**Studies on the Measurement of Impurities in Uranium sample with ICP-MS**

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**Abstract.** Extraction chromatography method was applied to separated impurities from uranium solution. The elution was measured by inductively coupled plasma mass spectrometry(ICP-MS).The concentration of impurities was obtained by using outernal standard method. The decontamination factor for uranium of the TBP, UTEVA and TEVA separation procedure is more than 3E104. The recovery of most impurities is between 90% and 110%. The results obtained by above three separation procedure agreed well with each other in their expanded uncertainty(K=2). The method developed can be applied for the analysis of nuclear material, which can provide useful signature for nuclear forensic investigations.

1. **Introduction**

At the beginning of the 1990s, cases of illicit trafficked nuclear materials were started being reported on newspaper. As a response to this situation, a new discipline –nuclear forensic science was emerged, whose aim was to solve the questions on the origin of the material, its intended use and the last legal owner. 1-3 It requires comprehensive analysis, using numerous nuclear analytical techniques and attribution analysis through a comparison of measured results and the data of known origin. The analysis usually proceeds step-by-step, until attribution can be achieved. But in most cases, the explicit conclusion can not be obtained. 4

The key parameters for uranium material are enrichment-levels, age, shape or morpholopy and impurities. The impurities in uranium sample vary slightly according to the produced method employed and local environment. By comparing the measured data to database information, this characterisic information can be used to trace to the source of uranium sample together with other useful clues.5

The origin attribution of unknown nuclear material is an important and challeging task. Fingerprint information usually involves many aspect of nuclear material. 4This work concerns on the measurement of impurities in uranium samples using TBP , UTEVA and TEVA6-8 extraction chromatography to separate impurities from uranium sample, and the recovery of impurities was obtained by the determination of separated sample using ICP-MS.

**2. Experimental**

***2.1 Reagents and materials***

For dilutions ultra-pure water was used(Milli-Q,USA). Suprapure grade nitric acid and hydrochloric acid were used for the sample separation. To decrease the influence of process blank, all lab ware was washed two times with diluted nitric acid and ultra-pure water successively, dried in a drying oven. A [[1]](#footnote-2)

natural uranium solution was used for MC-ICP-MS optimization,and a CRM030-A isotopic standard material was used to correct mass discrimination. An ICP standard solution(containing 28 elements) was purchased to prepare a series of standard solution .

To determine the uranium concentration in solution, isotopic dilution –mass spectrometer (ID-MS) was used. The spark of IRMM-0519 was added to uranium solution, and isotopic standard material IRMM-199 was used to correct the isotopic ratio 233U/238U.

The uranium sample used in this study was a mixed sample solution which have been used as an comparison sample in year 2013.

***2.2 Separation of impurities by extraction chromatography***

For TBP and UTEVA extraction chromatography , the resin was marinated in Mili-Q water for 24h after washing several times, then the resin was packed in a quartz column. Conditioning of the column was carried out by passing Mili-Q water, 0.5 mol L-1 HNO3 and Mili-Q water in sequence to convert the resin to be neutral. Finally 20 ml volume of 3M HNO3 was passed through the column to balance the resin. 1-2 ml uranium solution and 9 ml 3M HNO3 was passed through the resin , the elution was collected and converted to 2％HNO3(v/v)-solution that can be measured directly by ICP-MS. A blank test was carried out using the same procedure as the uranium sample.

For TEVA extraction chromatography ,the separation procedure is similar to the procedure mentioned above. The difference was that hydrochloric acid was used to replace the nitric acid. Before loading, the TEVA resin was pre-balanced with 3M HCl. After loading, the resin was washed with 9 ml 3M HCl. The collected elution was diluted for measurement by ICP-MS.

***2.3 Instrumentation***

A GV multi-collector inductively coupled mass spectrometer (MC-ICP-MS), equippped with 9 movable Faraday collectors , 7 ion counting and a fixed Daly detectors, was used for the isotopic ratio measurement of uranium . It was usually operated at low mass resolution mode(R=300). The samples were introduced into the plasma using Aridus introduction system or a concentric nebulizer.

The impurities measurement were performed by ICP-MS(NexION 300Q ,PerkinElmer,USA). The operating parameters of the ICP-MS are listed in table 1.

Table 1 Operating parameters of  NexION 300Q

|  |  |
| --- | --- |
| ICP-MS instrumental  Forward power  Cooling gas flow rate  Auxiliary gas flow rate  Nebulizer gas flow rate  Wriggle pump rate  Sample cone  Skimmer cone  Super cone  Scan type  Replicates | parameters  1000w  18L/min  1.2L/min  0.85L/min  20rpm  φ 1.1  φ 0.9  φ 1  peak jump  6 |

***2.4 Measurement of impurities by*** ***ICP-MS***

During the ICP-MS analysis, isotope with less isobaric interferences was choosed. For example, Cd has 106Cd,108Cd,110Cd,111Cd,112Cd,113Cd,114Cd,116Cd eight isotope, but each isotope has isobaric isotope except 111Cd, so 111Cd was measured to calculate the Cd concentration. Before sample measurement, a series of standard solution (0.05 ngg-1,0.5 ngg-1,1 ngg-1,5 ngg-1,10 ngg-1)was prepared and measured. The concentration of impurities in separated sample was obtained using external standard method. To correct the interferences of instrumental fluctuation, 10 ngg-1 In was added into sample online as an internal standard. 2% HNO3 solution was used for background correction. Between sample measurement, 2% HNO3 was introduced to wash the instrument for 3-5 minutes until the counts was approached to the background counts.

**3. Results and discussion**

***3.1 Uranium concentration analysis by ID-MS***

In order to normalize the impuritiesconcentration to be the content in 1g uranium, ID-MS was used to determine the concentration of uranium in sample solution. The isotopic ratio of uranium sample solution and the mixed solution(uranium sample and spike solution) was measured by MC-ICP-MS. Isotopic standard material CRM030-A and IRMM-199 was measured to correct mass discrimination between sample measurement.

The opeating parameters to determine the abundance ratio of uranium isotopes by MC-ICP-MS have been studied and optiminzed, such as gas flow rate of nebulizer, the position of torch, collision gas flow rate, the parameters of ion lenses and ion extraction modes etc. The sensitivity was optimized to acquire maximum signal intensity. Subsequently， the instrument was left to be stable for more than 2 hours. Typically，the sensitivity was approximately 2.5V for 200 ng g-1 238U.

Table 2 Optimized MC-ICP-MS intrumental parameters

|  |
| --- |
| MC-ICP-MS instrumental parameters  Forward power(W) 1350  Reflected power(W) <5  Cooling gas flow rate(L min-1) 13.4  Auxiliary gas flow rate(L min-1) 1.20  Nebulizer gas flow rate(L min-1) 0.95  Cones Ni  Sample uptake rate(ul min-1) 100  Collision gas flow rate(mL min-1) 1.5  Mass resolution 300  Ion Extration mode soft  Cup configuration for U measurement： 234U：Daly；235U：H1；238U：H2 |

The concentration of uranium can be derived using Eq.1.

 (1)

Where:

R(X) = amount ratio n(233U)/ n(238U) in the unknown sample X

R(Y) = amount ratio n(233U)/ n(238U) in the spike material Y

R(B) = amount ratio n(233U)/ n(238U) in the mixed sample

m(X) = mass of unknown sample used in the measurement

m(Y) = mass of spike solution used in the measurement

Rix = amount ratio of isotope i and reference isotope in the unknown sample X

Riy = amount ratio of isotope i and reference isotope in the spike sample Y

c(U,Y) = amount content of U g-1 spike solution

c(U,X) = amount content of U g-1 sample solution

Using the measured data and weighed data, a concentration of 0.01643 g g-1 sample solution was derived. Uranium concentration in the separaetd sample have been measured using the same method, and the value is less than 50 ng g-1. The decontamination factor for uranium is more than 3E104.

***3.2 Recovery of separation procedure***

The method of TBP extraction chromatography was applied for the uranium sample, the results are depicted in fig.1.

Fig.1 Recovery of impurities using TBP extraction chromatography

The recovery of impurities element using UTEVA extraction chromatography are depicted in fig.2.

Fig.2 Recovery of impurities using UTEVA extraction chromatography

The recovery of impurities element using TEVA extraction chromatography are depicted in fig.3.

Fig.3 Recovery of impurities using TEVA extraction chromatography

From the above three figures, the measured results agree well with each other in their expanded uncertainty(K=2). Among the three used resins, TBP is widely used in the world, for example in the purex to extract uranium and plutonium. For separated sample using TEVA extraction chromatography, Mo and Cd were not detected which requires further research.

**4. Conclusions**

A method has been researched for the measurement of impurities in uranium solution. The impurities was effectively separated using the method of TBP ,UTEVA and TEVA extraction chromatography. The decontamination factor for uranium is more than 3E104 which enable the elution to be directly measured by ICP-MS. It was found that the results obtained by three separation procedure agreed well with each other, which confirmed the feasibility of the method. The method can be applied to the determination of impurities in nuclear material, which can provide significant clues on the provenance, and thus trace them back to their source combining with other useful signature.

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