TRACE ELEMENT ANALYSES OF URANIUM MATERIALS

Donna M. Beals and Charles R. Shick
Savannah River National Laboratory
Aiken SC 29808 USA

ABSTRACT

The Savannah River National Laboratory (SRNL) has developed an analytical method to measure many trace elements in a variety of uranium materials at the high part-per-billion (ppb) to low part-per-million (ppm) levels using matrix removal and analysis by quadrapole ICP-MS. Over 35 elements were measured in uranium oxides, acetate, ore and metal. Replicate analyses of samples did provide precise results however none of the materials was certified for trace element content thus no measure of the accuracy could be made. The DOE New Brunswick Laboratory (NBL) does provide a Certified Reference Material (CRM) that has provisional values for a series of trace elements. The NBL CRM were purchased and analyzed to determine the accuracy of the method for the analysis of trace elements in uranium oxide. These results are presented and discussed in the following paper.

INTRODUCTION

The determination of trace elements in uranium is required to ensure specifications for nuclear fuel are met. The ASTM International provides specifications for the final fuel product as well as uranium hexafluoride, ore concentrate and other precursors to the final product [1]. These specifications define the impurity limits for material to feed the nuclear fuel cycle. In addition, some uranium has been defined as excess to the fuel cycle and it must meet waste acceptance criteria with regard to regulated trace elements prior to dispositioning. Because uranium is radioactive as well as toxic it must be handled in such a way as to prevent laboratory and personnel contamination. The analysis of trace elements in uranium often entails the use of regulated fume hoods to prepare the sample for analysis and radiologically contained instrumentation for quantification of the analytes of interest.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is a very useful tool for the quantification of many elements simultaneously. In order to perform trace element analyses in uranium by ICP-MS an enclosed instrument can be used. For this method the uranium material is dissolved, diluted and aspirated into the plasma. The uranium in solution can cause significant matrix interference and reduce the instrumental detection efficiency for the elements of interest unless a large dilution is performed, which in turn raises the obtainable method detection limit. The analysis of uranium solutions by ICP-MS requires frequent cleaning on the cones and quadrupoles. Maintenance on an enclosed ICP-MS is difficult due to the enclosure. In addition, the pump oil will become contaminated with uranium generating a mixed waste for disposal.

Another option is to remove the uranium matrix and analyze the trace elements remaining in solution. A separation method was developed based on an extraction chromatography column in which uranium is retained by the resin and most other elements of interest pass through the

column **[2]**. This method was tested for use with a variety of uranium materials. A rigorous validation was performed to determine the precision and accuracy of the analysis and to estimate the obtainable detection limits for various elements in uranium oxide.

ANALYTICAL METHOD

The desired sample size was approximately 100 mg of uranium. Initial tests used a column bed volume of 2 ml. Samples were dissolved in nitric acid (only high purity acids were used in the following tests and analyses), dried and reconstituted in 5 ml of 3M nitric acid. This was loaded onto the column which had been preconditioned with 3M nitric acid. The column was washed with three 10 ml portions of 3M HNO_3. The column load solution and wash were collected in a clean beaker and then taken to dryness; the column with the uranium was discarded as waste. The column effluent was brought up in 2% HNO_3 and analyzed for residual uranium As seen in Figure 1 at sample loading greater than 100 mg there was significant breakthrough of uranium.
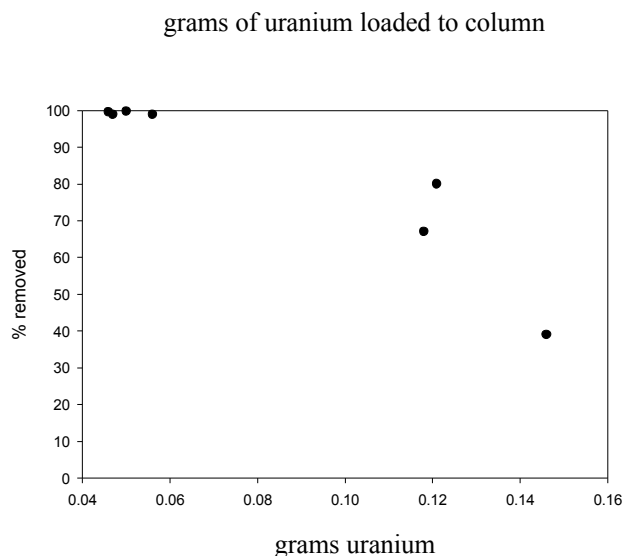
grams of uranium loaded to column

Figure 1. Percent of uranium retained on the 2-ml column versus column loading.

Increasing the resin bed volume to 5 ml resulted in nearly 100% retention of the uranium for most materials. However, for samples of low enriched uranium (LEU) produced at the Savannah River Site (SRS) 100% retention was not achieved. The LEU was reported to be nominally UO_3 but could also be U_3O_8. Only the more oxidized species of uranium, U^{6+}, will be retained by the extraction resin. To ensure that all the uranium was in the 6+ oxidation state about 1 ml of hydrogen peroxide was added when dissolving the sample. Following this protocol, the uranium retention was more consistently close to 100%.

To ensure quantitative recovery of the trace elements of interest, known amounts (equivalent to 10 ppb in the final solution) of selected elements were added to various uranium compounds. The matrices included uranium oxides (from various sources), acetate, ore and metal. Following

the matrix separation the final solution was analyzed using a commercial quadrupole ICP-MS. The system was used in a standard configuration consisting of a quartz concentric nebulizer, a thermoelectrically cooled quartz spray chamber, and a shielded quartz torch. All ICP-MS acquisitions were taken at three points per mass peak for a smapling time of 0.3 seconds per mass. Five replicate scans were collected, averaged, and reported as raw intensity. An internal standard (10 ppb [103]Rh) was added to each sample to correct the intensity to a concentration value.

The recovery of the trace element did not vary by starting material thus all the recoveries were averaged; the mean and standard deviation of the recovery for the elements tested are shown in Table 1.

element	mean	st.dev.	element	mean	st.dev.	element	mean	st.dev.
Li			Ge	0.45	0.06	Ce	0.89	0.05
Be	0.92	0.06	Rb			Pr		
Na	1.00	0.00	Sr	0.95	0.03	Nd		
Mg	0.96	0.06	Y	0.93	0.04	Sm		
Al	0.79	0.09	Zr	0.01	0.01	Eu	0.90	0.09
Ca			Nb			Gd	0.36	0.07
Sc	0.52	0.10	Mo	0.75	0.23	Tb		
Ti	0.35	0.21	Ru			Dy		
V	0.89	0.08	Rh	0.75	0.14	Ho	0.72	0.11
Cr	0.89	0.12	Pd			Er	0.75	0.12
Mn	0.92	0.08	Ag	0.91	0.07	Tm		
Fe			Cd	0.92	0.07	Yb		
Co	0.92	0.05	In	0.92	0.06	Lu		
Ni	0.94	0.09	Sn	0.53	0.33	Hf	0.02	0.01
Cu	0.91	0.09	Sb	0.12	0.03	Ta	<0.02	
Zn	0.97	0.07	Cs	0.94	0.03	W	0.08	0.05
Ga	0.94	0.04	Ba	0.87	0.07	Pb	0.96	0.06
			La			Bi	0.94	0.05

Table 1. Recovery of Added Trace Element from Uranium Matrix (Calculated Concentration divided by Known Added).

Yokoyama et al [3] had determined a recovery of greater than 0.99 for most elements, including the lathanides, except for Zr using a similar separation from silicate rocks. The non-quantitative recovery above for Al and Rh was also noted by Horowitz et al [2], and the recovery of the light lathanides were more variable than reported by Yokoyama et al [3]. Horowitz et al [2] noted no recovery for Th, Np and Pu, and a low recovery for Zr and Ru. The low recovery reported here for elements such as Ge, Sn, Sb could be due to their partial volatility. For the ICP-MS determination of Ti a low abundance mass peak must be used due to spectral interferences thus could contribute to the seemingly low recovery. If the determination of Zr, Hf or Ta were desired they can be stripped from the resin column using a small amount of HF added to the 3M HNO_3 (0.1M HF in 3M HNO_3) [2].

ANALYSIS OF UNKNOWN MATERIALS

Using the developed procedure duplicate samples of various uranium materials were analyzed to determine the ambient concentration of various elements. The ICP-MS result was corrected for weight of sample analyzed and for elemental recovery as noted in Table 1. The results of these analyses are shown in Figure 2. The DU and LEU ox (oxide) from Savannah River (SR), the DU and nat(ural) oxide from Oak Ridge (OR), the natural oxide from the New Brunswick National Laboratory (NBL) and the acetate from a commercial supplier all are very low in trace element content, as shown in Figure 2. The oxide of unknown origin has significantly more Ni than the other oxides. The metal contained about 0.5% of Pb and also Cu in greater abundance than any of the oxide or other chemical compounds analyzed.
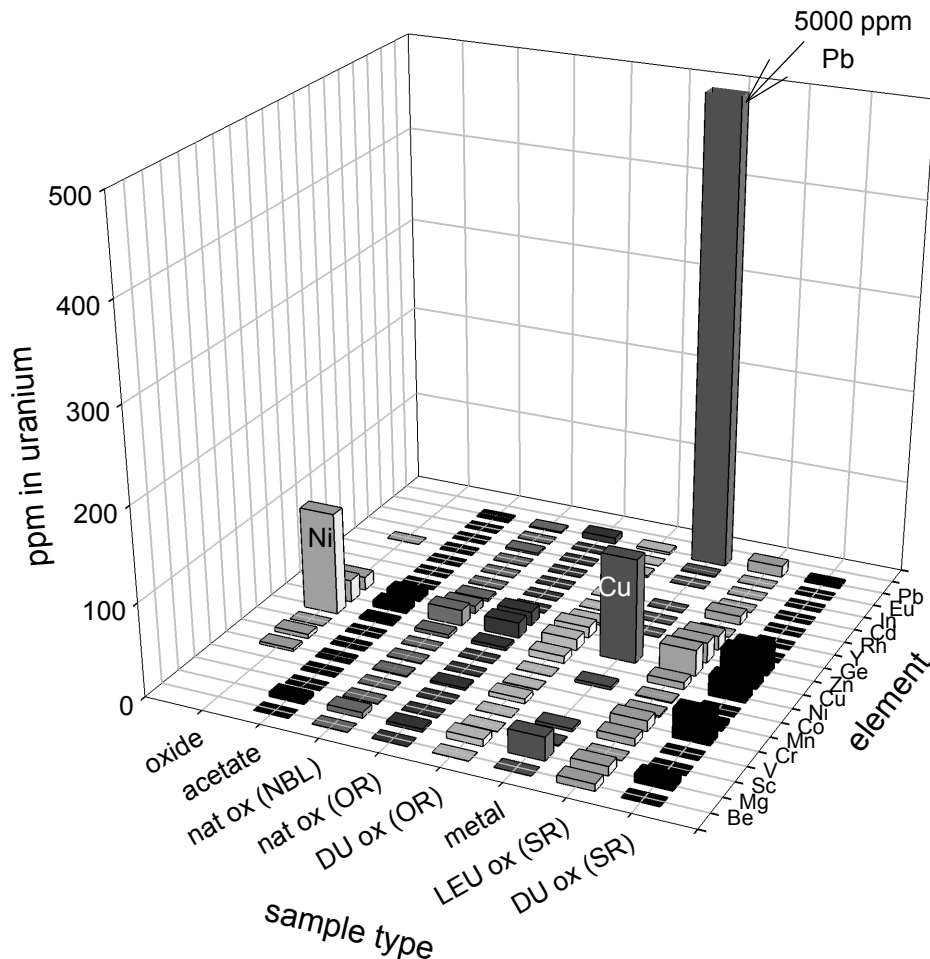

Figure 2. Trace element content of various uranium materials (see text for a description of sample type).

ANALYSIS OF NBL REFERENCE MATERIALS

The NBL Certified Reference Material (CRM) 124 is an impurity standard primarily for use in determining the non-volatile impurity content of uranium fuel materials [4]. It consists of six bottles containing uranium oxide to which 24 selected elements have been added in varying concentrations and a seventh bottle containing the unspiked oxide. The elemental values reported are provisional only at this time but can be used as the assigned values until a formal characterization is completed by the NBL. The range of the impurity content in the unspiked sample, CRM 124-7, is from <0.1 µg per g uranium (ppm) to <25 ppm. CRM 124-1 contains the largest quantity of impurities, ranging from a few tens of ppm to a few hundred ppm, with the remaining five bottles having values in between these two extremes.

Aliquots of the CRM were analyzed as described above. Results were evaluated as a fractional elemental recovery in which the calculated value was divided by the prepared value. Errors reported are the 2σ propagated errors with the ICP-MS result and chemical recovery being the largest source of error. Typical results for CRM 124-1, the highest concentration of impurities, and CRM 124-6, the lowest concentration of added impurities are shown in Figures 3, left and right, respectively. The different symbols are used to indicate results for unique samples; multiple use of the same symbol indicates a replicate ICP-MS measurement on the same generated sample solution.
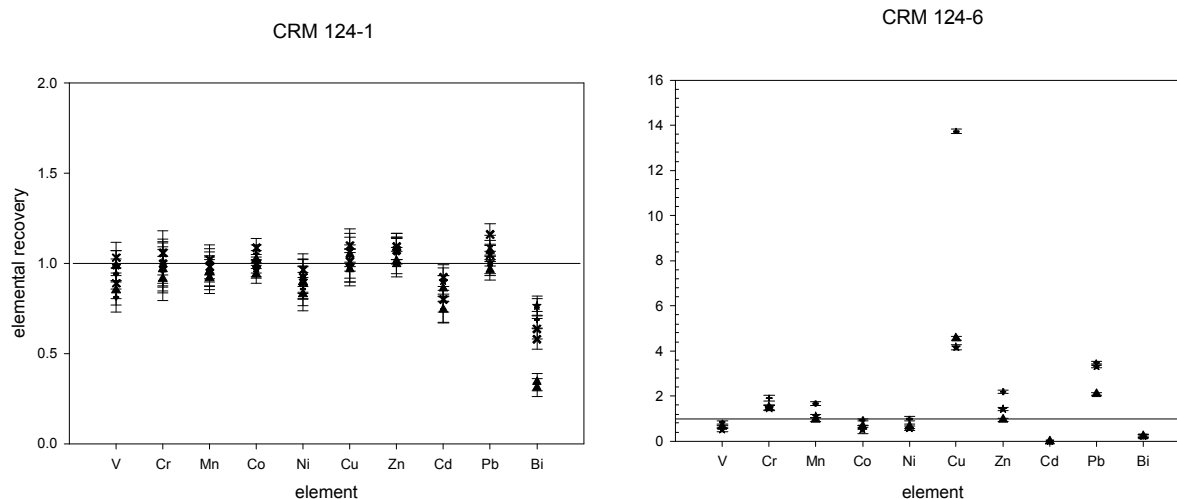

Figure 3. Results of the analysis of selected impurities in NBL CRM 124-1 (left, high impurity content material) and CRM 124-6 (right, low impurity content material). Elemental recovery is defined as the calculated value divided by the prepared value. (The line is the result at which the calculated value is equal to the known.)

As seen in Figure 3 (left) most of the elemental impurity values calculated for the high level impurities (CRM 124-1) were within the propagated error of the prepared value. Other values determined but not shown in the Figure were for Zr (negative bias), W (positive bias) and Sn (extremely variable from 0.5 to 1.5). The cause for the low bias in the calculated Bi values is unclear at this time. A positive bias was noted for many of the elements analyzed in CRM 124-6, the lowest impurity content material (Figure 3 [right]).

Following these results a study was undertaken to evaluate potential sources of contamination in the reagents being used to process the samples. A series of reagent blanks were prepared in which the 5 ml of nitric acid and 1 ml hydrogen peroxide were dried in a beaker, reconstituted in 3M HNO_3 and then passed through a resin column containing 5 ml of the extraction chromatography resin. The solution was collected and analyzed in the same manner as the previous samples.

For the elements analyzed in this study, many were found to be present above the instrumental detection limit. These included Cr, Mn, Ni, Cu, Zn, Zr, Sn, W and Pb. When the individual reagents were evaluated Cr, Zn and especially Sn were noted in the hydrogen peroxide (Sn is often used as a stabilizer in the solution). The deionized water and high purity nitric acid used were found to be free on contaminants at the detection limit. The extraction resin was found to be contributing the greatest impurities to the developed method.

Various options were then evaluated to clean the resin prior to use. Rinsing the resin with 3M HNO_3 or performing a batch extraction with the dilute acid did not completely eliminate the impurity contribution of the resin for all the elements being studied. Finally a test using 0.1M oxalic acid to wash the resin prior to use was found to provide the best elimination of the elements from the resin [5].

The reference materials were then reanalyzed using resin that had been washed with the 0.1M oxalic acid prior to use. Five-ml of resin was placed in the column and then rinsed with 20 ml of the oxalic acid solution, followed by 20 ml of 3M HNO_3, prior to loading the sample solution to the column. The oxalic acid and nitric acid washed were discarded. As before, the column was rinsed with 30 ml of 3M HNO_3 after the sample load to ensure the elements of interest had been washed through the column. The column load and rinse solution was dried and brought up in 25 ml of 2% nitric acid and analyzed as before by ICP-MS. A comparison of the results for a mid-range sample is shown in Figure 4. As seen in the figure the results are much more consistent after the column washing with the oxalic acid (graph on right) to remove impurities than with no wash (left graph).

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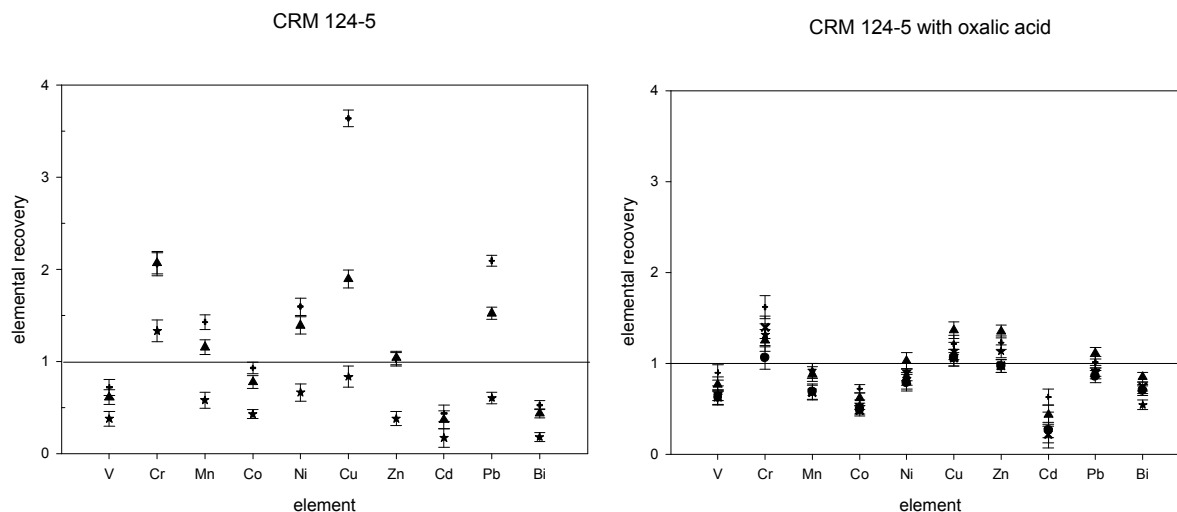CRM 124-5   CRM 124-5 with oxalic acid

Figure 4. Results of the analysis of CRM 124-5 without (left) and with (right) the
oxalic acid wash prior to sample loading.

As stated previously, the values reported by the NBL on the Certificate of Analysis are still
provisional. A comparison of the values obtained using this new method versus the prepared
value and the values obtained by other laboratories are shown in Table 2 for the analysis of CRM
124-5. As seen in Table 2 the SRNL results compare favorably with the range of values reported
by the other laboratories

element	mean this study	2s this study	range reported	mean	prepared value
Vanadium	1.8	0.3	2 - 2.8	2.4	2.5
Chromium	9.3	1.6	8 - 14	10	7
Manganese	2.6	0.4	2 - 5	4	3.2
Cobalt	0.8	0.1	1 - 2.6	1.5	1.4
Nickel	10.5	0.9	8 - 15	12	12
Copper	3.4	0.2	1.3 - 3.3	2.5	2.9
Zinc	13.6	1.8	9 - 15	12	12
Cadmium	0.2	0.1	0.25 - 0.5	0.38	0.45
Lead	3.2	0.3	2.3 - 3.4	2.8	3.3
Bismuth	1.8	0.2	1.8 - 2	2	2.5

Table 2. Results of analyses of CRM 124-5 (using the oxalic acid resin wash) by
this study versus values reported in the Provisional Certificate of Analysis, values
are in μg element per g uranium. The mean from the Certificate is calculated
based on the results reported to the NBL.

CONCLUSIONS

The SRNL has developed a new method for the analysis of non-volatile impurities in uranium materials. Using a matrix removal procedure impurities in uranium can be determined using a non-enclosed ICP-MS. The analysis of a series of provisionally Certified Reference Materials has demonstrated that the method is capable of providing reproducible results at the microgram per gram level of many impurities in uranium oxide. These results compare favorably with the provisional values provided and with the results reported by other laboratories. Working at these low levels it was determined that the extraction resin used did contribute to the reagent blank thus it is pre-cleaned prior to use. This method was demonstrated using a variety of uranium starting materials and should also be applicable to the analysis of impurities in plutonium; Pu^{4+} will be retained by the resin under the conditions

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