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## Determination of Impurities in Uranium Dioxide by Neutron Activation Analysis

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### 중성자방사화분석법에 의한 이산화우라늄중의 불순물정량

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#### Abstract

The preliminary concentration of trace elements in uranium dioxide using an anion exchange resin is presented for neutron activation analysis. The uranyl solution in sulfuric acid is adjusted to the acidity of about pH 2.7 and loaded on a column of the anion exchange resin. An appropriate volume of eluates obtained from the column shows good recoveries of trace elements. By combining this preconcentration with a radiochemical separation scheme, which was developed for the determinations of impurities in aluminum, it is possible to determine 21 trace elements in reactor grade uranium dioxide.

#### 요 약

이산화우라늄중의 미량불순물원소들의 중성자 방사화분석을 위하여 이들 원소들의 사전농축에 음이온교환수지를 사용하였다. 황산에 녹인 우라늄 시료용액의 산도를 pH 2.7에 맞춘다음 음이온교환수지통에 넣었다. 이 음이온교환수지통으로 부터 미량불순물 원소만을 정량적으로 회수할 수 있었다. 이 사전농축법과 알미늄중 미량불순물 원소의 정량을 위하여 개발한 방사화학적 분리법을 이용하므로써 원자로급 이산화우라늄 중의 21개 미량불순물을 정량할 수 있었다.

#### 1. Introduction

Uranium compound must be extremely pure and determined for the contents of

impurity elements in ppm or ppb levels. Neutron activation analysis is a sensitive and convenient method for that purpose. But uranium is not considered to be an appropriate matrix for the determination

of trace impurities by neutron activation analysis. Direct irradiation makes the sample difficult to handle because of very high activity due to fission products and neptunium.

One of the special behavior of uranium is that absorption strength of uranyl form on anion-exchange resin is very high at low concentration of sulfuric acid and that it decreases rapidly on the increase of the concentration.<sup>1</sup> This absorption function of uranyl ions in sulfuric acid differs markedly from those in hydrochloric acid or nitric acid. Kosta applied this behavior to neutron activation analysis for the determination of five impurity elements in uranium.<sup>2</sup>

Present authors study for the pre-separation of impurities and apply the results for the determination of 21 elements in a uranium dioxide. For this purpose, a radiochemical separation scheme along with a single comparator method<sup>3</sup>, which was developed for the determination of impurities in aluminum, is adopted.

## 2. Experimental

### 2-1. Separation of Impurities from Uranium

Ten grams of sample was dissolved in a 100ml solution made from 2N sulfuric acid and 1ml of H<sub>2</sub>O<sub>2</sub> solution. The solution was heated until fume of sulfuric acid was disappeared. After cooling, the dried sample was redissolved with water and stored in 500ml volumetric flask. Acidity of the solution was about pH 2.7.

An aliquot of 50ml was taken from the flask and loaded on an anion exchange resin column (Dowex 2×8, 100-200 mesh), 15cm long by 2.6cm diameter, which was pre-equilibrated with 0.001N sulfuric acid, and the flow rate was adjusted to ca. 0.7

ml/min. The column was then eluted with 150ml of 0.001N sulfuric acid. Successive 15ml portions of the eluates were collected. The content of uranium in each portion was analyzed by delayed neutron counting method<sup>4</sup>. The other four 50ml aliquots were taken separately from the flask and adjusted to 0.01N, 0.1N, 1N and 2N with 6N sulfuric acid, respectively. Each aliquot was loaded on a column, which was previously equilibrated with an appropriate sulfuric acid. Each column was treated similarly as described above under this section. The result shown in Table 1 indicates that the absorption strength of uranium (VI) is very high at low sulfuric acid concentration and decreases rapidly on the increase of concentration of the acid.

To find the feasibility of the separation of impurity elements from uranium by using these absorption characteristics on anion exchange resin, a study on the recoveries of impurities was carried out as follows.

Each radioactive trace element such as <sup>76</sup>As, <sup>24</sup>Na, <sup>42</sup>K, <sup>56</sup>Mn, <sup>64</sup>Cu, <sup>198</sup>Au, <sup>72</sup>Ga, <sup>65</sup>Ni, <sup>60</sup>Co, <sup>99</sup>Mo, <sup>144m</sup>In, <sup>115</sup>Cd, <sup>113</sup>Sn, <sup>51</sup>Cr, <sup>46</sup>Sc, <sup>140</sup>Ba, <sup>140</sup>La, <sup>141</sup>Ce, <sup>110m</sup>Ag, <sup>85</sup>Sr and <sup>95</sup>Zr was added to an aliquot of 50ml of the stocked solution and loaded on the column. This column was then eluted with 10×15ml aliquots of 0.001N sulfuric acid. Each eluate was analyzed by counting the radioactivity with 3''×3'' NaI(Tl) well type scintillation counter. The results are shown in Table 2.

On the basis of the results obtained from the above experiment, a procedure for preconcentration of impurity elements from uranium was proposed as follows.

One gram of uranium dioxide was dissolved in a 10ml solution made from 2N sulfuric acid and a few drops of H<sub>2</sub>O<sub>2</sub>

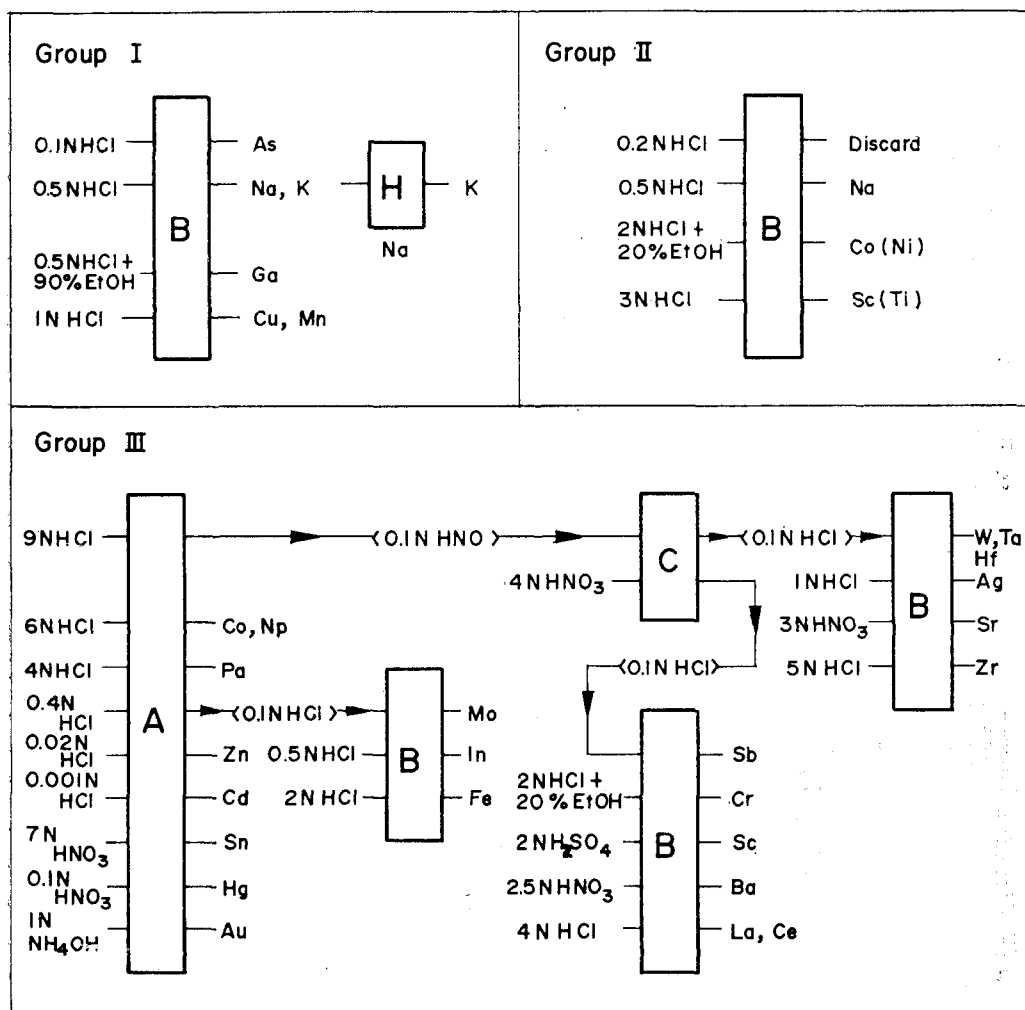


Fig. 1. Ion Exchange Resin Separation Scheme

solution. The solution was heated until fume of sulfuric acid was disappeared. The residue was redissolved with 30ml of water. This solution was loaded on an anion exchange resin column, which was preequilibrated with 0.001N sulfuric acid. The column was washed with 150ml of water. The eluate was evaporated and diluted to 10 ml.

## 2-2. Irradiation and Separation of Radioactive Impurity Element

In order to determine the contents of impurities in uranium dioxide, the procedure for their preconcentration, which has been developed in this study and described above under the section of "Separation of Impurities from Uranium", has been combined with a radiochemical separation scheme<sup>3)</sup>, which was previously developed by present authors for the determination of impurities in aluminum, as follows.

Ion exchangers used for the separation scheme are anion exchange resin (Dowex 1×8, 100-200 mesh), Cation exchange resin (Dowex 50×12, 100-200 mesh), Chelex-100 (100-200 mesh, BioRad) and HAP (hydrated antimony pentoxide, Carlo Erba, Italy). The exchange columns used in this procedure have the size of 15cm long by 1.2cm diameter. The flow rate was adjusted not to be higher than 0.7ml per minute.

The radiochemical separation scheme adopted is outlined in Fig. 1.

From the 10ml solution of uranium, a 3ml portion was taken into a polyethylene vial (capacity of 4ml) and irradiated along with a cobalt comparator for one day for the elements in group I in Fig. 1. The other 3ml portion was taken into the polyethylene vial, wrapped with cadmium sheet of 1mm thickness and irradiated similarly for 1

day for the elements in group II. Another 3ml portion was taken into silica vial (capacity of 4ml) and irradiated similarly for 1 week for the elements in group III. All the irradiations were done on Rotary specimen rack of TRIGA mark III reactor.

For group I; the irradiated solution was diluted with water to ca. 15ml and loaded on a cation exchange resin column. A 20ml volume of 0.1N hydrochloric solution was eluted through the column for collection of arsenic, and subsequently 100 ml of 0.5N hydrochloric solution for sodium and potassium, 40ml of 0.5N hydrochloric solution in 90% ethanol for gallium and 100 ml of 1N hydrochloric solution for copper and manganese. Eluates which contain sodium and potassium were collected, concentrated to 50ml and counted for sodium activities. After then, the 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 counted similarly for potassium activities.

For group II; the solution wrapped with cadmium was diluted with water to 15ml and loaded on cation exchange resin column. A 100ml volume of 0.5N hydrochloric solution was then eluted and eluates were discarded. A 50ml volume of 2N hydrochloric solution in 20% ethanol was eluted for <sup>58</sup>Co, which is produced from nickel, and 50 ml of 3N hydrochloric solution were then eluted for <sup>47</sup>Sc which from titanium.

For group III; the irradiated solution in silica vial was added to 10ml of conc. hydrochloric acid and loaded on an anion exchange resin column. Ten ml of 9N hydrochloric solution were eluted and the eluates (A) were kept for additional processing. A 150ml volume of 6N hydrochloric solution was eluted for Co and <sup>239</sup>Np (from

uranium), and subsequently 50ml of 4N hydrochloric solution for  $^{233}\text{Pa}$  (from thorium), 50ml of 0.4N hydrochloric solution for molybdenum, indium and iron (The eluates (B) were kept for more processing), 50ml of 0.02N hydrochloric solution for zinc, 50ml of 0.001N hydrochloric solution for cadmium and 50ml of 7N nitric solution for tin.

The eluates B were collected, evaporated to 20ml, adjusted to pH 1 and loaded on a cation exchange resin column. Ten ml of 0.1N hydrochloric solution were eluted for molybdenum, and subsequently 50ml of 0.5N hydrochloric solution for indium and 50ml of 2N hydrochloric solution for iron.

The eluates A were similarly collected, heated, converted to nitric solution, adjusted to pH 1 and loaded on a Chelex-100 resin-column. Ten ml of 0.1N nitric solution were eluted and the eluates (C) were kept for more processing. The 40ml of 4N nitric solution were eluted and the eluates (D) were kept for more processing.

The eluates D were heated, converted to hydrochloric solution, adjusted to pH 1 and loaded on cation exchange resin column. Ten ml of 0.1N hydrochloric solution were eluted and eluates were discarded. After then, the 50ml of 2N hydrochloric solution in 20% ethanol were eluted for chromium, and subsequently 50ml of 2N sulfuric solution for scandium, 50ml of 2.5N nitric solution for barium and 50ml of 4N hydrochloric solution for lanthanum and cerium.

The eluates C were heated, converted to hydrochloric solution, adjusted to pH 1 and loaded on cation exchange resin column. Ten ml of 0.1N hydrochloric solution were eluted for hafnium. A 50ml volume of 1N hydrochloric solution was eluted for silver, 50ml of 3N nitric solution for strontium

and 50ml of 5N hydrochloric solution for zinc.

### 2-3. Counting and Determination of Each Elements

All the eluates for each element were transferred to 50ml volumetric flask. Each flask as well as cobalt comparator was counted by 3'' $\times$ 3'' NaI (TI) crystal connected to 400 channel analyzer. From the gamma-ray spectra, characteristic photopeak area of the nuclei were measured at given geometry where the efficiencies of characteristic gamma-ray are known. The weights of the elements were calculated from the activities of the cobalt comparator and samples, using the comparator method as reported previously by present authors.<sup>3</sup>

### 3. Results and Discussion

The absorption strength of uranyl ions in sulfuric acid on anion exchange resin is drastically increased with decreasing the concentration of sulfuric acid as shown in Table 1 and this shows a good agreement with the result by Kraus and Nelson.<sup>1</sup> In order to decrease the concentration of sulfuric acid in the sample solution, the solution was heated until the fume of sulfuric acid was disappeared and the residue was dissolved with water. By doing these ways the acidity of the solution was found to be ca. pH 2.7. The sample solution thus obtained was loaded on the anion exchange resin column. The column was washed with 150ml of 0.001N sulfuric acid. The results shown in Table 1 show that the eluates contain such a small amount of uranium as 5.42 $\mu\text{g}$ . The amount of uranium is so low that radioactivities of neptunium and fission fragments which stem from

Table 1. Separation of Uranium by Anion Exchange Resin

acids	amount of uranium added, mg	uranium contents(ug) in seccessive 15-ml eluate											recovery (%)
		1	2	3	4	5	6	7	8	9	10	Total	
2NH <sub>2</sub> SO <sub>4</sub>	881.5	4210	4560	3980	3710	4120	3200	3850	4410	4620	4750	41410	4.7
1NH <sub>2</sub> SO <sub>4</sub>	"	1120	1280	810	670	600	510	390	290	320	280	6370	0.72
0.1NH <sub>2</sub> SO <sub>4</sub>	"	25	24	25	21	19	18	21	21	16	14	202	2.3×10 <sup>-2</sup>
0.01NH <sub>2</sub> SO <sub>4</sub>	"	5.0	3.1	2.4	2.4	2.5	2.0	2.4	2.6	2.9	3.2	28.5	3.2×10 <sup>-3</sup>
0.001NH <sub>2</sub> SO <sub>4</sub>	"	0.65	0.89	0.84	0.76	0.52	0.40	0.46	0.27	0.24	0.39	5.42	6.1×10 <sup>-4</sup>

Table 2. Recoveries of Trace Elements from Uranium Solution (The effluent is sulfuric acid of pH 3)

tracer											Total recovery (%)
	1	2	3	4	5	6	7	8	9	10	
<sup>76</sup> As	12.1	16.7	19.0	23.4	14.7	8.3	3.1	1.8	0.3	0.1	99.5
<sup>24</sup> Na	3.8	81.3	13.6	1.1	0.3	0.1	—	—	—	—	100.3
<sup>42</sup> K	2.5	79.6	14.0	2.1	0.6	0.3	—	—	—	—	100.0
<sup>56</sup> Mn	1.4	75.2	12.9	6.5	2.1	0.2	—	—	—	—	98.3
<sup>64</sup> Cu	0.7	33.7	48.9	12.7	2.5	1.0	0.5	0.2	0.1	—	100.3
<sup>72</sup> Ga	6.6	38.6	37.4	12.3	3.0	1.1	0.5	0.3	—	—	99.8
<sup>60</sup> Co	0.1	36.7	40.3	11.2	4.9	2.7	1.0	1.0	0.3	0.3	98.5
<sup>99</sup> Mo	29.1	51.3	6.6	6.0	3.8	2.2	0.8	—	—	—	99.8
<sup>114</sup> In	0.7	54.6	30.6	7.7	2.1	1.8	0.8	0.1	—	—	98.4
<sup>59</sup> Fe	2.7	75.6	17.1	2.4	1.1	—	—	—	—	—	98.9
<sup>65</sup> Zn	21.0	65.0	7.2	1.9	1.3	0.9	0.6	0.1	—	—	97.0
<sup>115</sup> Cd	5.6	28.7	43.3	10.0	5.3	2.1	1.0	1.0	—	—	97.0
<sup>115</sup> Sn	16.3	29.0	31.2	12.9	3.8	2.2	1.0	0.3	0.2	0.1	97.0
<sup>51</sup> Cr	1.9	36.5	21.4	13.3	7.1	3.6	2.0	2.0	0.2	—	88.0
<sup>46</sup> Sc	6.6	71.0	21.0	1.0	0.3	—	—	—	—	—	100.5
<sup>131</sup> Ba	0.3	64.7	31.7	2.3	0.9	—	—	—	—	—	99.9
<sup>140</sup> La	0.1	78.1	18.1	3.7	—	—	—	—	—	—	100.0
<sup>141</sup> Ce	3.9	89.1	3.3	1.3	0.7	0.4	—	—	—	—	98.1
<sup>110m</sup> Ag	17.3	69.2	10.1	1.4	0.6	0.3	—	—	—	—	98.9
<sup>85</sup> Sr	4.3	66.7	27.5	1.6	0.3	—	—	—	—	—	100.4
<sup>95</sup> Zr	4.1	72.7	11.1	5.6	3.1	1.2	0.6	0.3	—	—	98.4
<sup>198</sup> Au	4.7	3.6	1.1	0.3	—	—	—	—	—	—	9.7

uranium by irradiation are not interfered in the subsequent determination of impurities.

The recovery ratios of trace elements as shown in Table 2 indicate that the added amount of tracer, i.e., Na, K, As, Cu, Mn, Ga, Ni, Ti, Co, Mo, In, Fe, Sn, Zn, Cd, Sc, Ba, La, Ce, Zr, Ag and Sr have quantitatively recovered over 98%. However, recovery of chromium shows only about 88%

of yield within  $\pm 5\%$  of deviation. This result about chromium shows an agreement with those by Kosta<sup>2</sup>. Gold is absorbed quantitatively on anion exchange resin as expected.<sup>3</sup>

It was reported that the recoveries of trace elements in the radiochemical separation scheme which is adopted in this study are more than 95% with exceptions of Hg, As, Ag, Sr, and more than 90% for

**Table 3. Analytical Results of Impurities in Uranium Dioxide**

element	results(ppm), $\pm 1\sigma$
As	0.063 $\pm$ 0.009
Na	43 $\pm$ 3
K	11 $\pm$ 0.4
Cu	0.039 $\pm$ 0.02
Mn	0.017 $\pm$ 0.04
Ga	0.095 $\pm$ 0.004
Ni	0.84 $\pm$ 0.04
Ti	1.7 $\pm$ 0.2
Co	0.023 $\pm$ 0.003
Mo	1.7 $\pm$ 0.4
In	$\leq$ 0.1
Fe	4.8 $\pm$ 0.2
Sn	$\leq$ 0.1
Zn	13 $\pm$ 1
Cd	0.021 $\pm$ 0.005
Cr	0.43 $\pm$ 0.09
Sc	0.41 $\pm$ 0.02
Ba	1.8 $\pm$ 0.3
La	0.085 $\pm$ 0.012
Ce	0.019 $\pm$ 0.030
Zr	2.8 $\pm$ 0.7
Ag	$\leq$ 0.1
Sr	$\leq$ 0.1

these elements.<sup>3</sup>

By combining these results with the recoveries of trace elements shown in Table 2, it is found that the accuracies of the present method are more than 95% except Hg, As, Ag, Sr and Cr, but more than 90% for these elements. Using the present method, uranium dioxide sample was analyzed for their impurities and the results are shown in Table 3.

When employing our present irradiation conditions, it is found that 1 $\mu$ g of uranium produce the activity of <sup>115</sup>Cd equivalent to 2 $\times$ 10<sup>-4</sup> $\mu$ g of cadmium, that of <sup>99</sup>Mo equivalent to 1 $\times$ 10<sup>-1</sup> $\mu$ g of molybdenum, that of <sup>140</sup>La equivalent to 3 $\times$ 10<sup>-3</sup> $\mu$ g of lanthanum, that of <sup>141</sup>Ce equivalent to 6 $\times$ 10<sup>-2</sup> $\mu$ g of cerium and that of <sup>95</sup>Zr equivalent to 3 $\times$

10<sup>-2</sup> $\mu$ g of zirconium from uranium fission as shown on previous calculation<sup>3</sup> using the data of fission yields<sup>5</sup>. This means again that the fission fragments of uranium contribute about 5% to the analytical results of cadmium and zirconium, about 19% to that of lanthanum and 92% to that of cerium. The analytical results of Cd, Zr, La and Ce shown in Table 3 are those obtained by subtracting the contributions of uranium fission from analytical results. By employing acidities of 0.01N and 0.05N of sulfuric acid as like Kosta<sup>2</sup> instead of 0.001N acidity employed by present work, it is found by the similar calculation as described above that uranium contributions of the fission fragments to the results of those element indicated above are more than 50%.

As trace impurities are collected before irradiations and, therefore, the problems associated with keeping blank values at a negligible level are also important in this work. In order to minimize to blank values of impurities, redistilled water has been used and this was found to contain normally common elements such as Na, K, Cu and Mn below 10ppb levels. The elimination of the interference of these elements has been carried out by passing further through a column of cation exchange resin.

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