

Rapid separation method for protactinium from uranium using manganese oxide filter cake

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Abstract Adsorption and separation performance of protactinium (Pa) on a manganese oxide (MnO₂) filter cake was studied by measurements of α -, β -, and γ -rays and the results compared with those of solid-phase extraction using MnO₂ and TK400 resins. The MnO₂ filter cake method demonstrated excellent recovery. Radiochemical purity was comparable with that achieved by other newly developed methods, with only small amounts of contamination by Bi, Ra, Ac, Th, and U. The method, originally developed for recovering Pa from uranium solutions, has the merit of rapidity in chemical separation. It may be able to be applied to other purposes, such as investigation of the chemical properties of dubnium, a superheavy element.

Keywords protactinium, manganese oxide filter cake, MnO₂ resin, TK400 resin, chemical separation

1 Introduction

Adsorption behaviors of several cations on manganese oxide (MnO₂) filter cakes, prepared as layered manganese dioxide, have been investigated for several decades [1-4], and developed for practical applications such as collection of radium (Ra) ions [5,6]. With application to the study of actinides, the MnO₂ filter cake method has been used in a demonstration experiment [7] for the isolation of protactinium (Pa) from uranium (U) for students at Kanazawa University, Japan, because it can be performed using very simple and rapid procedures that yield a valuable method to measure even short-lived nuclides.

Solid-phase extraction methods, similar to the MnO₂ filter cake method, have recently been developed and have become very popular for separation of many elements, including actinides. Several methods utilize chromatographic materials, such as the TRU [8] and TEVA [9] resins, because of their excellent selectivity; however, the MnO₂ filter cake method still has advantages of rapidity, simplicity, and cost performance for particular elements.

Protactinium, the third actinide element, is a pseudo-Group V element. It has several oxidation states and thus complicated chemical behavior. The element is also notable for having properties that can be compared with those of dubnium (Db), a superheavy element. Such comparison is important to clarify the relativity effect that may cause deviation from the periodicity of the elements [10].

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In the present study, we performed an experiment to isolate Pa from uranium, including parent nuclides that decayed into Pa atoms and other daughter nuclides of the uranium series, as shown in Figure 1. It makes one able to obtain the Pa solution by a milking method, which is useful for the research work for chemical properties of Pa as well as a demonstration experiment for students learning the radioactive equilibrium of parent-daughter nuclides. We evaluated and confirmed the performance of the MnO₂ filter cake method with respect to recovery and radiochemical purity of Pa. We prepared a uranium solution from a uranyl nitrate reagent purchased several decades ago and which thus included many daughter nuclides of uranium.

TK400 [11] and MnO₂ [12] resins are commercially available. The former is used for isolation of Pa from other elements; the latter is modified with MnO₂ and used for Ra ion collection from environmental waters. We compared the resin performances with that of the MnO₂ filter cake using a revised procedure for Pa separation. We evaluated the radiochemical purity of each method from the relative radioactivities of nuclides, although the observed radionuclides depended on the emitted radiation, i.e., α -, β -, and γ -rays. We performed α - and γ -spectrometry in addition to β measurements to identify and measure the nuclides contaminating the MnO₂ filter cake.

2 Experimental

2.1 Reagents and apparatus

The reagents used for the chemical procedures included: uranyl nitrate solution (UO₂(NO₃)₂; 70–100 mg U/mL in 0.25 M nitric acid); thorium nitrate solution (Th(NO₃)₄; 40 mg Th/mL in 0.25 M nitric acid); 16 M HNO₃; manganese chloride solution (MnCl₂; 15 mg Mn/mL); potassium permanganate solution (KMnO₄; 5 mg Mn/mL); and wash liquids of 2 M nitric acid, H₂O, and acetone. The U sample used in the present study is not analyzed in detail on isotopic abundance but classified into depleted uranium, more enriched than natural uranium of 99.3% in the ²³⁸U content. The Th sample is ordinarily available sample of ²³²Th (100%).

The apparatus included a glass filter of 25 mm internal diameter, a suction bottle, aspirator, and a glass-fiber filter of 24 mm in diameter.

2.2 Chemical procedures

In any chemical procedure for separation of Pa from U solution that includes daughter nuclides of the same radioactivities due to radioactive equilibrium, contamination by ²³⁴Th, a daughter nuclide of ²³⁸U, should be used to purify the sample of Pa. Thus, a solution of Th as a retention carrier was prepared for addition to the U solution. A MnO₂ filter cake was prepared prior to the separation of Pa.

The basic procedures used in this study followed the method given in the textbook used for radiochemistry training courses at Kanazawa University, entitled “Experiments in Basic Chemistry B” [7]. Details of the chemical procedures are described below. The conditions are described as Methods 1 to 4 in Table 1. Methods 1 and 2 used MnO₂ filter cake, Methods 3 and 4 did MnO₂ resin, and Methods 5, TK400 resin. Methods 2 and 4 are performed with purified Th carrier, while Methods 1, 3 and 5 are done with Th carrier by the original procedure [7]. Preparation for the Th carriers is described in 2.2.1 in more detail.

2.2.1 Preparation of retention carrier of Th and MnO₂ filter cake

For preparation of the Th retention carrier, 1 mL of Th(NO₃)₄ solution, 2 mL H₂O, 1 mL of 16 M HNO₃, and 2 mL of MnCl₂ solution were mixed in a beaker before heating in a hot-water bath and adding approximately 20 drops of KMnO₄ solution to precipitate MnO₂. The Th-containing solution was

separated from the precipitate through a glass-fiber filter and stored as retention carrier solution for the Pa separation. A suction bottle connected to aspirator was used for this filtration, as well as for the other filtrations in this study. The remaining filtrate contained radioactive nuclides with chemical properties similar to those of Pa. After washing with a small amount of water and drying, it was subjected to measurements using a Geiger Müller (GM) counter. The solution was purified with another MnO₂ filter cake for Methods 2 and 4 to reduce contaminants other than Th. This was the only revised process that had an effect on the results in this study.

For preparation of the MnO₂ filter cake, 1 mL of 16 M HNO₃ and 2 mL of MnCl₂ solution were mixed in a beaker before heating in a hot-water bath and adding approximately 6 drops of KMnO₄ solution to precipitate MnO₂. A MnO₂ filter cake comprising the precipitate was thus uniformly prepared on a glass-fiber filter.

2.2.2 Isolation of Pa with MnO₂ filter cake

Five milliliters of UO₂(NO₃)₂ solution and 3 mL of the Th retention carrier, prepared as described in Section 2.2.1, were mixed in a beaker and allowed to stand for a while before the solution was slowly passed through the MnO₂ filter cake, prepared as described in Section 2.2.1, by suction for approximately for 30 s, i.e., using a flow rate of 16 mL/min. This filtration time is important because it affects the recovery. We determined the time by repeating the procedures so that as little radioactivity of Pa-234m as possible was lost during the measurement. The cake was then sequentially washed under suction with 1 mL of 2 M HNO₃, 1 mL H₂O, and 1 mL acetone until it was fairly dry. The filter cake was then placed in a sample dish for radioactivity measurements. For the methods used in this study, possible contaminants originated from the nuclides in the uranium and thorium series, except for the Pa isotopes shown in Figure 1.

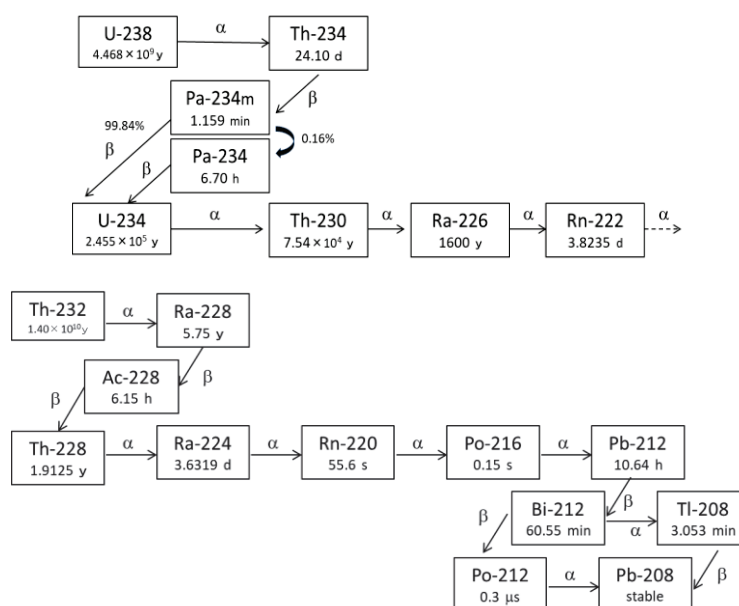


Figure 1 Decay chains and half-lives of nuclides in the uranium and thorium series [13,14].

2.2.3 Isolation of Pa with MnO₂ and TK400 resins

The MnO₂ and TK400 resins were used for comparison with the MnO₂ filter cake with respect to performance of the Pa separation. The MnO₂ resin (Eichrom Technologies, Inc., USA) [12] was modified with MnO₂. We prepared the same mass of resin in a suspension instead of as a cake under the same conditions and procedures as described in Section 2.2.2. The TK400 chromatographic resin (TrisKem International, France) [11] was modified with octanol for the separation of Pa. A resin cake was similarly prepared using a strong acid solution of HCl, which provided conditions for efficient

adsorption by the resin.

2.3 Measurement of radioactivities of Pa and contaminants

We measured the radioactivities of the samples using α -, β -, and γ -rays. Alpha spectrometry was performed using a silicon solid-state detector of 400 mm² active area, attached to an Octète PC alpha spectrometer (EG&G Ortec, USA). The data were passed through an analog-to-digital converter (ADC) with a 1k channel conversion gain that included energies up to 10 MeV. The measurement of β -rays was carried out using an Aloka GP-101GM counter (Hitachi, Japan) for analysis of the radioactive decay of nuclides. Gamma spectrometry was carried out using a BE2020 Ge semiconductor detector with 20% relative efficiency (Canberra, USA). The data were processed through an ADC with 4k channel conversion gain, covering energies up to 2000 keV.

3 Results and Discussion

Figure 2 shows a plot of counts per minute after subtraction of background counts as a function of elapsed time for the β measurements of MnO₂ filter cakes after elution of the sample solution. Decay curves derived from the plots demonstrated that the main β -radioactivity occurring immediately after separation was due to Pa-234m (1.159 min) except for longer components. Two-component analysis suggested that the latter components had half-lives of 10 to 47 min or more than 10 days. The data with lower purity (i.e., Method 1 in Table 1) were not reproduced well by calculated curves, possibly because of the involvement of more components or another component derived from a parent nuclide. Such analyses enabled determination of the recovery and radiochemical purity of Pa just after filtration through the MnO₂ filter cake, as listed in Table 1, where uncertainties of the data are from statistics in counting. Recovery values may be shifted to some extent due to uncertainties in the decay correction for the short-lived product.

These analyses demonstrated that Method 2, with a MnO₂ filter cake, had the best recovery of the methods tested. Suction time was crucial: about 30 s was needed. Less suction time resulted in loss of adsorption and more time resulted in loss of radioactivity due to decay of short-lived nuclides. We needed 1 to 2 min after filtration to start the β -measurement. The data in Table 1 were therefore corrected because of decay for this duration. Within the uncertainties, Method 2 and that using TK400 showed the best purity. These measurements only provided information concerning the half-lives of the isolated nuclides: we used γ - and α -spectrometry to identify the nuclides.

Table 1 Recoveries and radiochemical purities of Pa achieved for the three separation methods.

| Method | Adsorbent | Pa recovery (%) | Radiochemical purity (%) | Remark |
|--------|------------------------------|-----------------|--------------------------|---------------------|
| 1 | MnO ₂ filter cake | > 100 | 96.4 ± 1.5 | |
| 2 | MnO ₂ filter cake | > 100 | 98.9 ± 1.0 | Th carrier purified |
| 3 | MnO ₂ resin | > 100 | 96.6 ± 1.4 | |
| 4 | MnO ₂ resin | 84.5 ± 0.9 | 97.3 ± 1.5 | Th carrier purified |
| 5 | TK400 resin | 92.6 ± 1.0 | 98.3 ± 1.5 | |

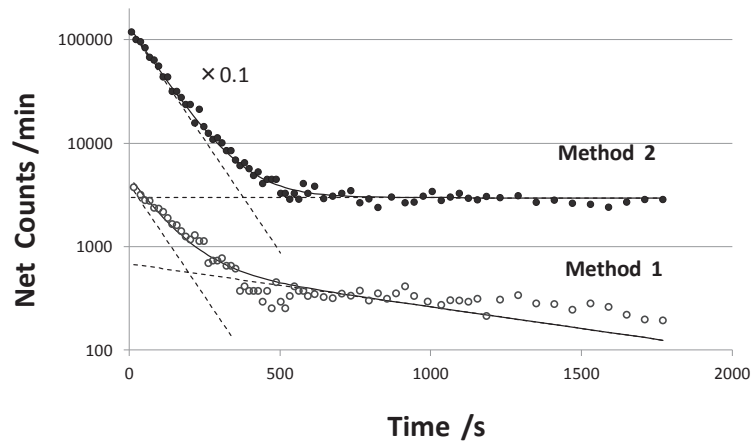


Figure 2 Decay curves of MnO₂ filter cake methods, as determined from Geiger Müller counter measurements.

Figure 3 shows a γ -spectrum as an example of the absorption of Pa by the MnO₂ resin. This was quite similar to the spectrum of the MnO₂ filter cake, but of better statistical quality. It enabled identification of the photopeaks of ²³⁴Pa (6.70 h), ²²⁸Ac (6.15 h), ²¹²Bi (60.55 min), and ²¹²Pb (10.64 h). In reference to the γ -ray data, ²⁰⁸Tl (3.053 min) originated from ²²⁴Ra (3.6319 d) [15]. Several peaks of ²³⁴Pa found in the spectrum demonstrated an excellent yield and purity of Pa, considering that radioactivity of the nuclide amounted to only 0.16% of that of ²³⁸U. It is noteworthy that observed nuclides were not always adsorbed on the cake in their original form, but adsorbed parent nuclides may have decayed into these nuclides. All contaminants except for ²³⁴Pa were nuclides of the Th series, from the Th carrier solution. A small amount of ^{234m}Pa was considered to originate from the decay of ²³⁸U contaminant because the initial ^{234m}Pa component was lost before starting the γ -counting.

The separation factor, SF , of the U concentration relative to the Pa concentration was obtained from Equation (1) according to the definition of Pa/U radioactivity ratios before and after a separation process, $(Pa/U)_{pre}$ and $(Pa/U)_{post}$, respectively, and the reasonable assumption that $(Pa/U)_{pre}$ was nearly unity because of its radioactive equilibrium. Thus, SF was estimated from the radioactivity ratio of ^{234m}Pa, a daughter nuclide of contaminant ²³⁸U, and ²³⁴Pa, which represented the separated Pa component after the process, as $SF \sim 130$.

$$SF = \frac{(Pa/U)_{pre}}{(Pa/U)_{post}} \quad (1)$$

$$\approx \frac{Pa-234/0.0016}{Pa-234m}$$

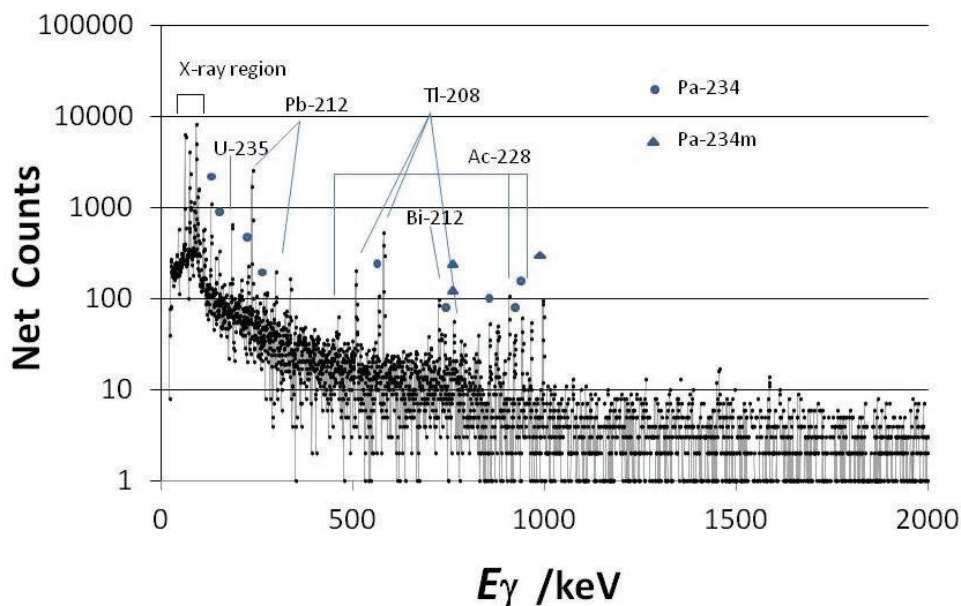


Figure 3 γ spectrum of absorption of Pa by MnO_2 resin, measured for 155 973 s after preparation by Method 4.

Figure 4 shows α -spectra of (a) Pa absorption and (b) Th daughters obtained in the preparation of the retention carrier solution of Th described in Section 2.2.1, both adsorbed by a MnO_2 filter cake. The spectra suggested that most of the nuclides observed in (a) were contaminants, because few nuclides of Pa are α -emitters, although a peak of ^{231}Pa , a daughter nuclide of ^{235}U , appeared in the spectrum. Nuclides from the Th series were assigned by comparison with (b), except for the U nuclides present at overwhelming material abundances. The nuclides of ^{232}Th , ^{228}Th , ^{224}Ra , and ^{212}Bi were concluded to be adsorbed on the MnO_2 filter cake, except for short-lived nuclides produced from parent nuclides and contaminants of the Pa separation using the MnO_2 filter cake.

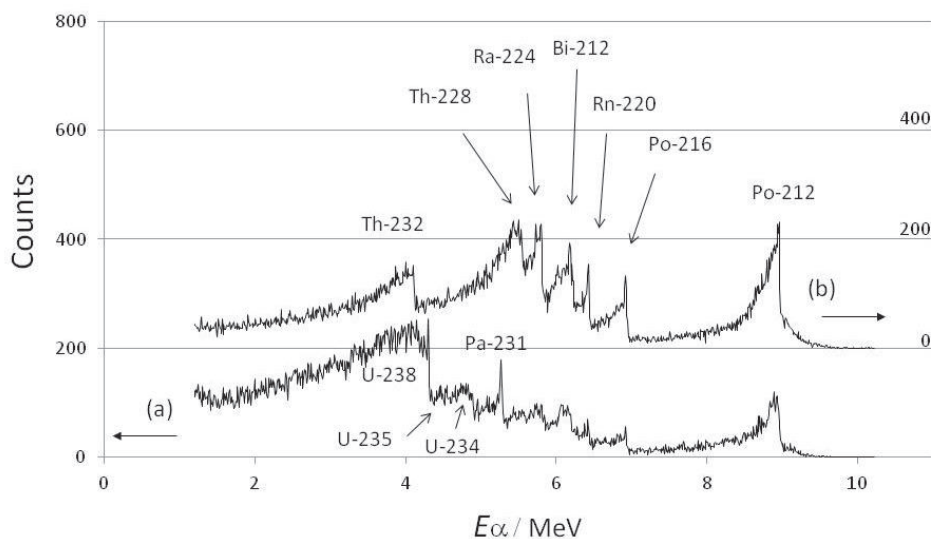


Figure 4 Alpha spectra for (a) Pa and (b) daughter nuclides in the thorium series adsorbed by MnO_2 filter cakes.

In short, the elements adsorbed on the MnO_2 filter cakes were deduced from these results to be Pb (Bi), Ra, Ac, and Th, present in small amounts of one order-of-magnitude less than the U contamination. The MnO_2 filter cake is understood to be a cation adsorbent, depending on the crystal structure of MnO_2 [2,3]. For this reason, it was interesting to note which species of Pa were adsorbed by the filter cake. It was reported that Pa and some non-metal elements adsorb on MnO_2 [1] and that Pa can be separated as PaO_2^+ ion with a cation-exchange resin in the same nitric acid system [16] as used in this study. The crystal structure of MnO_2 in the study is unclear although an XRD spectrum was taken for the MnO_2 filter cake made in the same procedure as the present study [4]. Therefore, the chemical species of Pa relevant for adsorption are not clarified in the study.

4 Conclusions

From β -measurement results, absorption using a MnO_2 filter cake showed excellent performance in recovery and radiochemical purity of Pa in comparison with the other methods studied. This may be somewhat unexpected because this is a conventional method that was developed many years ago. It should be noted, however, that many conditions for absorption by the TK400 and MnO_2 resins were not optimized in this study: it is possible that the newer methods would show better performance than the MnO_2 filter cake method under other conditions or for other purposes. Despite this, it is noteworthy that the conventional method using a MnO_2 filter cake has excellent performance in recovery, purity, and rapidity, and costs much less than the recently developed methods discussed in this study. The MnO_2 filter cake technique was originally developed for isolation of Pa-231, Pa-234g, and Pa-234m from U, although it may be also used for nuclide production of Pa from a Th target induced by a proton beam and spallation of a U target [17]. Pa atoms adsorbed to Mn oxides can be easily collected using an anion-exchange resin with 8 M HNO_3 eluant [18] after dissolving the oxide with hydrogen peroxide solution. This method can be easily scaled up because no target material should be adsorbed during the chemical procedures.

The method is useful not only for Pa separation, but also for the determination of ^{238}U determination in solution, where radioactive equilibrium between ^{238}U and $^{234\text{m}}\text{Pa}$ is achieved in a short time (less than 10 min) and $^{234\text{m}}\text{Pa}$ recovery is almost quantitative. For instance, the determination can be made using β -counting with a calibrated GM counter just after separation with a MnO_2 filter cake and decay analysis of the components at about 1.2 min, as done in this study. The deduced radioactivity of $^{234\text{m}}\text{Pa}$ at the separation is the same as that of ^{238}U , which can easily be converted to a material mass, because a daughter nuclide has the same radioactivity as its parent, according to the secular equilibrium law.

It is also worth emphasizing the possibility of utilizing this chemical system for research on superheavy elements, which need rapid chemistry because of their short half-lives. For the example of Db, a pseudo-homologue of Pa, the half-lives of the ^{262}Db (33.8 s) and ^{263}Db (27 s) isotopes often used for such research are comparable with that of $^{234\text{m}}\text{Pa}$ in this study. Furthermore, an α -source sample of a thin disc shape is easily prepared just after the separation process, which is convenient for superheavy element experiments mainly performed by α -spectrometry. For this reason, separation from possible alpha emitters, such as Po, Ra, Th, and U, is important: this capability was demonstrated in this study. Homologues of Db, such as V, Nb, and Ta, in addition to Pa, are reported to adsorb on MnO_2 in weak nitric-acid solution [1], so this method is suitable for experiments using superheavy elements in extremely low concentrations due to the absence of radiocolloidal adsorption. Further examination, including use of MnO_2 resin, is necessary to construct an experimental system suitable for such research.

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