

# Determination of Uranium and Plutonium in Metal Conversion Products from Electrolytic Reduction Process

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## 1. Introduction

Chemical characterization of process materials is required for the optimization of an electrolytic reduction process in which uranium dioxide, a matrix of spent PWR fuels, is electrolytically reduced to uranium metal in a medium of LiCl-Li<sub>2</sub>O molten at 650 °C [1]. A study on the determination of fissile materials in the uranium metal products containing corrosion products, fission products and residual process materials has been performed by controlled-potential coulometric titration which is well known in the field of nuclear science and technology [2~4]. Interference of Fe, Ni, Cr and Mg (corrosion products), Nd (fission product) and LiCl molten salt (residual process material) on the determination of uranium and plutonium, and the necessity of plutonium separation prior to the titration are discussed in detail. Under the analytical condition established already, their recovery yields are evaluated along with analytical reliability.

## 2. Experimental and Results

### 2.1 Reagent and Instrumentation

Chemical components of a simulated metal conversion products are as follows; U: 16.283 mg/g, Fe: 62.8 µg/g, Cr, Ni, Mg and Nd: 31.4 µg/g respectively and Li: 314 µg/g. In addition, chemical components of a metal conversion product sampled from the electrolytic reduction process are as follows; Fe: 0.74 mg/g, Nd: 2.62 mg/g, Li: 3.0 mg/g, Ni: 2.26 µg/g, Cr: 17.3 µg/g and Mg: 100 µg/g. A controlled-potential coulometric titration system consists of a coulometer (Scribner Associates, INC, Model: 279A), a potentiostat (EG&G Princeton Applied Research, Model: 253A) and a synchronous stirring motor (EG&G Princeton Applied Research, Model: 377).

### 2.2 Electrochemical determination of uranium and plutonium

An aliquot of an acidic solution (8 M HNO<sub>3</sub>) containing approximately 2 mg of uranium was transferred to a coulometric titration cell. Twenty five milliliters of a supporting electrolytic solution was added and argon gas was purged for 15 minutes to

remove oxygen dissolved in the electrolytic solution, Uranium was sequentially oxidized and reduced until residual current was reached down to 20 or 30 µA at the following controlled potentials, -250 mV, +200 mV, +650 mV, +200 mV and +650 mV (vs SCE), respectively. The amount of uranium was calculated by a difference in coulombs consumed through the following redox reactions; [U(IV) → U(VI) and Fe(II) → Fe(III) at +650 mV] - [Fe(II) → Fe(III) at +650 mV].

In the case of plutonium, an acidic solution containing approximately 0.5 mg of plutonium was taken to the beaker and evaporated down to 0.5~1 mL on a hot plate. This solution was transferred to a coulometric titration cell together with 25 mL of a supporting electrolytic solution by washing the beaker with the same electrolytic solution. After purging argon gas for 15 minutes to remove oxygen dissolved in the electrolytic solution, plutonium was sequentially oxidized and reduced until residual current was reached down to 50 or 30 µA at the following controlled potentials; +250 mV, +900 mV and +560 mV (vs SCE), respectively. The amount of plutonium was calculated by coulomb consumed through the anodic reaction of Pu(IV) → Pu(III) at controlled potential, +560 mV.

### 2.3 Interference elements on uranium and plutonium determination

An appropriate amount of Fe, Cr, Ni, Mg, Li, or Nd was added to the titration cell containing 2.3~2.5 milligrams of uranium, recovery yield of uranium was measured with varying the amount of individual metal. As shown in Figure 1, all the metal ions which are of interest in the study on the chemical characterization of process materials did not interfere in coulometric titration of uranium. So, uranium could be directly determined without its separation from co-existing metals in the sample solutions.

In the case of plutonium, the variance of coulomb consumed through the anodic reaction at +560 mV was measured with varying the interference elements such as uranium (25~750 mg) only and co-existing metals (0~1 mg). As shown in Figure 2. Iron and uranium interfered in the coulometric titration of plutonium when they were present more than 0.1 mg and 50 mg, respectively. Chromium did not interfere in plutonium determination in the presence of less than 0.5

milligrams. However, sample solutions containing a large amounts of chromium could not be continuously determined because a platinum electrode was seriously contaminated.

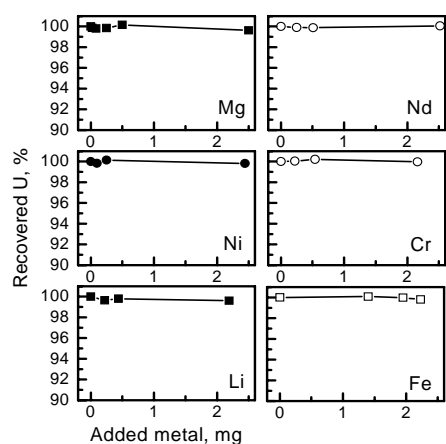


Figure 1. Effect of co-existing metals on uranium determination by coulometric titration.

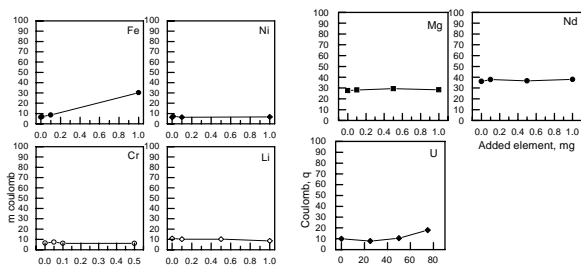


Figure 2. Effect of co-existing metals on the determination of plutonium by coulometric titration.

## 2.6 Plutonium separation

Plutonium was reduced to Pu(III) oxidation state with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in 1 M  $\text{HNO}_3$  and subsequently converted to Pu(IV) with  $\text{NaNO}_2$  in 8 M  $\text{HNO}_3$  [4]. The solution was passed through an anion exchange resin (Bio Rad AGMP-1, 200~400 mesh) column conditioned with 8 M  $\text{HNO}_3$ . Uranium and co-existing metals were removed with 10 mL of 8 M  $\text{HNO}_3$ , and plutonium was selectively recovered with  $\text{NH}_2\text{OH}\cdot\text{HCl}$  / 0.5 M  $\text{HNO}_3$ .

## 2.4 Evaluation of reliability in uranium and plutonium determination

An aliquot of the simulated metal conversion product dissolver solution (0.27~0.28 g) was transferred to the titration cell and the amount of uranium was determined by the same manner described in 2.2. As shown in Table 1, its recovery yield was 99.91% with relative standard deviation, 0.06%.

Plutonium was determined by the same manner described in 2.2 after it was separated from interferences using an aliquot of the simulated metal

conversion product dissolver solution containing 547.5  $\mu\text{g}$  of plutonium. As shown in Table 2, its recovery yield was 98.9% with relative standard deviation, 0.9%.

Table 1. Result of coulometric titration for uranium in simulated uranium metal product dissolved solution

Solution, g	Result, mg/g			
	U	Mean	SD	RSD, %
0.2770	16.281	16.268	0.009	0.06
0.2775	16.271			
0.2769	16.265			
0.2784	16.261			
0.2782	16.259			

Table 2. Result of coulometric titration for plutonium in a simulated uranium metal product dissolved solution

Added, $\mu\text{g}$	Result, $\mu\text{g}$			
	Found	Mean	SD	RSD, %
547.5	538.8	541.4	5.1	0.9
547.5	538.1			
547.5	547.2			

## 3. Conclusion

Controlled potential coulometric titration was applied for the determination of fissile materials (U and Pu) in uranium metal products from electrolytic reduction process. Co-existing metals such Fe, Cr, Ni, Mg, Nd and Li did not interfere in the uranium determination. However, Fe, U and Cr interfered in the plutonium determination. So, separation of plutonium from uranium matrix sample solutions was needed in advance of its determination. Both uranium and plutonium could be quantitatively determined by controlled-potential coulometric titration within the concentrations range of the interference elements checked with this study.

## REFERENCES

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