated by Pd and ^{239}Pu which was separated from Bikini ashes in a glass dish. As absorbers thin membranes of polyethylene and collodion were used. Collodion membrane was prepared as follows: collodion dissolved in isoamyl acetate was dropped on water surface and the produced film was taken up carefully and dried at room temperature.

A Lauritsen type electroscope made in Scientific Research Institute, Tokyo, was used for the measurement of radioactivity. In order to keep the geometry constant, the alpha sources were set on the same position and were measured the α -particles which passed through a central small hole (3 mm) in an aluminum disque.

The absorption curves of ^{210}Po and ^{239}Pu obtained under the same conditions depend on sample condition, thickness, sample dish, and back-scattering, but it is not able to discuss these relations. The absorption curves obtained by polyethylene film were exponential, on the other hand, by collodion film the more sharp curves were obtained. Effects by the back-scattering were examined. The range of α -particles were determined by these absorption method.

44. Studies on Counting Method of Tritium. I.
On the Nature of Flow Gases and Sampling of Tritium-tagged Substance

Tsunetaka Sasaki, °Mitsuo Muramatsu
and Shigeyoshi Imamura
(Department of Chemistry, Faculty of Science,
Tokyo Metropolitan University)

1. In order to establish a definite and reliable method of counting tritium, attempts have been made to determine the radioactivity of solid and liquid octadecane-1-^{3}H spread over the bottom of a stainless steel pan, using a 2π flow counter.
2. An excellent nature as flow gas was found in gaseous hydrocarbons such as methane, Stan PP (propane + propylene), Stan BB (butane + butylene), and commercial propane for fuel use. Their counting characteristics were highly reproducible and the range of plateau for each gas was wider than that for Q- or PR-gas.
3. Dissolution of flow gas into octadecane was observed but it did not affect the counting rate of the sample.
4. The counting characteristics were not affected by humidity

of flow gas over the wide region of plateau. This fact offers a possibility of using gaseous hydrocarbons as flow gas in performing the solid-or liquid-counting of tritium-tagged substances coexisting with or dissolving in an aqueous phase.

5. The counting rate increased proportionally with the increase of the sample thickness when the amount of the sample was less than that corresponding to the maximum range of β-ray.
6. Within this region the counting rate kept up its constancy for a given amount of the sample, irrespective of the manner of distribution of the sample over the bottom. This suggests a possibility of using octadecne-1-^{3}H as a standard for determination of tritium in an organic compound, taking account of quantitative reaction between octadecyl magnesium bromide and tritiated water which can be obtained by ignition of the compound.
7. Beyond this region, on the other hand, the counting rate was affected by several conditions such as an uneven distribution and the surface roughness of samples. This comes mainly from an extremely soft β-ray of tritium.

45. Measurement of Radioactivity of Natural Potassium

Isamu Koizumi

(Industrial Research Institute of Kanagawa Prefecture)

Radioactivities for different liquid thicknesses of soln. of potassium salt were measured with a thin walled cylindrical counter. It was found that ratios of γ counting rates to β were markedly variable with sample thickness. Hence, when sample thicknesses are very different, it is impossible to regard the counting rate as a linear function of the potassium content, then, it requires to obtain the correction curve for thickness or density of sample. Background sharply increased with decrease of sample thickness, within the max. range of K-40 β -ray. It is considered that the increasing is due to radiation of radioactive nuclide (K-40) in glass sample holder.

Geometrical efficiencies at each points in the cylindrical sample are variable with distances from the tube wall of counter In view of this consideration, the counting rates estimated agreed with the observation.

46. Studies on the Gamma Spectrum of Uranium Minerals in Japan

Yukio Murakami and Yoshie Suzuki
(Japan Atomic Energy Research Institute)

(OBJECT)

This study was performed for the purpose of developing a new simple instrument which indicates gamma spectrum of uranium and its decay products for field use to prospect uranium ores.

(INSTRUMENT USED)

Single Channel Gamma Spectrometer, NaI crystal 2" x 2" diameter, Nuclear Chicago Co. and 256 Channel Gamma Spectrometer, NaI crystal 3" x 2-3/4" well type, R.C.L. Co.

(SAMPLES INVESTIGATED)

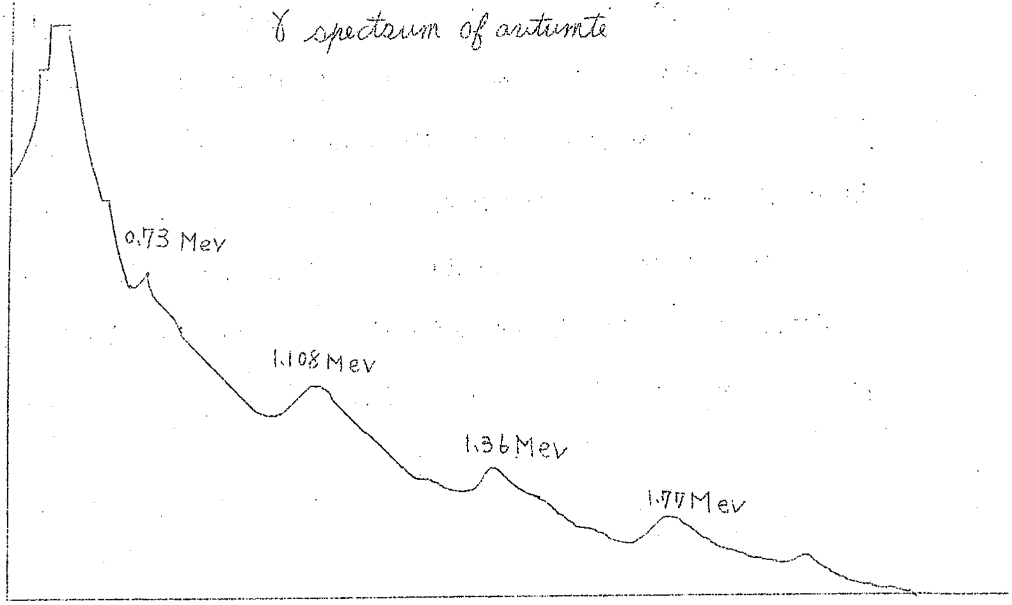
Pitchblende, Autunite and other uranium minerals. Uranium oxide, yellow cake, autunite occurred at Ningyo-Toge and other uranium minerals in Japan.

(RESULTS OBTAINED)

Among the gamma rays issued from uranium and its decay products, gamma ray of 1.78 Mev from RaC (^{214}Bi) can be remarkably detected without being disturbed by other effects caused by absorption of other gamma rays. The possibility of using this photopeak to fulfil the purpose above mentioned was thoroughly investigated in case of more than 10 samples cited beforehand. One of the charts obtained is shown in the following.

RaB and RaC were radiochemically isolated and the photopeak of both were examined to prove the presumption. The radiochemical separation of these decay products were made by the dithizon extraction method on the formation of $(BiCl_6)$ $(Co(NH_3)_6)$ that were formerly proposed by the author.

Special consideration should be paid on the appearance and interference of gamma spectrum due to ^{40}K (1.46 Mev) and ThC'' (2.20 Mev). Some remarks will be given on some charts of gamma spectrum that were obtained by several uranium minerals in Japan.



γ spectrum of autunite

47. Radioactivation by the (γ, γ)-Reaction IX. Application of the (γ, γ)-Reaction to the γ-ray Dosimetry. (Part 2)

Kenji Yoshihara and Nagao Ikeda

(Japan Atomic Energy Research Institute)

Previously, we studied (γ, γ)-reaction by the use of cobalt-60 γ-ray source, and applied this reaction to the dosimetry of cobalt-60 γ-ray. However, the previous method was somewhat inconvenient as it was based on the comparison of indium activities induced at different positions and it was necessary to determine the accurate dose rate at the appropriate position as the standard for the comparison by the other method at the same time.

In the present paper, we investigated the calculation method instead of the troublesome comparison method, by using the constant activation cross-section value for the resonance line of γ-ray which is responsible for the (γ, γ)-reaction.

The method of calculation is as follows: the saturated activity of ^{115m}In induced in the indium foil, A (dps), is expressed by the following formula,

$$A = N \sigma f \qquad (1)$$

where, N is the numbers of indium atoms, σ is the overall cross-section for the ^{115}In (γ, γ)^{115m}In and f is the γ-ray flux (quanta/cm^{2}sec).

Therefore, $$f = A/N\sigma \qquad (2)$$

The dose rate of cobalt-60 γ-ray (D) in the unit of r/hr is calculated from the γ-ray flux, f, using the following formula:

$$D = \frac{1}{4.35 \times 10^5} \frac{A}{N\sigma} = 4.56 \times 10^{-28} \frac{A_0}{\sigma} , \qquad (3)$$

where A_0 is the saturated value of the produced radioactivity in 1 gram of indium. The over-all cross-section, is expressed by the following formula$^{1)}$:

$$\sigma = \frac{1}{2} n_0 (\phi_1 + \phi_2) \frac{\sigma_a}{\mu} e^{(\mu - \mu')r_0} (1 - e^{-\mu r_0}), \qquad (4)$$

where n_0 is the electron density, ϕ_1 and ϕ_2 are the scattering cross-sections of the electron for the Compton scattering by which 1.04 MeV γ-ray (the resonance line for indium) is produced from 1.33 MeV and 1.17 MeV γ-ray of cobalt-60, respectively, σ_a is the activation cross-section of ^{115}In for the resonance line of 1.04 MeV, μ is the mean absorption coefficient of the substance for 1.33 and 1.17 MeV γ-ray, μ is the absorption coefficient for 1.04 MeV γ-ray, and r_0 is the thickness of the scatterer.

According to the equation (4), we can calculate σ for the various thickness of the various matters, and prepare the r_0 - σ diagram. From this diagram, we can obtain σ for the scatterer of a given thickness r_0.

σ was estimated to be in the order of 10^{-22} cm^2 by Miller and Waldman[2]. As this value was not accurate one, we attempted to estimate σ_a by the experiment of radioactivation of indium at the center of the 10 kC cobalt-60 γ-ray source of JAERI applying the equation (4). As the result, the value of 0.6×10^{-22} cm^2 was obtained for σ_a. Setting indium foils at the various positions arround the 10 kC cobalt-60 γ-ray source, we measured the dose rate at each position in the case of (a) no shielding, (b) shielding with 0.7 g/cm^2 brass, and (c) shielding with 3.8 g/cm^2 brass.

The dose rate obtained by the calculation in the above mentioned way agreed with the value obtained by Victoreen Roentgen rate meter within the error of about ± 15%. This is fairly good agreement considering that the error of the dose rate obtained by the Victoreen roentgen rate meter is ± 15%.

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1) K. Yoshihara, N. Ikeda; Radioisotopes, 7, 17 (1958)

2) W. C. Miller, B. Waldman; Phys. Rev., 75, 425 (1949)

48. Radioactivation Analysis of Indium Using Radium + Beryllium Neutron Source.

(Part II) Studies on Neutron Irradiation for Aqueous Solution of Sample.

Yuzuru Kusaka and Haruo Tsuji
(Dept. of Chemistry, Faculty of Science,
Konan University)

In general radioactivation analysis using low level neutron source, paraffin is used as neutron moderator and the sample to be analyzed is placed on the position in paraffin where maximum of thermal neutron flux is obtained and the radioactivity induced in the sample is measured after irradiation.

In this report, the authors studied the new method of neutron irradiation, in which the sample to be irradiated by neutron is the aqueous solution in the spherical flask of soft glass and the neutron source is placed on the centre of the flask and the flask is surrounded by water used as neutron moderator and reflector.

In this experiment, Ra 50mg + Be mixture was used as neutron source and indium as the element to be analyzed and the induced radioactivity (^{116m}In) was measured by GM tube or NaI scintillator of well type.

Firstly, the authors studied on the distribution of neutron flux in water. In this experiment, the neutron source was placed on the centre of a water-tank (48 x 33 x 33cm) and a metallic plate of indium (diameter: 22mm, weight: 2.1gr) was used as neutron detector. The induced radioactivity of the indium plate, which is placed on the definite position in the water, was measured for 10 minutes, starting at 5 minutes after the end of 2 hours' irradiation. The measurements with and without cadmium filter (thickness: 0.6mm) give the estimation of thermal neutron flux.

As a result of this experiment, it was found that a maximum point of thermal neutron flux is in existence at distance of about 1 cm from the neutron source.

Secondly, the authors sought for the volume of the sample solution suitable for neutron irradiation in this method. In this experiment, the definite quantity of indium (250 mg) was dissolved in the solution in the flask and the relation between the total radioactivity induced in the solution and the volume of the solution was studied.

The radioactivity was measured for 10 minutes by the well-type scintillator at 20 minutes after the end of 2 hours' irradiation.

As the results of this experiment, it was found that the maximum radioactivity was obtained at volume of about 200 cc.

Then, the relation between the induced radioactivity and the indium content in the solution of 200 cc was studied.

From this experiment, it was found that the induced radioactivity in this method is increased proportionaly with the indium content up to about 600 mg, and this relation is advantageous in the radioactivation analysis of indium.

Comparing this relation with in the usual method, in which paraffin is used as neutron moderator and solid sample (indium oxide in this report) is irradiated by neutron, it was found that the self-absorption effect of neutron in the solution method is smaller than in the solid method.

This solution method is also advantageous for rapid chemical procedure after irradiation of neutron, because it is not necessary for any procedure of dissolution of sample.

49. Neutron Activation Analysis of Halogens in Silicon

Tadashi Nozaki, Hideo Baba,
Hidemaro Araki and Toshi Kawashima
(Electrical Communication Laboratory)

On the last symposium on radiochemistry, we reported on the neutron activation analysis of iodine in silicon. Now a method for determination of chlorine, bromine and iodine in silicon by the same principle is shown. Alkali fusion of silicon with potassium iodide as carrier had been proved to be a suitable procedure for the determination of iodine in silicon. The same fusion with the corresponding carriers must be applied to the determination of bromine and chlorine successfully.

High purity silicon was irradiated in the JRR-1 with the activation standard of potassium bromide and ammonium chloride. The powdered silicon was gradually added to partly fused potassium hydroxide containing three alkali halides as carrier. The fused matter was dissolved in sulphuric acid, and then cromium trioxide and some concentrated sulphuric acid were added to this solution. Bromine was distilled out of the mixture in a few minutes, and most of chlorine in the following 20 minutes, while iodine remained in the residue as iodate. The bromine was lead into an aqueous solution of sodium sulfite containing phosphoric acid and oxidized with potassium permanganate to molecular bromine, which was extracted with carbon tetrachloride: while chlorine, if present, remained in the aqueous phase as chloride. The bromine was extracted back with an aqueous hydroxylamine and converted into silver bromide to be counted and weighed. The chlorine was also led into an aqueous solution of sodium sulfite and was converted into silver chloride without any purification. If the determination of iodine was necessary, addition of an excess of oxalic acid into the residue liberated molecular iodine, which could be obtained pure by distillation into an aqueous solution of sodium sulfite, oxidation with sodium nitrite and extraction with xylene. After this process the iodine could easily be converted into silver iodide for counting and weighing. The activity of bromine was determined easily with a simple G-M counter, while counting only of the high energy radiations from 38Cl using a scintillation counter with a large crystal and a single channel analyser was necessary for the determination of the chlorine, which contained inevitably some ^{31}Si and other impurities.

The chemical separation process necessitated about one hour, with the yield exceeding 50%. A silicon purified through the chloride process contained 0.4 ppm of chlorine 0.08 ppm of bromine and 0.05 ppm of iodine.

50. Activation Analysis of Selenium by Se-77m

Toshio Nakai, Seishi Yajima, Minoru Okada,
and Koreyuki Shiba
(Japan Atomic Energy Research Institute and
Government Chemical Industrial Research Institute, Tokyo)

Neutron activation analysis methods have been devised for the rapid analysis of selenium in sulfur and sulfur compounds. Sample was inserted through a pneumatic tube in a pile JRR-1, placed there for 20 seconds to be activated at a neutron flux of 3×10^{11} $cm^{-2} \cdot sec^{-1}$, cooled for 15 seconds, and counted for 20 seconds by a 256 channel gamma scintillation spectrometer. Sample was then cooled 20 seconds and counted again for 20 seconds. Thus two spectrographs were obtained and the identification for selenium was made from both a gamma energy and a half-life. A calibration curve was made over a range of concentration between 10^{-1} μ g and 10^{2} μ g of selenium by use of standard samples. The maximum and minimum concentration found in actual samples was 70 ppm and "less than 0.01 ppm" repectively.

With respect to half-life determination, it was found from Table of Isotopes that, in order to identify Se-77m (17.5 sec) from photopeaks in gamma spectra recorded, it was necessary that these photopeaks observed were confirmed not to be those of Ge-77m (54 sec). Since the half-life of Se-77m is considerably apart from that of Ge-77m, only two runs of gamma spectrometry per one sample may be enough to identify Se-77m.

The coefficient of variation of single analysis is assumed to be about 10% for a few microgram of selenium.

51. Activation Analysis of Indium in Sphalerite

Fumio Aoki and Teiji Okubo
(Government Chemical Industrial
Research Institute, Tokyo)

Indium often occurs in sphalerite, galena etc., and is recovered from those ore as a byproduct of zinc or lead. As the indium content in ores is generally very small the colorimetry and the fluorimetry are difficult to be applied to the determination of the element except when ores are relatively rich in indium.

In these circumstances a method of neutron activation analysis worked out using the JRR-1 reactor for the detn. of minute quantity of indium in sphalerite.

In a polyethylene tube (3mm i.d.) 300 mg of very fine powder of a sample is weighed and sealed. Five samples and two standards are put into a polyethylene capsule and irradiated for one week in the reactor.

The activity due to ^{114m}In, which is induced from ^{113}In by the (n, γ) reaction, is measured with a single channel spectrometer (Atomic Instrument) and a end-window type G.M. counter (Kaken). Self shielding effect is found to be neglibible even when a sample contains 1% of Cd.

The irradiated sample is dissolved in aqua regia, 2 mg each of Ag^+, Cu^{++}, and Sb^{3+}, as scavenger, and 5 mg of In^{3+}, as carrier are added. The solution is evaporated on a sand bath to remove nitrus fumes and heated with conc. HCl, then diluted with water and filtered. The acidity of the filtrate is adjusted to 0.3N, H_2S is passed into the solution, filtered and washed. Indium is precipitated twice as the hydroxide by use of NH_4Cl and NH_4OH leaving zinc and others in the solution

The ppt. is dissolved in 3N H_2SO_4, the same volume of 3M KI is added and indium is extracted with ethyl ether. The ether layer is evaporated on 100 ml of 0.1N HCl. Indium is precipitated as the oxinate and the latter is mounted for counting.

The oxinate is confirmed to be radiochemically pure by measureing the γ ray spectrum, the β energy and the half-life.

As small as 1 ppm. of indium can be determined by this method when the sample is irradiated for 15 hours (net.) by the JRR-1 reactor of which neutron flux is approximately 3×10^{11}n/sec/cm^2.

Results obtained by this method show satisfactory agreement with those by the oxine colorimetric method as for samples which are relatively rich in indium.

52. The Activation Analysis of the Impurities in Bismuth Metal

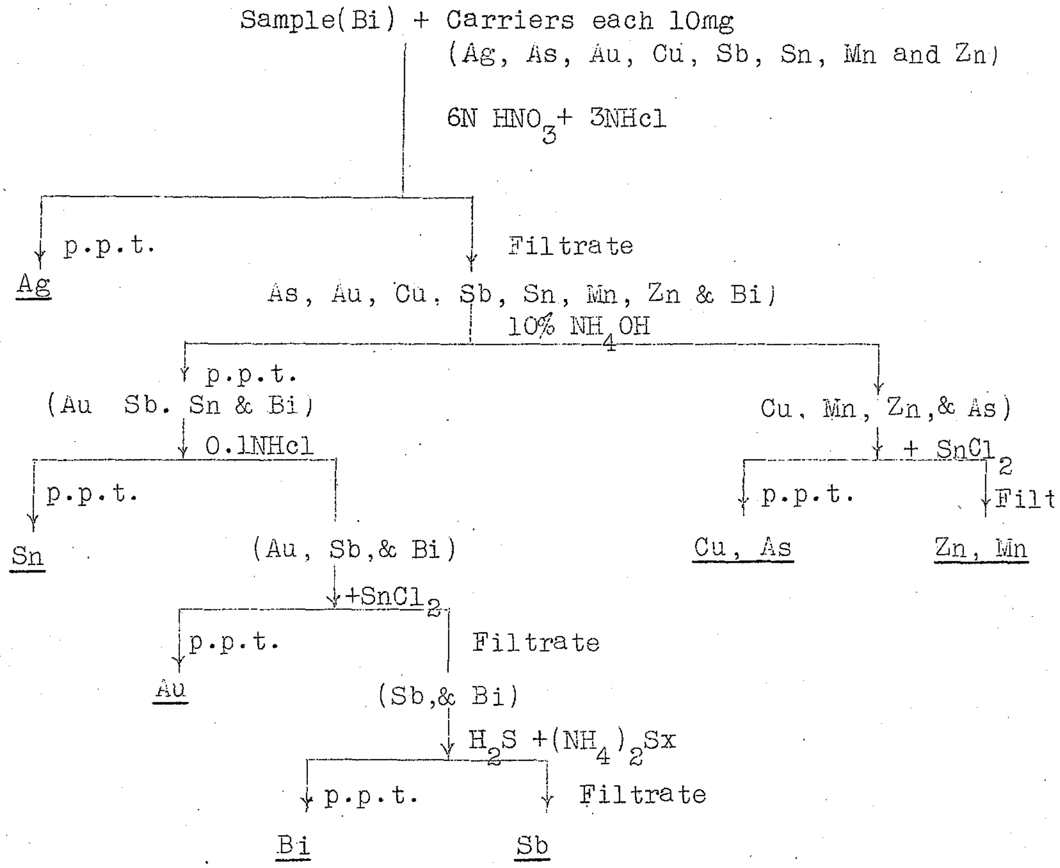
Toshio Nakai, Seishi Yajima and Ryuhei Kurosawa
(Japan Atomic Energy Research Institute and
Waseda Science and Engineering Research)

Recently, the demand of bismuth metal has been increased for the uses of semiconductor and reactor coolant. For these utilities, the ultra micro concentrations of impurities in bismuth metal should be checked, especially, for the use of coolant. Therefore, concentrations of silver, gold, cadmium and copper which have comparatively large neutron adsorption cross section will be important problem.

In our experiment, the impurities in the bismuth samples which were produced by the several kinds of production methods were determined using activation analysis and gamma ray spectrometry.

The samples were irradiated in the reactor of JRR-1 under the thermal neutron flux of about 5×10^{11} neutrons/cm^2sec. for three days (the irradiation time in one day was 5 hours, and therefore, the total irradiation time was 15 hours).

After irradiation, the sample was treated by the chemical separation procedures as follows:



The separated fractions were transfered into a polyethylene bottle and the gamma ray spectrum of each fraction was obtained by the use of a gamma ray scintillation spectrometer with a well type sodium iodide scintillator. The standard samples which were irradiated under the same condition as the bismuth samples were assayed by gamma spectrometry as above mentioned, By comparing spectra of the fractions and the standard samples, the impurities contained in the bismuth sample were determined.

Analytical results on two bismuth samples are shown in the next table.

Impurities Samples	Ag	Au	Cu	Sb	As
Purified by zone refining	ppm -	ppm -	ppm 2.2	ppm 0.4	ppm <0.004
Purified by electrolysis refining	60	0.5	30	0.03	<0.004

53. Activation Analysis of Impurities in Germanium and Other Metals of High Purity

Toshio Nakai, Seishi Yajima,
Minoru Okada and Teruo Imai
(Japan Atomic Energy Research Institute,
The Government Chemical Industrial Research Institute
and Research Institute of Sumitomo Metal
Mining Co. Ltd., Tokyo)

1) The distilling method for the separation of impurities in germanium from matrix was studied.

It was desirable to remove germanium as germanium tetrachloride with the distillation rate of 100 ml per 2 hours und under the circumstances of hydrochloric and nitric acid solution. The ratio of both acids was as follows:

i) first experiment; 30-50 ml of concd. HCl + 30-40 ml of concd. HNO_3 + 20 ml of water. ii) Second and third experiments; 20 ml of concd. HCl + 10 ml of concd. HNO_3.
iii) Final experiment; 20 ml of concd. HCl only.

The distillation was carried out until the residual solution was evaporated down to 15 - 5 ml. The separation of arsenic from germanium was considered to be complete.

The last residual solution containing impurities to be determined was separated into several groups by using the anion exchange resin of Dia Ion SA #100, and the determination by gamma ray spectrometry was taken for each group.

Some trace elements in metallic germanium and germanium dioxide were determined by using this method.

2) On the activation analysis of sodium in aluminum or magnesium, the following reactions caused up the interferece; i) $^{27}Al(n, \alpha)^{24}Na$, ii) $^{24}Mg(n,p)^{24}Na$. Using a cadmium sheet, we studied the possibility of the elimination of (n, γ) reaction which produces ^{24}Na.

The samples, one of which was wrapped with the cadmium sheet, were irradiated simultaneously and the amount of ^{24}Na produced was compared to the unwrapped sample.

54. Activation Analysis of Individual Rare Earth Element in Thorium as Nuclear Fuel

Isao Fujii and Haruo Natusme
(Tokyo Shibaura Electric Co. and
Japan Atomic Energy Research Institute)

Neutron-activation analysis has been applied to the determination of individual rare earth element in thorium nitrate (Nuclear grade) using the automatic recording instrument for drawing elution curve and the cation exchange chromatography.

Sample of the thorium nitrate was irradiated in the Saclay reactor EL-2 (Centre d'Etudes Nucleaires de Saclay, CEA.) for a period of 150 hours at a flux of about 1.8×10^{12} neutrons per sq.cm per second.

The radiochemical separation after the addition of carrier was based on anion exchange chromatography to separate thorium and protoactinium from sample solution, and on cation exchange chromatography for separation of individual rare earth elements using 0.5M solution of lactic acid (pH-3.30 and 3.44). The radiochemically pure rare earth element separated by above treatments was finally precipitated and counted at the oxalate.

In the application of this method, it is important to put the mind on the nuclear fission reaction occuring with the overwhelming number of thorium atoms, as compared to the n, γ reaction on the smaller numbers of rare earth elements atoms.

55. Determination of Rare Earth Elements in Thorium Metal and Oxide by Neutron Activation

Toshio Nakai, Seishi Yajima,
Yuichiro Kamemoto and Koreyuki Shiba
(Japan Atomic Energy Research Institute)

Previously, we reported the determination of Dy, Sm and La in thorium metals using neutron activation technique (at 2nd. Symposium on Radiochemistry, 1958). In the present investigation, the above technique has been modified and extended to the determination of Eu, Dy, Sm and La in thorium metals and oxides.

The major modifications in this report include (1) the irradiation of sample for 3 days (5 hours at longest each day) in addition to the irradiation for 2 hours, (2) the addition of La as a carrier with the aim of eliminating the loss of rare earth elements during the chemical procedure, (3) the reduction of interfering activities using more steps of chemical decontamination, and (4) the determination of Eu by an analysis of the decay curve of rare earth mixture, etc.

The outline of procedures are as follows. Samples and standards were sealed separately in polyethylene tubes which were placed side by side in a capusule for irradiation. Irradiations were carried out in JRR-1 reactor. The flux was $\sim 2 \times 10^{11}$ neutrons/sq. cm/sec, and the irradiation lasted two hours (for the determination of Eu and Dy) or three days (for the determination of La and Sm). After irradiation, the samples and standards were respectively dissolved in hydrochloric acid solution in the presence of La carrier by adequate method. The amount of each rare earth element in the thorium metal and oxide samples were determined by comparing the peak height of gamma ray spectrum of sample with those of standards after chemical decontamination.

Radiochemical separation process consisted of the dissolution of the irradiated sample by the adequate chemical procedures, precipitation of the hydroxide of rare earth elements by adding of NH_4OH, and separation of rare earth elements from ^{233}Pa by ion exchange method. Pouring the 11M-HCl solution containing rare earth elements, thorium and ^{233}Pa to a Cl-type anion exchange resin column (Diaion SA #100, 100-200 mesh, $\phi \sim 6$ mm x 60 mm), the rare earth elements and thorium passed through the resin column and ^{233}Pa was retained, Leaked fraction was concentrated to a suitable volume and ready for measurement of gamma activity using a gamma ray spectrometer.

In the determination of Sm and La, further decontamination process was adopted. Rare earth elements were separated from thorium by thiosulfate method, precipitated with NH_4OH, dissolved in HCl and reprecipitated with oxalic acid.

A example of the results obtained by this method is as follows:

Sample	Dy	Eu	Sm	La
Th metal	1 ppm	1 ppm	not det.	not det.

56. Determination of Trace Elements in Silicate Rocks and Stony Meteorites by Neutron Activation

Hiroshi Hamaguchi, Yuichiro Kamemoto,
Eikichi Ideno, Tadashi Endo and Tsutomu Yasunaga
(Tokyo Univ. of Education, Tokyo)

Some trace elements, i.e. palladium, iridium, platinum, arsenic, antimony and tungsten in rocks and stony meteorites were determined using neutron activation technique. The radioactivation procedure involves thermal neutron irradiation of the sample powder along with a monitor. The irradiations were carried out in JRR-1 reactor. The flux was $\sim 3 \times 10^{11}$ n/cm^2/sec, and the irradiation lasted 2 $\sim$ 3 days (5 hours irradiation each day). After irradiation the samples were fused with sodium peroxide in the presence of carriers. The melt was dissolved in hydrochloric acid, and the solution was evaporated up to dryness to remove silica. The trace elements were isolated from the resulting solution by the same procedure as reported previously. The amount of the respective elements was then determined by comparing the activity of the radiochemically pure nuclides isolated from the samples with those from the monitor. The results obtained for stony meteorites are summarized in Table 1.

Table 1

Trace elements in some stony meteorites (p.p.m.)

	Forest City (chondrite)	Modoc (chondrite)	Nuevo Laredos (achondrite)	Admire County (pallasite; silicate phase)
Pd	1.0 ±0.3 (3)	0.73 ± 0.09 (3)	*	0.04
Ir	0.4 ±0.25 (3)	0.3 ± 0.08 (3)	*	*
Pt	1.0 ±0.2 (3)	1.0 ± 0.1 (3)	*	*
As	2.59 ± 0.31 (3)	1.79 ± 0.30 (3)	0.0179±0.008(3)	0.0168
Sb	0.124±0.013(3)	0.118±0.033(3)	0.0096±0.001(2)	0.0214
W	0.24 ± 0.06 (4)	0.13 ± 0.02 (2)	0.11	

* not detectable

The values in parenthesis are number of determinations.

The sensitivities of the method, the cosmic abundance of the respective elements, the distribution of the elements among the metal and silicate phases, and the geochemical charcter of the elements are discussed.

57. The Solubility Determination of Tributyl Phosphates in Water by Activation Analysis

Hirokazu Umezawa, Shinzo Nomura and Reinosuke Hara
(Chemistry Division,
Japan Atomic Energy Research Institute)

In view of the small solubility and the difficulty in chemical analysis for the minute content of organic phosphorus, the activation analysis was applied to the solubility determination of tributyl phosphates.

The experiment was proceeded with tri-n-butyl, iso-butyl and sec.-butyl phosphates which were carefully purified by vacuum distillation. One ml of phosphate was shaken with 1.5 ml of ion-exchange water.

The aqueous phase was first discarded, and again the phosphate was shaken with ion-exchange water for 1 hour at 20°C. After the separation of two layers, 1 ml of aqueous phase was taken on a filter paper, and left standing at room temperature to evaporate off water. The filter paper was then sealed in a polyethylene sheet, and irradiated by JRR-1 for 15 hours. Several day cooling was provided to die off short lived activities due to impurities in polyethylene as well as

^{31}Si produced by (n,p) reaction, then ^{32}P content was radiochemically determined.

The reference was prepared by dissolving pure phosphates in benzene to make approximately 5 g/l solution. Each 10 λ, 50 λ, 100 λ and 150 λ solutions were taken, and the same procedure and experimental condition as applied to samples were taken for the reference. The references prepared corresponded to 50, 250, 500 and 750 μg phosphate respectively, and the calibration curves were prepared.

Both filter paper and polyethylene contained long lived impurities which gave the back-ground counting of $\sim$ 100 cpm. The sample activity of 50 μg phosphate was approximately twice as much as the back-ground counting.

The solubility of tri-n-butyl phosphate was determined to be 0.3 g/l which is in fairly good agreement with McKay's value, 0.5 g/l.

Both tri-iso and sec.-butyl phosphates showed higher solubilities as compared with tri-n-butyl phosphate, and the solubility of approximately 2 g/l was determined for tri-sec. butyl phosphate.

58. Excitation Functions for the Reactions, $^{40}A(\alpha,p)^{43}K$ and $^{40}A(\alpha,pn)^{42}K$

Shigeo Tanaka, Takashi Mikumo, Michiaki Furukawa,
Masuo Yagi, Shiro Iwata and Hiroshi Amano
(Institute for Nuclear Study, University of Tokyo)

Excitation functions for (α,p) and (α,pn) reactions on argon-40 were measured by the activation method using a "stacked-gas" technique. We used a target chamber with a platinum wire along the beam path. The wire was negatively charged to collect radioactive products on it. Alpha-particle bombardments were made with monoenergetic beam from 160 cm INSJ cyclotron.

The beam was collected in a Faraday cup and measured by a beam current integrator. After the bombardment, argon gas was pumped out and let through a washing bottle filled with 0.1 N hydrochloric acid. After the platinum wire was removed from the chamber, the wire was cut into several pieces and washed with 0.1 N hydrochloric acid. Radioactive products remained in the gas chamber were recovered with 0.05 N potassium hydroxide solution. These samples were counted with an NaI scintillation counter. The relative yields of ^{43}K were obtained by counting photo-peaks of 0.37- and 0.62-MeV gamma rays after subtraction of Compton tails of 1.52 MeV gamma ray emitted from ^{42}K. Relative yields of ^{42}K were given by counting with a scintillation counter so biased as to cut gamma rays below 1 MeV.

The disintegration rate of ^{43}K was given by applying $4\pi\beta$-counting to a sample below the threshold of $^{40}A(\alpha,ph)$ reaction.

The disintegration rate of ^{42}K was also obtained by $4\pi\beta$-counting after the contribution from ^{43}K was subtracted. Results are shown in the table. More than 85% of radioactive products were collected onto the platinum wire when the negative high voltage of 300 V was supplied to the wire.

Energy of alpha-particles	Cross section (mb)	
$(E_\alpha)_{lab}$MeV	(α,p)	(α,pn)
36	10	119
33.5	13	158
31	15	165
28	21	174
26	25	135
22	46	59
18.5	67	8

Energy of alpha-particles	Cross section (mb)	
$(E_\alpha)_{lab}$MeV	(α, p)	(α, pn)
15	41	0
11.5	15	---

59. Alpha Excitation Functions on Iron

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1) Introduction

It may be certain that the nuclear reactions on medium weight nuclei at intermediate energies follow the statistical theory which assumes the formation of compound nucleus. Recently, however, the contribution of direct interaction process for the nuclear reaction has been discussed. In this point of view, alpha excitation functions on ^{54}Fe, proton excessive nuclei, was chosen as the main purpose of the present study. The measurements of the excitation functions on ^{54}Fe, ^{56}Fe and

^{57}Fe were done with alpha-particles of energies up to 40 MeV. The ratio of the cross sections for ^{56}Fe(α,pn)^{58m}Co reaction to those for ^{56}Fe(α,pn)^{58g}Co was also measured.

2) Experiments

Bombardements were made with monoenergetic beams of 32 MeV and 40 MeV from the 160 cm INSJ cyclotron. Energy dependence of cross sections from 10 MeV to 40 MeV was measured by the "stacked-foil" technique in which thin iron foils (of about 7.7 mg/cm^2 thickness and natural isotopic abundance) were interspaced with aluminum absorbers. The targets were bombarded for 6 hours at an average beam intensity of 0.5 μA. The impurities in the target foil processed by a roller were determined by spectrographical analysis. The contents of impurities were as follows; less than 0.1% for aluminum and nickel, nearly 0.1% for calcium, manganese and silicon and trace for chromium and titanium.

After the bombardment, nickel, manganese, cobalt and iron were chemically separated by an anion exchange resin Dowex 1X 8(200 $\sim$ 400 mesh) in the 13mm ϕ x 150mm column. All fractions were counted with GM counter and NaI scintillation counter (2" ϕ x 2" or 1-3/4 ϕ x 2" -well-type). The correction of "recoil loss" for the relative yield of each reaction was made. The relative and the absolute yields of ^{57}Co (half-life 270 days) were obtained by counting the photo-peaks from 0.122 MeV gamma rays in a well type NaI crystal, Compton tails being subtracted. For 0.163 MeV gamma ray from ^{52}Fe (half-life 8.3 hours) produced by ^{54}Fe(α, α'2n)^{52}Fe, nearly the same counting procedures were applied. The relative yields of ^{56}Co (half-life 77 days) and ^{58}Co(half-life 71 days) were calculated by comparing the samples with the standard sources of ^{56}Co and ^{58}Co. These cobalt standards were produced by the reactions ^{56}Fe(p,n)^{56}Co and ^{55}Mn(α,n)^{58}Co and standardized by taking photo-peaks of 0.845 gamma ray from ^{56}Co and 0.810 MeV gamma ray from ^{58}Co in a defined geometry. These results were checked by $4\pi\beta$-counting of positrons. The nickel fractions, ^{56}Ni(half-life 6.5 days) and ^{57}Ni(half-life 37 hours) were allowed to decay to produce ^{56}Co and ^{57}Co, and nearly the same counting procedures were applied. The disintegration rate of ^{57}Ni was cross-checked by comparing β^+- β^+ coincidence count with that of ^{22}Na standard calibrated by $4\pi\beta$-counting. The absolute yield of ^{56}Mn(half-life 2.58 hours) and ^{52}Mn(half-life 18.2 hours) was determined with a calibrated GM-counter and that of ^{54}Mn was determined by taking photo-peaks from 0.845 MeV γ-ray in a defined geometry.

3) Results

Excitation functions for the next reactions were obtained.

^{54}Fe(α,n)^{57}Ni, ^{54}Fe(α,2n)^{56}Ni, ^{54}Fe(α,p)^{57}Co, ^{54}Fe(α,pn)-^{56}Co, ^{54}Fe(α,p2n)^{55}Co (As ^{55}Ni may immediately decay to ^{55}Co, ^{54}Fe(α,3n)^{55}Ni reaction can not discriminate against ^{54}Fe(α, p2n)^{55}Co reaction. The sum of the cross sections for both reactions was given.), ^{54}Fe(α, α'pn)^{52}Mn, ^{54}Fe(α, α'2n)^{52}Fe, ^{56}Fe(α,pn)^{58}Co, ^{56}Fe(α, α'pn)^{54}Mn and ^{57}Fe(α, α'p)^{56}Mn.

It is interesting that the measured branching ratio $\sigma(\alpha,p)/\sigma(\alpha,n)$ and $\sigma(\alpha,pn)/\sigma(\alpha,2n)$ for ^{54}Fe are larger than the predicted ones based on the statistical theory.

Reaction Energy	$^{54}Fe(\alpha,n)^{57}Ni$	$^{54}Fe(\alpha,p)^{57}Co$	$^{54}Fe(\alpha,2n)^{56}Ni$	$^{54}Fe(\alpha,pn)^{56}Co$	$^{56}Fe(\alpha,pn)^{58}Co$	
(E_α)lab MeV	σ (mb)	σ (mb)	σ (mb)	σ (mb)	σ (mb)	σ_m/σ_g
31.0			3.83	433	560	1.7
29.3	11.4		3.44	470	640	2.6
27.6	13.4		3.09	475	595	3.0
25.8	19.8	125	2.23	457	573	2.7
24.0	30.4	166	2.15	397	544	3.1
22.0	47.5	206	2.05	314	446	2.8
19.9	83.5	309	1.64	182	255	2.7
17.9	126	432	0.15	68	77	2.1
16.3	152	490				
15.6	142	509				
13.3	107	388				
10.0	45	147				

60. Alpha Excitation Functions on Manganese

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1) Introduction

We have reported the alpha excitation functions on ^{54}Fe, proton excessive nucleus. It is of interest that the comparison of the excitation functions on ^{54}Fe with those on ^{55}Mn, which has nearly the same mass number and is neither proton excessive nor neutron excessive.

2) Experiments

Bombardments were made with monoenergetic beams of 32 MeV and 40 MeV alpha-particles from 160 cm INSJ cyclotron. Energy dependence of the cross sections from 10 MeV to 40 MeV was measured by the "stacked-foil" technique in which manganese targets were interspaced with aluminum absorbers. The targets were prepared by spattering manganese metal onto 20 μ thick aluminum foils. The purity of manganese metal used was approximately 99.9%. The targets were bombarded for 3 hours at the average beam intensity of about 0.5 μ A of 32 MeV alpha-particles and for 4 hours at the average beam intensity of about 0.25 μA of 40 MeV alpha-particles. After bombardment, the target foil was digested in fuming nitric acid and only manganese was dissolved.

Chemical separations and counting procedures were nearly the same for the measurements of alpha excitation functions on iron. The correction of "recoil loss" was performed by measuring the activities in the aluminum backing foils.

3) Results

Excitation functions for the next reactions were obtained. $^{55}\mathrm{Mn}(\alpha,n)^{58}\mathrm{Co}$, $^{55}\mathrm{Mn}(\alpha,2n)^{57}\mathrm{Co}$, $^{55}\mathrm{Mn}(\alpha,3n)^{56}\mathrm{Co}$, $^{55}\mathrm{Mn}(\alpha,\alpha n)$-$^{54}\mathrm{Mn}$ and $^{55}\mathrm{Mn}(\alpha,2pn)^{56}\mathrm{Mn}$.

Reaction Energy	$^{55}\mathrm{Mn}(\alpha,\alpha' n)^{54}\mathrm{Mn}$	$^{55}\mathrm{Mn}(\alpha,3n)^{56}\mathrm{Co}$	$^{55}\mathrm{Mn}(\alpha,2n)^{57}\mathrm{Co}$	$^{55}\mathrm{Mn}(\alpha,n)^{58}\mathrm{Co}$	$^{55}\mathrm{Mn}(\alpha,n)^{58}\mathrm{Co}$
(E)lab MeV	σ (mb)	σ (mb)	σ (mb)	σ (mb)	$\sigma m/\sigma g$
38.5	125	115	118	6.52	
36.8	164	91.3	136	6.60	
34.2	146	76	219	12.8	
32.5	151	55	275	16.2	
31.3	153	40.8	343	19.3	2.40
30.7	134	37.4	364	21.0	
29.4	140	17	392	22.1	2.54
27.4	118	3.9	470	32.8	
25.3	73.2	0.8	565	48.2	4.43
23.0	28.5		552	75.3	4.48
21.0	6.6		562	134	5.00
18.5			482	227	4.38
16.0			357	388	3.69
13.1			31	569	1.39
9.9				332	1.20

The data of cross sections for (α,3n) and (α,n) reactions are the values from gamma-ray measurements. The values from $4\pi\beta$ -countings are about 1.5 times larger for (α,3n) reaction and 1.2 times larger for (α,n) reaction than the above values.

The errors for relative yields are less than ± 5%.

61. Excitation Functions of the (Ag+ α) Reactions (I)

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In the series of studies on the nuclear reaction by "the activation method", the reactions between the medium-weight nuclei and α -particles are much interested in. Here the excitation functions of the (Ag+α) reactions have been measured as the examples.

Several reports on some of the (Ag+α)reactions have already appeared in literature, but the authors' intention is mainly to obtain some new data of the reactions, of which datum has never been obtained, and also to improve the accuracy of the existing data of cross sections or to extend the energy region of α-particles in past experiments.

As the exact knowledge of the decay scheme of the product nuclei is essential for these researches on the reaction cross-sections, these works were carried out under close co-operation with a decay-scheme researching group.

The reactions included in the present report are given in the following table:

Reaction / Target nuclei	(α,n)	$(\alpha,2n)$	$(\alpha,3n)$	(α,pn)	$(\alpha,\alpha' n)$	$(\alpha,\alpha' 2n)$	$(\alpha,2p)$
^{107}Ag	^{110}In, ^{110m}In	^{109}In	^{108}In, ^{108m}In	^{109}Cd	^{106}Ag (8.2d)	^{105}Ag	---
^{109}Ag	---	^{111}In	^{110}In, ^{110m}In	---	---	---	^{111}Ag

The conditions of the bombardment and the methods of chemical separations are given here, but the methods of measuring radio-activities will be given in following Part II.

Targets of the bombardment were the stacked foils of silver metal, each one of which was 7 ~ 11 mg/cm^2 thick and pasted upon the aluminum frame for the easiness of handling.

The 63' cyclotron of the Institute for Nuclear Study of Tokyo University was mainly used for the acceleration of α-particles and the beam, after being passed through the analyser-magnet, was collimated by 1 cm x 1 cm graphite slit mounted in front of the target stack. The beam current was received in a Faraday cup and measured by an integrating micro ammeter. Activations of the order of 10^3 micro coulomb were done in $5 \sim 30$ min for short-life activities and of 5×10^3 micro coulomb in $3 \sim 4$ hr. for long-life ones. The incident energies of the -particles were regulated to either 40 or 30 Mev., and the energy at each foil was estimated by the existing range vs. energy curves.

The 44' cyclotron of Osaka University was also used for certain experiments, where the external target system was used and the maximum energy of the α-particles was 23 Mev. The beam current was measured by a recording micro ammeter.

For calculating the cross sections the adequate accounts were made on the beam fluctuations and the disintegration of the product activity during the bombardments.

In some cases the mutual chemical separation of activities of In, Cd and Ag was needed. Indium was first collected on ferric hydroxide from an ammoniacal solution, and Ag was precipitated as chloride and Cd as sulphide, individually. After repeats of each procedure twice or thrice, such efficiency of separation was attained as given in the following table;

Specified element	Chemical yield (%)	Decontamination coefficient		
		In	Cd	Ag
In	99		$> 1.3\text{x}10^3$	$> 1.3\text{x}10^3$
Cd	97	$1.3\text{x}10^2$	---	$1.0\text{x}10^3$
Ag	99	$1.0\text{x}10^3$	$2.5\text{x}10^2$	---

Samples for activity measurement were either a definite quotient of the solution of a separated precepitate or a dried residue of the solution.

62. Excitation Functions of (Ag+α) Reactions (II)

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Based upon the conditions described in part I, relative excitation functions have been obtained by measuring the characteristic radiations of reaction-products and the absolute cross-sections have been calculated with absolute measurements of activities.

A) Relative excitation functions

1) ^{107}Ag(α,n)^{110}In; ^{109}Ag(α,3n)^{110}In; ^{107}Ag(α,3n)^{108}In

2.3 Mev β^+ from ^{110}In (66 min) and 3.5 Mev β^+ from ^{108}In (40 min) were measured with the activated silver foil using GM-counter. 1.5 Mev β^+ from ^{110m}In and 1.4 Mev β^+ from ^{109m}In were separated by an adequate aluminum absorber. Countings with a thick absorber were substracted as γ -components. By analysing decay curve, activities of ^{110}In and ^{108}In were obtained separately.

2) ^{107}Ag(α,n)^{110m}In; ^{109}Ag(α,3n)^{110m}In; ^{107}Ag(α,3n)-^{108m}In 0.88 Mev γ from ^{10m}In (4.9h) and 0.89 Mev γ from ^{108m}In were measured with scintillation spectrometer. ^{110m}In and ^{108m}In were measured independently by analysis of the decay curve and the interference was negligible with non-separated samples.

3) ^{109}Ag(α,2n)^{111}In Measurements on 0.17 Mev-and 0.24 Mev γ of ^{111}In of the chemically separated In-fraction were done after 3 days decay and no interference was met.

4) ^{107}Ag(α,2n)^{109}In $\rightarrow$ ^{109}Cd As ^{109}Cd was the only activity observed in the chemically separated In-fraction after 3 months decay, the well type scintillation counter was used to measure the activity. Correction had to be made upon the activity transformed into Cd before the time of chemical separation.

5) ^{107}Ag(α,pn)^{109}Cd Cd-activities was separated immediately after the bombardment and measured with a well scintillation counter after a while. ^{109}Cd coming from the above (α,2n) reaction was corrected.

6) ^{107}Ag(α,α'n)^{106}Ag(8.2d); ^{107}Ag(α,α 2n)^{105}Ag ^{106}Ag and ^{105}Ag in the separated Ag-fraction after several days decay were measured γ-spectrometrically. But some error might not be avoided owing to ambiguities included in the

present decay scheme.

B) Absolute values of reaction cross-sections

1) Absolute measurements of ^{110}In, ^{110m}In, ^{108}In, ^{108m}In With silver foil bombarded at α -energy of 14 Mev (α,n) region, the conversion electron of 0.66 Mev γ by the use of a beta-ray spectrometer. An absolute measurement of ^{110m}In was done by γ - γ coincidence counting with 0.94 and 0.88 Mev cascade gammas. And then absolute value of ^{110}In could be calculated. On the other hand, ^{108}In/ ^{108m}In/ ^{110}In ratio in the target bombarded with 40 Mev α was obtained by the Kurie-analysis of the β -ray spectrum and the absolute values of ^{108}In and ^{108m}In were thus calculated.

Through these procedures the absolute cross-sections of the reactions, ^{107}Ag(α ,n)^{110}In, ^{110m}In; ^{107}Ag(α,3n)^{108}In, ^{108m}In; ^{109}Ag(α ,3n)^{110}In, ^{110m}In were estimated.

2) Absolute measurements of ^{109}Cd The defined geometry measurement of 0.088 Mev γ of ^{109}Cd was adopted. A strong ^{109}Cd source produced by the ^{109}Ag(α,2n)^{109}Cd reaction was used to aid the measurement of weak (α,2n) and (α,pn) products. Thus the absolute values of the cross-section of the reactions, ^{107}Ag(α ,2n)^{109}In; ^{107}Ag(α,pn)^{109}Cd were obtained.

3) Miscellaneous Approximate yields of ^{105}Ag, ^{106}Ag and ^{111}Ag were estimated from the measurements with the GM-counter

and the approximate cross-sections were calculated.

Conclusion

Absolute measurements were done on the excitation functions of the reactions: $^{107}Ag(\alpha,n)^{110}In$, ^{110m}In; $^{107}Ag(\alpha,2n)^{109}In$; $^{107}Ag(\alpha,pn)^{109}Cd$; $^{107}Ag(\alpha,3n)^{108}In$, ^{108m}In; $^{109}Ag(\alpha,2n)^{111}In$; $^{109}Ag(\alpha,3n)^{110}In$, ^{110m}In. And some informations with the cross-sections of the reactions: $^{107}Ag(\alpha,\alpha'n)^{106}Ag$; $^{107}Ag(\alpha,\alpha'2n)^{105}Ag$; $^{107}Ag(\alpha,2p)^{111}Ag$ were obtained.

Several discussions have been given as to the accuracy of various measurements and the excitation function obtained.

63. Excitation Function of $^{115}In(\alpha,pn)^{117m}Sn$ Reaction and Production of Carrier-free ^{117m}Sn.

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The carrier-free ^{117m}Sn necessary for research on decay scheme is used to be produced by ^{114}Cd(α,n)^{117m}Sn reaction, where other activities such as ^{113}Sn and ^{119m}Sn should be simultaneously produced and radiochemically pure ^{117m}Sn can not be obtained. Among reactions which yield ^{117m}Sn in the product (In$+\alpha$) reaction has attracted our attention, because bombardment of In with α-particles of about 40 Mev should give no other RI of Sn besides product of ^{115}In(α,pn)^{117m}Sn reaction. However, very little have been known about the cross-section of (α,pn) reactions. Herewith, the excitation function of the above (α,pn) reaction and the corresponding thick target yield have been studied in the first place and the conditions of the target and method of chemical preparation of carrier-free ^{117m}Sn on the other hand.

1) Measurement of the excitation function

Indium metal ($\sim$ 10 mg/cm^2 thick) electro-deposited from the cyanide solution upon silver foil ($\sim$25 mg/cm^2) were stacked and used as the target in experiments of measuring excitation function.

Alpha-beam accelerated to 40 Mev by 63' cyclotron of the

Institute for Nuclear Study of Tokyo University was used for the bombardment. The beam current was measured by an integrating microammeter. Activations of the order of 10^3 micro coulomb were done in about 3 hrs. Energies of α-particles at each foils were estimated by the range vs. energy curve.

The activated foils were dissolved in hot 18 N-sulphuric acid and carriers of Sn and Cd were added. Indium and Sn were precipitated from ammoniacal solution holding Ag and Cd in the solution, and then Sn was separated from In and Cd by introducing H_2S into a 0.5 N- HCl solution.

Precipitate of Sn was dissolved in HCl and the activity of an aliquot of the solution was measured by the well type scintillation counter and the reaction cross-section was calculated with adequate considerations.

The excitation function obtained has a peak of 130 mb in the vicinity of 33 Mev. Nuclear reaction yield can be calculated by combining the excitation function with the range-energy data.

2) Production of the carrier free ^{117m}Sn

For production experiments In metal (1mm thick) deposited on the silver plate soldered with indium metal on the water cooled copper block was bombarded by α-beam accelerated to 23 Mev in the 44' cyclotron of Osaka University. No damage of the target was observed when bombardment with beam current of $2 \sim 4\ \mu$A was continued.

After a few days cooling of Sb-activities, the activated indium was demounted together with silver plate. Indium part was selectively dissolved by HCl and Sn activity was coprecipitated with $In(OH)_3$ by NH_4OH, then separated from In by CuS collector with H_2S in a 0.5 N-HCl solution. Separation from the Cu could be achieved by the use of anion exchanger with HCl medium. By elution with HNO_3 the carrier-free ^{117m}Sn was obtained. Precautions were made to avoid the formation of radio colloid of Sn.

The α -spectrum of the final product indicated the expected purity in radio chemical sense.

As to the reaction yield the experiments are now being carried out.

64. Studies on Radionuclides of Osmium and Rhenium

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The study presented here was undertaken with the intent of obtaining new and additional information on the radionuclides of rhenium, osmium and iridium.

The 160-cm synchrocyclotron in the Institute for Nuclear Study, University of Tokyo was used for bombardment with alpha particles, while the JRR-1 reactor was utilized for neutron irradiation.

Materials used in this investigation were metallic rhenium, potassium perrhenate, ammonium perrhenate, and metallic osmium.

The metallic rhenium and ammonium perrhenate were carefully purified by conventional process before they were used as target materials.

The target materials used in the cyclotron bombardment were metallic rhenium, potassium and ammonium perrhenates.

After bombardment, chemical separations were made with some samples. Some of the irradiated perrhenates were dissolved in water. To the resulting solution was added iridium salt as a carrier, metallic iridium was then precipitated by reduction with formic acid.

The rhenium in the filtrate was recovered as sulfide precipitate. The separation of osmium was made with separate samples. After the addition of osmium carrier and nitric acid, the solutions of irradiated perrhenate were subjected to distillation. Osmium tetroxide was distilled out from the solutions.

The target materials irradiated with neutrons were ammonium perrhenate and osmium. The irradiated osmium was fused with alkali and then dissolved in nitric acid. To the resulting solution was added rhenium carrier. A large fraction of osmium in the solution was removed by repeated distillation.

The separation of the rhenium from the osmium in the residual solution was carried out by solvent extraction using thiourea and isoamyl alcohol. The rhenium was extracted in alcohol layer, while the osmium remained in aqueous phase.

The results can be summarized as follows:

a) In the bombardment with alpha particles of 37 - 43 Mev, an activity with a half-life of about 28 min. was found in the osmium fraction separated from potassium perrhenate target.

Further experiment is needed, however, to clarify the chemical nature of this activity.

b) The 28-min. activity was not observed in the osmium fractions from neutron-irradiated metallic osmium.

c) An activity with a half-life of approximately one hour was found in the cyclotron experiment. This activity might be identical with one-hour rhemium nuclide of unknown mass number which appears in the new Seaborg's isotope table.

d) The one-hour activity was never detected in the neutronirradiated rhenium.

65. Studies on the Hot Atom Chemistry of Arsenic-76 Using Phenylarsonate

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In order to produce arsenic-76 having high specific activity and to investigate the behaviour of the high excited recoil arsenic atoms resulting from neutron capture reaction, zirconium phenylarsonate, irradiated with thermal neutrons (1-2 x 10^{11}n/cm^2/sec) for two hours, was shaken with 0.6 N hydrochloric acid, and the radioactivity of the residue and filtrate were measured separately after filtration. Some results obtained are as follows.

1) Radioactivity, extracted into hydrochloric acid, was about 1μ C per 10 mg of the irradiated sample and the half life of it was approximately accord with that of Arsenic-76(26.4 hours). 2) Radiochemical purity of it was about 99.97%. 3) Specific activity, determined with molybdenum blue method, is about 1.5 x 10^6c/g. 4) Oxidation state of the recoil atom was seemed to be tervalent state (90% or more) in the moment of extraction, but tervalent arsenic was gradually oxidized by air and after standing for two days it was completely turned into quinquevalent state. 5) The retention was about 10% for a sample standing for 11 hours after irradiation, and was exponentially increased with the elapes of time.

66. Retention of Arsenic-76 in Ion-exchange Resin by Neutron-irradiation of Arsenate-loaded Resin

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In the previous investigations,[1-3] it was found that a fraction of hot-atoms, such as As-76, Br-82, I-128, was enriched in anion exchange resin phase by the neutron irradiation of oxyacid-loaded anion exchangers. The enrichment of radioactive halogen in the resin phase may be interpreted as a result of the reaction of hot-atoms with one of organic radicals formed in the resin. In the case of radioarsenic, however, it seems unlikely that such reaction takes place in the resin phase, because carbon-arsenic bond is less stable than carbon-halogen bond. In an effort to clarify the retention of As-76 in the resin phase, a series of experiments have been performed as follows. Anion or cation exchanger, Dowex-1 x-8 (Cl-form) or Dowex-50W x-8 (H-form) consisting of 100-200 mesh beads were dried in an Abderhalden's desiccator. Three grams of the dried resin was added to 30 ml. of the following solutions: aqueous arsenate solution, arsenate-tartaric acid solution, arsenate-ammonia solution, arsenate-ammoniumtartrate solution, and solutions of arsenic trichloride in various media such as absolute ethanol, ethanol-water, petroleum ether, 6 N hydrochloric acid, etc. In addition, some experiments were conducted with a system containing arsenic trichloride and resin.

The neutron-irradiation of these samples lasted 2 to 3 hr. The flux and maximum energy of neutrons produced by Be-D reaction were $\sim 10^7$ n/cm^2 sec. and $\sim$ 7 Mev, respectively. Then, each irradiated sample was poured into a column of 0.8 x 1.0 cm size. After the solution was passed through the column, the resin was treated successively with 50 ml. of ethanol, 50 ml. of 8 N hydrochloric acid, 50 ml. of 1.5 N hydrochloric acid, and finally with 50 ml. of water. The gross γ -activities of both the effluent and the resin were measured with a well-type scintillation counter. The fraction of total activity retained in the resin phase was calculated on each sample.

The results of the experiments are summarized as follows. (1) Radioarsenic is retained in the resin phase with enrichment factors of the order of 10^3. (2) In aqueous systems, the fraction of As-76 remaining in the resin phase is larger than in non-aqueous systems. (3) More activity is retained in anion exchanger than in cation exchanger. (4) The presence of tartrate in solution reduces the fraction of As-76 retained in the resin phase. (5) A tracer study using As-74 shows that the fraction of arsenate retained in the irradiated resin after the elution is several times larger than that in non-irradiated resin. The phenomenon of the retention of As-76 in the resin phase may be interpreted as such that some polymerized anions of arsenic are produced by recoil process and then adsorbed irreversibly on anion exchange resin.

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67. Effect of Cation and Water of Crystallization on Retention of Radioarsenic in Neutron-irradiated Arsenates

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Previously, the present authors studied the effect of irradiation temperature on the retention of radioarsenic in neutron-irradiated sodium arsenate crystals. In order to investigate other factors which may affect the retention, the following compounds were subjected to neutron irradiation: arsenates of sodium, lithium, ammonium, potassium, barium, cesium, cobalt and rubidium in anhydrous or hydrated form. These salts were irradiated for 2.5 hours at room temperature with neutrons produced by Be-D reaction ($\sim 10^7$ n/sec.cm^2).

After the end of irradiation each of the irradiated samples was stored for one hour at room temperature and then dissolved in water containing As (III) carrier. To this solution were added magnesia mixture and ammonia water to precipitate ammonium magnesium arsenate. The precipitate was dissolved in hydrochloric acid and then the precipitation was repeated in the presence of hold-back carrier of As (III). Hydrogen peroxide was added to the combined filtrate to oxidize As (III). The precipitate formed in the filtrate contained radioarsenic which was originally in the valence state of III as a result of recoil process. The precipitates were dissolved in hydrochloric acid and then diluted to 25 ml. The β-activity was measured with a dipping counter. Finally, the retention value of radioarsenic was calculated on each salt.

It was found that each salt has its characteristic retention value. Even when the salts contain the same kind of metal, their retention values are different, depending upon the number of metal atoms or water of crystallization in unit molecule.

It seems that the salt containing much water of crystallization has generally low retention value and the anhydride has higher retention than the hydrate of the same compound.

The effect of cation on the retention in the solid compound seems rather complex. When the irradiated sample was stored for more than one hour at room temperature, the increase in the retention resulted. Such increase seems to be commonly observed in irradiated solid arsenates.

The irradiation of the sample at low temperatures (for instance --195°C) resulted generally in lower retention values than those obtained by irradiation at room temperature.

It is noticeable that the retention value of sodium arsenate ($Na_2HAsO_4.7H_2O$) is exceptionally high in spite of high content of the water of crystallization. This value is also high as compared with other arsenates containing relatively light cations such as lithium, ammonium and potassium. In addition, the value is higher than those of other sodium arsenates.

68. Hot-Atom Chemistry of Bromine in Cobalt Complex Salts

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Very little attention has so far been paid to the hot-atom effect of ligand atoms in metal complex salts. In order to clarify the hot-atom behavior of radiobromine (^{80m}Br and ^{82}Br) arising from (n, γ) reaction on bromine-containing compounds, the present authors investigated the effect of various ligands on the "ligand yields" 1) of radiobromine in cobaltammine complex salts.

Experimental -- Solid complex salts ($[Co(NH_3)_5Br]X_2$, X = Cl, NO_3, etc.; $[Co(NH_3)_5Y]Br_{2,3}$, Y = NH_3, Cl, etc.; and $[Co(en)_2Y_2]Br_{1,3}$, Y = NH_3, Cl, etc.) were irradiated for two to three hours with neutrons (flux 10^7 n/cm^2.sec) which were produced by Be-D reaction and thermalized through paraffin. Each salt was dissolved in water after the irradiation, and the resulting solution was poured into a column of cation exchange resin, Dowex 50W X-8 (hydrogen or potassium form), 100-200 mesh. Most radiobromine atoms were leached out as anions into the effluent, while some fraction remained with the complex cations on the resin. The latter fraction was presumed to be combined with cobalt as ligand. These radiobromine atoms in the resin could be extracted through aquation by refluxing with water at elevated temperatures. Bromide was determined either by the Mohr's method or by colorimetric method.

Results -- (1) $[Co(NH_3)_5Br]X_2$: More than 80% of total radiobromine was leached out in water with enrichment factors of the order of 10^2. No significant differences were observed among the ligand yields of the salts containing different anionic species ($X = Cl$, Br, NO_3, 1/2 C_2O_4) except that the iodide showed considerably low yield. It is interesting to note that $[Co(NH_3)_5Br]Br_2$ showed almost the same yield as other salts. When $[Co(NH_3)_5Br]^{2+}$ adsorbed on the cation exchange resin was irradiated, the ligand yield was somewhat smaller than those of the corresponding solid samples, and appreciable activity remained in the resin even after long refluxing. The ligand yield dropped nearly to zero in the irradiation of aqueous solutions of the salt.

(2) $[Co(NH_3)_5Y]Br_{2,3}$: Radiobromine atoms resulting from anions were enriched in ligands through replacement by hot-atom effect. Enrichment factors of the radiobromine in ligands were 10^2-10^3. The ligand yield in the form of $[Co(NH_3)_5Br^*]^{2+}$ (obtained through replacement of Y by hot bromine, Br^*) increased in the following order: $Y = NH_3$, NCS, (F), NO_2, OH_2, ONO, ONO_2, Cl, I, Br.

(3) $[Co(en)_2Y_2]Br_{1,3}$: Enrichment of radiobromine in ligands was also observed with these salts. For $[Co(en)_3]Br_3$, the ligand yield was almost zero. For the other salts, the ligand yield increased in the following order: $Y = NH_3$, NCS, Cl, Br. No significant differences were observed between the

ligand yields of cis- and trans isomers of both $[Co(en)_2(NCS)_2]$ Br and $[Co(en)_2Cl_2]$ Br.

Discussion -- If the mass of the donor atom in ligand Y, and of bromine is, M, M', respectively, the fraction of the maximum possible loss in the recoiling energy of bromine for a collision with the donor atom is given by $\gamma = 4MM'/(M+M')^2$. For the salts $[Co(NH_3)_5Y]$ $Br_{2,3}$ and $[Co(en)_2Y_2]$ $Br_{1,3}$, the ligand yield seems to increase as the value of γ of ligand Y increases: the efficiency of replacement of Y by hot bromine depends mainly on γ. It may be presumed that the Kinetic processes play an important role in the hot-atom effect of bromine in ligands of the complex salts.

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1) Ligand yield is the fraction of total produced activity retained in ligands of a complex.

69. Hot-atom Chemistry of Metallic Ammine Complex Salts (III)

On the Radiosynthesis of Chloropentamminecobalt (III) Chloride

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Introduction

The application of the chemical effects of the nuclear recoil to the synthesis of organic labelled compounds is becoming familiar in these few years by the name of "radiosynthesis". In this report, the authors tried to expand the application of radiosynthesis to the inorganic field, and found that about 7% of radioactivated chlorine ^{38}Cl was produced in the form of chloropentamminecobalt(III) chloride $[Co(NH_3)_5{}^{38}Cl_2]Cl$ when hexamminecobalt(III) chloride $[Co(NH_3)_6]Cl_3$ was irradiated by slow neutrons.

Experimental

The radiochemical yield of chloropentamminecobalt(III) chloride produced in the irradiated hexamminecobalt(III) chloride was determined in the following way.

The irradiated hexammine salt was dissolved in the known volume of water containing the definite amounts (about 50 mg) of chloropentammine salt as the carrier. 5 ml aliquot of the radioactive solution thus obtained was taken for counting. To the remainder of the solution, hydrochloric acid was added and the acidity of the solution was adjusted to 1.5 N. The precipitated chloropentammine salt was then centrifuged and washed with 1.5 N hydrochloric acid. The precipitate was dissolved in water, and then was passed through the Amberlite-IRA400 resin bed (RNO_3-form, 100 ~ 200 mesh, 1 cm ϕ x 7 cm) to eliminate any radioactive chlorine in the chloride form, if present in the precipitate. A part of the effluent was taken for counting of radioactivity and for determination of the amount of chloropentammine salt. The specific activity of the separated chloropentammine salt was then readily calculated. From these data, applying the principle of the reverse isotope dilution method, the radiochemical yield of chloropentammine salt was calculated.

The exchange between Cl^- and $[Co(NH_3)_5Cl]^{2+}$ was checked, on the other hand, using ^{38}Cl as the tracer. It was revealed that the exchange occur only by a very small and negligible extent.

For the neutron irradiation, the cyclotron at the Physical and Chemical Research Institute and the JRR-1 nuclear reactor at the Japan Atomic Energy Research Institute were used. The radioactivity was measured with the scintillation γ -ray spectrometer made by Baird-Atomic Co.

Result

The values of radiochemical yield of chloropentammine-cobalt(III) chloride thus obtained are tabulated in Tables 1 and 2.

Table 1. When irradiated by the cyclotron.

(neutron flux: 10^6 n/cm^2.sec)

	Irradiation time (hr)	Deuteron beam (μA·hr)	Radiochemical yield of (%)
I	1	7	6.5
II	2	12	6.2

Table 2. When irradiated by the reactor.

(neutron flux: 3×10^{12} n/cm^2.sec)

	Irradiation time (min)	Radiochemical yield of (%)
I	3	6.7
II	5	7.3

Table 2 (Cont'd)

	Irradiation time (min)	Radiochemical yield of (%)
III	7	7.1
IV	10	7.3
V	15	7.2
VI	20	5.9

The radiochemical yield is about 7% for each case independently on the neutron flux and irradiation time. This suggests that radioactivated chlorine hot-atoms collide in the crystal with ammine groups and cause replacement of these groups by an almost constant probability.

From the viewpoint of ^{60}Co-labelling, a few percent of ^{60}Co was produced in the form of $[Co(NH_3)_5Cl]^{2+}$ when hexamminecobalt(III) chloride was irradiated by neutrons.

70. Hot Atom Effects of Metal Complexes 8-Hydroxyquinoline

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Preparation of some radioisotopes in a high specific activity is studied utilizing the hot atom effects of some metal oxinates (8-hydroxyquinolates). The experimental results obtained about manganese, tungsten and calcium oxinates will be given.

Dehydrated oxinates irradiated in JRR-1 were dissolved in an organic solvents. The organic solution of manganese or tungsten oxinates was shaken with Michaelis' buffer solution of various pH values. Comparing activities of both layers, an extractability was caluculated. On the other hand, amounts of metals come into the aqueous phase was determined colorimetrically. Basing upon these values the enrichment factor was determined.

Irradiation of calcium oxinate for more than 1 month did not give sufficient activity. Besides that, any nice water-immiscible solvent was not found for this oxinate. Accordingly, the n-butylamine solution of the oxinate was passed through a cation exchange column in order to pass n-butylamine and the oxinate away, keeping calcium ion in the column. After washing the column with distilled water, calcium ion on the resin was eluted by 3N-hydrochloric acid. Calcium was precipitated as phosphate for the measurement of radioactivity.

Although numerous studies had been carried out on the hot atom effects of inorganic manganese compounds such as permanganates, manganese oxide, and carbonate, that of organic manganese compounds was not studied except that of manganese chlorophyll. Manganese ion is extracted with an aqueous solution of pH $8 \sim 9$, whereas the oxinate is kept in the organic phase. The experiment showed that about 10% activity was found in the aqueous solution after shaking with the organic solution. The total amount of manganese was determined by the color of permanganate. Thus, the enrichment factor of 10^3 was obtained.

There is no report on the hot atom effect of tungsten. Shaking the organic solution of tungsten oxinate with an aqueous solution of pH 3.0   4.3 results about 30% activity in the aqueous solution showing the enrichment factor of 130   150. As the pH value of the aqueous solution is increased, the extraction of the oxinate into the aqueous phase is decreased keeping the partition of the activity almost constant.

Accordingly, shaking with an aqueous solution of pH 7 is preferable.

Trials to obtain the calcium radioisotope by the hot atom effect have not been succeeded by this time. As mentioned above, calcium ion is isolated by an ion-exchanger, showing about 8% activity extracted and the enrichment factor of 40 ~ 120.

71. The Chemical Reactions of Recoil Tritium with Water

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Tritium atoms recoiling from the nuclear reactions ^{6}Li (n,α) ^{3}H and ^{3}He (n,p) ^{3}H undergo chemical reactions while still possessing some of the kinetic energy of nuclear recoil. When reacting with H_2O, two reactions are possible:

$$T^* + H_2O \rightarrow HTO + H \quad (1)$$

$$T^* + H_2O \rightarrow HT + OH \quad (2)$$

Reaction (2) is endothermic by 0.3 e.v. and does not take place with thermal hydrogen atoms; however, it is an important reaction for recoil tritium atoms.

The competition between reactions (1) and (2) has been investigated in aqueous solutions containing Li^+ ions, and in gas mixtures containing ^3He, by irradiating the samples with thermal neutrons. The analysis has involved measuring the relative amounts of HT and HTO produced during irradiation. The samples were opened on a vacuum line HT withdrawn with ^4He carrier gas, while the HTO with H_2O carrier was held at -196° C in a liquid nitrogen trap. The HT was counted in a proportional counter with propane added. The H_2O was combusted to H_2 by the zinc combustion method, and its tritium content determined in the same way.

Aqueous solutions (pH 1 ~ 13) with many different dissolved salts present all give HT/HTO ratios of 0.10 ± 0.02. This ratio measures the competition between reactions (2) and (1) in liquid phase. These reactions are unaffected by solutes, as shown by the constant ratio.

Gas phase measurements have been made with H_2O, H_2 and O_2 present, as well as ^3He as the tritium source. In these systems, two additional reactions occur:

$$T^* + H_2 \rightarrow HT + H \qquad (3)$$

$$T^* + O_2 \rightarrow ? \rightarrow HTO \qquad (4)$$

The ratio HT/HTO represents the competition of reactions (2) and (3) with reactions (1) and (4). Approximate values for these rates in the gas phase are: $k_1/k_2 \sim 20$, $k_1/k_3 \sim 5$, $k_4/k_1 \sim 2$. These ratios will change with the energy of the recoiling tritium atom.

72. The Preparation of Iodine-131 by the Use of Fission Recoil Method

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Muneo Handa and Terutomi Moki
(Japan Atomic Energy Research Institute)

When a mixture of uranium dioxide powder and adequate medium of which amounts are sufficiently greater than that of uranium dioxide is irradiated with neutrons, the most portion of fission products are recoiled out of uranium dioxide and captured by the medium. If the medium is soluble in water, fission products can be easily transfered to the aqueous phase, and it makes the elimination of the troublesome procedure of the dissolution of uranium dioxide by the use of nitric acid and the following complicated purification processes connected with nitrogen oxide gas evolution.

In our experiment the pellets of uranium dioxide and oxalic acid (1:10 in weight ratio) are irradiated in a experimental hole of JRR-1 reactor for two hours. After 8 days cooling, it is treated with water and iodine is distilled out of the solution by sparging. Since the yield of I-131 depended on the sparging conditions such as temperature of air, flow rate of air, sparging period and concentration of the oxalic acid solution, these conditions were studied to obtain the optimum condition for the treatment.

The chemical yield was determined by a gamma-ray spectrometer comparing peak heights (0.364 Mev. gamma energy) of the spectra of the distillated I-131 and that of I-131 extracted from the residual solution by the carbon tetrachloride extraction method.

The optimum cooling period which is required to decay I-133 activity to less than 2% of I-131 activity was also investigated by experiment and calculation.

In this experiment, it was shown that about 70% of the I-131 can be obtained by the fission recoil method, and the subsequent purification process was much more simplified than the previous procedures.

73. Electronic Theoretical Consideration of Organophosphorus Compounds for Uranium Extraction Power

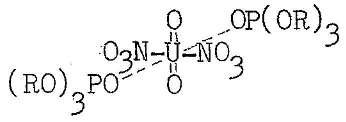
Tomota Nishi and Mitsuru Asano
(Engineering Research Institute, Kyoto University)

The authors already reported that uranyl and thorium nitrate could be extracted into various trialkylphosphates from aqueous nitric acid solution, that the longer the alkyl groups of phosphate, the larger the distribution coefficient was, and that the triiso-alkylphosphates extracted nitrate more easily than the corresponding trin-alkyl phosphates. These effects can be explained by electronic configuration of organophosphorus compounds, and thus we can presume the configuration of effective extracting agent of uranium.

For example, uranyl nitrate is extracted by trialkylphosphates as a following formula

$$UO_2(NO_3)_{2\ aq} + 2(RO)_3PO_{org} \rightleftarrows UO_2(NO_3)_2 2(RO)_3PO_{org}$$

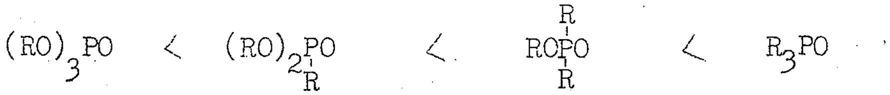
and the configuration of compound extracted is



$$(RO)_3PO \cdots O_3N-\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{U}}-NO_3 \cdots OP(OR)_3$$

The limit formulas of $(RO)_3$ PO are $\equiv P = D$, $\equiv P \rightarrow O$, $\equiv P^{+}- O^{-}$, and the higher electron density of oxygen in $\equiv$ P O group is preferable to get a stable compound with uranyl nitrate. Assuming that the effect of steric hindrance of the alkyl groups would not be so large, the alkyl group must be electron donative, and the longer the alkyl groups are, the stronger the electron donative property of alkyl groups and the higher electron density of oxygen in $\equiv$ P O group become. Therefore the phosphate of long alkyl groups will be more effective. The electron donative property of alkyl group of the phosphate will steeply increase in the short chain members and then gradually as the chain length becomes longer. As the iso-alkyl group is a stronger electron doner than the n-alkyl, the tri iso-alkylphosphates extract uranium more easily than the corresponding tri n-alkylphosphates. Indeed, triisopropylphosphate extract uranium much better than trin-propylphosphate.

The electron donative effect of the alkyl group of the trialkylphosphate is partly screened by -O- bond. Therefore, the organophosphorus compound having $\equiv$ P O group in which alkyl groups combine directly to phosphor, i.e. trialkylphosphine oxide is more effective than the others. The extraction power of the compounds will increase in the following order:



$$(RO)_3PO < (RO)_2\underset{R}{P}O < RO\overset{R}{\underset{R}{P}}O < R_3PO$$

trialkyl phosphate	dialkylalkyl phosphonate	alkyldialkyl phosphinate	trialkyl phosphine oxide

Above all, phosphine oxide compound of branched alkyl groups will have the most excellent extraction power.

Triphenyl and tricresylphosphate can not extract uranyl and thorium nitrate from aqueous nitric acid solution. This would be attributed to the electron attractivity of phenyl group and the fewer electron density in oxygen of $\equiv$ P O group. In tribenzylphosphate, the electron attractive effect of phenyl group is somewhat screened by $-CH_2-$ group, but this compound could not extract uranyl nitrate at all.

Tricycrohexylphosphate is presumed to extract uranyl nitrate from aqueous nitric acid solution more than triiso-propylphosphate.

The authors are trying to verify this theory, synthesizing many kinds of organophosphorus compounds and measuring the extraction power of those compounds.