

《Original》

## Determination of Impurities in Aluminum by Neutron Activation Analysis

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### Abstract

A radiochemical separation scheme for the neutron activation analysis is developed for the determination of 28 elements in aluminum. The scheme is based on a group separation using ion-exchange resin and mineral exchanger. Present work has employed mineral acids and their partly organic mixture excluding HF as the media as well as common glass wares. For the determination, gamma-ray spectroscopy using 3"×3" NaI (Tl) detector and a single comparator method are used.

### 요 약

중성자 방사화분석법으로 알루미늄중 28개의 미량원소들의 분석을 위하여 방사화학적 분리방법을 개발하였다. 이 분리법은 이온 교환수지와 무기질 이온 교환체를 사용한 군분리에 기초를 둔 것으로서 이온교환용은 유리관을 사용하였으며 용매는 불산용액을 제외한 무기산용액 혹은 유기용매와 혼합된 무기산 용액을 사용하였다. 함량은 분리된 각 원소들의 방사능을 3"×3" NaI(Tl) 검출기로 감마선 스펙트럼을 구한 다음 단일비교 방법으로 결정하였다.

### 1. Introduction

Aluminum is widely used in various industrial fields because of its convenient chemical properties, such as, lightness, no chemical toxicity, good thermal and electrical conductivities and resistance to corrosion. More over, as its neutron absorption cross section is low and the half-life of its radioisotope is short, its metal of high purity is one of the important mater-

ials for nuclear fields. The presence of some other elements, even at the trace levels, may limit its use. Neutron activation analysis is sensitive and convenient method for determination of these elements.<sup>1~4)</sup>

When the highest sensitivity is needed, radiochemical separation may be required in order to eliminate some interfering radioactivity or to make group separations. In this case, the counting of the separated sources is very often performed by means of a NaI (Tl) crystal connected to multi-

channel analyzer. A large variety of radiochemical separation techniques ranges from classical methods of precipitation, solvent extraction and ion-exchange to a variety of derived techniques.

Girardi and Pietra developed a separation scheme for the analysis of aluminum, which is based on neutron activation followed by a group separation using ion-exchange resin and HCl or HF medium.<sup>2)</sup> Beurton et al. have extended this separation scheme for the determination of 30 elements in aluminum.<sup>4)</sup> These authors combined the separation by ion-exchange resin with separation methods such as solvent extraction, gravimetry or distillations. They employed polymethylmetacrylate column and other special wares instead of common glass wares in order to protect from HF corrosion.

The radiochemical scheme which is developed in the present studies is based on a group separation using ion-exchange resins, i.e., Dowex 1, Dowex 50 and Chelex-100, and a mineral exchanger, i.e., HAP (hydrated antimony pentoxide). Present work has employed mineral acids or their partly organic mixture, excluding HF acid, as the media as well as common glass wares to determine 28 elements in aluminum.

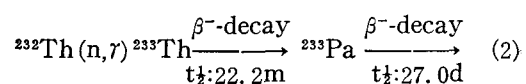
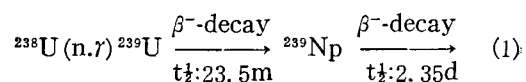
To avoid the preparation, irradiation and measurement of large number of standards which are very cumbersome and source of errors, single comparator method was used for all elements except Ni, Ti, U and Th. These elements are determined relatively, i.e., by comparing the activities of samples with those of standards.

#### Nuclear Data and Interference

The elements determined in the present

work are shown in Table 1. The  $^{24}\text{Na}$  activity is produced by (n, $\gamma$ ) reaction of sodium impurities as well as by the fast-neutron reaction of  $^{27}\text{Al}$  (n, $\alpha$ )  $^{24}\text{Na}$ . The sodium concentration have been determined by means of double irradiations, i.e., one sample is irradiated with cadmium cover and the other is irradiated without cadmium cover, and by using the activity difference between these two irradiations.

Uranium and thorium have been determined by the activities of  $^{239}\text{Np}$  and  $^{233}\text{Pa}$ , which are produced by following reactions, respectively;



Ni and Ti have been determined by measuring activities of  $^{58}\text{Co}$  and  $^{47}\text{Sc}$ , respectively.

For the determination of Zr, Mo, Cd, La and Ce, the contribution from uranium fission products was corrected in order to determine the trace amounts of these impurities.

#### Single Comparator Methodology

When large number of elements is determined by neutron activation analysis, the preparation, irradiation and measurement of such large number of standards are very cumbersome and introduce source of errors. For this reasons, the single comparator method which was first used by Girardi et al.<sup>5)</sup> has come into prominence in the recent year.<sup>6-9)</sup> In this work, Co was used as the comparator as described in the previous report.<sup>9)</sup> When the samples are irradiated together with the comparator, the amounts of the determined elements in sample are given by the following relations,

Table 1. The Elements Determined in This Work

element	nuclear reaction	separation subgroup*	limit of sensitivity (ug)**	possible interference (g/g)***
As	$^{75}\text{As}(n,r)^{76}\text{As}$	1B	$1 \times 10^{-4}$	
Na	$^{23}\text{Na}(n,r)^{24}\text{Na}$	1B, 2B	$5 \times 10^{-3}$	Al( $5 \times 10^{-6}$ ) Mg( $5 \times 10^{-6}$ )
K	$^{41}\text{K}(n,r)^{42}\text{K}$	1B	$5 \times 10^{-1}$	
Ga	$^{71}\text{Ga}(n,r)^{72}\text{Ga}$	//	$1 \times 10^{-3}$	
Cu	$^{63}\text{Cu}(n,r)^{64}\text{Cu}$	//	$1 \times 10^{-3}$	
Mn	$^{55}\text{Mn}(n,r)^{56}\text{Mn}$	//	$1 \times 10^{-2}$	
Ni	$^{58}\text{Ni}(n,p)^{58}\text{Co}$	2B	$1 \times 10^{-1}$	
Ti	$^{47}\text{Ti}(n,p)^{47}\text{Sc}$	//	$1 \times 10^{-1}$	
Co	$^{59}\text{Co}(n,r)^{60}\text{Co}$	3A	$5 \times 10^{-3}$	
Zn	$^{64}\text{Zn}(n,r)^{65}\text{Zn}$	//	$1 \times 10^{-1}$	
Cd	$^{114}\text{Cd}(n,r)^{115}\text{Cd}$ $\rightarrow^{115}\text{In}$	//	$1 \times 10^{-2}$	U( $2 \times 10^{-4}$ )
Sn	$^{112}\text{Sn}(n,r)^{113}\text{Sn}$	//	$1 \times 10^{-1}$	
Hg	$^{196}\text{Hg}(n,r)^{197}\text{Hg}$	//	$1 \times 10^{-3}$	
Au	$^{197}\text{Au}(n,r)^{198}\text{Au}$	//	$5 \times 10^{-6}$	
U	$^{238}\text{U}(n,r)^{239}\text{U}$ $\rightarrow^{239}\text{Np}$	//	$5 \times 10^{-4}$	
Th	$^{232}\text{Th}(n,r)^{233}\text{Th}$ $\rightarrow^{233}\text{Pa}$	//	$5 \times 10^{-4}$	
Mo	$^{98}\text{Mo}(n,r)^{99}\text{Mo}$ $\rightarrow^{99\text{m}}\text{Tc}$	3AB	$1 \times 10^{-2}$	U( $1 \times 10^{-1}$ )
In	$^{113}\text{In}(n,r)^{114\text{m}}\text{In}$	//	$1 \times 10^{-1}$	
Fe	$^{58}\text{Fe}(n,r)^{59}\text{Fe}$	//	$1 \times 10^{-2}$	
Cr	$^{51}\text{Cr}(n,r)^{52}\text{Cr}$	3ACB	$1 \times 10^{-2}$	
Sc	$^{45}\text{Sc}(n,r)^{46}\text{Sc}$	//	$1 \times 10^{-3}$	
Ba	$^{130}\text{Ba}(n,r)^{131}\text{Ba}$	//	$1 \times 10^{-1}$	
La	$^{139}\text{La}(n,r)^{140}\text{La}$	//	$5 \times 10^{-3}$	U( $3 \times 10^{-3}$ )
Ce	$^{140}\text{Ce}(n,r)^{141}\text{Ce}$	//	$1 \times 10^{-3}$	U( $6 \times 10^{-2}$ )
W	$^{184}\text{W}(n,r)^{185}\text{W}$	//	$5 \times 10^{-2}$	
Hf	$^{180}\text{Hf}(n,r)^{181}\text{Hf}$	//	$5 \times 10^{-4}$	
Ag	$^{109}\text{Ag}(n,r)$ $\rightarrow^{110\text{m}}\text{Ag}$	//	$1 \times 10^{-1}$	
Sr	$^{84}\text{Sr}(n,r)^{85}\text{Sr}$	//	$1 \times 10^{-1}$	
Zr	$^{84}\text{Zr}(n,r)^{85}\text{Zr}$	//	$1 \times 10^{-4}$	U( $3 \times 10^{-2}$ )
Ta	$^{181}\text{Ta}(n,r)^{182}\text{Ta}$	//	$5 \times 10^{-3}$	

\*: Symbols of I, 2, 3, A, B and C are group I, group II, group III, anion exchange resin, cation exchange resin and chelex-100 resin, respectively.

\*\*: Detection limits were calculated according to Currie's method<sup>20</sup>.

\*\*\*: The value in parenthesis is the grams of the element in column 1 which is produced by one gram of interfering element.

$$W = W' \cdot \frac{A \cdot S' \cdot D'}{A' \cdot S \cdot D} \cdot K_1 \cdot (C_2 \cdot C_3)^{-1}, \quad (3)$$

$$\text{where } K_1 = \frac{f' \cdot M \cdot b'}{f \cdot M' \cdot b}, \quad C_2 = \frac{\epsilon}{\epsilon'}, \quad C_3 = \frac{\hat{\sigma}}{\hat{\sigma}'},$$

A=activity of a nuclide of interest

$\hat{\sigma}$ =effective activation cross section

W=weight of element

f=fractional isotopic abundance of target nuclide

M=atomic weight of element

b=gamma-abundance in decay scheme

S=saturation factor;  $1 - e^{-\lambda t_1}$

D=decay factor;  $e^{-\lambda t_2}$

$t_1$ =irradiation time

$t_2$ =decay time

$\epsilon$ =efficiency of the detector for a particular gamma-ray measured

and the indication (') refers to cobalt comparator.

The effective cross section,  $\hat{\sigma}$ , is given by the following equation<sup>10)</sup>

$$\hat{\sigma} = \sigma_0 \cdot (g - r \cdot \sqrt{T/T_0} \cdot S_0), \quad (4)$$

where  $\sigma_0$  is the cross section for 2200m/sec neutrons, and  $r \cdot \sqrt{T/T_0}$  is spectral index.  $r$  is epithermal index which represents the relative strength of the epithermal  $1/v$  component in the neutron spectrum, and  $T_0$  and  $T$  are temperature equivalent to energy of 2200m/sec neutron and epithermal neutron, respectively.  $g$  and  $S_0$  are the factors depending on the departure of the cross section law from  $1/v$  form. The spectral index is related to cadmium ratio (CdR) as follows,

$$r \cdot \sqrt{T/T_0} = \sigma_0 \cdot \frac{g}{(CdR - 1) S_0 + CdR \cdot 1/K}, \quad (5)$$

where the constant  $K$  is 2.293 for 0.040 inch thickness of cadmium.<sup>11)</sup> For calculation of the spectral indices, the data used are shown in Table 2. Once constant  $K$  and the spectral index are known,  $S_0$  values of all elements can be determined if their

Table 2. Spectral Index in the Rotary Speciman Rack of TRIGA Mark II Reactor

nuclide	half-life	$S_0$	$\sigma_0$	K	Cd ratio	$r \cdot \sqrt{T/T_0}$
$^{60}\text{Co}$	5.27y	$37^{16,18}$	$1.78^{16,18}$	2.2931	$13.8 \pm 0.1$	$0.0347 \pm 0.002$
$^{198}\text{Au}$	2.70d	$98.8^{17,18}$	$17.31^{17,18}$	"	$2.60 \pm 0.06$	$0.0347 \pm 0.008$
$^{56}\text{Mn}$	2.58h	$13.3^{16,18}$	$0.697^{16,18}$	"	$25.8 \pm 0.2$	$0.0350 \pm 0.003$

Table 3. Cd Ratios and  $S_0$  Values

reaction	$\sigma_0$	$g^{19*}$	Cd ratio	$S_0$ in this work	$S_0$ in other work
$^{75}\text{As}(n,r)^{76}\text{As}$	$4.4^{16,18}$		$2.58 \pm 0.03$	$14.9 \pm 0.2$	$15.1^{16}$
$^{23}\text{Na}(n,r)^{24}\text{Na}$	$0.528^{16}$		$48.8 \pm 1.5$	$0.158 \pm 0.005$	$0.155^{16,18}$
$^{41}\text{K}(n,r)^{42}\text{K}$	$1.46^{16,18}$		$31.5 \pm 0.6$	$0.494 \pm 0.009$	$0.468^{16,18}$
$^{71}\text{Ga}(n,r)^{72}\text{Ga}$	$4.7^{16,18}$		$5.84 \pm 0.07$	$5.40 \pm 0.07$	$5.49^{18}$
$^{63}\text{Cu}(n,r)^{64}\text{Cu}$	$4.4^{16,18}$	1.000	$24.1 \pm 1.0$	$0.793 \pm 0.003$	$0.774^{18}$
$^{55}\text{Mn}(n,r)^{56}\text{Mn}$	$13.3^{16,18}$	1.000	$26.1 \pm 0.2$	$0.695 \pm 0.005$	$0.680^{16,18}$
$^{59}\text{Co}(n,r)^{60}\text{Co}$	$37^{16,18}$	1.000	$13.8 \pm 0.1$	$1.78 \pm 0.01$	$1.78^{16,18}$
$^{98}\text{Mo}(n,r)^{99}\text{Mo}$	$0.14^{16,18}$		$1.42 \pm 0.10$	$76.1 \pm 4.8$	$60.0^{18}$
$^{113}\text{In}(n,r)^{114}\text{In}$	$8.1^{16,18}$	1.0211	$1.85 \pm 0.05$	$33.6 \pm 0.9$	$35.44^{16,18}$
$^{58}\text{Fe}(n,r)^{59}\text{Fe}$	$1.14^{16,18}$		$2.60 \pm 0.30$	$0.699 \pm 0.008$	$0.680^{18}$
$^{64}\text{Zn}(n,r)^{65}\text{Zn}$	$0.82^{18}$		$13.7 \pm 0.5$	$1.67 \pm 0.24$	$1.69^{18}$
$^{114}\text{Cd}(n,r)^{115}\text{Cd}$	$0.30^{18}$	1.3945	$1.50 \pm 0.19$	$79 \pm 10$	$86.9^{18}$
$^{112}\text{Sn}(n,r)^{113}\text{Sn}$	$1.22^{16}$		$1.83 \pm 0.13$	$33.8 \pm 2.4$	$38.3^{16}$
$^{50}\text{Cr}(n,r)^{51}\text{Cr}$	$16.0^{18}$		$53.0 \pm 4.3$	$0.108 \pm 0.009$	$0.0917^{18}$
$^{45}\text{Sc}(n,r)^{46}\text{Sc}$	$25^{18}$		$55.2 \pm 4.0$	$0.0876 \pm 0.0064$	$0.0790^{18}$
$^{130}\text{Ba}(n,r)^{131}\text{Ba}$	$13.5^{18}$		$2.40 \pm 0.04$	$19.8 \pm 0.3$	$22.1^{18}$
$^{139}\text{La}(n,r)^{140}\text{La}$	$9.0^{17}$		$21.5 \pm 0.5$	$0.948 \pm 0.022$	$1.02^{17}$
$^{181}\text{Ta}(n,r)^{182}\text{Ta}$	$21.5^{17}$	1.814	$2.44 \pm 0.06$	$35.6 \pm 0.9$	$37.0^{17}$
$^{140}\text{Ce}(n,r)^{141}\text{Ce}$	$0.58^{18}$		$34.2 \pm 0.7$	$0.419 \pm 0.009$	$0.446^{18}$
$^{184}\text{W}(n,r)^{185}\text{W}$	$1.8^{17}$		$4.12 \pm 0.03$	$8.66 \pm 0.06$	$8.27^{17}$
$^{180}\text{Hf}(n,r)^{181}\text{Hf}$	$12.6^{17,18}$	1.023	$10.5 \pm 0.2$	$2.55 \pm 0.05$	$2.36^{18}$
$^{109}\text{Ag}(n,r)^{110m}\text{Ag}$	$4.7^{16}$	1.006	$2.32 \pm 0.05$	$21.1 \pm 0.5$	$18.9^{16}$
$^{84}\text{Sr}(n,r)^{85}\text{Sr}$	$0.80^{16,18}$		$2.83 \pm 0.05$	$15.1 \pm 0.9$	$14.4^{16}$
$^{94}\text{Zr}(n,r)^{95}\text{Zr}$	$0.075^{16,18}$		$6.30 \pm 0.08$	$4.92 \pm 0.06$	$5.20^{16,18}$
$^{196}\text{Hg}(n,r)^{197}\text{Hg}$	$3092^{17}$			0	$0^{17,18}$

\*: g values which do not listed in this column are treated as 1.00

cadmium ratios are measured.<sup>11)</sup> The effective cross section,  $\hat{\sigma}$ , are then calculated by using the equation (4). For this purpose the used data are given in Table 3.  $K_1$  values are shown in Table 4.  $C_2$  values were measured experimentally as described previously.<sup>9)</sup>

## I. Experimental

### Determination of Cd Ratio

An amount of 10-100mg of each metal or metal oxide (Johnson and Matthey, "spec. pure") were accurately weighed, dissolved in a hot mixture of 3ml concentrated nitric acid and 0.5ml hydrofluoric acid, evaporated to expel hydrofluoric acid by heating and finally diluted to 25ml in volumetric flask

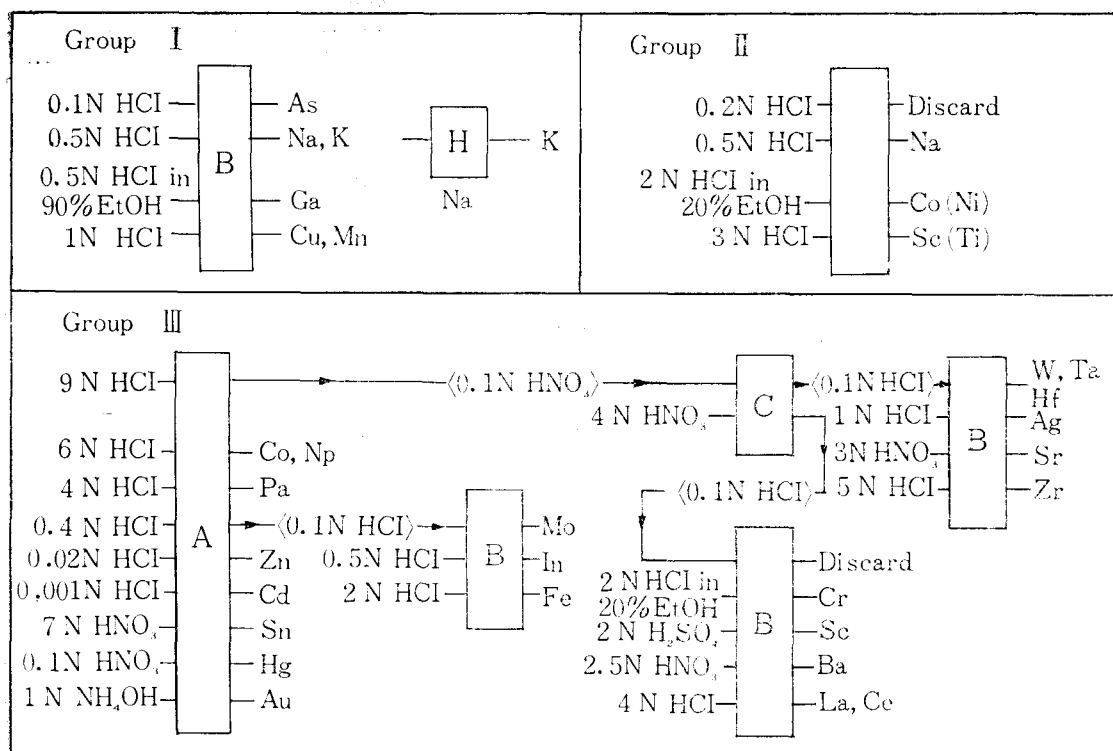


Fig. 1. Ion Exchange Resin Separation Scheme

A: Anion exchange resin (Dowex 1)  
 B: Cation exchange resin (Dowex 50)  
 C: Chelex-100 H: Hydrated antimony pentoxide  
 < > Evaporation and exchange of solvent

by distilled water. From this solution, the amount of 100 lambda was each pipetted onto polyethylene foil and dried by the heat of an infrared lamp. The polyethylene foil was wrapped and inserted into the small polyethylene bag. This polyethylene bag was irradiated with and without cadmium cover at the rotary specimen rack of TRIGA Mark III reactor for 1 day. The irradiated sample was counted by 3"×3" NaI (Tl) crystal connected to 400 channel pulse height analyzer (Hitachi, RAH-403 Model, Japan). From the gamma spectra, characteristic photopeak area of each nuclide is calculated and cadmium ratio thus obtained are shown in Table 3.

#### Irradiation of Aluminum

For the removal of the contaminated impurities on the surface of aluminum sample, the sample was dipped into 6 N HCl solution for a few minutes, transferred into redistilled water and washed by ethyl-alcohol. About 0.7–1.0 gram amount of the decontaminated sample was weighed accurately and wrapped with aluminum foil. An accurate weight of about 100μg of cobalt comparator was attached on each sample. The samples were irradiated in the neutron flux of  $1 \times 10^{13}$  neutrons per square cm per sec using rotary specimen rack of TRIGA Mark III reactor. Irradiation times

Table 4. The  $K_1$  Values and Nuclear Data

nuclide	E(MeV)*	T	f	b	M	$K_1$
$^{76}\text{As}$	0.559	26.4h	1.00	0.431	74.92	2.96
$^{24}\text{Na}$	1.37	15h	1.00	1.00	22.99	0.390
$^{42}\text{K}$	1.52	12.4h	0.0677	0.18	39.10	54.4
$^{72}\text{Ga}$	0.834	14.1h	0.399	1.19	69.72	2.49
$^{64}\text{Cu}$	0.511	12.8h	0.691	0.38	63.55	4.11
$^{56}\text{Mn}$	0.845	2.58h	0.99	1.00	54.94	9.42
$^{60}\text{Co}$	1.33	5.27y	1.00	1.00	58.93	1.00
$^{99}\text{Mo}$	0.143(d)	66h	0.241	1.00	95.93	6.75
$^{114\text{m}}\text{In}$	1.30(d)	49.5d	0.043	0.965	114.8	47.0
$^{59}\text{Fe}$	1.10	44.6d	0.003	0.56	55.85	564
$^{65}\text{Zn}$	1.115	243.8d	0.486	0.49	65.38	4.66
$^{115}\text{Cd}$	0.336(d)	53.5h	0.287	0.95	112.4	7.00
$^{113}\text{Sn}$	0.392	115d	0.0101	1.00	118.7	200
$^{198}\text{Au}$	0.412	2.67d	1.00	1.00	197.0	3.34
$^{51}\text{Cr}$	0.320	27.7d	0.0435	0.090	52.00	225.4
$^{46}\text{Sc}$	0.889	83.8d	1.00	1.00	44.96	0.763
$^{131}\text{Ba}$	0.496	11.7d	0.0011	0.294	137.3	7206
$^{140}\text{La}$	1.597	40.2h	0.999	0.60	138.9	3.93
$^{141}\text{Ce}$	0.145	32.5d	0.8848	0.70	140.1	3.84
$^{185}\text{W}$	0.1254	75.1d	0.3067	0.003	183.9	3391
$^{182}\text{Ta}$	0.100	115d	1.00	1.00	180.9	3.07
$^{181}\text{Hf}$	0.482	42.4d	0.352	0.83	178.5	10.4
$^{197}\text{Hg}$	0.077	65h	0.00146	0.999	200.6	2334
$^{110\text{m}}\text{Ag}$	0.884	252d	0.4817	0.74	107.9	5.14
$^{85}\text{Sr}$	0.514	65.2d	0.0056	1.00	87.62	265.5
$^{95}\text{Zr}$	0.756	64.0d	0.174	0.49	91.22	18.2
$^{58}\text{Co}(\text{Ni})$	0.810	70.8d	Relative Method			
$^{47}\text{Sc}(\text{Ti})$	0.1594	3.41d	"	"		
$^{233}\text{Pa}(\text{Th})$	0.312	27.0d	"	"		
$^{239}\text{Np}(\text{U})$	0.106	2.35d	"	"		

\*: (d) in this column means radioisotope of daughter.

were on the range of 8 hours-one week which are depended on groups given in the Fig. 1.

#### Recrystallization of Aluminum and Separation Procedures

The irradiated aluminum sample was dissolved in 6 N HCl solution and a 0.3ml amount of concentrated  $\text{H}_2\text{O}_2$  solution was added. This solution was saturated by passing the gaseous hydrogen chloride. The crystallization of the aluminum chloride

occurred spontaneously in 12M HCl solution. The precipitates of aluminum were filtered with filter paper (Wattmann No. 5) and washed three times with 3ml aliquots of 12M HCl solution.

Ion exchangers used in this work are anion exchange resin (Dowex 1 $\times$ 8, 100-200 mesh), cation exchange resin (Dowex 50 $\times$ 12, 100-200 mesh), Chelex-100 (100-200 mesh, BioRad) and HAP (hydrated antimony pentoxide, Carlo Erba, Italy). Each

ion exchange resin column is 1.2cm in diameter and 15cm long. The elution rate was adjusted not to higher than 0.7ml per minute.

The separation scheme in the present work consists of some procedures which have been adopted routinely in this laboratory for the analysis of biological samples<sup>12)</sup> and water<sup>13)</sup> as well as other procedures which are based on Beurton's<sup>4)</sup> but a little modified by Strelow's distribution data<sup>14, 15)</sup>. The separation scheme is outlined in Fig. 1.

For group I, the filterates obtained by filtering the precipitates of aluminum were collected and adjusted to pH 1 by adding 6 N  $\text{NH}_4\text{OH}$  solution and loaded on a cation exchange resin column. The 20ml of 0.1 N HCl solution were eluted through the column for the collection of arsenic and subsequently 100ml of 0.5 N HCl solution for sodium and potassium, 40ml of 0.5 N HCl in 90% ethanol for galium and 100ml of 1 N HCl solution for copper and manganese. The latter part of this procedure is based on Strelow's distribution coefficient (Kd), i.e., Kd of Ga, Cu and Mn are 3.5, 36 and 730 in the medium of 0.5 N HCl solution in 90% ethanol, respectively.<sup>14)</sup> Eluates which contain sodium and potassium were collected, adjusted to 50ml by diluting with distilled water and counted for sodium activities. After then, this solution was adjusted to pH 1 and loaded on HAP resin column for removal of sodium. The eluates from HAP resin column were collected and similarly counted for potassium activities.

For group II, some portion of filterates were also converted to pH 1 as like group I and loaded on a cation exchange resin column. The 40ml of 0.2 N HCl solution was eluted and eluates were discarded. Then the 50ml of 0.5 N HCl solution

was eluted for  $^{24}\text{Na}$  which was produced mostly from aluminum and subsequently 50ml of 2 N HCl solution in 20% ethanol for  $^{58}\text{Co}$  and 50ml of 3 N HCl solution for  $^{47}\text{Sc}$  which were produced from nickel and titanium respectively. This procedures are also based on Strelow's data, i.e., Kd of Co and Sc are 8.9 and 57 in the medium of 2 N HCl solution in 20% ethanol, respectively.<sup>14)</sup>

For group III, another portion of the filterates were diluted to 9 N HCl solution and loaded on a cation exchange resin column. Ten ml of 9 N HCl solution were eluted and the eluates(A) were kept for additional processing. The 150ml of 6 N HCl solution were eluted for Co and  $^{239}\text{Np}$  (from uranium), and subsequently 50ml of 4 N HCl solution for  $^{233}\text{Pa}$  (from thorium), 50ml of 0.4 N HCl solution for Mo, In and Fe (This solution (B) was kept for more processing), 50ml of 0.02 N HCl solution for Zn, 50ml of 0.001 N HCl solution for Cd, 50ml of 7 N  $\text{HNO}_3$  solution for Sn, 80ml of 1 N  $\text{HNO}_3$  solution for Hg and 50ml of 1 N  $\text{NH}_4\text{OH}$  solution for Au.

Filterates B were collected, heated to 20ml, adjusted to pH 1 and loaded on a cation exchange resin column. Ten ml of 0.1 N HCl solution were eluted for Mo, and subsequently 50ml of 0.5 N HCl solution for In and 50ml of 2 N HCl solution for Fe.

The eluates A were collected, heated, converted to  $\text{HNO}_3$  solution, adjusted to pH 1 and loaded on a Chelex-100 resin column. Ten ml of 0.1 N  $\text{HNO}_3$  solution were eluted and eluates(C) were kept for more processing. The 40ml of 4 N  $\text{HNO}_3$  solution were eluted and these eluates(D) were kept for more processing.

The eluates D were heated, converted

Table 5. The Accuracy of the Present Method

element	amount added ( $\mu\text{g}$ ), $W_a$	amount recovered ( $\mu\text{g}$ ), $W_r$	$W_r/W_a$	number of determination
As	10.1	$9.0 \pm 0.5$	$0.900 \pm 0.051$	3
Na	26.3	$24.5 \pm 0.6$	$0.932 \pm 0.021$	3
K	108.7	$109.0 \pm 3.3$	$1.01 \pm 0.03$	3
Ga	30.0	$29.1 \pm 0.3$	$0.970 \pm 0.010$	3
Cu	29.5	$29.4 \pm 0.2$	$0.997 \pm 0.005$	3
Mn	88.1	$88.1 \pm 2.7$	$1.00 \pm 0.03$	3
Ni	49.9	$49.3 \pm 0.8$	$0.988 \pm 0.016$	4
Ti	51.7	$51.9 \pm 1.0$	$1.00 \pm 0.02$	4
Co	53.0	$53.0 \pm 1.6$	$1.00 \pm 0.03$	7
Mo	52.5	$52.4 \pm 1.0$	$0.992 \pm 0.018$	4
In	50.3	$48.1 \pm 0.5$	$0.956 \pm 0.010$	4
Fe	250.1	$249.7 \pm 2.2$	$0.998 \pm 0.009$	4
Zn	106.2	$104.8 \pm 1.3$	$0.987 \pm 0.012$	2
Cd	102.1	$100.2 \pm 1.0$	$0.981 \pm 0.009$	2
Sn	253.7	$250.3 \pm 5.3$	$0.897 \pm 0.021$	2
Cr	50.9	$48.7 \pm 4.1$	$0.957 \pm 0.081$	4
Sc	15.8	$15.8 \pm 1.1$	$1.00 \pm 0.07$	4
La	26.0	$25.7 \pm 0.4$	$0.988 \pm 0.017$	4
Ce	25.7	$25.6 \pm 0.2$	$0.996 \pm 0.007$	4
Hf	15.7	$15.7 \pm 1.4$	$1.00 \pm 0.09$	3
Hg	25.0	$22.8 \pm 1.9$	$0.912 \pm 0.083$	4
Ag	152.3	$145 \pm 12$	$0.953 \pm 0.081$	3
Sr	150.4	$141.2 \pm 1.4$	$0.939 \pm 0.009$	3
Zr	52.1	$53.2 \pm 2.3$	$1.02 \pm 0.05$	3
Au	10.7	$10.5 \pm 0.3$	$0.981 \pm 0.030$	3
Ba	62.0	$60.3 \pm 2.7$	$0.972 \pm 0.040$	3
U	10.1	$10.0 \pm 0.7$	$0.990 \pm 0.030$	3
Th	53.9	$53.0 \pm 0.6$	$0.983 \pm 0.011$	4

to HCl solution, adjusted to pH 1 and loaded on cation exchange resin column. Ten ml of 0.1 N HCl solution were eluted and eluates were discarded. After then, the 50ml of 2 N HCl solution in 20% ethanol were eluted for Cr, and subsequently 50ml of 2 N  $\text{H}_2\text{SO}_4$  solution for Sc, 50ml of 2.5 N  $\text{HNO}_3$  solution for Ba and 50ml of 4 N HCl solution for La and Ce. This procedures are based on Strelow's data, i.e., Kd values of Cr, Sc, Ba and La are 7.5, 57, 74 and 68 in medium of 2 N HCl solution in 20% ethanol, respectively.<sup>14)</sup> The Kd values of Sc, La and Ce

are 8.5,  $10^4$  and  $10^4$  in 2 N  $\text{H}_2\text{SO}_4$  medium, respectively and Kd values of Ba, La and Ce are 8.4, 30 and 30 in 2.5 N  $\text{HNO}_3$  medium, respectively.<sup>15)</sup>

The eluates C were heated, converted to HCl solution, adjusted to pH 1 and loaded to cation exchange resin column. Ten ml of 0.1 N HCl solution were eluted for Hf. Subsequently, the 50ml of 1 N HCl solution were eluted for Ag, 50ml of 3 N  $\text{HNO}_3$  solution for Sr and 50ml of 5 N HCl solution for Zr. (Kd values of Sr and Zr are 6.1 and 112 in 3 N  $\text{HNO}_3$  medium, respectively.<sup>15)</sup>)

#### Activity Counting

All the eluates for each element were transferred to 50ml volumetric flask and diluted to 50ml. Each flask as well as cobalt comparator was counted by 3'' $\times$ 3'' NaI (Tl) crystal connected to 400 channel pulse height analyzer (Hitachi, Model RAH-403, Japan). From the gamma-ray spectra, characteristic photopeak areas of the nuclei, A, were measured at given geometries where the efficiencies of characteristics gamma-rays are known as described previously.<sup>9)</sup>

#### Determination of Each Elements

The weights of the elements were calculated from the activities of cobalt comparator and samples by Eq. (3) using the values of  $K_1$ ,  $C_2$ ,  $C_3$  S and D.

## II. Results and Discussion

#### Recrystallization of Aluminum

To check the absorption of ions on the surface of aluminum chloride during recrystallization of aluminum by passing hydrochloride gas, an experimental procedure was applied.



**Table 6. Recoveries During Recrystallization of Aluminum**

added radioactive element	activities (%)	
	crystal of $\text{AlCl}_3$	solution
Ga	0.02	100.0
In	0.06	99.99
Fe	—	100.1
Ni	—	100.0
Co	—	100.3
Sn	0.03	99.97
Cr	0.03	100.1
Mo	0.02	99.99
Zn	0.01	99.99
Hf	—	99.98

One gram of nonactive aluminum metal was dissolved as described in the procedure of "the recrystallization of aluminum and separation". To this solution, some radioactive trace ions were added and aluminum chloride was recrystallized by passing hydrochloride gas. The precipitates of aluminum chloride were filtered as described in the procedure. Activities of precipitates and filtered solution were each counted using well type scintillation counter. Absorption of ions on surface of  $\text{AlCl}_3$  crystal was found negligible as shown in the Table 6.

#### Ion Exchange Separation

Fifty ml solution was sufficient for the elutions of most elements, however, 150ml of 6 N HCl and 80ml of 0.1 N  $\text{HNO}_3$  solution were needed for the collection of Co and Np, and for mercury in group III, respectively. When mercury solution was heated for the concentration to 50ml, it was found that some mercury was vaporized. For the determination of mercury that eluates were therefore transferred to 100ml volumetric flask and counted.

It was found that tungsten and talium

**Table 7. The Analytical Results of Impurities in Aluminum**

element	results(ppm)	
	sample 1	sample 2
Na	$0.037 \pm 0.016$	$0.31 \pm 0.08$
K	N.D.	N.D.
Cu	$0.54 \pm 0.01$	$1.2 \pm 0.2$
Mn	$0.71 \pm 0.01$	$0.95 \pm 0.02$
As	$2.8 \pm 0.3$	$1.9 \pm 0.1$
Ga	$4.1 \pm 0.1$	$4.8 \pm 0.3$
Ni	$0.41 \pm 0.03$	$4.8 \pm 0.3$
Ti	$0.31 \pm 0.01$	$0.31 \pm 0.01$
Co	$1.3 \pm 0.1$	$1.6 \pm 0.1$
Mo	$3.2 \pm 0.2$	$5.0 \pm 0.2$
In	N.D.	N.D.
Fe	$12 \pm 1$	$68 \pm 2$
Zn	$394 \pm 15$	$735 \pm 37$
Cd	N.D.	N.D.
Sn	N.D.	N.D.
Hg	N.D.	N.D.
Cr	$0.10 \pm 0.10$	$0.15 \pm 0.01$
Sc	$0.018 \pm 0.003$	$0.21 \pm 0.01$
Ba	$0.71 \pm 0.02$	$2.1 \pm 0.3$
La	$0.22 \pm 0.01$	$0.25 \pm 0.01$
Ce	$0.028 \pm 0.001$	$0.100 \pm 0.003$
Au	N.D.	N.D.
Hf	$0.014 \pm 0.001$	$0.027 \pm 0.001$
Zr	$1.3 \pm 0.3$	$3.9 \pm 0.5$
U	$0.13 \pm 0.01$	$0.23 \pm 0.01$
Th	$0.100 \pm 0.003$	$0.11 \pm 0.1$

were collected in eluate C. When eluates C were loaded on cation exchange resin, these two elements were eluted simultaneously below 0.2 N concentration of HCl. Because of similar gamma-ray energy of the nuclides produced from these elements, it was not possible to determine these elements in the present work.

#### Accuracy of the Present Method

It was certified by tracer work that recoveries of all elements were above 98% in the ion exchange separation. In order to verify the accuracy of this work, a mixture

of the known amounts of all the elements was irradiated by neutron along with Co comparator. The radioactive mixture was dissolved in 20ml of 6 N HCl solution with 1 gram of inactive aluminum sample. Then, each elements was separated as described in the procedures. The results of this trace work are shown in Table 5. Amounts added and determined agreed within ca. 5% relative deviation for all the elements except Hg, As, Ag and Sr, and within ca. 10% for these elements.

#### Analysis of Aluminum Sample

Two aluminum samples were analyzed by this method. The results given in Table 7 show that the present scheme for separation and determination enables one to determine the amount of trace elements with the accuracy of less than 10% relative standard deviation. It was notable that present scheme has employed mineral acids or their partly organic mixture, excluding HF acid as the media as well as common glass wares to determine 28 elements, whereas, the works reported by previous authors<sup>2,4)</sup> generally employed HF mixture and special wares such as polymethylmetacrylate column in order to protect from HF corrosion. The maximum duration for the radiochemical separation was 15 hours in this work. This time is shorter than those of other procedures.<sup>2,4)</sup>

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