Determination of impurities in uranium oxide by inductively coupled plasma mass spectrometry (ICPMS) by the matrix matching method

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An analytical procedure was developed to determine the concentration of some elements regarded as trace impurities in nuclear fuel using inductively coupled plasma mass spectrometry (ICPMS) associated to the matrix matching method. The assessment of this approach was carried out using a set of certified reference materials produced by the New Brunswick Laboratory (NBL). Eighteen out of the twenty-four elements in the reference materials could be easily determined. It was found that the mean values for reproducibility and accuracy were 5.0% and 15.0%. The remaining six elements provided mean values of 11.0% and 37.0%, respectively. They could not be adequately determined due to the effects of analyte signal suppression and spectral interference.

Introduction

The nuclear fuel cycle consists of a series of operations that produces chemical, physical and isotopic transformations in uranium from raw to a pure and well characterized material, usually uranium dioxide (UO_2), necessary to feed nuclear reactors.[1]

The uranium dioxide produced must comply with a standard specification that indicates several requirements that must be met before the material is sintered and mounted into the fuel rods that eventually are introduced in the nuclear reactor.[2]

Several analytical techniques have been developed to determine the trace impurities in uranium dioxide. The excitation of the uranium samples with DC current was tried but the interference due to the spectral lines limited the number of elements that could be detected.[3] Besides its reproducibility was very poor. Carrier distillation was also used in the past but did not have the sensibility to determine the concentration of volatile and non-refractory elements.[4]

Although inductively coupled plasma atomic emission spectrometry (ICP-AES) is still the most used technique, it has also limitations. The excitation of uranium in the plasma generates a complex optical spectrum forming thousands of emission lines that interfere with the lines of the trace impurities to be detected. The solution to this problem was found by removing the uranium matrix.[5]

A new analytical alternative came into the scene with the introduction of the inductively coupled plasma mass spectrometry (ICPMS). Its advantages over the traditional techniques are the higher sensibility, higher sample throughput, higher dynamic range, lower detection limit, simpler spectra and ease of operation.[6] Nevertheless, this technique has also limitations due to the existence of spectroscopic and non spectroscopic interferences.[7]

Several possible methods were considered to tackle this problem.[8] The dilution of the sample is the simplest one but would compromise the quantification limits for some elements. Standard addition might be very efficient but it is more suitable to cases where just a lower number of elements are involved. For sure isotopic dilution can provide highly precise and accurate results but requires the use of isotopic reference materials for each element of interest, which is not applicable when a large number of elements is involved.

Considering that there is no definitive method, it was decided to assess the reliability of the determinations provided by the matrix matching method.

The analytical procedure assessment was carried out using a set of certified reference material (CRM 124) provided by the New Brunswick Laboratory (Chicago, IL , USA). It consists of six samples in the form of pure uranium trioxide (U_3O_8) to which twenty four elements regarded as impurities were added at different concentrations.

Experimental

Instrumentation

The instrument used was a PlasmaQuad PQII Plus manufactured by VG Elemental (Winsford, Cheshire, UK). It is equipped with a MiniPlus 2 peristaltic pump from Medical Electronic Company (Middletown, WI, USA), mass flow controller model FC 260 from Tylan (Rancho Dominguez, CA, USA), double pass water cooled quartz spray chamber, De Galan cross flow nebulizer, quartz torch of the Fassel type, Channeltron continuous dynode electron multiplier from Galileo Electro Optics Corporation (Stunbridge, MA, USA) and a 2.0 kW, 27.1 MHz solid state radio frequency generator from RF Power Products (Marlton, NJ, USA).

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Reagents, standards and samples

The 18 MΩ deionized water used in this study was supplied by an Elgastat Maxim ultrapurifier from Elgast Scientific (Bucks, England). Nitric acid Suprapur 65% and single element standards of Ag, Al, B, Be, Bi, Ca, Cd, Co, Cu, Cr, Fe, In, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, Ti, V, W, Zn and Zr at a concentration of 1.000 μg/ml were supplied by Merck (Darmstadt, Germany).

The matrix matching method requires that the standards and the samples have the same uranium concentration. Previous studies showed that a concentration of 1.0 g/l U would be suitable for this experiment.[9] As the instrument requires the use of an internal standard to correct the instrumental drift, indium at a concentration of 100 ng/ml was selected and used in every solution. The three calibrations solutions contained the 24 elements to be determined in the CRM oxide samples. Each of the six oxide samples was weighted, heated at a rate of 120 °C/hour, transferred to a platinum dish and dissolved in nitric acid. Then they were diluted to the desired concentration. All the solutions were prepared in 2% nitric acid. The running solutions were:

Reagent blank (100 ng In/ml),

Matrix blank (1 g/l U, 100 ng In/ml),

Calibration solution 1 (1 gU/l, 100 ng In/ml, 100 ng element/ml),

Calibration solution 2 (1 gU/l, 100 ng In/ml, 200 ng element /ml),

Calibration solution 3 (1 gU/l, 100 ng In/ml, 500 ng element /ml)

Sample 1 to 6 (1 gU/l, 100 ng In/ml)

Measurement procedure

The instrument was calibrated using a multielement solution containing Be, Mg, Co, In, La, Pb, Bi and U at a concentration of 10 ng/ml, 2% nitric acid, to assure that the peaks were centered at their correct position. The sensitivity for each element in the calibration solution was also verified. Typical values were $1.0 \cdot 10^5$ counts per second. Finally short-term and long-term stability tests were carried out to see whether the system was able to give stable ion count rates.

The operating parameters are summarized in Table 1. The measurement parameters were selected, as shown in Table 2.

It was very important to set correctly the solution processing times to avoid cross contamination as well as undesired ion count rate fluctuations. The selected values are shown in Table 3.

The matrix matching method required that the solutions were processed in the order presented in Table 4.

Table 1. Instrument operating parameters

Source	
Cooling gas	Argon
Forword RF power, W	1.350
Reflected RF power, W	2
Cooling gas flow rate, l/min	14.0
Auxiliary gas flow rate, l/min	1.0
Nebulizer flow rate, l/min	0.96
Sample uptake, ml/min	0.80
Interface	
Plasma sample depth, mm	10
Sampling cone diameter, mm	Ni, 1.0 mm
Skimmer cone diameter, mm	Ni, 0.7 mm
Nebulizer pressure, p.s.i.	20
Spray chamber temperature, °C	4.2

Table 2. Measurement parameters

Scan mode	Peak jumping
Dwell time per scan, s	1.35
Dwell time per peak, ms	10.24
Number of points per mass peak	5
Number of repeats	3
DAC steps	10

Table 3. Solution processing times

Uptaking time, s	120
Acquisition time, s	60
Washing time, s	120

Table 4. Solutions processing order

Number	Sample	Code	Subtraction
1	Reagent blank	BR	
2	Matrix blank	BM	
3	Calibration solution 1	P1	P1-RB
4	Calibration solution 2	P2	P2-RB
5	Calibration solution 3	P3	P3-RB
6	Sample 1	S1	S1-MB
7	Sample 2	S2	S2-MB
8	Sample 3	S3	S3-MB
9	Sample 4	S4	S4-MB
10	Sample 5	S5	S5-MB
11	Sample 6	S6	S6-MB

Results and discussion

Vocabulary and estimation of uncertainty

The technical vocabulary used followed recommendations of BIPM[10] and ISO.[11] The expanded uncertainty for the experimental data was estimated according to ISO-GUM[12] and Eurachem/Citac Guide.[13] A coverage factor (*k*) of 2 was used throughout this work.

Table 5. Limits of quantification

Element	Quantification limit, pg/ml
Be	90
B	700
Na	8,000
Mg	900
Al	26,000
Si	400,000
Ca	100,000
Ti	400
V	300
Cr	800
Mn	700
Fe	550,000
Co	50
Ni	1,500
Cu	2,500
Zn	3,500
Zr	100
Mo	100
Ag	50
Cd	50
In	50
Sn	50
W	250
Pb	300
Bi	50

Limits of quantification

The limits of quantification presented in Table 5 were calculated as 10 times the standard deviation of the reagent blank count rate. These values just give an indication of the reachable quantification level since they were taken from the blank and do not include the effects of the uranium matrix.

Sample measurement

The results for each sample of CRM 124 are presented in Tables 6 to 11. In these tables, the certified value means the prepared concentration for each element in the reference material. The experimental value is the mean of *n* independent determinations and the accuracy is the relative difference between the experimental and certified value.

In order to evaluate the quality of our analytical data produced, the values of reproducibility and accuracy for each element are presented in Tables 12 and 13, respectively.

Table 12 shows that in general the measurements are very reproducible over the concentration range studied. This is a clear demonstration that all the instrumental and analytical parameters involved are under perfect control.

Table 13 shows that in general the accuracy or error of measurement increases when the concentration decreases. This is due to the fact that the limits of quantification associated to the procedure are being reached.

Table 6. Experimental results for CRM 124-1

Element	n	Certified, µg/g U	Experimental, µg/g U	Bias, %
Be	10	25	24 ± 1	5
B	6	5.1	5.7 ± 0.8	12
Na	10	400	194 ± 44	51
Mg	10	101	107 ± 13	6
Al	4	205	209 ± 48	2
Si	8	202	341 ± 72	69
Ca	5	200	196 ± 18	2
Ti	10	50	49 ± 2	2
V	5	50	30 ± 5	40
Cr	10	102	93 ± 5	9
Mn	10	51	46 ± 6	10
Fe	8	210	183 ± 13	13
Co	10	25	24 ± 2	5
Ni	10	202	197 ± 6	3
Cu	8	50	51 ± 3	3
Zn	10	202	179 ± 17	11
Zr	10	200	209 ± 7	5
Mo	10	100	99 ± 8	1
Ag	10	5.0	4.8 ± 0.8	4
Cd	10	5.2	5.0 ± 0.4	4
Sn	10	51	43 ± 1	16
W	10	200	188 ± 4	6
Pb	10	51	49 ± 1	4
Bi	10	50	50 ± 1	1

Table 7. Experimental results for CRM 124-2

Element	*n*	Certified, μg/g U	Experimental, μg/g U	Bias, %
Be	10	12.5	13.2 ± 0.8	6
B	5	2.6	3.2 ± 0.2	23
Na	10	200	140 ± 21	30
Mg	10	51	66 ± 15	30
Al	10	105	97 ± 53	7
Si	5	102	162 ± 15	59
Ca	5	100	190 ± 18	90
Ti	10	25	24 ± 3	2
V	5	25	24 ± 2	4
Cr	10	52	56 ± 13	8
Mn	10	26	26 ± 2	2
Fe	8	110	146 ± 27	33
Co	10	12.5	13.3 ± 2.4	6
Ni	10	102	106 ± 19	4
Cu	10	25	25.1 ± 2.4	0
Zn	5	102	122 ± 5	20
Zr	5	100	128 ± 4	28
Mo	10	50	53 ± 10	6
Ag	6	2.5	2.9 ± 0.2	16
Cd	10	2.7	2.8 ± 0.2	4
Sn	5	26	34 ± 0.2	31
W	10	100	108 ± 10	8
Pb	5	26	25 ± 2	5
Bi	5	25	25 ± 2	0

Table 8. Experimental results for CRM 124-3

Element	*n*	Certified, μg/g U	Experimental, μg/g U	Bias, %
Be	10	5.0	4.8 ± 0.4	4
B	5	1.1	1.4 ± 0.2	27
Na	10	100	84 ± 3	16
Mg	10	21	30 ± 3	42
Al	6	55	42 ± 17	23
Si	5	52	114 ± 20	118
Ca	5	51	73 ± 60	44
Ti	10	10.3	9.7 ± 0.4	6
V	10	10	9 ± 2	14
Cr	10	22	23 ± 3	4
Mn	10	11	10 ± 2	5
Fe	10	60	64 ± 30	6
Co	10	5.0	4.6 ± 0.2	8
Ni	10	52	45 ± 11	13
Cu	8	10	9 ± 1	12
Zn	10	52	51 ± 6	1
Zr	10	50	50 ± 7	0
Mo	10	20	19 ± 1	6
Ag	10	1.0	1.1 ± 0.2	10
Cd	10	1.2	0.9 ± 0.2	25
Sn	10	10.6	8.7 ± 0.6	18
W	10	50	50 ± 2	1
Pb	10	10.8	10.5 ± 3.0	3
Bi	10	10.0	11.5 ± 1.5	15

Table 9. Experimental results for CRM 124-4

Element	n	Certified, μg/g U	Experimental, μg/g U	Bias, %
Be	10	2.5	2.4 ± 0.4	4
B	5	0.6	0.8 ± 0.2	33
Na	5	40	24 ± 3	40
Mg	5	11	18 ± 2	65
Al	1	25	11 ± 3	56
Si	5	22	57 ± 3	158
Ca	6	21	69 ± 6	227
Ti	10	5.3	5.0 ± 0.2	6
V	5	5.0	4.2 ± 0.2	16
Cr	10	12	12 ± 1	2
Mn	5	5.7	5.8 ± 0.2	2
Fe	5	30	51 ± 5	71
Co	10	2.6	2.6 ± 0.2	0
Ni	5	22	23 ± 1	5
Cu	5	5.4	5.1 ± 0.2	6
Zn	9	22	21 ± 4	4
Zr	10	20	19 ± 1	5
Mo	10	10.0	10 ± 1	2
Ag	5	0.5	1.6 ± 0.2	220
Cd	10	0.7	0.5 ± 0.2	29
Sn	10	5.6	3.9 ± 0.2	30
W	10	20	21 ± 2	4
Pb	10	5.8	4.7 ± 0.2	19
Bi	10	5.0	4.6 ± 0.2	8

Table 10. Experimental results for CRM 124-5

Element	n	Certified, μg/g U	Experimental, μg/g U	Bias, %
Be	10	1.30	1.3 ± 0.2	2
B	5	0.35	0.5 ± 0.2	43
Na	5	20.00	40 ± 9	99
Mg	5	6.00	14.8 ± 3	147
Al	1	15.00	67.00	347
Si	2	12.00	31 ± 5	158
Ca	3	11.00	11 ± 6	2
Ti	10	2.80	2.8 ± 0.1	1
V	10	2.50	1.9 ± 0.1	24
Cr	10	7.00	8.3 ± 0.2	19
Mn	7	3.20	3.2 ± 0.8	0
Fe	10	20.00	64 ± 12	220
Co	10	1.40	1.3 ± 0.2	7
Ni	10	12.00	15 ± 1	23
Cu	5	2.90	2.4 ± 1.2	17
Zn	10	12.00	19 ± 1	55
Zr	10	10.00	14 ± 1	40
Mo	10	5.00	5.5 ± 0.4	10
Ag	10	0.25	0.19 ± 0.20	24
Cd	10	0.45	0.29 ± 0.20	36
Sn	10	3.10	2.5 ± 0.20	19
W	8	10.00	11 ± 1	15
Pb	10	3.30	2.80 ± 0.20	13
Bi	10	2.50	2.38 ± 0.20	5

Table 11. Experimental results for CRM 124-6

Element	n	Certified, µg/g U	Experimental, µg/g U	Bias, %
Be	6	0.5	0.7 ± 0.2	40
B	5	0.2	0.3 ± 0.2	50
Na	10	10.0	28 ± 3	177
Mg	5	3.0	6.8 ± 0.6	127
Al	0	10.0	–	
Si	0	7.3	–	
Ca	0	5.8	–	
Ti	10	1.3	1.2 ± 0.2	8
V	5	1.0	1.0 ± 0.2	0
Cr	10	4.3	5.2 ± 0.4	21
Mn	7	1.7	1.2 ± 0.6	29
Fe	7	15.0	41 ± 7	173
Co	10	0.6	0.6 ± 0.2	0
Ni	5	7.0	7.2 ± 0.2	3
Cu	1	1.4	2.3 ± 0.2	64
Zn	10	6.6	13.7 ± 1.6	108
Zr	10	5.0	7.4 ± 0.4	48
Mo	8	2.0	2.4 ± 0.2	20
Ag	0	0.1	–	
Cd	10	0.3	0.1 ± 0.1	67
Sn	10	1.6	1.3 ± 0.2	19
W	7	5.0	5.8 ± 0.6	16
Pb	10	1.8	1.4 ± 0.2	22
Bi	10	1.0	1.1 ± 0.2	10

Table 12. Reproducibility of measurements for CRM 124

Element	124-1, %	124-2, %	124-3, %	124-4, %	124-5, %	124-6, %	Mean, %
Be	2.1	3.0	4.2	8.3	6.8	0.0	4
B	8.8	3.1	7.1	12.5	14.0	33.3	13
Na	7.5	4.9	1.3	5.4	*	*	5
Mg	3.9	7.4	4.3	4.4	*	*	5
Al	7.7	27.2	13.2	*	*	*	16
Si	7.0	3.1	*	*	*	*	5
Ca	3.1	3.2	41.7	*	52.6	*	25
Ti	1.6	5.3	2.1	2.0	2.2	8.3	4
V	8.0	4.2	12.8	2.4	3.7	0.0	5
Cr	2.9	7.6	3.9	3.3	1.4	3.8	4
Mn	7.0	4.2	4.8	1.7	13.2	50.0	13
Fe	2.4	6.2	15.9	3.5	*	*	7
Co	2.1	6.0	2.2	3.8	0.0	0.0	2
Ni	1.6	6.2	12.2	1.7	2.8	1.4	4
Cu	2.9	4.8	5.4	2.0	42.5	*	12
Zn	4.7	2.0	5.6	8.5	3.8	5.8	5
Zr	1.7	1.5	6.8	0.0	0.0	2.7	2
Mo	4.4	9.6	2.1	5.1	4.0	4.2	5
Ag	8.3	3.4	9.1	*	10.5	*	8
Cd	2.0	0.0	0.0	0.0	6.9	0.0	1
Sn	1.4	0.0	3.4	2.6	0.0	0.0	1
W	1.2	4.8	1.4	5.7	4.6	5.2	4
Pb	1.0	3.2	15.2	2.1	1.4	7.1	5
Bi	1.4	2.8	4.3	2.2	1.7	0.0	2

Table 13. Accuracy of measurements for CRM 124

Element	124-1, %	124-2, %	124-3, %	124-4, %	124-5, %	124-6, %	Mean, %
Be	5.2	5.6	4.0	4.0	1.5	40.0	10
B	11.8	23.1	27.3	33.3	42.9	50.0	31
Na	51.4	30.3	15.5	39.5	–	–	34
Mg	6.3	30.2	42.4	65.5	–	–	36
Al	1.9	7.3	23.1	–	–	–	11
Si	68.7	59.2	–	–	–	–	64
Ca	2.0	90.4	43.9	–	–	–	45
Ti	1.6	2.0	5.8	5.7	0.7	7.7	4
V	40.0	4.0	14.0	16.0	23.6	0.0	16
Cr	9.3	8.3	3.6	1.7	18.6	20.9	10
Mn	9.8	1.9	4.5	1.8	0.3	29.4	8
Fe	13.0	32.8	6.0	70.7	–	–	31
Co	5.2	6.4	8.0	0.0	7.1	0.0	4
Ni	2.6	4.4	13.1	5.5	23.3	2.9	9
Cu	2.6	0.4	11.5	5.6	17.2	64.3	17
Zn	11.2	19.6	1.0	3.6	55.0	–	18
Zr	4.7	28.2	0.4	5.0	40.0	48.0	21
Mo	0.9	6.0	6.0	2.0	10.0	20.0	7
Ag	4.0	16.0	10.0	–	24.0	–	14
Cd	3.8	3.7	25.0	28.6	35.6	66.7	27
Sn	16.1	30.8	17.9	30.4	19.4	18.8	22
W	5.9	8.2	1.0	4.5	15.0	16.0	8
Pb	3.3	4.6	2.8	19.0	12.7	22.2	11
Bi	0.8	0.0	15.0	8.0	4.8	10.0	6

It can also be seen from Tables 12 and 13 that the elements can be divided into two groups. The first one includes eighteen elements (Be, B, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Zr, Mo, Ag, Cd, Sn, W, Pb and Bi) with a mean value of reproducibility and accuracy of 5.0 and 15.0%, respectively. The second one is composed by six elements (Na, Mg, Al, Si, Ca and Fe) with mean values 11.0 and 37.0%.

The reasons for the different behavior between these two groups are the effects of analyte signal suppression and spectral interference. The former is due to the action in the skimmer region of heavy uranium ions over low molecular weights ions (Na, Mg and Al).[15] The latter to the presence of species formed in the plasma that essentially have the same mass of sample ions being transmitted (Si, Ca and Fe) and cannot be resolved by the mass spectrometer. These species are either isobars, poliatomic ions, refractory oxides or double ions.[16]

Several approaches have been tried to overcome the related problems: collision cells, cold plasma, mixed gases, desolvation of aerosols, electrothermal vaporization and high mass resolution.[17] These highlight the effort to solve the limitations of the ICPMS technique. On the other hand, they indicate that the limitations are associated with the technique itself and not with the selected method.

It is important to note that the results provided by this work are comparable to other analytical procedures applied to uranium compounds.[18,19] It can be seen that the limitations pointed here are present there on the same group of elements.

Conclusions

The analytical procedure described allows the determination of the concentration of eighteen elements regarded as impurities in nuclear fuel. The sample preparation is straightforward and the measurement procedure is simple and fast, based on the good dynamic range and sensibility of the ICPMS. Six elements cannot be determined at an acceptable level of reproducibility and accuracy, which is due to interferences verified in the ICPMS. Other techniques like atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-AES) seem more indicated to be used for the determination of these elements.

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