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Trace Metal Determination in a Uranium Matrix by Sector Field ICP-MS

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Key Words

- **ELEMENT 2**
- **Glovebox**
- **Nuclear**
- **Uranium**

Introduction

The determination of trace impurities in a uranium matrix is of great importance in the nuclear industry and demands the very highest analytical performance. Impurity levels in fresh nuclear fuels are critical as they define the quality of the fuel. Very low levels of impurities of neutron absorbing elements such as B, Cd and Gd must be achieved as otherwise they act as fuel 'poisons', reducing the efficiency of the fuel for energy production. The halides (Cl, Br, I) should also be low because, at the working temperature of a reactor, they may corrode the fuel cladding (zircaloy metal tubing, > 90% Zr) in which the fuel pellets are held. Other impurities (e.g. transition metals) can be at slightly higher levels than the neutron absorbers and halides, since they only influence the mechanical and thermal characteristics of the fuel. Another reason to keep the level of impurities low is that, after the fuel has been used, their activation products can be costly to dispose of/store. An example for this is Co, where high impurity levels will increase the formation of the hard gamma-emitting radionuclide ^{60}Co.

Summing up these factors for fresh nuclear fuels, a complete elemental analysis at ultra-trace levels, as well as over a large measurable concentration range, is necessary to fulfill the requirements in process and quality control. Moreover, since research is mostly performed with glove-box equipped instruments, highly sensitive instrumentation allows for the analysis of more dilute radioactive samples, lowering the dose for the researchers.

Therefore, the general requirements for a multi-elemental technique for the analysis of radioactive fuels are low pg/ml detection limits and background equivalent concentrations in a heavy uranium sample matrix. The sector field technology implemented in the Thermo Scientific ELEMENT 2, with its unique high sensitivity at high mass resolution, fulfills these needs, especially when coupled to user definable glove box environments (Figure 1). This report presents analytical data from examples of the quantification of trace and ultra-trace metals in uranium samples.

Figure 1: Thermo Scientific ELEMENT 2 adapted to a customer defined glovebox configuration.

Detection Limits

As a basic parameter to evaluate instrument performance, limits of detection were measured in a uranium matrix. Table 1 lists the sample introduction system and operating conditions used for all experiments.

Sample introduction:	PFA spray-chamber, PFA self-aspirating nebulizer at 0.05 ml min^{-1} (PFA µflow, ESI, Omaha, NE, USA)
Plasma:	1200 W
Sample:	200 µg ml^{-1} U solution, diluted in 2% HNO_3, (Baseline, Seastar Chemicals, Canada)

Table 1: Sample introduction and operating conditions used for all analyses.

The measurement of detection limits for the analysis of uranium samples was designed to take into account any effect of the high uranium matrix; i.e., would the uranium matrix cause a decrease in sensitivity that would lead to deterioration in detection limits. In order to assess this, the standard deviation from ten replicate blank measurements in 2% ultra-pure nitric acid solution, prepared from Baseline quality (Seastar Chemicals, Canada) nitric acid and water, was compared to the instrumental sensitivity obtained from a spiked sample of 200 µg ml^{-1} uranium (prepared from the dilution of a 1000 µg ml^{-1} uranium standard, Merck KGgA, Darmstadt, Germany). The standard deviation was measured in a 2% HNO_3 blank in order to avoid any contamination from measuring a 'blank' U matrix solution that would degrade detection limits. The resulting 'matrix effect compensated' detection limits are shown in Table 2.

This multi elemental analysis is an example of monitoring the lowest levels of impurities in nuclear fuels. Typically, detection limits in the single digit pg ml^{-1} range are obtained. The somewhat elevated B, K, Fe, and Br levels in the 10 pg ml^{-1} range indicate contamination introduced from the chemicals used. For all elements measured, the background from impurities was distinctly higher than the instrumental background (dark noise) of < 0.2 cps (counts per second). What is important to note from this data is that the Thermo Scientific ELEMENT 2 instrumental sensitivity is sufficiently high that low detection limits can still be obtained with relatively low U matrix content (high dilution factors) - a highly desirable feature for the analysis of radioactive sample matrices.

ISOTOPE	RESOLUTION	DETECTION LIMIT (pg ml^{-1}) IN 200 µg ml^{-1} URANIUM
^{7}Li	LR	0.530
^{11}B	LR	5.7
^{23}Na	LR	8.40
^{24}Mg	LR	0.350
^{27}Al	LR	1.74
^{60}Ni	LR	12.5
^{63}Cu	LR	0.110
^{71}Ga	LR	0.170
^{88}Sr	LR	0.031
^{89}Y	LR	0.020
^{90}Zr	LR	0.060
^{93}Nb	LR	0.110
^{95}Mo	LR	0.430
^{101}Ru	LR	0.160
^{103}Rh	LR	0.010
^{105}Pd	LR	0.076
^{107}Ag	LR	0.034
^{111}Cd	LR	0.160
^{118}Sn	LR	0.410
^{121}Sb	LR	0.100
^{133}Cs	LR	0.015
^{137}Ba	LR	0.120
^{139}La	LR	0.029
^{140}Ce	LR	0.029
^{149}Sm	LR	0.004
^{153}Eu	LR	0.033
^{157}Gd	LR	0.003
^{163}Dy	LR	0.039
^{182}W	LR	0.053
^{208}Pb	LR	2.60
^{209}Bi	LR	0.023
^{28}Si	MR	77.4
^{44}Ca	MR	6.42
^{47}Ti	MR	0.280
^{52}Cr	MR	0.270
^{55}Mn	MR	0.140
^{56}Fe	MR	7.27
^{59}Co	MR	0.315
^{66}Zn	MR	1.46
^{79}Br	MR	45.3
^{39}K	HR	28.7

Table 2: Detection limits calculated from 10 replicate measurements of 2% HNO_3 (Baseline, Seastar Chemicals, Canada) and an intensity determination in 200 µg ml^{-1} U solution. LR = Low Resolution (R = 300), MR = Medium Resolution (R = 4000) and HR = High Resolution (R = 10000).

Quantification of Trace Elements in a Uranium Matrix

As an example of the application of the Thermo Scientific ELEMENT 2 to the determination of trace elements in a uranium matrix, the U_3O_8 certified reference materials NBL 124-6 and 124-7 were analyzed. These two materials (CRM) represent the lowest concentration levels of the CRM series NBL 124-1 to 124-7. The latter is the base material from which the other standards were prepared by subsequent spiking, and CRM 124-6 is the lowest spiked sample. Analytical parameters used for these experiments are listed in Table 1.

The two reference materials were digested using Baseline nitric acid in inert PFA bottles. Approximately 50 mg of each material was accurately weighed and digested with 2.5 ml HNO_3 in an ultrasonic bath for 1 h at 50 °C. After digestion, the samples were made up to 25 ml with high purity Baseline water, resulting in a dilution factor of approximately 500. This solution was further diluted 10-fold prior to analysis, to give a final sample matrix concentration of 200 µg ml^{-1} uranium. Such a relatively high dilution factor (*5000) is preferable when it comes to the analysis of uranium samples in order to reduce the amount of active material which the instrument and operators are exposed to. Quantification was carried out by standard addition with 0.5 mg l^{-1} Indium as an internal standard. Standard addition was preferred over external calibration as any attempt of matrix-matching would inevitably result in irreproducible blank levels when doing analyses at the single-digit ng/l level.

The results from the CRM measurements are shown together with the target concentrations in Table 3. The concentrations shown are those in the solid, i.e. a factor of 5000 higher than measured in the actual sample solution.

ISOTOPE	RESOLUTION	124-7	124-6	[(124-6) - (124-7)]	REFERENCE 124-6 µg g^{-1}
^{27}Al	MR	<LoD	4.7	4.7	5
^{11}B	LR	0.3	0.4	0.1	0.1
^{9}Be	MR	0.003	0.46	0.46	0.5
^{114}Cd	LR	0.006	0.13	0.12	0.1
^{59}Co	MR	0.01	0.52	0.51	0.5
^{52}Cr	MR	2.1	3.9	1.8	2
^{63}Cu	MR	0.14	1.05	0.91	1
^{56}Fe	MR	5.1	10.0	4.9	5
^{24}Mg	MR	0.4	2.3	1.9	2
^{55}Mn	MR	0.27	1.21	0.93	1
^{60}Ni	MR	0.9	5.6	4.7	5
^{208}Pb	LR	0.21	1.08	0.87	1
^{28}Si	MR	15.8	20.3	4.6	5
^{120}Sn	LR	0.14	0.93	0.79	1
^{47}Ti	MR	0.001	0.76	0.76	1
^{51}V	MR	0.013	0.91	0.9	1
^{184}W	MR	0.06	4.35	4.29	5
^{68}Zn	MR	<LoD	5.1	5.1	5
^{90}Zr	LR	0.001	4.9	4.9	5

Table 3: Concentrations determined in NBL uranium reference materials 124-6 and 124-7. All values shown have units of µg g^{-1}.

While there is no certified value for the base material 124-7 itself, the difference in determined concentrations between this material and the spiked sample, 124-6, should give the certified spike concentrations for 124-6. Therefore the difference $[(124\text{-}6) - (124\text{-}7)]_{\text{concentration}}$ is compared with the reference data for 124-6. These recovery data are shown in Figure 2.

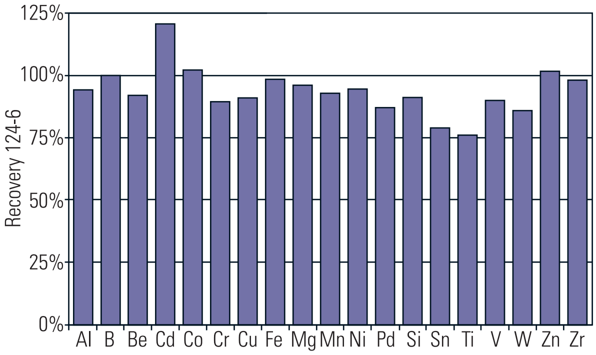

Figure 2: Recovery (expressed as a percentage) for CRM NIST124-6.

For all the elements determined, the ELEMENT 2 gave accurate results that showed excellent recoveries for this low-level material. For Sn, W, and Ti, recoveries are slightly low indicating an incomplete digestion (of refractory components as no HF was used in the digestion).

Conclusions

The high sensitivity of the Thermo Scientific ELEMENT 2 allows for relatively high dilution factors to be routinely used for the analysis of high uranium matrices (e.g. nuclear fuels etc). Even with the high dilution factors used here for the routine analysis of nuclear fuels, which are preferred to minimize the contamination to the instrument and dose to its users, the high sensitivity and resistance to matrix effects allows the ELEMENT 2 to provide high quality data at the lowest concentration levels.

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The TRITON sets a new standard in high precision TIMS isotope ratio measurements. The TRITON's unique capabilities have earned it the reputation of the "natural choice" in TIMS instrumentation.

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- Magnetic ion separating system employing stigmatic focusing for high ion transmission and enhanced mass dispersion.

Thermo Scientific XSERIES 2 ICP-MS

The XSERIES 2 ICP-MS is a robust analytical instrument capable of meeting the most challenging requirements. It is a powerful and precise measurement tool designed to maximize productivity in the laboratory across a wide range of applications.

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