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Activation Analysis of Impurities in Reactor Materials.

Toshio Nakai, Seishi Yajima, Minoru Okada and Isao Fujii (Japan Atomic Energy Research Institute)

1. Activation Analysis of Hafnium in Zirconium by Hafnium-179 m.

A method has been developed for the quantitative determination of hafnium in zirconium based on the use of neutron activation analysis. The sample was irradiated in the reactor of JRR-1 under the neutron flux of 2×10^{11} n/cm^2/sec. The gamma ray spectrograph of the irradiated sample was continually followed by RCL 256 channel pulse height analyzer, and the appropriate condition for the measurement of peak in 215 KeV gamma ray of Hf-179 m was found to be 60 second irradiation, 10 second cooling and 10 second measurement.

This procedure was applied to the determination of hafnium in the reactor grade zirconium and the appropriate analytical method was developed for the determination of hafnium of few ppm in zirconium with the accuracy of ±2%. The experimental results indicate that this method has an advantage over the conventional methods of microanalysis such as spectroscopic analysis, colorimetric analysis and others, because the former is not time consuming, taking only a few minutes for the analysis including sample preparation time, and has higher sensitivity and accuracy than the others.

2. Activation Analysis of Impurities in Aluminum and Magnesium.

Neutron activation analysis which includes neutron irradiation, anion exchange resin chromatography and gamma spectrometry has been developed for the determination of trace elements in Aluminum and Magnesium metals of high purity in the concentration range of 10^{-1} to 10^{-3} ppm. The elements determined are: copper, zinc, manganese, and antimony.

Dtermination of Uranium in Low Grade Ores by Neutron Activation.

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

Microgram amounts of uranium in minerals have been determined by neutron activation.

About 0.1 gr. of sample was irradiated in JRR-1 at a flux of approximately 2×10^{11} neutrons/sq.cm./sec. for two hours. Neptunium-239 formed was leached with aqua regia and then extracted by 100% TBP. Finally neptunium was purified by sorption on an anion exchanger from strong nitric acid solution.

Measurements of radiations were carried out by gamma scintilation spectrometry. Gamma ray spectra of Neptunium-239 have two large photopeaks at 0.10 and 0.21 Mev, both of which serve to identify and examine purity of neptunium isolated.

The method has a sensitivity of 0.01 microgram U_3O_8 and can be applied to minerals in which uranium is extractable with aqua regia.

Determination of Impurities in Thorium Metal and Oxide by Radioactivation.

Toshio Nakai, Seishi Yajima, Isao Fujii and Koreyuki Shiba (Japan Atomic Energy Research Institute)

In this study, the quantitative determination of rare earth elements in the thorium samples has been investigated by the use of neutron activation analysis.

A sample was irradiated in JRR-1 at a flux of approximately 2×10^{11} neutrons/sq.cm./sec. for two hours. The irradiated sample was dissolved in 8M-HCl by the adequate chemical procedures and poured to a Cl-type anion exchange resin column to separate rare earth elements from the activity of ^{233}Pa formed. By this treatment, rare earth elements and thorium passed thorugh the resin column and ^{233}Pa was retained. Leaked fraction was concentrated to a suitable volume and ready for measurement of gamma activity using gamma ray spectrometer.

The results obtained by this method are as follows:

Sample	Dy	Sm	La
1. (ThO_2)	410 ppm	250 ppm	110 ppm
2. (Th)	18	15	
3. (〃)	7	6	
4. (〃)	5	5	
5. (〃)	<1	2	

Sample 1) Raw material 2) Metal prepared by the electolysis of the fused salts 3)~5) Metals purified by the electrolysis.

Activation Analysis of Impurities in Semiconductor Materials.

Toshio Nakai, Seishi Yajima (Japan Atomic Energy Research Institute) Isao Fujii (Matsuda Research Laboratory, Tokyo Shibaura Electric Co. Ltd.,) and Minoru Okada (The Government Chemical Industrial Research Institute, Tokyo.)

In order to detect and determine many kinds of impurities with the minimum chemical procedure, neutron activation analysis which includes neutron irradiation, ion-exchange chromatography and gamma spectrometry was studied.

In gamma-spectrometry two or more kinds of radionuclides can be determined without chemical separation, if their γ-energy values are so apart from each other that they can be resolved by spectrometer. Therefore, the separation procedure is considerably simplified, and so, error caused by the separation can be avoided. Since the photopeaks of copper, antimony, cadmium and arsenic are in the narrow range of 0.51 to 0.57 MeV, which is little more than the resolution power of spectrometer used, these elements are, in their chlorocomplex, separated with each other by anion exchange resin chromatography.

Samples of silicon and germanium were irradiated by neutrons having a flux of 2×10^{11} n/cm^2/sec in JRR-1 reactor.

The method possesses a sensitivity of $4\times10^{-3}\mu g$, $3\times10^{-3}\mu g$, $1\times10^{-3}\mu g$, $2\times10^{-2}\mu g$, $1\times10^{-1}\mu g$, $3\times10^{-3}\mu g$, $3\times10^{-3}\mu g$, $4\times10^{0}\mu g$ for arsenic, copper, antimony, cadmium, zinc, natrium, gallium, and iron, respectively.

Activation Analysis of Silver using Radium-beryllium Neutron Source.

Yuzuru Kusaka and Haruo Tsuji (Department of Chemistry, Faculty of Science, Konan University, Kobe)

A method of radioactivation analysis by measurment of short-lived radioisotope was developed to determine the silver content in various samples. In this work, 50mg radium-beryllium mixture was used as activation source, and paraffin as neutron moderator.

In order to perform simply the activation operation and to measure efficiently the short-lived radioactivity induced by thermal neutrons, a special apparatus was constructed. After the end of neutron irradiation, the polyethylene tube, in which a neutron source is inserted, is slided out and the neutron source is exactly placed at the definite position in the lead shield and then the counting operation is followed by increasing the applied voltage of G. M. tube to its working voltage. By means of these procedures, it was possible to start the counting operation at five seconds after the end of neutron irradiation.

For obtaining as many counts of the induced radioactivity as possible in the definite time, we adopted the repeating operation of short time irradiation and measurment. The method was applied to determining the silver content in the japanese silver coins and the by-products in copper refining process. In the former a method using a calibration curve and in the latter an addition method, in which the known amount of the element was added in the sample and it was used as standard, were applied.

The method would be applicable to the radioactivation analysis of the other elements which produces the measurable amounts of the short-lived radioisotopes (half-life : ten seconds order) by means of a portable neutron source.

Utilization of Graphs for Presumption of Interfering Activity in Redioactivation Analysis.

Minoru Okada and Teiji Ōkubo (The Government Chemical Industrial Research Institute, Tokyo)

In activation analysis interfering activity always comes into question. In order to pervent the interference of a nuclide, which is a little different, from nuclide to be determined, in its half-life or radiation energy, it is required that all elements be compared with each other in their property mentioned above. For the convenience of the comparison of all elements with each other the authors have drawn five graphs. These show, against half-life of induced nuclide, such factors as (1) product of thermal neutron activation cross-section per unit mass of naturally occurring element and the ratio of the number of gamma emitters to that of disintegrations, (2) energy of gamma-ray emitted from radionuclide induced by thermal neutron irradiation, (3) energy of beta-ray emitted from radionuclide induced by thermal neutron irradiation, (4) threshold energy of (n, p), (n, α), or (n, 2n) reaction, and (5) activetion cross-section per unit mass of element for 14 MeV neutrons.

When the kinds of interferences are found by use of these graphs, necessary chemical procedures can be applied without the other chemical procedures. Therefore, the procedures in activation analysis can be simplified.

Radioactivation-analysis of Iodine in Silicon.

Tadashi Nozaki, Hideo Baba and Hidemaro Araki (Laboratory for Electro-communication, Tokyo)

Trace quantity of iodine in silicon purified through iodide method was determined by radioactivation-analysis. Silicon sample prepared from decomposition of silicon iodide was irradiated in JRR1 for an hour at the neutron flux of 2×10^{11}n/cm^2/sec with standards of iodine and arsenic. Fortunately, at that condition, there was no element to interfere measurement of γ-ray of iodine-128, whose energy and half-life are 0.46 Mev and 25.0min. respectively. The irradiated sample was measured repeatedly at short time intervals by a scintillation counter with 20-channel pulse-height analyser to obtain change of the γ-ray spectrum with time. Spectra due to sillicon having been substructed, the remaining spectra coincided with those of the standard both in shape and half-life. The standard was potassium iodide, from which after oxidation iodine was extracted with carbontetrachloride. Content of iodine in this silicon was 4 to 5ppm. 0.6ppm of arsenic was also determined through chemical separation and counting. Chemical separation of iodine was also studied, and was shown that, starting from alkali fusion, one could convert the iodine in one hour with good yield into siver iodide ready for counting. With this method, limiting quantity of iodine in silicon for determination should be 3×10^{-9} g.

Separation of Radioactive Anitomony from Tin Target Irradiated by 14 Mev Protons.

Kunio Seto, Nobuo Suzuki and Kazuo Saito (Institute for Nuclear Study, University of Tokyo)

In order to prepare a source for the measurement of angular correlation of gamma-rays of ^{120}Sb, chemical separation of this element from a large amount of tin was studied. The specific actitvity of the source must be 30 to 500 μc in 0.05 cc. Since commercial tin always contains a small amount of antimony, the source cannot be carrier-free.

Two methods, cation exchnage[1] and solvent extraction[2] were employed and their applicability was for the first place examined with the aid of commercial ^{124}Sb. It was elucidated that the former is satisfactorily effected when both elements are in the lower valency state, whilst the latter when they are in the higher valency state.

Irradiation was substantiated in INS cyclotron with 14 Mev protons, for 5 hr. with 40 μA beam and for 8 hr. with 15 μA beam (total 200 and 120 μA-hr. respectively); tin metal is spread on an aluminium slab and attached to the head of an inner target holder. Irradiated tin is either dissolved in 6 N hydrochloric acid or in a mixture of 6 N hydrochloric and nitric acid; the former solution is submitted for ion exchange separation and the latter to the solvent extraction method. Satisfactory separation of antimony was effected by extraction with amyl acetate from a 10 N hydrochloric acid solution (200 ml) containing ca. 20 mg. tin per cc. and the amyl acetate solution was washed with 10 N hydrochloric acid evaporated and mounted in a plastic sample holder. On the other hand some ambiguity was involved in the case of ion exchange separation.

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1) Kimura et al., Nippon Kagaku Zassi **74**, 305, (1953).

2) White et al., Anal. Chem., **25**, 351, (1953).

Excitation Functions for the Reactions ^{58}Ni (p, pn) ^{57}Ni, ^{58}Ni (p, 2p) ^{57}Co, and ^{58}Ni (p, α) ^{55}Co up to Ep=14 Mev

S. Tanaka (Inst. for Nuclear Study, Tokyo Univ)

The absolute values of excitation functions for the reactions ^{58}Ni (p, pn) ^{57}Ni, ^{58}Ni (p, 2p) ^{57}Co, and ^{58}Ni (p, α) ^{55}Co have been measured by the activation method.

Proton bombardments at energies up to 14 Mev were carried out by the analyzed beam of the INS cyclotron (Tokyo) using stacked foils of natural nickel. The irradiated targets were dissolved in hydrochloric acid, and the nickel, the cobalt and the copper were chemically separated by anion exchange resin. After 36-hr. ^{57}Ni was allowed to decay into ^{57}Co, ^{57}Co was separated from nickel, fraction. ^{57}Ni was thus measured as ^{57}Co. The absolute amount of 270-d. ^{57}Co was determined by counting on the 137-and 123-kev gamma peaks with a scintillation spectrometer. The absolute amount of ^{55}Co (18.2-hr.) for one sample was counted in a 4π constant-flow methane proportional counter. (This was also counted in a Geiger region using Q-gas.) The relative amounts of ^{55}Co for the other samples were measured by a Geiger counter.

The contribution of the ^{60}Ni (p, α) ^{57}Co reaction on σ (p, 2p) curve should be considered, but this is indistinguishable by this method. The important conclusion is that the (p, 2p) cross sections are much larger than the (p, pn) cross sections over the whole proton energy range from threshold to 14 Mev, as has been pointed out at 21.5 Mev by Cohen et al. (P. R., **99**, 723 ('55)).

Excitation Functions for the Reactions ^{61}Ni (p, n) ^{61}Cu and ^{64}Ni (p, n) ^{64}Cu up to Ep=14Mev

S. Tanaka, M. Furukawa and T. Mikumo (Inst. for Nuclear Study, Tokyo Univ.)

The absolute values of excitation functions for the reactions ^{61}Ni(p, n) ^{61}Cu and ^{64}Ni(p, n) ^{64}Cu have been measured by the activation method.

Proton bombardments at energies up to 14 Mev were carried out by the analyzed beam of the INS cyclotron (Tokyo) using stacked foils of natural nickel. The incident flux was measured by a Faraday cup. The irradiated targets were dissolved in hydrochloric acid, and the copper was chemically separated by anion exchange regin. The absolute amount of ^{64}Cu(12.8-hr.) was counted in a 4π constant-flow Q-gas Geiger counter. The relative amounts of ^{64}Cu for other samples were measured by a Geiger counter. The absolute amount of ^{61}Cu(3.3-hr.) was determined from ^{61}Cu/^{64}Cu ratios which were obtained by analyzing the gross decay curves.

Sensitivities of Neutron Activation Analysis Using JRR-1 Reactor.

Hiroshi Hamaguchi, Toshio Nakai (Tokyo University of Education, Tokyo and Japan Atomic Energy Research Institute, Tokaimura, Ibaragi Pref.)

Sensitivities of neutron activation analysis are determined by several factors, i.e. the nature of the nuclides in question, the irradiation conditions, the time necessary for chemical procedures, the chemical yield, and the counting efficiency of the activity isolated. An attempt to calculate the sensitivities was made based on the following assumptions :

sensitivity : define as the amount of the element in μg which gives 100 cpm activity at the time of isolation.
neutron flux : 3×10^{11}n/cm^2/sec.
decay time : 48 hours
chemical yield : 50%
counting efficiency : 10% (using usual GM counter)

Results are shown below :

sensitivity (μg)	element
0.001 ~ 0.01 ········	Eu, Au, Lu, Ho, Ir
0.01 ~ 0.1 ········	Sm, Re, Yb, La, Pr, As, W, Sb, Tm
0.1 ~ 1 ········	Y, Br, Sc, Cu, U (via Np^{239}), Tb, Pd, Na, Ga, Ta, Os, Gd, P, Cd, Nd, Hf
1 ~ 10 ········	Cr, Cs, Co, Pt, Ce, Hg, Ru, K, U (via Ba^{140}), Mo, Sn, Ag
10 ~100 ········	Rb, Te, Bi, Tl, Zr

The calculated values are compared with those obtained experimentally in the case of Ir, As, W, Sb, Pd, Pt and Zr.

Determination of Tungsten in Iron Meteorites by Neutron Activation.

E. Ideno, T. Nakai and H. Hamaguchi (Tokyo University of Education, Tokyo and Japan Atomic Energy Research Instiute, Tokaimura, Ibaragi pref.)

So far no reliable analytical data have been established for tungsten in iron meteorites. We report here the result of the determination of a trace amount of the element in two typical iron meteorites by neutron activation technique.

The radiochemical procedure involves thermal neutron irradiation of the samples (0.5~1.0 g block) along with a monitor, both sealed in quartz tubes. As a monitor, a solution containing the same principal metallic constituents as iron meteorites, together with a known added amount of tungsten, was evaporated in a quartz vial.

Irradiations were carried out in JRR-1 reactor. The flux was $\sim 3\times 10^{11}$n/cm^2/sec, and the irradiation lasted from 2 to 3 days (5 hours at longest each day).

After irradiation the sample and monitor were dissolved in aqua regia in the presence of tungsten carrier. The amount of tungsten was then determined by comparing the radiochemically pure ^{187}W and ^{185}W activities isolated from the samples with those from the monitor. In the decontamination chemistry, special care was taken of the removal of phosphorus and molybdenum activities, because these elements and tungsten are liable to behave similarly in the usual chemical procedures. After radiochemical separation, the tungsten was precipitated as oxinate, dried at 120°C and mounted for counting. Total time required for the chemical process was 10~15 hours and the overall yield was 25~50%. Correction for the counting efficiency with different sample thickness was made because of the rather weak β energy (0.62 Mev) of ^{187}W.

Two iron meteorites, Canon Diablo and Henbury, showed the mean value of 1.0 and 0.8 ppm respectively, but indicated variation by a factor of 2 and 4, respectively, with separate irradiations.

The latter fact seems to suggest the uneven distribution of the element in the samples.

Determination of Arsenic and Antiminy in Iron Meteorites by Neutron Activation.

T. Endo, T. Nakai and H. Hamaguchi (Tokyo University of Education, Tokyo and Japan Atomic Energy Research Institute, Tokaimura, Ibaragi Pref.)

A number of determinations on arsenic and antimony in iron meteorites have already been reported. However, as they showed wide variations by different authors, more studies are highly desirable. The present authors report here the results of arsenic and antimony assay by neutron activation technique.

The radioactivation procedure involves thermal neutron irradiation of the samples along with a monitor. As a monitor, a solution containing the same principal metallic constituents as iron meteorites together with a know added amount of arsenic and antimony, was evaporated in a quartz vial.

Irradiations were carried out in JRR-1 reactor. The flux was $\sim 3\times 10^{11}$n/cm^2/sec, and the irradiation lasted from 2 to 3 days (5 hours at longest each day). After irradiation the sample and monitor were dissolved in aqua regia in the presence of carriers. The amount of the two elements was then determined by comparing the radiochemically pure ^{76}As and ^{122}Sb activities isolated from the samples with those from the monitor.

For the radiochemical separation, arsenic and antimony sulfide were precipitated from the solution by thioacetamide, dissolved in fuming HNO^3 ; then arsenic trichloride and antimony tribromide were distilled at oil bath temperatures of 115 and 225°C respectively. Finally the arsenic was reduced to the metal with $SnCl_2$ and the antimony was precipitated as sulfide with H_2S, and both were mounted for counting.

Two typical iron meteorites, Canon Diablo and Henbury, gave mean values of 12.5 and 14.3 ppm for As and 0.34 and 0.45 ppm for Sb respectively. Separate irradiations on the same meteorite gave the same value to within 20%, thus showing the evidence of an even distribution of the elements in the samples.

Determination of Platinum Group Metals in Iron Meteorites by Neutron Activation.

Y. Kamemoto, T. Nakai and H. Hamaguchi (Tokyo University of Education; Japan Atomic Energy Research Institute.)

Platinum, Palladium and Iridium in iron meteorites were determined using neutron activation techique. The radioactivation procedure involves thermal neutron irradiation of the samples along with a "mock", i.e. a monitor of meteoritic composition spiked with a known amount of elements to be determined. After irradiation the sample and monitor are dissolved in the presence of carriers. The amount of the respective platinum metals in the meteorite are then determined by comparing the radiochemically pure ^{197}Pt, ^{109}Pd, ^{194}Ir and ^{192}Ir activities isolated from the samples with those from the monitor.

All irradiations were carried out in JRR-1 reactor. The flux was $\sim 3 \times 10^{11}$ n/cm^2/sec, and the irradiation lasted from 2 to 3 days (5 hours at longest each day). Samples weighing less than 1.4 g were found to have no self-shielding effects.

Radiochemical separations consisted of the precipitation of the metals by reduction with Mg, fusion with $NaOH$-Na_2O_2 mixture, precipitation with NH_4Cl, dissolution in aqua regia and separation into fractions by ion exchange. For further decontamination, Ir and Au holdback carriers were added to the Pt fraction and the Pt was extracted with ethyl acetate, followed by the precipitation of the metal fraction and the Pt with Mg. From the Pd fraction Pd glyoxime was precipitated, dissolved in aqua regia, put in a ferric hydroxide scavenge, and was reprecipitated. Ir was precipitated as the metal from its fraction by reduction with Mg.

The results obtained are the following :

Meteorite	Pt		Pd		Ir	
	No. of detens.	content (ppm)	No. of detens.	content (ppm)	No. of detens.	content (ppm)
Canon Diablo	3	12.6	2	4.1	3	0.3
Henbury	3	9.8	3	4.7	3	1.3
Carbo	2	30	2	3.4	2	3.5

Separation of the Fission-Recoiled Fragments from the Uranium Oxide

Toshio Nakai, Seishi Yajima and Isao Fujii (Japan Atomic Energy Research Institute)

Introduction: In the field of nuclear physics, the momentum properties of fission products have been intensively investigated with a view of determination of kinetic energies, angular distributions, and modes of energy loss.

However, except a few studies, the nuclear recoil of fission products has not been applied to the complete separation of fission products from their parent fissile material. If a fission reaction is carried out in particles of fissile material with maximum dimensions smaller than the range of the fission products, fission products will necessarily recoil out of the parent material. On the other hand, the heavier nuclei formed by neutron capture and beta decay will have a very much shorter recoil range and will remain within the original particle unless it is extremely small. This means that in a suitable heterogeneous system the fission products will completely separate themselves from the actinides, eliminating the need for complex chemical processing.

Procedure: In this study, uranium oxide powder (chemical form U_3O_8, weight 30 mg, diameter less than 0.5μ) were mixed uniformly with graphite powder (weight 0–2100 mg, diameter about 70μ), and these prepared samples were irradiated for about three minutes in the central portion of JRR 1 (thermal neutron flux was about 2×10^{11}n/cm^2/sec.). Fifty ml portions of saturated zinc bromide solution were added to the irradiated samples respectively and these mixtures were centrifuged to separate the graphite powder to upper layer and the uranium oxde powder to the bottom portion. After separation, these fractions were collected in polyethylene bottles respectively and the separation degree of the fission products was investigated by the use of gamma ray scintillation spectrometer (R.C,L. 256 channel, well type crystal attached).

Results:

1. The separtion degree of fission products was about 75% in the range of the weight ratio 1(U_3O_8) : 3(graphite) and approximately 95% in the range of 1 :30.
2. The Np-239 formed by neutron capture and β-decay was retained completely in the uranium oxide powder.
3. The fission products fixed to the graphite powder were not leached by boiling 7N nitric acid.

Preparation of High Specific Activity ^{51}Cr by the Szilard-Chalmers Process.

Nagao Shibata and Kenji Yoshihara (Japan Atomic Energy Research Institute)

High specific activity ^{51}Cr has been prepared by neutron irradiation of electromagnetically enriched ^{50}Cr in the pile ; but this method offered only poor enrichment. Recently, it was found that the state of ^{51}Cr, produced when chromate or dichromate was irradiated by neutron, was a trivalent form; and high specific activity ^{51}Cr was prepared by the procedure based on this effect, but its yield was not so high.

We studied the method of separation of ^{51}Cr recoiled from a highly stable dye Palatine Fast Blue GGN, a sort of chromium complexes of 0, 0′-dioxy diazo compounds.

The sample which was irradiated in the reactor, JRR 1 (neutron flux: 10^{11}n/cm^2/sec) was dissolved in water, then it was passed through a cation exchanger column. A main part of activity was absorbed in the resin, and the dye itself was passed through the column. It was observed that the absorbed part was Cr* (III) separated from mother dye material by the hot atom effect, and eluted by 200 ml of 2N hydrochloric acid. Its eluent was composed of three peaks, corresponding $Cr^*(H_2O)_6^{+++}$ $Cr^*(H_2O)_4Cl_2^+$ and $Cr^*(H_2O)_5Cl^{++}$ respectively.

These cationic parts were oxidized to chromate or dichromate, and its yield was totally over 70%. Another small part of activity which was originally $Cr^*O_4^{--}$ was absorbed by anion exchanger, and was collected from it. The concentration factor of thus separated ^{51}Cr was over 10^3. In conclusion, we think this method by hot atom effect is useful for production of high specific activity ^{51}Cr, because its high yield and high concentration factor.

Fraction of Sulfur Isotopes during Oxidation of Sulfite Ion.

I. Iwasaki, H. Fukutomi and H. Shimojima (Tokyo Institute of Technology, Tokyo)

The present authors carried out an experiment to make up clear the fractionation of sulfur isotopes during oxidation of sulfite ion. Sodium sulfite labelled with sulfur-35 is prepared by the absorption of radioactive sulfur dioxide with granular sodium hydroxide. Radioactive sulfur dioxide is produced by the reaction of radioactive lead sulfate (labelled with sulfur-35) and pyrite powder in vacuum at 600~700°. A definite volume of bromine water is added to sodium sulfite solution and small part of sulfite is oxidized to sulfate. Acidifying a mixed solution of sulfite and sulfate with hydrochloric acid and introducing nitrogen gas, sulfite is decomposed to sulfur dioxide. This sulfur dioxide gas is introduced into sodium hydroxide solution and partly oxidized again with bromine water by the same manner as described above. The sulfate ion is precipitated as barium sulfate. The experiment was carried out successively till the sulfite is consumed. About ten samples of barium sulfate for the determination of the radioactivity were obtained. If the fractionation of sulfur isotopes had not taken place during these processes, these samples should have had the same specific activity. However, there is a small variation beyond the experimental errors in their radioactivity, and the barium sulfate obtained in earlier stage in one series of fractional oxidation is larger specific activity than the later. The isotope effect will be considered as a factor for the explanation of these phenomena.

Fractionation of Isotopes during Oxidation and Reduction of Some Sulfur Compounds.

H. Shimojima, H. Fukutomi and I. Iwasaki (Tokyo Institute of Technology, Tokyo)

Following processes of oxidation and reduction have been carried out.

Sulfate ——→ Sulfide
Sulfide ——→ Sulfate
Sulfur ——→ Sulfate
Sulfite ——→ Sulate

Isotope effects on the reaction velocity as well as on the thermal equilibrium should be considered to explain the experimental results.

Oxidation of sulfur to sulfate was made as follows. A carbontetrachloride solution of crystalline sulfur labelled with sulfur-35, was made to react with an aqueous solution of hydrochloric acid and bromine. After a definite time interval, aqueous layer which contains sulfate produced, is separated from a carbontetrachloride solution. Barium sulfate is prepared and mounted for the measurement of radioactivity. About 10% difference in the specific activity was found in the barium sulfate samples obtained in earlier and later stages of the reaction.

Simultaneous Production of Silicon-31 and Phosphorous-32 by Szilard-Chalmers Process.

Nagao Ikeda and Hiroshi Ebihara* (Department of Chemistry, Faculty of Science, Tokyo University of Education; Japan Atomic Energy Research Institute*)

Since L. Szilard and T. A. Chalmers had prepared the carrier-free radiohalogens from organohalogen compounds in 1934, this method has been applied to the first stage of nuclear chemical experiments.

On the concentration of radioisotopes which is prepared by the common process (n, γ) reaction, the Szilard-Chalmers process is still more practical ways.

In order to prepare Silicon-31 and phosphorous-32 in high specific activity, the authors investigated the possibility of the Szilard-Chalmers process relating with tributylphosphate.

Tributylphosphate was bombarded with neutron by the cyclotron (neutron flux: 10^7n/cm^2/sec.), and radioactive ^{31}Si and ^{32}P recoiled out was extracted from tributylphosphate by various extracting agents.

The percentage yield of separable ^{31}Si activity showed maximum value 87.5% when potassium hydroxide solution of pH 12.5 was used; and the percentage yield of ^{32}P also showed maximum value 54.3% in the same conditions, Both anion and cation exchange resin were studied about the separation of ^{31}Si and ^{32}P, and the cation exchange resin Daiaion SK-1 (feric type) gave the most preferable results. ^{31}Si and ^{32}P got by the procedure mentioned above were almost carrier-free state, and the radiochemical purity of ^{31}Si was 99.9% and of ^{32}P was 100.

Thus, we could prepare radioactive ^{31}Si and ^{32}P in high specific activity and high radiochemical purity in a short while.

Hot-atom Effects in Neutron-irradiated TBP.-Phase Effect for (n, γ) and (n, p) Reaction.

Nobufusa Saito and Hirotoshi Sano (Department of Chemistry, Faculty of Science, University of Tokyo; Scientific Research Institute, Tokyo)

It was shown by other investigators that the "organic yield" was higher for (n, γ) reactions carried out at temperatures below the freezing point of a compound than for the reactions conducted at temperatures, above such point. This fact indicated the presence of "phase effect" which might be attributable to the difference in density or structure of solid from that of liquid. In this report, the phase effects were studied for ^{32}P and ^{31}Si produced by the $^{31}P(n, \gamma)$ ^{32}P and the $^{31}P(n, p)$ ^{31}Si reaction on TBP, respectively.

At room temperature or liquid-nitrogen temperature, 20 ml. of TBP was subjected to neutron irradiation. The neutrons produced by Be-D reaction in a cyclotron were used, its flux being approximately 10^7 neutrons/cm^2. sec. The irradiation of the sample in or out of a Dewar's vessel containing liquid nitrogen lasted 2 to 3 hours. After the bombardment, the sample was shaken with 20 ml. of petroleum ether and 20 ml. of water at room temperature and the resulting aqueous layer was separated. The organic layer was extracted repeatedly with 20 ml. of water. The aqueous and organic layers were separately transferred into each of two 50 ml. volumetric flasks, and diluted to the mark with water or ethanol. The gross activities were measured on each fraction with a G-M liquid counter. From the decay curves observed, the relative amounts of the radioactivities in these fractions were determined. It was found that the "organic yield" of ^{32}P resulted from the (n, γ) reaction at liquid-nitrogen temperature was makedly higher than that at room temperature, whereas the "organic yield" of ^{31}Si resulted from the (n, p) reaction was nearly independent on the nature of the phase or the temperature during irradiation.

Radioactivation Analysis of Phosphorus in Biological Materials by (n, p) Reaction.

Hirotoshi Sano, Eikō Sairenji and Nobufusa Saito (Department of Chemistry, Faculty of Science, University of Tokyo; Scientific Research Institute, Tokyo)

Phosphorus in biological materials is usually determined spectrophotometrically.

However, most of the analytical methods used are so complicated that the results obtained are not reproducible. In recent years, the activation analysis employing (n, γ) reaction have been applied to the determination of phosphorus in biological materials. To obtain sufficient activity of ^{32}P for counting, however, fairly long irradiation of the samples is needed. Moreover, ^{32}P will be produced from the coexisting chlorine in such materials, since ^{35}Cl (n, α) ^{32}P reaction takes place even by thermal neutron irradiation. This will interfere with the determination of phosphorus.

An attempt was made by the present authors to estimate phosphorus in biological samples by counting ^{31}Si activity prduced by the ^{31}P (n, p) ^{31}Si reaction. For irradiation, fast neutrons (flux : 10^6–10^7 n/cm^2/sec.) from the cyclotron at the ScientificResearch Institute were used. Irradiation periods varied from one to three hours. In addition to the desired samples, a reference standard of calcium phosphate was irrdiated and the redioactivity produced in them were compared each other.

In the present study, basic factors were investigated, such as the relationship between the amounts of phosphorus and the activity of ^{31}Si induced in a sample, self-absorption and the influence of some other elements which may coexist in a sample. If ^{31}Si is produced from other elements than phosphorous, it may greatly interfere with the determination. For example, the ^{34}S(n, α)^{31}Si reaction may occur in a sample containing sulfur. But, the interference will not serious because of the low content of sufur in biological materials. The interference by silicon resulting from the ^{30}Si(n, γ)^{31}Si reaction is also negligible. The effect of the presence of sodium, chlorine and potassium in samples was also studied. If the amounts of these elements in samples are small, the ^{31}Si can be identified by the analyses of composite decay curves, whereas the analyses of the curves is difficult if they exist in large amounts.

The Influence of Irradiation Temperature on the Retention Value of Radioarsenic in the Szilard-Chalmers Reaction with Crystalline Sodium Arsenate.

Nobufusa Saito and Isao Tomita (Department of Chemistry, Faculty of Science, University of Tokyo; Scientific Research Institute, Tokyo)

Retention of radioarsenic as arsenate after the neutron irradiation of crystalline $Na_2HAsO_4 \cdot 7H_2O$ was found previously to be about 67 % by J. Malý and R. Šimáňová, and 65 % by H, Müller and E. Broda and, independently, by the present authors.

In the present investigation, the "recombination" of the fragments produced by neutron capture in these compounds has been studied : that is, the irradiation was carried out at different temperature, so that the reaction rate of recombination process may be different enough to effect on the retention values.

Temperatures of bombardment site were −195°C (liquid nitrogen), −72°C (mixture of dry-ice and ethanol) and room temperature. The neutrons produced by Be-D reaction were thermalized through a paraffin block or water. In some cases, they were slowed down through ethanol.

Retention values at lower two temperatures were nearly the same, about 50%, showing a fairly large difference from the value, 65%, obtained in the irradiation at room temperature. When the irradiated crystals were stored for 18 hours at liquid nitrogen or dry ice-ethanol temperature, retention values remained almost constant. On the other hand, the storage of the crystals at room temperature resulted in gradual oxidation of radioarsenic in+3 oxidation state to +5 and the retention values increased.

The above experimental data are not contradictory to the assumption of "recombination process" that the recoil fragments of irradiated salts would recombine after they were ejected from the parent molecules.

Hot-atom Effects in the Neutron Irradiation of Iodate.

Nobufusa Saito, Hirotoshi Sano and Reiko Shiomi (Department of Chemistry, Faculty of Science, University of Tokyo; Scientific Research Institute, Tokyo)

Hot-atom effects have been studied by Cleary et al. on the neutron-irradiated iodate in solid state and in aqueous solution. The present investigation was undertaken to study the behavior of hot atoms of ^{128}I produced by the neutron irradiation of iodate, the effects of temperatures during irradiation upon the retention value.

The iodate samples were irradiated for 2.5 hours with a neutron flux of approximately $10^7 n/cm^2.sec$. Irradiations were performed at room temperature, −72°C (dry ice-ethanol) and −196°C (liquid nitrogen). For the separation of iodide from iodate, precipitation and ion exchange methods were employed.

The retention of ^{128}I in iodate crystals was approximately 70% at room temperature, while that in aqueous iodate solution was 25%. The decrease in the retention value observed, when irradiations were made at low temperatures. The retention in the resin phase was only 5%, being much smaller than those in other phases. This might be attributable to the reducing nature on ion-exchanger. The ^{128}I of high specific activity was obtained by the use of anion-exchanger. It was observed that approximately 10% of the total activity remained in the resin even after the elution process was completed. It is likely that the radioactive iodine atoms are bound to resin in organic form.

On the Hot-Atom Chemistry of Uranium Salts (1)

Nobufusa Saito and Tatsuya Sekine (Department of Chemistry, Faculty of Science, University of Tokyo, Tokyo,)

Previously, J. W. Irvine, Jr., reported that ^{239}U in neutron-irradiated uranyl ammonium acetate solution is enriched in the first fraction of a hydrolytic precipitation by a factor of approximately ten and that ^{239}U formed in the solution is probably settled down in the tetravalent state. The present reporters made some experiments using a cyclotron (Be-d reaction) instead of Ra-Be mixture as a much stronger neutron source than that of Irvine's work. The procedures are as follows; neutron-irradiated ammonium uranyl acetate solution is poured into boiling water containing small amounts of ammonium acetate. A precipitate of basic uranyl acetate is filtered and dissolved with a hot mixture of nitric acid and acetic acid, then to the solution is added a large excess of sodium acetate to precipitate sodium uranyl acetate. The precipitate is filtered, dried and its β activity is measured. After repeated experiments, the reporters could not observe such a ^{239}U enrichment as described by Irvine.

The reporters also have made an experiment on the hot-atom chemistry of uranium sulfate solutions. The procedures are as follows; three kinds of solutions, (A) U(VI), (B) U(VI)+U(IV), (C)U (IV) sulfate, are irradiated with neutrons and carrier of either U(IV) or U(VI) is added to the solutions (A) and (C), then U(IV) is extracted with chloroform as cupferronate and this U(IV) cupferronate is heated with nitric acid to obtained U(VI) nitrate solution. Sodium uranyl acetate was precipitated from each of the U(VI) solution, then its β activity is measured. The results are as follows; (1) almost all of ^{239}U in the neutron-irradiated U(VI) solution is in the (VI) state. (2) more than half of ^{239}U in the U(IV) solution is not in the (IV) state but in the (VI) state. In another experiment on solution (C), ^{239}U is enriched in the U(VI) fraction by a factor of approximately 50, and from these data, the reporters have concluded that hot-atom effect plays an important role in the formation of ^{239}U in the (VI) state.

Hot-atom Chemistry of Tellurium. IV.

Chemical State and Enrichment of Radioactive Tellurium in Neuton-irradiated Tellurite.

Nobufusa Saito and Mariko Inarida (Department of Chemistry, Faculty of Science, University of Tokyo; Scientific Research Institute, Tokyo)

This is to report the chemical state and the enrichment of radioactive tellurium produced by neutron irradiation of tellurite.

Tellurite was adsorbed on a strong-base anion exchange resin, Amberlite IRA-400 (RCI form, 100-200 mesh, column size: 3 cm long and 1.0 cm in diameter) to make up samples of tellurite-loaded resin. In addition, tellurium (IV) was extracted with TBT (100%) from hydrochloric acid solutions of 4 and 6N to prepare samples of TBP containing tellurium (IV). These samples were irradiated with thermal neutrons (flux: 10^6-10^7n/cm^2/sec) for two to three hours. For the separation of tellurium (IV) from tellurium (VI), anion exchange and TBP extraction methods were empolyed. The activities of radioactive tellurium of both tellurium (IV) and tellurium (VI) fractions were measured and the distribution, specific activity of radioactive tellurium in these fractions were calculated. In the samples of tellurite-loaded resin, approximately 95 % of the total activity was found in the tellurium (IV) fraction, while in TBP samples about 80 % was found in corresponding fraction. The enrichment of radioactive tellurium was observed in tellurium (VI) fractions from the samples of both kinds.

The authors studied also the stability of tellrium (IV) in the resin and TBP phases, using Te-127 m as an indicator. No appreciable change was observed after five hours standing of the resin and TBP containing tellurium (IV).

Studies on the Szilard-Chalmers' Reaction of Manganese-Chlorophyll

Yoshie Suzuki (Dept. of Chemistry, Univ. of Tokyo) and Yukio Murakami (Radiosiotope School, Japan Atomic Energy Research Institute)

OBJECT: This study was undertaken to find out the producing method of radioisotope of divalent metals in high specific activity by applying the Szilard-Chalmers' reaction to the chlorophyll related compounds that the central metal atom of chlophyll was replaced by the divalent atoms.

METHOD AND RESULTS: At first, manganese-chlorophyll was used in water solution as target material. This compound was irradiated for a definite time with the thermal neutron by the KAKEN-Cyclotron. The following nuclear reaction will be expected: $^{55}_{25}\mathrm{Mn}(n, \gamma)^{56}_{25}\mathrm{Mn}$

After the irradiation, the solution was slightly acidified with nitric acid. This treatment made the compound water soluble form and easily extractable form with organic solvent, such as ether. The extraction was repeated until any green colour of chlorophyll could not be found in water solution. The organic and water layers thus formed were dried up and their radioactivity were measured with scintillation counter. After that, manganes content of these two samples was determined colorimetrically, and the specific activity was calculated.

In water layer the specific activity is higher than that in organic layer. The ratio of specific activity in both layers varied between the ranges of 1 to 3. However sometimes the completely reverse results were obtained.

The discussion on the pH of target material solution, the promising separation method, the oxidation state of the recoiled manganese atom and the extent of exchange reaction will be given in detail.

A New Fluorescent Substance for the Measurement of Charged Particles......Sexiphenyl

Kazuo Saito, Koichi Suga, Tadashi Nozaki and Michiko Tamura (Institute for Nuclear Study, University of Tokyo, and Laboratory for Electro-communication)

It has long been recognized that para-polyphenyl compounds are useful for scintillator or wave-length shifer and that the efficiency of the compound increases with increasing number of the phenyl ring. Nevertheless, no infomation is available concerning higher members of this series than quater phenyl. Hence attempts have been made to synthesise sexiphenyl and to examine its properties as scintillator.

Sexiphenyl was synthsised by two methods : commercial terphenyl is nitrated and then converted into p-iodoterphenyl which was condensed with silver powder by Ullmann's method; p-nitrobiphenyl is converted into p-iodobiphenyl and similarly condensed with pp'-diiodobiphenyl obtained from benzidine. Both products were purified by vacuum distillation and recrystallisation. For the solvent, only those liquids having high boiling points (e.g. α-methylnaphthalene, tetraline, o-dichlorobenzene and nitrobenzene) were available. By repeated recrystallisation, followed by vacuum sublimation, pure crystalline sexiphenyl was obtained with a poor yield.

Characteristics of this compound as scintillator were examined with polonium -210 as actitvity source. The fine crystalline powder is immersed in a mixture of α-bromonahthalene and α-chloronaphthalene, having the same reflective index with sexiphenyl and the photo-pules is introduced into a photomultiplier, the output of which is amplified and submitted to pulseheight analysis. The results compare favourably with those for quaterphenyl.

Radioactivation by (γ, γ)-Reaction. VII. Dosimetry of Cobalt-60 γ-Ray Source by the Use of $^{115}In(\gamma, \gamma)^{115m}In$ Reaction.

Nagao Ikeda, Kenji Yoshihara, Kazuo Shimada (Japan Atomic Energy Research Institute)

Previously, we applied (γ, γ)-dosimetry using $^{115}In(\gamma, \gamma)^{115m}In$ reaction as a standard in the determination of the cross-sections of the reactions, $^{107,109}Ag(\gamma, \gamma)^{107m,109m}Ag$ and $^{111}Cd(\gamma, \gamma)^{111m}Cd$. In this work, we attempted to obtain a more distinct outline on this method using 10 Kc cobalt-60 γ-ray source which was set at Japan Atomic Energy Research Institute.

Indium foils (2 cm × 3 cm) are mounted at the difinite positions around the γ-ray source. The dose rate at each position was measured by the Victoreen Roentgen Rate Meter and by chemical dosimetric method. Induced radioactivities in indium foils at various positions were measured, and it was found that these values were proportional to the dose rate obtained by other methods. At the position near the wall, however, the proportionality was not so good because of the scattering effect of the wall. Above the desk on which the γ-ray source was put, this proportionality holds good to the height of 30 cm. This (γ, γ)-dosimetry is convenient for the measurement of the high dose rate near the large amounts of γ-ray source, and gives good indication of dose rate of γ-ray over 1.04 MeV.

Tracer-chemical Studies on Actinide Elements II. Distribution of Neptunium between TBP and some mineral acids.

Tomitaro Ishimori and Eiko Nakamura (Japan Atomic Energy Research Institute)

Neptunium-239 is used as the tracer for studies on solvent extraction behaviors of neptunium in the following systems :

1. Nitric acid solution and TBP 2. Hydrochloric acid solution and TBP
3. Sulphuric acid solution and TBP 4. Perchloric acid solution and TBP

Kd values are measured by combinations of scrubbing techniques and the chemical treatments. In nitric, hydrochloric and sulphuric systems, neptunium gives three kinds of Kd, distribution ratio, which could be assigned to oxidation states of IV, V, and VI. On the other hand, in perchloric system neptunium does not show Kd value which should be assigned to oxidation state IV.

Some of these results are compared with those of uranium, plutonium and other elements. In nitric system, neptunium (VI) shows a similar acid dependence of Kd value with those of uranium (VI) and plutonium (VI). Kd values of neptunium (IV) and plutonium (IV) vary almost in the same way against the acid concentration of nitric acid. There is also a strong similarity between acid dependences of uranium (VI) and neptunium (VI) in the hydrochloric system.

Behaviors of neptunium (V) are compared with those of protactinium.

Tracer-chemical Studies on Actinide Elements III. Solvent Extraction of Pa and Np with Cupferron.

Kan Kimura (Japan Atomic Energy Research Institute)

Partitions of both Pa and Np are studied on systems of acidic aqueous solution and chloroform solution of cupferron.

Tracers used are Pa-233 and Np-239. These are prepared by irradiating thorium and uranium nitrates in JRR-1 respectively.

(1) Hydrochloric systems :

In the presence of zinc metal, Np is easily extracted from (0.5-4)N hydrochloric acid showing Kd values of about 10. Behaviors on less than 0.5N hydrochloric acid is not checked. On the other hand, the pressence of gaseous chlorine makes Kd values very small.

Pa is also extractable from (0.5-4)N hydrochloric acid. In this case, Kd values are not affected by zinc or chlorine gas, however.

Solvent dependencies of Kd values for both Pa and Np are studied at 1N hydrochloric acid.

(2) Nitric systems :

Np can be extracted from (0.5-1.5)N nitric acid giving Kd values of about 10, whereas Pa can not be extracted from nitric acid of higher acidities than 1 N. These acid dependencies are compared with that of thorium. UX_1 is used as the tracer of thorium.

(3) Perchloric systems :

From 2.5 N perchloric acid, Np is extracted with Kd values of about 1.

As mentioned the extractions with cupferron may be carried out at rather high acidity. Accordingly it would find some applications in making these elements pure.

Distribution of Zirconium between Tributyl Phosphate and Nitric Acid System.

K. Umezawa and R. Hara (Japan Atomic Energy Research Institute.)

By determining the distribution coefficient of zirconium into TBP-HNO_3 system, the extraction mechanism of zirconium into TBP and its equilibrium constant were studied. The study was extended to the extraction by such relating phosphate esters as tripropyl and trioctyl phosphates. The experiment of extraction was carried out at the temperature of 10°C, 23°C and 50°C, by means of Zr-95 in the carrier free form and also with the addition of non-active zirconium (5×10^{-5} M). The acid concentration was varied over 1~10 M HNO_3, and the solvent was diluted by CCl_4 to the concentration of 20%. For the study of solvent dependency, the solvent concentrations of 2, 5 and 10% were also employed.

The results on acid and solvent dependencies obtained with tributyl, propyl and octyl phosphates indicate that the increase in acid or solvent concentration resulted in the increase of Kd values. The effect of alkyl radical is that the slightly increased extractability is found with the increase in alkyl group chain. The equation of zirconium extraction is,

$$\underset{(aq)}{Zr^{4+}} + n\,\underset{(aq)}{NO_3} + m\,\underset{(org)}{TBP} \rightleftarrows \underset{(org)}{Zr\,(NO_3)_n(TBP)_m}$$

$$K=\frac{[Zr\,(NO_3)_n\,(TBP)_m]}{[Zr][NO_3]^n\,[TBP]^m}=\frac{Kd}{[NO_3]^n\,[TBP]^m}$$

The measurement of Kd values was made under the following conditions;

Acid concentration, variable —— TBP concentration, constant.
Acid concentration, constant —— TBP concentration, variable.

The result indicates the composition of extracted species, $Zr\,(NO_3)_4\,(TBP)_2$, and the estimated K value, $2\sim3\times10^{-3}$.

Some Investigation on the Separation of Sr-90 (Y-90) by Solvent Extraction with TTA.

Nobuo Suzuki and Toyoaki Kato (Department of Chemistry, Faculty of Science, Tohoku University, Sendai)

In order to establish the procedure for carrier-free separation of Sr-90(Y-90) by solvent extraction with TTA (2-Thenoyltrifluoroacetone), the authors investigated various conditions having effects on the extraction of both elements.

The procedure was, unless otherwise stated, as follows. The aqueous solution containing Sr-90(Y-90) or Sr-89 (ca. 0.1 μc) was transfered to the separatory funnel and buffered to suitable pH adjusting to a volume of 15 ml. Then 2 ml.

of 0.1 M TTA in suitable solvent was added. After shaking for 2 minutes, the phases were separated by centrifuge and the organic phase was dried and counted and pH of the aqueous phase was measured. When benzene was used as the organic solvents, 93~95% of Y was extracted at pH 6-9 in a single extraction, while Sr remained in aqueous layer completely. When 6 ml. of dioxane was added to aqueous phase previously, Sr was also extracted and 95~98% of it was found in organic phase at a pH of 9-11.

Using various solvents instead of benzene, the extractability of Sr was examined. When hexone or iso-amyl acetate was employed, up to 90% of Sr was extracted at a pH of 9.

These results were applicable to the carrier-free separation of Sr-90(Y-90): After the repetition of extraction at a pH of 8 with TTA benzene solution in twice, Y-90 was extracted completely. Next, Sr-90 was extracted at a pH of 10 with additional TTA benzene solution from the aqueous phase containing suitable amount of dioxane. Both elements extracted up to 99%.

Behavior of Yttrium-90 in the Solvent Extraciton from Aqueous Solution Containing Various Organic Acids. I

Toshiyasu Kiba, Takuji Kawashima (Kanazawa University, Kanazawa)

Simple and rapid method for the separation of yttrium-90 from a solution containing strontium-90 and yttrium-90 has been desired particularly when the solution contains various organic acids or their salts. However, the behavior of the nuclides has been less pronounced in the liquid-liquid extraction. The authors attempted to examine the behavior of the nuclides by carrying out the extraction with 2 ml. of 0.05 M TTA-hexone and 0.05 M TTA-benzene from 5 ml. of the aqueous solution containing 5% ammonium citrate or 0.25 M ammonium oxalate. Both of organic and aqueous phases separated in a separatory funnel were drained into a dish separately and evaporated to dryness. The activity was measured by a β-counting set, and the percentage extraction was computed as a ratio of the activity of the organic phase to that of the original solution. The radiochemical purity of the separated nuclides was estimated by drawing

		From citrate solution		From oxalate solution	
		By TTA-benzene	By TTA-hexone	By TTA-benzene	By TTA-hexone
The lowest pH at which extraction takes place		7	7	8	8
pH at which max. extraction takes place		8.0--8.5	8	9	9
Composition of the org. phase	Y-90	70%	88%	76%	81%
	Sr-90	33%	21%	17%	24%

a Harley plot in each case. As a result of the experiments it was found that the separation of the two nuclides by the solvent extraction is less satisfactory than in the case of the solution containing acetate. Some data are shown in the following table.

Extraction of Uranium as Acetylacetonate.

Tsunenobu Shigematsu, Masayuki Tabushi (Institute for Chemical Research, Kyoto University. Kyoto)

Optimun condition for extraction of uranium as acetylacetonate were studied. The uranium solution was treated with 1 ml of 10% EDTA (disodium salt) solution, 5 g of sodium chloride, and 20 ml of 5% acetylacetone solution, the pH was adjusted to 7, the volume was adjusted to 50 ml with water, and the solution was extracted with 20(10+5+5) ml of 1% solution of acetylacetone in chloroform, or with butyl acetate in the presence of calcium chloride equivalent to EDTA and absence of sodium chloride. The uranium in organic layer was determined spectrophotometrically by the thiocyanate method or by the acetylacetonate method. The recovery of uranium was about 90% in chloroform extraction, and was almost complete in butyl acetate extraction. These methods were applied to sepration of uranium from fission products and from thorium.

Studies on the Anionic Exchange of Pertechnetate.

M. Kojima and N. Matsuura (College of General Education, University of Tokyo)

An interesting conclusion derived by Gerlit on the existence of a valency state of Tc lower than VII was based on the extraction of Tc by organic solvent from well concentrated acid HCl. The distribution of Tc between amylalcohol and inorganic acid attains to a maximum at the concentration of aqueous HCl not far from 2 N., but in the case of sulfuric acid it increases continuously without maximum. He has attributed this difference to the hydrochloric acid acting as a reducing agent, though, to our experiments, a similar maximum was also obtained even in the extraction effected from the non-reducing acid, $HClO_4$ or HNO_3.

In this point of view the ion exchange of pertechnetic acid with several different forms of anionic resines was effected by batch method. For the bisulfate or chloride resines the logarithumic curve of partition cofficient is effectively distinguished, because of its more complex feature, from that for nitrate or perchlorate resines as a weaker adsorbant, and the latter shows the typical uni-uni anion exchange in the acid from 0.01 to 3 N. From our experimental results we permit that in the sulfuric and hydrochloric acid the uni-uni valent anion exhange of Tc is superposed with some other process. We can separate this superposed curve from one to another with the aid of a relation worked by on the thermodynamical treatment of partition constant K for the resines subtracting the contribution due to the uni-uni anionic exchange actually observed in the perchlorate and nitrate resines. One of the separated log K_d curve pararel to the absissa makes us to believe that a molecular adsorption of Tc is prevalent of the bisulfate and chloride resines. To interpret the both extraction and exchange behavior of pertechnetic acid we prefer the process $RCl + TcO_4^- + H^+ = RTcO_3(OH)Cl$ as an exchange of technetate on the anionic resine from weak HCl or H_2SO_4 solution.

Solvent Extraction of Ruthenium. (1) Extraction of Ruthenium with Several Nitroso-Compound Solvent System.

Kichizo Tanaka, Yoshio Koda (Goverment Industrial Research Institute of Nagoya)

The importance of the separation of radioactive ruthenium from the fission products has brought demands for furthur more detailed study on ruthenium chemistry. Among several organic nitroso-compounds which was tested for color formation with ruthenium salts, 1-nitroso-2-naphthol, 2-nitroso-1-naphthol, o-nitroso resorcine monomethyl ether and cupferron were selected as the reagents, and several organic-aqueous system was also tested for effective extraction of ruthenium.

Procedure: Rutheniumtetroxide was recovered by distillation of ruthenium red added with radioactive nitrosyl ruthenium with potassium permanganate-sulfuric acid. Deep red ruthenium nitrate solution was prepared by the action of hydroxide on ruthenium tetroxide which was in 2N nitric acid. The ruthenium nitrate, the organic reagent, and a buffer solution were mixed and boiled in a glass stoppered tube until the color change finished and then cooled. The equal volume of organic solvent was added to the solution and stirred vigorously for 1 min.. 1cc aliquots of both the layers were dried in glass dishes, 1 dia., under a infra-red lamp. Their activities were counted with a Kaken end-window type GM counter. Light absorption spectra were obtained with Shimadzu spectrophotometer.

Results: The dark brown ruthenium nitroso-naphtholates were precipitated by heating the mixture of ruthenium nitrate and nitrosonaphthols.

Brown red color was formed by the reaction between ruthenium nitrate and o-nitroso resorcine monomethyl ether. These salts were easily extracted with a solvent such as hexone or ethyl acetate-amylalcohol. Rates of these reaction were rapid above 90°C but very slow under the temperature. Faint color formation was observed by the addition of cupferron to the ruthenium nitrate solution. Distribution ratio of ruthenium between organic solvent and aqueous solution was a trend to show minimum at about 1M nitric acid concentration.

Tracer-chemical Studies on Actinide Elements 1. Oxidation of Neptunium (IV) in Nitric Acid Solution.

Tomitaro Ishimori and Eiko Nakamura (Japan Atomic Energy Research Institute)

1N nitric acid solution of neptunium containing both neptunium (IV) and (V) is contacted with 10% TBP.

Resulting organic phase is scrubbed many times with fresh nitric acid. Kd value becomes higher and then approaches to a constant value. The variation of Kd is expressed roughly by following equation:

$$\mathrm{Kd}_n=\frac{(\mathrm{Kd}^{\mathrm{V}})^{n+1}(1+\mathrm{Kd}^{\mathrm{V}})^{-n}+(\mathrm{Kd}^{\mathrm{IV}})^{n+1}(1+\mathrm{Kd}^{\mathrm{IV}})^{-n}\mathrm{k}}{(\mathrm{Kd}^{\mathrm{V}})^{n}(1+\mathrm{Kd}^{\mathrm{V}})^{-n}+(\mathrm{Kd}^{\mathrm{IV}})^{n}(1+\mathrm{Kd}^{\mathrm{IV}})^{-n}\mathrm{k}} \tag{1}$$

where, Kd_n : Kd value for nth scrubbing,

$\mathrm{Kd}^{\mathrm{IV}}$: Kd for Np (IV)

Kd^{V} : Kd for Np (V)

k : the ratio Np(IV)/Np(V) in original solution

On the other hand successive scrubbing of the aqueous phase (obtained by the first scrubbing) with fresh TBP gives low constant Kd for neptunium (V). The Kd value varies as Eq. (2).

$$\mathrm{Kd}_n=\frac{\mathrm{Kd}^{\mathrm{IV}}\mathrm{k}(1+\mathrm{Kd}^{\mathrm{IV}})^{-n}+\mathrm{Kd}^{\mathrm{V}}(1+\mathrm{Kd}^{\mathrm{V}})^{-n}}{\mathrm{k}(1+\mathrm{Kd}^{\mathrm{IV}})^{-n}+(1+\mathrm{Kd}_v{}^{\mathrm{V}})^{-n}} \tag{2}$$

The fractions which give the constant Kd value are assigned to neptunium(IV) and (V) respectively according to chemical behaviors against TTA, zinc, potassium bromate and other reagents.

As can be seen in Eq. (1) and (2), k, the ratio between neptunium (IV) and (V), can be obtained by scrubbing mentioned above. Accordingly oxidation of neptunium (IV) caused by heating 3N nitric acid several minutes is studied by tracing the variation of k value.

On the Hexavalent Polonium.

N. Matsuura and M. Haissinsky (College of General Education,
University of Tokyo, Tokyo.)

The partition of tetravalent polonium at the concentrations of an order of 10^{-10}M between its acid solution, nitric or hydrochloric, and methylisopropyl ketone depends little on the acidity from 1 to 6N. Extraction percentages fall not far from 80 at ordinary temperature. From sulfuric acid the polonium IV extracted into organic solvent varies in the function of the acidity with a minimum and a maximum. Regardless the nature of the acid, if the aqueous solution of polonium is treated with a strong oxydant, for example Ce^{+4} or $\mathrm{Cr}^{\mathrm{IV}}$, the partition equililbrium is transfered in favor of the aqueous phase, that is, the major part of Po rest in the aqueous solution. Destructing the oxydant with hydrogen peroxide the partition recovers to its initial value. We found in the same time that the partition depends on the relative quantities of the reductant and oxydant in the solution. Accordingly, these experiments and an analogy with the element Te permit to confirm the existence of the valency state VI of polonium. We tried to determine the oxydation potential of Po(VI) related to Po (IV) with several oxydants and found it to be near 1.5 volt for the ionic forms of Po VI assumed.

Separation of Neptunium-239 from Fission Products with Nitrate form Anion Exchanger.

Fujio Ichikawa (Japan Atomic Energy Research Institute)

Uranium nitrate irradiate in J. R. R. -1 for two hours at 10^{11}n/cm^2/sec is dissolved in 1 N hydrochloric acid. A few mg of hydroxylamine hydrochloride or ascorbic acid is added to this solution in order to reduce neptunium. After drying up the solution, the residue is taken up in 7.5 N nitric acid and poured into the nitrate form Dowex 1 resin column. The fission products are washed out with 7.5 N nitric acid and then neptunium is eluted with 0.7 N nitric acid.

Np (IV) and (VI) are prepared by reduction with zinc and oxidation with ceric sulfate respectively. Neither Np (IV) nor Np (VI) is adsorbed on the column. From these facts, it is likely that neptunium (V) forms nitrate complex in 7.5 N nitric acid.

Distribution coefficients of neptunium are measured in systems of nitric acid and nitrate form anion exchanger.

A Study on Ion-exchange Equilibrium of Sodium Isotopes on Cation Exchange Resins.

H. Ohtaki, H. Kakihana, and K. Yamasaki (Faculty of Science, University of Nagoya, Nagoya)

Selectivity coefficients, K'', between Na^{23} and radioactive Na^{24} on differently cross-linked sulfonated resins were determined at 25°C in ethanol-water mixtures containing variable amounts of sodium chloride.

As the cation exchange resins Dowex 50-X1, X4, X8, and X12 were used. The concentrations of sodium chloride were 0.01, 0.1, and 1M and the volume percentage of ethanol-water mixtures were 0 (water), 20, 34, 50, and 74 % ethanol.

The batch method was adopted to attain the equilibrium.

The distribution of the solvents in the resin was measured with an isopiestic method. The dielectric constants in the resin phase were calculated on a few assumptions and the following experimental equation was derived :

$$\log K'' = a(m-b)\left(\frac{1}{D_{soln}} - \frac{1}{D_{resin}}\right) + c$$

where a, b, and c are empirical constants, m is the molarity of the external solution, D_{soln} and D_{resin} represent the dielectric constants of the external solution and the resin phase, respectively.

Separation of Rare Earths by Ionexchnge Method.

Shinzo Okada, Tomota Nishi, and Ichiro Fujihara (Engineering Research Institute of Kyoto University, Kyoto)

The separation of rare earths with cation exchanger and citric acid solution was studied by Spedding et al. We improved their method and reached complete separation of individual rare earth and thorium from the mixture of rare earths, which was obtained from monazite.

Rare earch commonly contains slight thorium and have weak activity, therefore it is not adaptable to use as stable carrier for radioisotope which have weak activity. The α and β activity of rare earths, i. e. La, Ce, Pr, Nd, separated by ionexchange, were measured with GM-counter and gas-flow 2 proportional counter.

They did not show any activity above natural background. They are sufficient to use as a carrier for weak activity. Besides we used these rare earths which have no activity as carrier for separation of rare earths infission products, three years old. Y-91, Pm-147 and Ce-144 were separated, especially the separaton of Pm-147, which emits low energy β radiation, was pursued.

Ion-exchange Separation of Heavy Alkali-metals.

Masayoshi Ishibashi, Taitiro Fujinaga, Mutsuo Koyama and Taiji Naito. (Department of Chemistry, Faculty, of Science, University of Kyoto. Kyoto)

Ishibashi and co-workers have previously reported on the gravimetric, spectrometric and colorimetric determination of heavy alkali-metals after separating them as precipitates [J. Chem. Soc. Japan, **63**, 211, 767 (1942); **64**, 976 (1943)]. In this work, rubidium and cesium were separated by the use of ion exchange resin in the presence of other alkaline elements and the optimum condition was investigated using ^{86}Rb and ^{137}Cs as their indicators.

Batch method Ion exchange resine (Dowex 50, 200~400 mesh) was used in all the experiments. The distribution ratio of Rb and of Cs were determined with the resine in a solution of 0.1~2.0 N HCl. By this preliminary experiments, the better separation was expected, smaller the concentration of HCl.

Column method After all alkaline elements were adsorbed on the column resin, the elution was performed by HCl solution and the activity of the eluent passed under a GM tube was recorded automativally by a recording rate meter.

Individual elution curves of Rb and Cs were recorded in the presence or absence of nonactive isotopes and other alkaline elements. The elution curve shows better separated peaks with smaller concentration of HCl. With increasing the concentration of Rb or Cs, the front of their peaks appears earlier. Considering the time required, the best results were expected by eluting with 0.5 N-HCl at the flow rate of 0.2 ~ 0.25 ml/min. with regard to the column of 25.5 cm in height and 0.6 cm in diameter. 7 mg of RbCl and 9.8 mg of CsCl were quantitatively separated under the condition mentioned.

Effect of other alkaline elements on the elution curve Sodium (38 mg) or ammonium (31 mg) has little influence on the elution curve of rubidium or cesium, showing two well-separated peaks of their own. Potassium (40 mg) advances the elution peaks of rubidium and of cesium. Rubidium (70 mg) advances the peaks more than potassium does.

Utilizing the results obtained the isolation of cesium from a lepidolite was examined.

Separation of Carrier-free Sulfate and Phsophate by Cation Exchang Resin.

Eiji Shikata and Chizuko Yamaguchi. (Japan Atomic Energy Research Institute)

Radioisotope of sulfur. S-35 is produced from chlorine by the nuclear reaction, $^{35}Cl\,(n, p)^{35}S$. As the sametime, radioisotope of phosphorus, P-32 is produced, $^{35}Cl\,(n, \alpha)^{32}P$. To get pure S-35, it is necessary to separate P-32. The authors carried out a study separating them by the cation-exchange resin. Solution of iron chloride (0.5 mg. Fe/ml) was passed through the Diaion SK-1 resin bed (H-form, 100-200 mesh, 0.6 cm × 10 cm, dried weight 1g) and then the resin bed was washed with 10 ml water. 10 ml of sample solution of 0.5% ammonium chloride containing carrier-free sulfate, $^{35}SO_4^{-2}$ and phosphate $^{32}PO_4^{-3}$ was passed through the resin bed and then 1 ml of washing water, 10 ml of 2N-hydrochloric acid was passed successively.

All the sample solution, washing water and hydrochloric acid were collected, and a small amount of sulfate and phosphate was added as carriers to each solution. Sulfate and phosphate was separated by the usual precipitation method and their activities were mesured. Similar experiment was carried out using lanthanum instead of iron. The results were as follows : 1) In the case of the La-form resin $^{32}PO_4^{-3}$ was completely adsorbed at pH over 8, 2) In the case of Fe-form resin $^{32}PO_4^{-3}$ was adsorbed independent of pH, 3) $^{35}SO_4^{-2}$ was obtained in each case at yield of 95%.

Quantitative Isotope Dilution Analysis—Determination of Silver in Plant Materials.

Nobuo Suzuki (Department of Chemistry, Faculty of Science, Tohoku University. Sendai)

Quantitative isotope dilution analysis is as follows. After addition of known amount of radioisotope (radioactivity A, and mass Mi, in suitable unit) to the sample solution containing unknown amount of element (Ms), suitable amount of reagent, which is able to react with a fixed and partial quantity of element (Mr) in question and the resultant of this reagent with element can separate easy, is added, separate the resultant and radioactivity is measured, then nexed relation is obtained between radioactivity of the resultant (Ae) and quantity of element :

$$Ae = A \cdot Mr/(Mi + Ms)$$

This method depends on the same principle as isotope dilution method, permits of course correction to be made due to loss of the element in question, and is convenient in operation and superior both in sensitivity and accuracy to the chemical methods hitherto in practice, because the final determination is possible only by radioactivity measurement and do not require any other auxiliary chemical method.

The author chooses mint in Japan as sample plant and succeeded in determination of silver in mint by this method. Silver content in leaves and in stems per dry materials was 0.86 p.p.m. and 0.15 p.p.m. respectively.

Study on the Chemical Analysis of Metals by Applying the Backscattering of β-Particle.

Hidehiro Gotō and Shigerō Ikeda (The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai)

The reflected intensity of β particle increases with the increase of the atomic number of the reflecter.

The investigation was intended for the application of this specific property of β particle to the non-distractive quantitative analysis of the element in binary alloy. Y-90 and P-32 were used as β source and is put in the small vessel consist of lead and solder alloy, not to allow primary β particle count. The sample specimen was placed on the polyethylene plate, the center of which was holed so as to let β particle strike the specimen, and the scattered particle was measured by G. M. counter.

Determination of Hafnium in Zirconium with Isotope Dilution Mtheod.

Hiroshi Amano (The Reaseach Institute for Iron, Steel and Other Metals, Tohoku Universitty, Sendai)

The Hf contents of Zr metal or compound were determined with isotope dilution method using radioactive isotope Hf-181.

In preliminary experiments, varied volumes of Hf standard solution were mixed with the fixed volume of Hf* solution and diluted to fixed volume. The aliquots of these solutions were taken and counted. With alizarin-red S method, the Hf contents per ml were determined. From counts and Hf contents the specific activities of Hf solutions were calculated. The versus of specific activities and Hf mg were linear from 0.012 mg to 1.0 mg/50 ml. In order to isolate Hf from Zr, cation exchange methods were investigated. From the solution of 0.05∼0.1-M acidity, Zr and Hf were absorbed on the resine, Zr was first eluted with 0.045 M-nitric acid+0.095 M-citric acid solution continued with Hf. However, less than the weight ratio Hf/Zr of 1/100, the eluted Hf fraction was contaminated with Zr, and with two times separation, Hf was isolated up to 1/1000 of Hf/Zr. Finally the thiocyanate-hexone extraction method was adapted to concentrate Hf followed by two times ion-exchange separation and 0.016 % Hf in Zr could be determined.

Studies on Separation of Ruthenium from Fission Products.

Kiyoshi Kudō (Department of Chemistry, Faculty of Science, Tohoku University)

In order to separate carrier free ruthenium from fission products by precipitation method, the investigation was carried out.

The fission products were precipitated from acidic medium with copper, tellurium, and selenium carrier. About 7 per cent of fission products was coprecipitated to cupuric sulfide, but each of nuclides could not been identified.

Analysis of fission products was carried out by precipitation method in consideration of behavior of ruthenium. After alkali fusion, nuclides were separated by systematic analysis. Then, ^{106}Ru—^{106}Rh, ^{137}Cs—^{137m}Ba, ^{90}Sr—^{90}Y, ^{144}Ce—^{144}Pr were detected. Rare earth and alkali earth nuclides were not removed to the water soluble part, but some part of ^{106}Ru—^{106}Rh were contaminated in rare earth precipititation part. And, ^{106}Ru—^{106}Rh was not collected completely by one time of hydroxide precipitation.

In the experiments using ^{106}Ru—^{106}Rh tracer, following result were obtained: By fusion, 10 to 15 per cent of ruthenium were absorbed to nickel crucible. In lanthanum, iron, and calcium carrier, about 80 per cent ruthenium was removed to water insoluble part. For that reason sepaparated carrier free ^{106}Ru—^{106}Rh hydrochloric acid solution was only 10 per cent, but by addition of tellurium carrier, 70 to 80 per cent ruthenium was separated to water soluble part.

Radiometric Determination of Gallium—Especially in Presence of Thallium (III) and Indium.

Yoshimasa Takashima (Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka)

A series of analytical methods of several ions by means of hexaamminecobolt (III) chloride (luteo salt) and sodium fluoride have been proposed by this author.

In earlier years, the radiometric determination methods of thallium (III) and indium that are based upon the quantitative precipitation of the metals in dulute hydrochloric acid solution with hexamminecobalt (III) chloride was reported by Ishimori et al. Though gallium is also precipitated by the reagent in the solution more than 6 N hydrochloric acid, it is not be able to apply for the determination of gallium, because the solubility of the gallium complex is rather large and the precipitate is accompanied with a lot of precipitate of reagent itself. The present work is analogous to the above method, but it was designed to make possible the quantitative determination of gallium with the aids of sodium fluoride instead of hydrochloric acid.

According to the preliminary gravimetric test, it is shown that gallium give quantitative results in pH range of 3～6. And it is also proved that this insoluble precipitate has the composition represented by $[Co(NH_3)_6]GaF_6$. Improving the above method with the help of Co-60 tracer, microamount of gallium can be determined radiometrically. If these two procedures that include the system of luteosalt—hydrochloric acid and luteosalt-fluoride respectively are combined, gallium can successfully determined in presence of thalliun (III) and indium.

Separation of Zirconium and Hafnium by Solvent Extraction.

Sinzo Okada, Tomota Nishi and Chiehiro Matsumoto (Engineering Research Institute of Kyoto University, Kyoto)

The distribution ratio for zirconium and hafnium between the sulfate or chloride solutions and salicylic acid-metyl isobutyl ketone solution were determined at various concentrations. Hafnium-181 was used as tracer to follow the extraction process and determine the concentration of hafnium radiochemically.

The sepration factors varied from 1.5 to 10 and distribution ratio from 3.4 to 300 with increase of concentration of ammonium salt.

Zirconium and hafnium was recrystallized 3 times as hydrated sulfate from conc. sulfuric acid known as the best method. Gas flow 2π counter was employed for measuring hafnium activities. Salicylic acid used as chelating agent is slightly soluble in acidic aqueous solution but very soluble in MIBK.

10 mls of aqueous solution and the same amount of organic were shaken in 50 mls separatory funnel for 5 minutes, and after separating to two phases the amount of extracted zirconium and activities of hafnium were determined as oxide.

Effect of salicylic acid concentration in MIBK was not so large and cnocentration of salicylic acid was used at 1 M/l. Concentration of acids and ammonium salts were so effective as changing pH value of the aqueous solution. pH was the most important factor for zirconium and hafnium salts hydrolize at pH -3-.

Carrier-free Separation of ^{140}La from ^{140}Ba by the Use of Mercury Cathode.

Masayoshi Ishibashi, Taitiro Fujinaga, Atsuyoshi Saito and Kunzo Matsuda (Faculty of Science, University of Kyoto, Kyoto)

The authors have previously reported on the carrier-free separation of ^{90}Y from ^{90}Sr-^{90}Y mixture of radioactive equilibrium by the use of mercury cathode [J. Chem. Soc. Japan, **79**, 978 (1958)]. In the present work, similar technique was applied to the separation of ^{140}La from ^{140}Ba-^{140}La equlibrium mixture.

Experiments Hildebrand's double cell was used for the separation. A mercury pool served as cathode and a silver plate as anode. A 20 ml of electrolytic solutions containing 1 ml of ^{140}Ba-^{140}La mixture (6000 cpm/ml) was electrolysed in the inner compartment and a 40 ml of distilled water was filled in the outer compartment of the cell to decompose the amalgam formed in the inner compartment. Aliquots of the solution before and after the electrolysis were pipetted out and ferric chloride (carrier of La^{+++}) and barium chloride (hold back carrier of Ba^{++}) were added. Ammonium hydroxide were added to the solution to precipitate ferric hydroxide. Activities and half-lives of both the precipitate and the solution were measured. Identical measurements were carried out with the solution of outer compartment.

Results Barium ions in the inner compartment form the amalgam by electrolysis and dissolve again into the water of outer compartment. Lanthanum ions seem to deposit partially on mercury cathods, however, transfer of them to the outer compartment was hardly observed and most of them was recovered by shaking the amalgam with the inner electrolyte solution.

As a result, a carrier free lanthanun can successfully be obtained by the electrolysis of 1-2 hours duration with the cell voltage of 10-15 volts by the use of mercury cathode separation technique.

Study of the Production of Iodine-131.

Eiji Shikata (Japan Atomic Energy Research Institute)

Extracting I-131 from the tellurium metal, which had been irradiated in the pile, was studied. I-131 is produced as follows, $^{130}\mathrm{Te}(n, \gamma)^{131}\mathrm{Te} \xrightarrow{\beta} {}^{131}\mathrm{I}$. The irradiated tellurium was heated and dissolved with concentrated nitric acid in a small flask, provided with a reflux condenser. I-131, which was produced in tellurium, was oxidized to iodic acid. Iodic acid or potassium iodide was added as a carrier and iodine was isolated by the reduction with hydrogen peroxide or potassium iodide (in the former case), or by the oxidation with hydrogen peroxide (in the latter case). The solution was shaken with carbon tetra-chloride a few times and isolated iodine was extracted into the organic phase, which was back-extracted sequently with sodium sulfite solution into the water phase. Experimental conditions, such as sort and quantity of the carrier, concentration of the nitric acid solution and the time of refluxing, was studied. 80%~90% extraction ratio was obtained at optimum condition.

Studies on Condensed Phosphate from the view-point of Analytical Chemistry (VII), Several Condensed Phosphate (Ortho-, Pyro-, Tri-, Trimeta-, and Hexameta-Phosphate) Complexes with Calcium Ion.

Yoshiyuki Kiso (Department of Chemistry, Faculty of Science,
Hiroshima University, Hiroshima)

The aim of present experiment was the comparison of behavior between several orth-, pyro-, tri-, trimeta-, and hexameta-phosphate complex formation with calcium ion, and the caluculation of their stability constant with measuring of distribution coefficient.

Calcium chloride labeled with radioactive Ca^{45} was equilibrated with several concentration of above-mentioned phosphates and the used resin was cation exchanger, Dowex 50, (60~100 mesh), in the sodium form. The detection of calcium ion carried out with Geiger-Muller counter. Then their distribution coefficient of calcium ion between the solution and the resin was measured by Batch method besed on Schubert's theory.

From this experiment result, their stability constant of phosphate complexes were calculated, and their order of stability were hexameta-, tri-, pyro-, ortho-, and trimetaphosphate.

A Simple Method for the Preparation of Carrier-free ^{90}Y by Adsorption.

Nagao Ikeda, Jun Akaishi and Yoshitaka Ono (Department of Chemistry, Faculty of Science, Tokyo Universty of Education; Japan Atomic Energy Research Institute)

To investigate how much of radioactivity in solution would be adsorbed on the wall of container, the authors examined the adsorption of several kinds of radioisotopes on brass, aluminum, stainless steel, vinyl, polyethylene, glass, etc. In the course of this study, vinyl sheet was found to be a good adsorbent for ^{90}Y from ^{90}Sr ^{90}Y solution. So that, the further study was carried out to attain the suitable conditions for the separation and preparation of carrier-free ^{90}Y by this simple method.

A vinyl sheet of 3×3 cm size, one side of which was coated by paraffin to prevent the adsorption of radioctive substances, was inserted into the aqueous solution of ^{90}Sr-^{90}Y solution. After standing at the room temperature for 48 hours, the sheet was taken out, washed with water, and the decay curve of the radioactivity was observed. The amount of adsorption of ^{90}Y showed its maximum value at about pH 9. The amount of ^{90}Sr simultaneously adsorbed on the vinyl sheet was 0.5-2% of ^{90}Y at the time when the sheet was taken out from the solution.

The distribution of ^{90}Y was observed by the autoradiographic method using the X-ray film. It was revealed that the distribution was not homogeneous, but many spots were irregularly distributed on the film.

Thus, we can prepare ^{90}Y in the carrier-free form by inserting a vinyl sheet into ^{90}Sr-^{90}Y solution for 2-3 days. The ^{90}Y adsorbed on the sheet is then readily soluble in dilute hydrochloric acid.

Rapid Determination of Cs-137 in Human Urine.

Takahisa Hanya and Eiichi Yanagihara (Chemistry Department, Faculty of Science, Tokyo Metropolitan University, Tokyo)

PURPOSE. It is a urgent demand for us to estimate rapidly a degree of invasion of Cs-137 into human body for the investigation of the effect of the radio-Substances produced by peaceful use of atomic energy as well as by atomic explosions. The purpose of this experiment is to measure rapidly the activity of Cs-137 in human urine.

METHOD. Into a certain quantity of human urine acidified by nitric acid are first poured cesium chloride as carrier and Cs-137 as tracer, then phosphoric acid and ammonium molybdate are added. Cs in human urine precipitates as cesium ammonium phosphomolybdate.

RESULT. The amount of Cs-137 found in comparison with that of the added in the case of various experimental conditions is shown in the following table. The experiment of No. 15 is the best. The determination of Cs-137 in human urine in the natural condition is under investigation.

Table

No. of Experiment	Human urine (ml)	Nitric acid added (ml)	CsCl added (mg as Cs)	Ammonium molybdate added (10% soln, ml)	Phosphoric acid added (10%, ml)	Cs-137 added (cpm)	Cs-137 found (cpm)	Cs-found/Cs-added (%)
No. 1	1800	400	10	20	2.5	123	0	0
2	1800	400	20	40	10	123	0	0
3	1800	400	40	80	10	123	0	0
4	1800	400	60	120	15	123	137	111
5	1800	400	80	160	20	123	125	102
6	1800	400	100	200	25	123	124	101
7	1800	400	150	300	40	123	134	109
11	1800	400	80	10	2.5	231	0	0
12	1800	400	80	20	2.5	231	0	0
13	1800	400	80	40	5.0	231	2	1
14	1800	400	80	80	10	231	155	67
15	1800	400	80	120	15	231	239	103
16	1800	400	80	160	20	231	250	108
17	1800	400	80	200	25	231	241	104

Radiochemical Analysis of Cesium 137 in Fall-out.

Noboru Yamagata, Toshiko Yamagata and Shunji Matsuda (Kiriu College of Technology, Gunma Univ., Kiriu)

A simple and rapid separation method for cesium 137 in fall-out has been presented. It is composed of three steps, phosphate-sulfate precipitation, ammonium phosphomolybdate precipitation and chloroplatinate precipitation. Overall yield of cesium is over 85% and the decontamination from other fission activities in more than 10^5 for cerium and strontium. The contribution of the activities of rubidium 87 and potassium 40 is negligibly small in the determination of cesium 137 in fall-out by beta counting.

The fall-out collected during the period from July 1 to July 31, 1958 in the area of 1 m^2 contained $350\mu\mu c$ of cesium 137. It means the fall-out rate in July '58 is 0.35 $mc/km^2/month$ or 4.2 $mc/km^2/y$. for cesium 137. The ratio of ^{137}Cs activity/Gross activity was approximately 1%.

The Concentration of Sr^{90} in Radioactive Rain Water from April, '57 to March, '58 Observed in Niigata City.

S. Koyama and T. Sotobayashi (Faculty of Science, Niigata University)

The distribution and separation constants for calcium and strontium, were examined with eluants of various molarities of ammonium formate and acetate. The acetate was found to be somewhat more effective than formate as eluating agent. By the addition of several organic solvents, the separation factor became larger by forty per cent. From these experiments 1.6 M ammonium acetate solution containing ethanol (H_2O : $EtOH=1$: 1) is recommended as an eluant for the separation of strontium from calcium by ion exchange method. This method was applied to the determination of Sr^{90}-concentration in rain water and snow. Data are summarized on the following table. From the table it is shown that in winter (from Nov. to Apr.) the concentration of Sr^{90} in rain (or snow) water is larger by several times as that of summer (from June to Oct.) and average concentration of Sr^{90} in rain water is estimated to be 5 μμc/l.. The Sr^{90} carried down by rain water and snow was estimated about 8.2 mc./km^2..

Period of collecting	Sr-90 μμc/l	Period of collecting	Sr-90 μμc/l	Period of collecting	Sr-90 μμc/l
4-20~ 5- 7	8.84	8-29~ 9- 7	1.00	11-23~12- 8	4.44
5-11~ 6- 8	4.66	9- 8~ 9-20	1.62	12- 9~12-28	5.84
6-19~ 7- 3	1.34	9-24~10- 6	3.16	12-30~ 1-20	11.00
7- 4~ 7-20	0.24	10- 8~10-20	3.40	1-21~ 2- 3	6.96
7-21~ 7-31	0.52	10-21~11- 9	2.80	2- 7~ 2-20	12.20
8- 3~8-10	1.92	11- 3~11- 7	2.14	2-23~ 3- 6	10.56
8-12~ 8-25	0.84	11- 8~11-22	10.08	3- 7~ 3-28	11.20

Analysis of ^{137}Cs in Rain- and Fallout Samples.

Takashi Nagai, Yoko Ajiki and Masami Izawa (National Institute of Health, Tokyo.)

In order to establish the practical method of ^{137}Cs analysis in rain- and fall-out samples, the applicability of silicotungstate separation followed by two $Fe(OH)_3$ scavenges and perchlorate precipitation was examined. Cesium was extracted completely by one HCl-extraction process from evaprorated residue of the sample collected for a month. Actually, however, HCl extraction was performed three times to analyze Sr activity simultaneously. Contamination in Cs perchlorate precipitate was checked by using a number of radionuclides as the contaminants, and the following result was obtained :

RI added	Activity added cpm	Activity in $CsClO_4$ precipitate cpm
^{90}Sr+^{90}Y	5,200	−2.8±1.3
^{45}Ca	8,200	2.1±1.3
^{59}Fe	5,600	−0.2±0.9
^{106}Ru+^{106}Rh	13,200	8.1±1.0
^{127}Te	7,400	1.4±1.2
^{147}Pm	7,200	−0.6±0.9
^{22}Na	9,700	48.5±1.7

From the table it can be seen that contamination of nuclides other than alkali could be effectively eliminated from the final precipitate by this procedure. As far as the rain- and fallout samples are concerned, contamination of radioactive alkali does not become a problem. It was found that the recovery of the Cs activity and that calculated from the sample weight was the same whithin experimental error. Therefore, it was concluded that contamination of nonactive alkali metals was negligible.

Radiochemical Studies on "Bikini Ashes", Part III. Determination of Some Long Lived Nuclides by the Recent Chemical Analysis.

Takanobu Shiokawa and Masuo Yagi (Radiochemical Laboratory, Shizuoka University, Shizuoka)

In the previous papers, the results of the radiochemical studies on "Bikini Ashes" were reported. At that time, however, the long lived fission products and induced active nuclides were not investigated in detail, so that the analysis has been carried out again in the recent, four years after the fission on March 1, 1954, when the most of the short lived nuclides had decayed away.

In the present analysis, the separation of elements was carried out in usual manner by employing carriers, and the identification of the nuclide was made by observing the radioactive charactor of the nuclide by means of the G-M counter and the gamma ray spectrometer.

The helm-palms taken off from the top of bambo-poles of the boat were ignited, and the ashes of them were used as the sample of the analysis. 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 of Co, Cu, Zn, Sr, Ru, Sb, Te, Ce and Cs were added to the combined solution and evaporated to dryness. At the first step Ru was distilled with $HClO_4$, and then silicates were removed by a dehydration process. Then, the sulfide group was separated by H_2S in the acidity of 0.3 N. The filtrate was scavenged twice with Sb_2S_3 precipitation, and from it the next group was precipitated as hydroxides. The hydroxide precipitates were dissolved into HCl and reprecipitated as before. From the filtrate, Zn and other sulfides were precipitated. The filtrate was scavenged with ZnS precipitation, and the Sr and other element were precipitated as carbonates from it. Finally, Cs was precipitated with H_2PtCl_6.

The further separation of individual element in the each groups were carried out respectively by employing carriers.

As the result, ^{90}Sr, ^{90}Y, ^{106}Ru, ^{125}Sb, ^{125}Te, ^{144}Ce and ^{137}Cs in fission product and ^{60}Co in induced active nuclide, were detected. The contents of ^{90}Sr and ^{137}Cs were rather small in comparison with the general composition of the fission product of same age likely as the last analysis in the previous paper. And Tc was not found in the present analysis of the helm-palms ashes.

Radioactive Contamination of Several Metals.

Hidehiro Goto and Hiroshi Amano (Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai)

The radioactive contamination of several metal surfaces was investigated.

Each metal was punched to the disc 1~15 mm thick 25 mm in diameter. These discs were mounted in metacryl resine, and their surface was polished to 0000 amelie paper. The specimens were dlipped into the fission products solution which was adjusted to pH 1.4 and had the activity of about 27,000 cpm. After one week test, the surface was washed through with the water stream and the activity remained on the surface was measured. Then the specimen was anodically electrolyzed in 3.0 N-H_2SO_4, and the surface activity was measured. The solution was analysed and the nuclei in the solution were determined. Iron, stainless steel, copper and brass were tested. From the experiences, it was found that activity was absorbed on the metal surfaces homogeneously, and there was no relation between the contamination and the corrosion state of surface, and that there was no element which was absorbed on the metal surface specifically according to the metal tested.

A Study on the Decontaminant of Radioactive Matter from Cotton Clothing.

Hiroshi Hotta, Yoshiki Wadachi, and Haruto Fukuta (Japan Atomic Energy Research Institute)

In order to establish the method of decontamination of radioactive matter, we measured the residual radioactivity of cotton clothing contaminated by $^{60}CoCl_2$ and treated by various decontaminants (polyphosphates, organic polyacid salts, and surfactants). It is concluded from the present experiment that the chelating agents, having the larger chelate stability constant, are the better decontaminant against inorganic salt, and surfactant is a poor decontaminant. Furthermore, the action of chelating agent as the decontaminant is dependent on the pH of the solution.

Rediochemical Polarography I. The Role of Cobalt on the Catalytic Wave of Protein.

Mutsuaki Shinagawa, Hiroyuki Nezu and Tetsuya Yamada (Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima)

The most delicate point in the interpretation of the whole catalytic electrode process involved in the polarographic "protein wave" consists in the elucidation of the role of cobalt. Consequently, the present experiments were initiated quantitatively in order to examine the following three points ;

1) During the period of voltage sweep at which the peak wave is furnished, is cobalt reduced constantly or in other fashion ?

2) The cobaltous wave is shifted to more positive potential by the presence of gelatin, cystine or serum protein and under some conditions it becomes into two steps. During the peried of such reduction, how about the net reduction of cobalt ?

3) How about the net reduction of cobalt during its maximum period, which

can be seen in the absence of gelatin?

In the present investigation, the measurements of the net amounts of reduced cobalt are taken by the method of radiochemical polarography using Love's method after improving some points. Radioactivity per one drop of mercury is plotted against applied potential. Thus obtained radiochemical polarograms correspond to the ordinary polarogram, but the kinetic factors are eliminated and the net reduction of cobalt can be illustrated.

As the result the following facts were observed;

1) No elevation of the reduced amounts of cobalt was recognized.

2) The detail explanation about (2) was difficult experimentally, but some possible explanations of the phenomena are presented.

3) A maximum in the radiochemical polarogram was corresponded to the ordinary polarographic maximum.

In summerizing above three points, the role of cobalt on the mechanism of "protein wave" will be discussed.

Coprecipitation of Barium Ions with Ferric hydroxide Precipitate.

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

The authors have previously studied on the coprecipitation of strontium ions with ferric hydroxide precipitate and have demonstrated that the coprecipitation is mainly due to the adsorption. In the present work, similar experiments were carried out with regard to the barium ions using ^{140}Ba as indicator and the following results were obtained.

1) On the adaptability of Freundlich's adsorption isotherm: Ferric chloride (1 mg as Fe) and barium ions (from carrier free amount to 1 mM as Ba) were dissolved in 15 ml of 0.1N-HCl and NH_4OH was added to the solution until pH 9.0-9.5 in N_2 atmospher. Aliquots of the solutions before and after the addition of NH_4OH were pipetted out and the activities of ^{140}Ba corrected for ^{140}La were measured. As a result, in the Freundlich's equation,

$$\ln\frac{x}{m}=\ln C=\ln a+\frac{1}{n}\ln C$$

n=1 holds when Ba^{++} is below 10^{-4}mM and the n value becomes larger with increasing Ba^{++} over 10^{-4}mM.

2) On the effect of other ions present together: Sodium ions have little effect to the coprecipitation of Ba^{++} until 0.1 mM. On the other hand, calcium and strontium ions when present over 1 mM, completely prevent the coprecipitation of Ba^{++} with $Fe(OH)_3$. Aluminum ions precipitate together with $Fe(OH)_3$ at the pH described, however, the coprecipitation of Ba^{++} decreases.

3) On the cation exchange reaction: A solution of sodium, calcium, strontium or aluminum was added to the precipitate of $Fe(OH)_3$ and of Ba^{++} and similar effects to the case of above experiments were observed.

On the Effect of Beta-rays on the Gamma-ray Spectroscopy Measurement.

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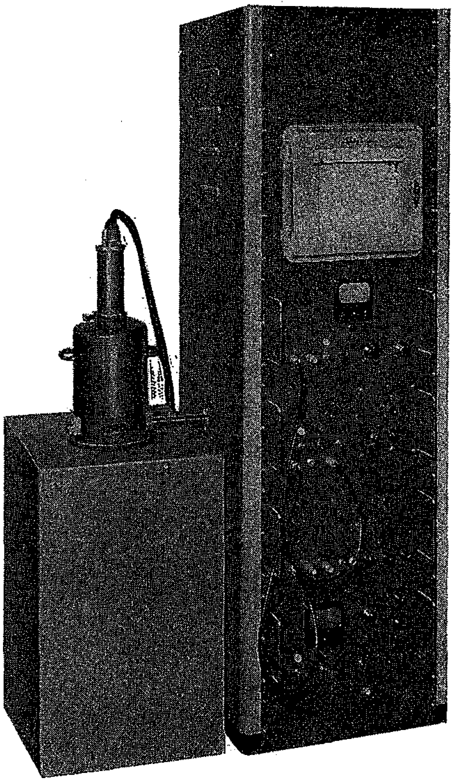
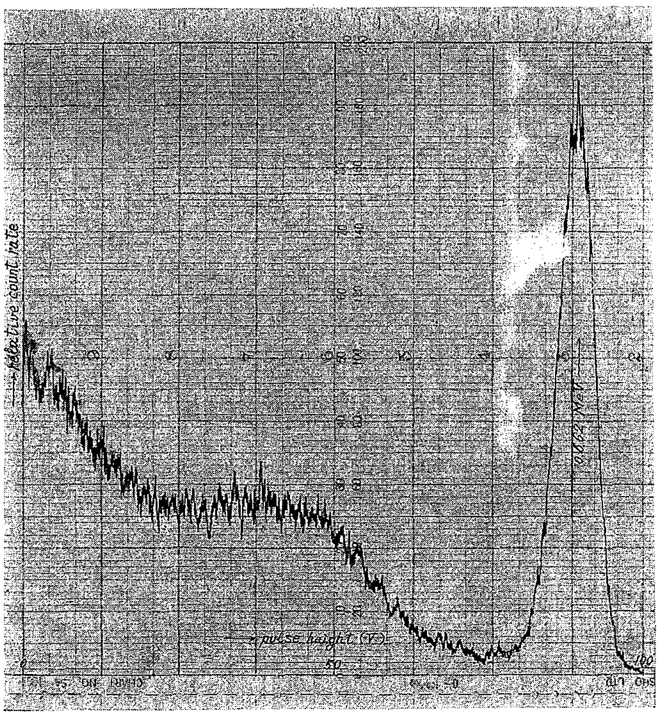
Recent year, on the fields of energy measurements of gamma-ray from nucleus, or determination of impurities in the radioctive isotopes, the gamma-ray spectroscopy are more utilized. It's principle are based on fact that the output pulse height of light from scintillator are proportioned to secondary electron intensity emitted from scintillator by the incident gamma-ray. The most scintillator are sensitive not only the gamma-rays but also the beta-rays. The NaI scintillator, which is most used to measure the gamma-ray energy, are canned in thin aluminum capsule. A soft beta-ray cannot penetrates the capsule, but a hard beta-ray can easily penetrates it. Consequently, for a emitter of gamma-ray with hard beta-ray, the gamma-ray spectrum are materially affected by the beta-rays; that is, some small photo-peaks in gamma-ray spectrum are coverd in hard beta-ray spectrum and do not clearly recognized. To avoid this gamma spectrum distortion, the NaI scintillator are covered with the thick plastic plate, such as acryl-resin plate, and hard beta-rays are absorbed by this plastic plate and beta-ray cannot reach the scintillator. Thereby, gamma-ray spectrum do not distorts by beta-rays.

A example, arsenic-76 disintegrates with the half-life of 26.9 hours, beta-rays of 3.04, 2.49, 1.29 Mev. and gamma-ray of 0.56, 1.21, 1.70, 2.06 Mev.; gamma-ray of 0.56, 1.21, 1.70, 2.06 Mev. gamma-ray are weak. In case of no beta-ray shield, photo-peak for 2.06 Mev. gamma-ray do not almost records, but it's peak are clearly recognized by use of the beta-ray shield (1.5 cm. thickness of acryl-resin plate).




→ relative count rate
→ pulse height (V)
0
50
100
0.662 MeV

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