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Activation Analysis of Uranium and Thorium Contained in High Purity Niobium Oxides.

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Uranium and thorium in high purity Nb₂O₅ were determined by neutron activation analysis followed by radiochemical separation (RNAA). A separation procedure combined with anion exchange, solvent extraction with TBP and coprecipitation with LaF₃ was developed and proved to have quantitative yields for the activation products of ²³⁹Np and ²³³Pa. The decontamination factors of major impurities were determined. The detection limit for both elements was less than several ppms when a high flux reactor such as JMTR was available for activation. The method is useful to the other composition materials containing niobium as a matrix element.

KEYWORDS: activation analysis, high purity niobium oxide, radiochemical analysis

1. Introduction

The α -particles from U and Th in semiconductor materials may cause "soft errors"¹⁾. Therefore, their contents in composition materials must be as low as possible.²⁾ Present authors have concerned the neutron activation analysis (NAA) focused on to U and Th contained in wide variety of composition materials, which might be used for the fabrication of d-RAM and the other highly integrated circuits. The products ²³⁹Np ($t_{1/2}=2.35$ d) and ²³³Pa ($t_{1/2}=27$ d) were measured to determine U and Th by NAA. Instrumental neutron activation analysis without chemical separation (INAA) was applied to the determination of several ppms of U and Th in composition materials such as silica/Si, in which no γ -emitters were formed from matrix element by neutron irradiation. To get higher sensitivity, it was necessary to remove interfering γ -emitters produced from impurities.³⁻⁵⁾ Anion exchange chromatography and LaF₃ coprecipitation method were developed and proved effective to remove majority of interfering γ -emitters from a mixture of ²³⁹Np and ²³³Pa. The outline of the separation method for ²³⁹Np and ²³³Pa recovery is expected to be useful for many other irradiated samples for U and Th analysis. This is a report of such analysis for Nb containing materials. We used high purity Nb₂O₅ for irradiation. As expected and described below, all samples contained Ta as an impurity and the contents were larger than 1 ppm. We describe mainly the chemical separation and the decontamination of the activation products made from impurities in this report.

2. Experimental

2.1 Niobium Sample and Neutron Irradiation

Nb₂O₅ samples used were semiconductor grade and stored in a desiccator. Two reactors, the MITRR of the Musashi Institute of Technology and the Japan Materials Testing Reactor (JMTR) were used for irradiation. The neutrons of MITRR were well moderated having a flux $4 \times 10^{16} \text{m}^{-2} \text{s}^{-1}$ and those of JMTR were $1 \times 10^{18} \text{m}^{-2} \text{s}^{-1}$.

About 1g of Nb₂O₅ sample, which was wrapped doubly in polyethylene film for the activation in MITRR or encapsulated in a quartz tube for JMTR irradiation, was irradiated with standard quartz samples that contained 1 μ g aliquots of U and Th. The irradiation time was 5 hours for the activation in MITRR and much longer irradiation up to 140 hours was possible for JMTR irradiation. After standing for 3-10 days to wait for the decay of short life activation products, the samples irradiated in MITRR were supplied to INAA for impurity analysis before the decomposition of Nb₂O₅.

2.2 γ -ray Spectrometry

For the accumulation and the analysis of γ -ray spectra, a personal computer assisted γ -ray spectrometer system, consisting of a high purity coaxial Ge detector with 80 cm³ of active volume, a 4096ch pulse height analyzer with 200MHz Wilkinson ADC was used. Dead time ratios of the accumulation system were below 10%. Contents of Th and U were calculated from the γ -ray counting rate ratio at 312keV for ²³³Pa and 106 or 228keV of ²³⁹Np, respectively.

2.3 Chemical Separation

2.3.1 Decomposition of Nb₂O₅

Irradiated Nb₂O₅ sample was taken into a Teflon crucible that had an inner volume of 70cm³ and was made wet by the addition of 10cm³ of a 10M (mole/dm³) HF and 6M HCl mixed acid solution. The crucible was set in an autoclave made of stainless steel. The Nb₂O₅ in the autoclave was decomposed by heating at 150°C for more than 2 hours.

2.3.2 Anion Exchange Chromatography

The mixed acid solution obtained by the decomposition of Nb₂O₅ was passed through a 18mm ϕ column packed with 30cm³ of Dowex 1x8 100-200mesh in Cl⁻ form. ²³³Pa and ²³⁹Np were not caught by the column, while Nb and its activation products as well as the most intense γ -emitter ¹⁸²Ta were caught by the column. The column was washed by eluting 30cm³ of 10M HF-6M HCl solution to ensure the complete recovery of ²³³Pa and ²³⁹Np.

2.3.3 Extraction with TBP

All effluent was evaporated to dryness in a Teflon beaker by

*IMR, Report No. 1968

heating. The evaporated residue was dissolved in 5cm³ of 5M HNO₃ solution. 13mg of Fe²⁺ and 70mg of hydroxylamine was added into the solution and left to stand for 5 hours to adjust the oxidation state of Np to be IV. ²³³Pa and ²³⁹Np were coextracted with 7cm³ of undiluted TBP. After washing with 7ml of 6M HNO₃, TBP was diluted by the addition of 7cm³ of benzene. ²³³Pa and ²³⁹Np were stripped from the diluted TBP solution by washing twice with 14cm³ of 1M HNO₃-0.5M HF solution.

2.3.4 LaF₃ Coprecipitation

Finally, ²³³Pa and ²³⁹Np were coprecipitated with LaF₃ by the addition of 200mg of La³⁺ and excess HF acid. The precipitate was collected onto a membrane filter with the pore size of 4.5x10⁻⁷m and supplied directly for γ-ray spectrometry after wrapping with polyethylene film.

The chemical yields of ²³³Pa and ²³⁹Np were examined prerinarily using a mixed acid solution prepared from an irradiated Nb₂O₅ containing known quantities of ²³³Pa and ²³⁹Np.

3. Results and Discussion

3.1 Impurity Analysis by INAA

An example of INAA γ-ray spectrum is shown in Fig. 1 for a Nb₂O₅-D sample irradiated in MITRR. All γ-rays were assigned to ^{92m}Nb and activation products made from impurities. No γ-rays of ²³³Pa and ²³⁹Np were observed because of strong interference due to ^{92m}Nb and ¹⁸²Ta. Thus, INAA could be used only for the determination of impurities Ta, W, As, Sb, Na, Mo, and Br but even the detection limits of these elements strongly depend on the content of Ta. It can be said that the removal of ¹⁸²Ta is necessary to detect the γ-rays of ²³³Pa and ²³⁹Np.

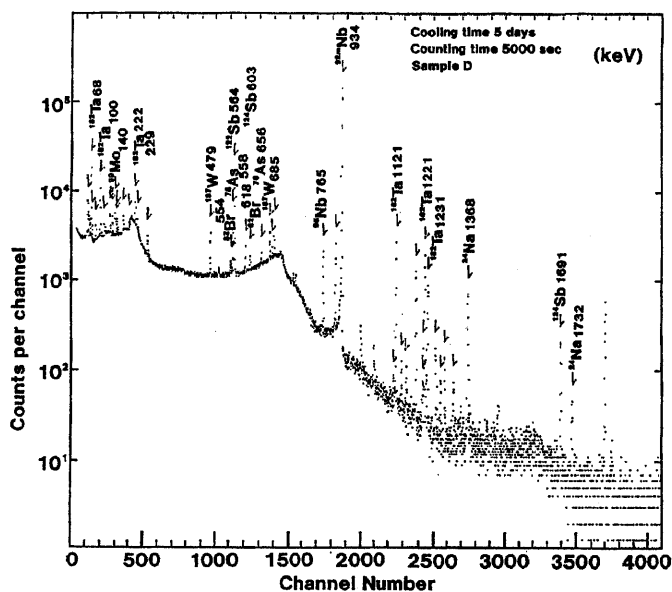


Fig. 1 γ-ray spectrum of Nb₂O₅-D for INAA

3.2 Chemical Yield and Decontamination Factors

Fig 2 illustrates the elution curves of main impurities. The (n,2n) reaction products of matrix Nb, ^{92m}Nb, and ¹⁸²Ta

were absorbed strongly in the anion exchange column. ²³³Pa and ²³⁹Np were eluted out in the first 30cm³ elution with 10M HF-6M HCl. The yield of ²³³Pa was 99±1% and that of ²³⁹Np was 96±2% in this fraction. The γ-rays of ¹⁸⁷W, ¹²²Sb, and ⁷⁶Sb as well as ¹⁸²Ta that were observed in Fig. 1 was removed effectively. The existence of the other activation products made from trace of Na, Ba, Cr and lanthanides were pronounced in Pa-Np fraction and they interfere the precious determination of ²³³Pa and ²³⁹Np.

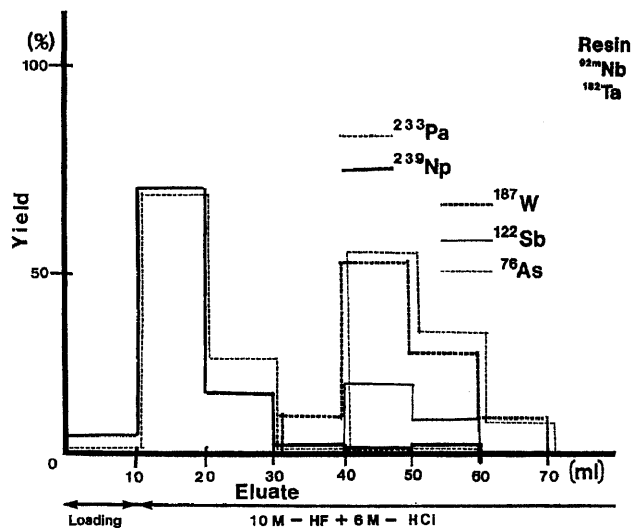


Fig. 2 Elution of impurities in Nb₂O₅

The extraction with TBP was found effective to remove such activation products as ²⁴Na, ¹⁴⁰La, ¹⁴¹Ce, ¹³¹Ba, ⁸²Br, and ⁵¹Cr. The extraction of Pa was quantitative and the coexistence of reductants did not affect to the recovery yield. The quantitative extraction for ²³⁹Np could not be attained unless the reductants was not added. The chemical yield in the extraction step was 97±3% for ²³³Pa and 99±2% for ²³⁹Np, respectively.

The coprecipitation yield in LaF₃ was supposed to be quantitative because ²³³Pa and ²³⁹Np were not found at all in the filtrate.

Total yield of ²³³Pa was 96±4% and that of ²³⁹Np was 95±5%, respectively. Table 1 shows the analytical results for impurities obtained by INAA and Table 2 shows the decontamination factors of impurity activation products concerning finally isolated Np-Pa coprecipitates.

Table 1. Analytical results for impurities

elements	Concentration (ppm)			
	A	B	C	D
Ta	150	92	41 ±0.4	3.0 ±0.2
W	<0.5	<0.3	3.2 ±0.02	1.0 ±0.1
As	<0.3	<0.1	12 ±0.2	0.92±0.09
Sb	<0.05	1.3	0.35±0.01	1.2 ±0.1
Na			8.1 ±0.9	5.8 ±0.4
Mo				2.4 ±0.1
Br	<0.8	<0.1	<0.1	0.47±0.02

Table 2. Decontamination Factors

	Ion-exchange	Extraction	Coprecipitation	Total of process
^{92n,95} N b	>8. 5 × 10 ⁴	—	—	>4. 6 × 10 ⁷
^{182,183} T a	>3. 7 × 10 ³	—	—	>5. 1 × 10 ⁶
¹²² S b	>1. 0 × 10 ³	—	—	>1. 7 × 10 ⁸
¹⁸⁷ W	—	> 53	—	>3. 2 × 10 ³
⁹² B r	—	> 140	—	>5. 9 × 10 ³
⁷⁶ A s	—	> 69	—	>9. 3 × 10 ³
²⁴ N a	—	> 230	—	>2. 2 × 10 ⁴
⁶³ C o	—	—	> 220	> 220

— :Not detected before and after each process

Table 3. Analytical Results for U and Th

Samples	Concentration		Detection limit	
	U	Th	U	Th
MITR INAA A	ND	ND	7.4	14
MITR RNAA A	2.0 ± 0.2	35 ± 2	0.13	0.094
B	0.16	1.0	0.13	0.085
C	0.97	0.56	0.11	0.15
D	0.23	0.24	0.14	0.12

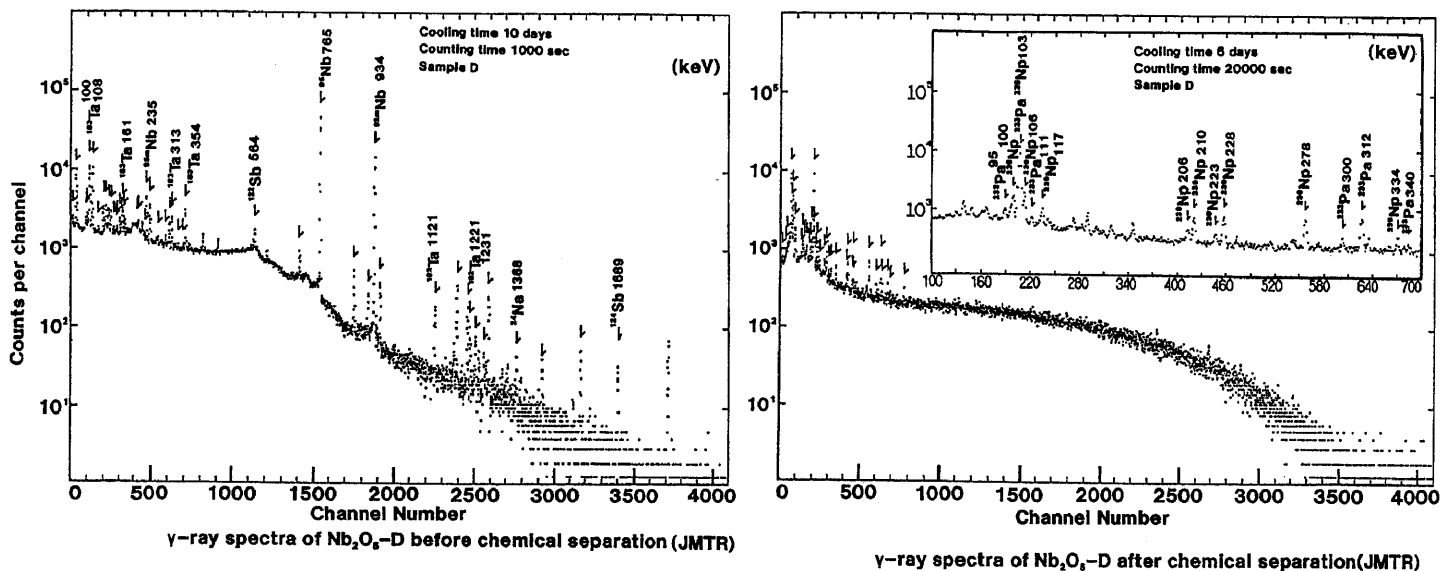


Fig. 3. Effect of Chemical Separation

Fig. 3 is an example of the effect of RNAA. A sample Nb₂O₅-D, which has the highest purity among the samples presently examined, was irradiated in JMTR for 24hours. ¹⁸¹Ta that has relatively large activation cross section leads to the formation of strong γ -ray emitter ¹⁸²Ta. The use of JMTR resulted to the unnecessary production of ¹⁸²Ta as shown in the spectrum before chemical separation. The effect of the chemical separation is quite valid and the detection limit was reduced to 4ppt for U and 1ppt for Th, respectively.

The analytical results for U and Th are summarized in Table 3. It seems interesting to compare the results shown in Table 3 with those shown in Table 1. The content of Ta, homologue of Nb in the periodic table, was the highest for sample A and decreases in the order of B, C, and D.

This finding implies that the purification of Nb certainly has the effect for the reduction of the content of Ta. To overview roughly the contents of the other impurities, the contents were reduced in the same order but the highest content of W was observed in sample C. In addition, the content of U seems to be abnormally high in the sample C. We consider the contamination with W including appreciable U along with the purification process of Nb₂O₅. It can be said that the materials such as vessels for the purification and the heater for calcination must be examined for the contents of U and Th to get the highest grade Nb₂O₅.

4. Summary

RNAA method for the analysis of U and Th in high purity Nb₂O₅ were developed. The chemical yields of the activation products ²³⁹Np and ²³³Pa were almost

quantitative. The method have high ability of the decontamination for ^{182}Ta and $^{92\text{m}}\text{Nb}$. It is possible to analyse sub ppb contents of U and Th by using the method developed in this work.

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