Analysis of twenty five impurities in uranium matrix by ICP-MS with iron measurement optimized by using reaction collision cell, cold plasma or medium resolution

Alexandre Quemet [a], Rene Brennetot [a,*], Emilie Chevalier [a], Edwina Prian [a], Anne-Laure Laridon [a], Clarisse Mariet [b], Pascal Fichet [a], Ivan Laszak [b], Florence Goutelard [a]

[a] Analysis and Support to Facilities Laboratory, Department of Physics and Chemistry, Division for Nuclear Activities, CEA Saclay, DEN/DPC/SEARS/LASE, 91191 Gif sur Yvette, France
[b] Elementary, Nuclear and Isotopic Analysis Laboratory, Department of Physics and Chemistry, Division for Nuclear Activities, CEA Saclay, DEN/DPC/SEARS/LANIE, 91191 Gif sur Yvette, France

A B S T R A C T

An analytical procedure was developed to determine the concentration of 25 impurities (Li, Be, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Ag, Cd, In, Sm, Eu, Gd, Dy, W, Pb, Bi and Th) in a uranium matrix using the quadrupole inductively coupled plasma mass spectrometry (Q-ICP-MS). The dissolution of U_3O_8 powder was made with a mixture of hydrochloric acid and nitric acid. Then, a selective separation of uranium using the UTEVA column was used before measurement by Q-ICP-MS. The procedure developed was verified using the Certified Reference Material "Morille". The analytical results agree well except for 5 elements where values are underestimated (Li, Be, In, Pb and Bi). Among the list of impurities, iron was particularly investigated because it is well known that this element possesses a polyatomic interference that increases the detection limit. A comparison between iron detection limits obtained with different methods was performed. Iron polyatomic interference was at least reduced, or at best entirely resolved in some cases, by using the cold plasma or the collision/reaction cell with several gases (He, NH_3 and CH_4). High-resolution ICP-MS was used to compare the results obtained. A detection limit as low as 8 ng L^{-1} was achieved.

1. Introduction

The determination of trace (mg L^{-1}) and ultra-trace levels (µg L^{-1} and ng L^{-1}) is very important for different applications such as: environmental, industrial, forensic, medical and nuclear. Impurities in uranium oxide are of prime interest for the International Atomic Energy Agency (IAEA) in the monitoring of nuclear installations to verify the material conformity to the nuclear grade specifications, to identify material origins, etc. [1–5].

Because uranium oxide samples are received in a solid form and are to be studied with Inductively Coupled Plasma (ICP), a dissolution procedure needed to be found. Various procedures are available to dissolve uranium oxide samples, such as: dissolution in acid mixture [6–9], oxidizing conditions [10,11], photochemical reaction [12], supercritical fluid carbon dioxide [13] and microwave dissolution [14,15] can be used.

However, measurement of impurities at trace or ultra trace level in the presence of uranium at several g L^{-1} levels is very challenging due to possible matrix effect affecting the accuracy of impurities concentration measurement. This is the reason why some separation methods have been developed in order to extract or eliminate the uranium matrix, among them: solvent extraction [16–18] or column extraction chromatography [19,20].

Several studies for impurities measurement in uranium matrix have been reported in literature. There are mainly two principal techniques used for this kind of measurement: Inductively Coupled Plasma-Atomic Emission Spectrometry [2,16,18,19] (ICP-AES) and Inductively Coupled Plasma-Mass Spectrometry [1,3,17,21] (ICP-MS). Depending of the concentration level that has to be reached, either can be used to determine the concentration of interest. In the case of µg L^{-1} and ng L^{-1} level, ICP-MS is more appropriate.

ICP-MS became a versatile tool since it gives good detection limit for many elements with short time analysis. The main limitation is the presence of many interferences for m/z below 80 amu. Isobaric interferences arise from elements having equal mass isotopes (for instance $^{40}Ar^+/^{40}Ca^+$) whereas polyatomic interferences are due to the combination of an element M or Ar, from the gas used to generate the plasma, with sample or matrix ions like C^+, N^+ and O^+ to form MO^+, ArC^+, ArN^+ and ArO^+ species.

There are several ways to suppress interferences. First, chemical separation can be used to resolve isobaric interferences: [22,23] interfering elements are separated and mono-elemental

purified fractions are obtained. An alternative way for multi-isotopic elements is to use another isotope, free of interferences but it has to be compatible with the desired concentration level of the element. For a mono-isotopic element, an interference correction equation can be useful to resolve some interference ($^{35}Cl^{16}O^+$/$^{51}V^+$ with the measurement of $^{37}Cl^{16}O^+$ at mass 53 for instance). Nevertheless, these methods cannot be used to resolve the interferences generated by the plasma.

One approach to reduce these polyatomic interferences is to use cold plasma operating conditions [24,25]. However, these conditions are not robust and a decrease of sensitivity is commonly observed. Moreover, it is limited to elements presenting a low ionization potential.

A similar decrease of sensitivity is observed with high resolution using a sector field ICP-MS (SF-ICP-MS), although it presents the ability to separate ions with very close m/z ratios (typically, when a resolution lower than 10,000 is required) [26–28].

Recent studies have shown the great potential of collision/reaction cells implanted in ICP-MS to perform direct isobaric–polyatomic interferences resolution [29–33]. This system is based on the addition of a collision and/or reaction gas after the ions extraction. Gas molecules collide or react with the ion beam and the interferences are eliminated or reduced. The choice of the gas is crucial and is based on the difference of behavior between the analyte and the interfering species [33].

Iron measurements by ICP-MS with a collision and/or reaction cell have been performed on various matrices and instruments. Gases such as CH_4, NH_3, N_2O, H_2, H_2 in He have been tested to resolve the $^{40}Ar^{16}O^+$/$^{56}Fe^+$ interference and achieve the lowest detection limit [26,34–37].

Several mechanisms have been proposed to explain the reaction between the ions and the reaction gas molecules, among them: association or clustering reaction, atom transfer reaction and charge transfer reaction [33]. For example, when ArO^+ reacts with H_2, the species $ArOH^+$ and H_2O^+ are observed because of an hydrogen transfer reaction and an association reaction, respectively. Meanwhile, Fe^+ ions are not impacted by H_2 and can be analyzed at mass 56 [34,38,39]. Conversely, N_2O reacts with Fe^+ to form FeO^+ by means of an oxygen transfer reaction: iron measurement is performed at the corresponding mass of 72 [34,39]. On the other hand, due to their low energy potential, NH_3 and CH_4 can react with ArO^+ by a charge transfer mechanism whereas Fe^+ ions are not impacted [40,41]. Alternatively, the low dissociation energy of the Ar–O bound (0.31 eV) [42] could be broken by collision with the use of an inert gas, for instance He.

After a brief description of the microwave dissolution and separation procedure on a UTEVA resin, the results obtained for measurement of 25 impurities in the Certified Reference Material (CRM) Morille (CETAMA, France) will be discussed in terms of limit of detection and % of recovery.

A particular focus will then be done for iron measurement in 2 M HNO_3 solution. On the one hand, the resolution of the Fe^+/ArO^+ interference by using the collision/reaction cell in the Q-ICP-MS was studied with three different gases to determine the detection limit (He as collision gas and NH_3 and CH_4 as reaction gases). On the other hand, we use the medium resolution of a sector field ICP-MS to resolve the interference. For each instrument, a comparison between standard and cold plasma conditions was performed.

2. Experimental

2.1. Materials and reagents

A microwave-assisted reaction system furnace (Speedwave, Berghof, Germany) with Teflon (PTFE) vessels was used for the dissolution of the CRM at 1300 W with 2.45 GHz microwave field. The solution temperature in the vessel was automatically controlled with an infrared sensor regulating the power output. Likewise, the pressure inside each vessel was measured to avoid any build-up.

UTEVA resin (Triskem, France) with 100–150 μm particle size in 2 mL prepackaged columns was used for the separation procedure in order to fix the uranium matrix.

An Agilent Technologies 7700x Q-ICP-MS was used for this study, together with a Thermo Fischer Scientific Element 2 SF-ICP-MS to compare the detection limits of iron (in medium resolution, near 4000). The SF-ICP-MS has three nominal resolutions ($R = M/\Delta M$ at 10% peak height) settings: low (LR: $R = 300$), medium (MR: $R = 4000$), and high (HR: $R = 9000$). For this method we configure the mass spectrometer to perform in MR.

The main operating parameters are summarized in Table 1. First, in standard mode with the 7700x ICP-MS (i.e. without gas in the collision/reaction cell) sensitivity maximization and short term stability tests were performed on a daily test using a 1 μg L^{-1} solution of U and In. Typical sensitivities were better than 150,000 counts s^{-1} (μg L^{-1})$^{-1}$ with a residual standard deviation better than 1% for 10 measurements of 1 min. Under such optimum conditions, the formation levels of the oxide ions ($^{140}Ce^{16}O^+$/$^{140}Ce^+$) and of the double charge ions ($^{138}Ba^{++}$/$^{138}Ba^+$) were found to be lower than 2% and 3% respectively. Then, in gas mode, a blank solution (the acid of preparation) was used to optimize the gas flow rate and the instrumental parameters in order to reduce the ArO^+ interference. A 1 μg L^{-1} indium solution, presenting no gas reaction, was used to maximize sensitivity for each collision/reaction gas flow rate.

High purity standards were used for the preparation of the external calibration curves. They were prepared from single element SPEX (SPEX Certiprep, France) solutions (1000 mg L^{-1}) diluted in a 2 M nitric acid solution. This 2 M nitric acid solution was prepared by diluting a sub-boiling 15 M nitric acid solution with deionized water (resistivity 18.2 MΩ.cm). Sub-boiling nitric

Table 1
Typical ICP-MS operating conditions. Gas flow rate are in L min^{-1} and plasma power is in W.

	7700x Agilent	Element 2 Thermo Fisher
Plasma power	1550	1200
Cooling gas flow rate	15	16
Auxiliary gas flow rate	0.90	0.80
Nebulizer gas flow rate	1.05	1.20
Nebulizer	Quartz concentric	Quartz concentric
Spray chamber	Scott chamber	Scott chamber
Torch shield	Yes	Yes
Cell geometry	Octopole	–
Standard mode	–	–
Octopole bias	−8	
Quadrupole bias	−3	
He mode	–	–
Octopole bias	−18	
Quadrupole bias	−15	
Gas flow rate	6.1	
He high energy mode	–	–
Octopole bias	−100	
Quadrupole bias	−86	
Gas flow rate	10	
CH4 mode	–	–
Octopole bias	−18	
Quadrupole bias	−15	
Gas flow rate	1.4	
NH3 mode	–	–
Octopole bias	−18	
Quadrupole bias	−15	
Gas flow rate	1.4	

– Not applicable.

acid solution was achieved by distillation of a 65% HNO_3 Norma-tom solution (Prolabo, France) using an EVAPOCLEAN system (Analab, France). 12 M sub-boiling hydrochloric was achieved by distillation of a 35% HCl Ultrex solution (Fischer Scientific, France) and was used for the dissolution. A 45% HF Ultrex solution (Fischer Scientific, France) was used for the separation process. ^{45}Sc (5 µg L^{-1}), ^{139}La (1 µg L^{-1}) and ^{205}Tl (1 µg L^{-1}) are used as internal standard for ICP-MS measurements. Dilutions were performed gravimetrically with high precision balance.

The assessment of the procedure investigated was carried out on a CRM "Morille" provided by the CETAMA. It consists in a U_3O_8 powder to which 25 elements concentration is certified.

High purity of helium (99.9999% purity), methane (99.9995% purity) and ammonia (99.98% purity) were used as collision or reaction gases in the cell of the ICP-MS (Messer, France).

2.2. Dissolution procedure

Dissolution procedure includes the cleaning of all the vessels used to prepare dissolution. The same acids were used for cleaning and dissolution. The CRM was dried at 110 °C for at least 3 h in a drying oven, prior to any sampling. 0.6 g of U_3O_8 was precisely weighted before the digestion process. Dissolution program begins with a temperature ramp of 1 °C/min and a first stage of 5 min at 90 °C. A second ramp is then performed to reach 110 °C during 30 min. 15 mL of 8 N hydrochloric acid and 6 N nitric acid (50/50 v/v) both of sub-boiling quality was used to perform dissolution of the CRM. This acid mixture was chosen to ensure a maximum stability of the elements of interest in the dissolution solution and to ensure a complete dissolution of the sample.

2.3. Separation procedure

UTEVA column was first conditioned and then by washing the column with 20 mL of deionised water (resistivity 18.2 MΩ.cm) and 10 mL of HNO_3 3 M, and then equilibrated with 20 mL of the HNO_3/HF (8 M/0.1 M) acid mixture used for the separation. The conditioning was optimized to ensure that the separation blanks were as low as possible for all the element of interest. The solution obtained after dissolution with the microwave furnace was weighed and evaporated to dryness. Sample was deposited on the column with 3×200 µL of the HNO_3/HF acid mixture and the elution was performed with 10 mL of the acid mixture. The solution obtained after separation is purified in uranium and the uranium decontamination was checked by ICP-MS measurement. As a result, up to 99.997% uranium was eliminated. All impurity measurements, which were in 10 mL of the acid mixture, were performed using a diluted acid (typically by a factor of 4) to be more suitable with the ICP-MS. This procedure was optimized to ensure a maximum recovery for Zr and Th.

3. Results and discussion

3.1. Estimation of the analytical measurement

The limits of detection (Table 2) were estimated from the linear calibration curves (correlation coefficient > 0.999) in the range tested (0.010–7 µg L^{-1}) and were expressed in amount of the element in the U_3O_8 material. The limit of detection was calculated according to the IUPAC (3 standard deviation of blank signal/slope). These values gave an indication of the reachable performance. They did not include the matrix effect as they were obtained with a 2 M HNO_3 matrix, nor the separation yield as they were calculated considering a yield of 100%.

Table 2

Detection limits in the solid (LD (CRM)) in µg kg^{-1} U, and experimental results (mg kg^{-1} U) of the Certified Reference Material "Morille" by Agilent 7700x Q-ICP-MS and Thermo Fischer Element 2 SF-ICP-MS.

Element	Certified mg kg^{-1} U	Measured mg kg^{-1} U	Recovery %	LD(CRM) µg kg^1 U	
				Without U	With U
Agilent 7700x Q-ICP-MS					
Li	5.0 ± 0.2	3.8 ± 0.2	76 ± 5	9	–
Be	5.4 ± 0.6	4.0 ± 0.2	76 ± 5	4	–
Ti	49.2 ± 2.6	45.5 ± 2.4	92 ± 5	65	155
V	48.7 ± 2.8	41.8 ± 2.2	86 ± 5	2	12
Cr	99 ± 2	95 ± 6	96 ± 6	17	62
Mn	24.5 ± 0.5	24.4 ± 1.6	100 ± 6	9	25
Fe	211.6 ± 6.5	189.1 ± 23.0	89 ± 12	52	205
Co	9.8 ± 2.0	9.4 ± 0.8	96 ± 9	2	4
Ni	147 ± 3	144 ± 5	98 ± 4	34	62
Cu	50.2 ± 1.0	47.7 ± 2.0	95 ± 4	9	75
Zn	98.6 ± 5.5	97.7 ± 9.0	97 ± 7	4	124
Zr	59.9 ± 4.1	64.1 ± 1.2	107 ± 7	90	–
Mo	147 ± 5	136 ± 17	93 ± 13	9	6
Ag	10.4 ± 1.6	11.7 ± 1.0	112 ± 9	1	–
Cd	4.9 ± 0.7	4.9 ± 0.2	100 ± 3	2	12
In	9.4 ± 1.0	7.5 ± 0.4	80 ± 5	1	2
Sn	18.5 ± 5.6	16.5 ± 2.2	89 ± 14	13	633
Sm	0.50 ± 0.12	0.51 ± 0.02	102 ± 2	1	3
Eu	0.52 ± 0.03	0.52 ± 0.02	100 ± 2	1	1
Gd	0.56 ± 0.06	0.58 ± 0.02	103 ± 2	2	19
Dy	0.50 ± 0.06	0.46 ± 0.02	92 ± 4	1	1
W	100 ± 9	89 ± 4	90 ± 2	2	2
Pb	101 ± 3	86 ± 5	89 ± 4	4	2
Bi	24.4 ± 1.9	19.9 ± 1.0	81 ± 5	1	1
Th	6.2 ± 0.8	6.4 ± 0.2	103 ± 2	1	3
Thermo Fischer Element 2 SF-ICP-MS					
Fe	211.6 ± 6.5	207.4 ± 13.6	98 ± 3	34	–

– not determined.

The limits of detection were also estimated from the linear calibration curves, by using the matrix matching method, using an uranium matrix around 0.1 g L^{-1} (corresponding to a sample dilution of 100 after the dissolution). They were also expressed in amount of the element in the U_3O_8 material. The limits of detection of Li, Be, Zr and Ag were not determined by the matrix matching method.

The separation procedure allowed to decrease the uranium content by a 30,000 factor and therefore, the matrix effect. As a matter of fact, detection limits were improved by a 5–50 factor for the following elements: V, Cu, Cd, Sn, Gd and Th, and slightly less than a 5 factor for all the other elements. It confirmed that the elimination of the uranium matrix allows for a lower level quantification, but that it is correlated to the nature of each element. The matrix separation prevents a pollution of the ICP also used to investigate trace uranium measurement in other research programs. It also increases the productivity by avoiding a complete wash of the instrument during a few days.

3.2. Procedure check for the quantification of impurities in uranium matrix

The procedure developed was assessed using the CRM "Morille" (CETAMA, France). Once the separation process was realized, a standard external calibration was used to determine the concentration of the following trace elements: Li, Be, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Mo, Ag, Cd, In, Sn, Sm, Eu, Gd, Dy, W, Pb, Bi and Th. All the impurities were in the mg kg^{-1} U concentration range, matching perfectly the operational key use of the Q-ICP-MS. A quality check control at 1 µg L^{-1} and a blank solution, prepared in HNO_3, were run before and after the sample in order to control

the calibration curve and the pollution of the instrument. The results obtained are listed in Table 2 together with the quantitative recoveries. Each measured value is the average of 8 different separations on the same dissolution. The uncertainties values are given at $k=2$. The dissolution procedure was previously validated from 4 dissolutions of the CRM.

As shown, the analysis results agree satisfactorily with 19 of 25 certified values, whereas they are slightly underestimated (around 20%) for Li, Be, In, V, Pb and Bi.

When agreement was achieved with the certified value, recoveries are between $89 \pm 12\%$ and $112 \pm 9\%$. For the six other elements, recoveries are between $76 \pm 5\%$ and $89 \pm 4\%$. Nonetheless, some elution tests were performed to improve their separation and recoveries about 90% were completed for V, In, Pd and Bi. Improvement on the separation of Li and Be are currently under investigation.

The repeatability was calculated for each element in order to estimate the quality of our analytical results: it was systematically below 6%, thus demonstrating the validity of our analytical procedure.

3.3. Study of the possibilities of the elimination of $^{56}Fe^+/^{40}Ar^{16}O^+$ isobaric interferences

Among all impurities, iron is the only one presenting a polyatomic interference that deteriorates the detection limit. Other elements, with potentially overlapped by polyatomic interferences ($^7Li^+/^{14}N^{++}$, $^{51}V^+/^{38}Ar^{13}C^+$, $^{52}Cr^+/^{40}Ar^{12}C^+$, $^{53}Cr^+/^{40}Ar$ $^{13}C^+$, $^{59}Co^+/^{35}Cl^{24}Mg^+/^{40}Ar^{19}F^+$, etc.), have their limits of detection sufficiently low to allow their measures in the CRM without interferences resolution. The possibility to measure iron by ICP-MS at a concentration level compatible with the CRM was assessed: its analytical performance was evaluated in terms of detection limit, background intensity, sensitivity and measurement error. All calibration curves were made in HNO_3 with twelve calibration points in the $0–2 \, \mu g \, L^{-1}$ range. Two quality check controls (at 0.5 and $1 \, \mu g \, L^{-1}$), prepared independently in HNO_3, were run with the samples in order to control drift and precision. Two different ICP-MS were used to evaluate the detection limit of iron: a Q-ICP-MS and a sector field ICP-MS. To estimate the iron detection limits three different conditions of ICP-MS were tested: the standard mode and the cold plasma conditions for the two ICP-MS (Q-ICP-MS and SF-ICP-MS), the use of the collision/reaction cell for the Q-ICP-MS and the medium resolution for the SF-ICP-MS. The results are presented in Table 3.

3.3.1. Standard mode

In the standard mode, the iron measurement by Q-ICP-MS was made at mass 57 because the $^{40}Ar^{16}O^+$ intensity was higher than 4,000,000 cps in the blank at mass 56, and chromium interfere at mass 54. The detection limit at mass 57 was determined at $215 \, ng \, L^{-1}$.

The iron measurement by a SF-ICP-MS was made also at mass 57 using the low resolution. An improvement of the detection limit was achieved with a value of $44 \, ng \, L^{-1}$ confirming the better sensitivity of the SF-ICP-MS over the Q-ICP-MS.

The measurement errors were determined between 2 and 10% for the two quality check controls for the Q-ICP-MS and the SF-ICP-MS. The limit of detection of the Q-ICP-MS is close to the concentration of the two quality check controls explaining the high measurement errors, similar for both instruments.

3.3.2. Cold plasma operating conditions

One approach to overcome the $^{40}Ar^{16}O^+/^{56}Fe^+$ interference is to reduce the plasma power to reach the cold plasma conditions [43].

Table 3
Detection limits (LD) in $ng \, L^{-1}$ of iron in HNO_3 and the measurement error (%Bias) for the Agilent 7700x Q-ICP-MS and the Thermo Fischer Element 2 SF-ICP-MS and for different configurations instruments. Level 1 and 2 are the quality check control at 0.5 and $1 \, \mu g \, L^{-1}$, respectively.

Analysis condition	LD ($ng \, L^{-1}$)	Quality check control	
		Level	% error
Agilent 7700x Q-ICP-MS			
Standard (^{57}Fe)	215	1	8
		2	2
Cold plasma	15	1	9
		2	3
He high energy mode	22	1	2
		2	3
He	12	1	5
		2	1
CH_4	8	1	2
		2	1
NH_3	74	1	6
		2	5
Thermo Fischer Element 2 SF-ICP-MS			
Standard (^{57}Fe)	44	1	3
		2	10
Cold plasma	132	1	9
		2	22
Medium resolution	10	1	4
		2	4

Hence, analyte can be easily detected since the background caused by argon species is reduced. In the present study, the plasma power was reduced to 600 W for the Q-ICP-MS. Within these conditions, a $15 \, ng \, L^{-1}$ detection limit was obtained at mass 56 which is significantly lower than the ones obtained at mass 57 in the standard mode and in close agreement with the value of Huang and Lin ($16 \, ng \, L^{-1}$) [43]. The measurement errors for the Q-ICP-MS were higher for the first quality check control (9%) and acceptable for the second one (less than 3%).

On the other hand, when the plasma power was reduced to 700 W for the SF-ICP-MS, the detection limit was deteriorated to $132 \, ng \, L^{-1}$ compared to the $44 \, ng \, L^{-1}$ in the standard mode. The loss of sensitivity can explain the deterioration of the detection limit. However this type of set-up is not suitable for this apparatus when medium resolution can be used to make the measurement in good conditions.

For the SF-ICP-MS, the measurement errors were higher (more than 9%) and are incompatible with the measurement of iron at low level.

3.3.3. Medium resolution

In theory, a 2500 resolution is required to separate $^{40}Ar^{16}O^+$ from $^{56}Fe^+$ and can be reached using the medium resolution of the SF-ICP-MS. Indeed, a detection limit of $10 \, ng \, L^{-1}$ was achieved which is of the same order of magnitude than the one obtained with the collision/reaction cell ICP-MS. The measurement errors were less than 4% for the two quality check controls, showing that it is the best way to measure iron with a SF-ICP-MS.

3.3.4. Collision/reaction cell

Different gases were tested to try to overcome the $^{40}Ar^{16}O^+$ interference on $^{56}Fe^+$ in order to improve the detection limit in HNO_3 solution and also for trace analysis in uranium: CH_4 [26], NH_3 [34,36] and He [44].

Using the gas mode, the ArO^+ intensity was decreased by more than 99.95% and was lowered below 1000 cps.

The use of He as a collision gas, or CH_4 as a reaction gas provided the best detection limits. With these two gases, a

10 ng L^{-1} detection limit was obtained at mass 56, which is considerably lower than the one obtained at mass 57 in standard mode (215 ng L^{-1}). This illustrates the capacity of the gas mode to eliminate interferences and to lower the limit of detection.

However, NH_3 was not suitable to decrease lower the detection limit (74 ng L^{-1}), value in the same order of magnitude than the one of Iglesias et al. (24 ng L^{-1}) [34]. As CH_4 and NH_3 have close masses (16 and 17 g mol L^{-1}) and react with the same mechanism, we could have expected to obtain very similar detection limits of iron. A decrease by a factor 2 of the iron intensity was observed using NH_3. Beside, Koyanagi et al. [39] observed $FeNH_3^+$ and $FeCH_4^+$ species. However, one explanation could be that the formation of $FeNH_3^+$ has a reaction efficiency 20 times higher than the formation of the $FeCH_4^+$ species [39,45]. Furthermore, the formation of $FeNH_3^+$ is 4 times more exothermic than $FeCH_4^+$, and the Fe–N bonding energy is more than 4 times stronger than Fe–C. Even if the $FeNH_3^+$ and $FeCH_4^+$ species were not observed in the present study (lack of sensitivity), it is very likely that the $FeNH_3^+$ species was formed as a secondary reaction and hindered the analysis.

The 7700x (Q-ICP-MS) integrates also a high energy mode. The potential applied to the collision/reaction cell was fixed at a higher negative value (-100 V) and a higher helium gas flow rate was applied. These new conditions gave an ion energy around 100 eV and allowed for a greater dissociation of ArO^+ by collision with helium. However, the detection limit of iron was slightly decreased (22 ng L^{-1}) due to a reduction of the iron intensity.

The iron interference was properly reduced, leading to the accurate measurement of $^{56}Fe^+$ with measurement errors better than 6% for the two quality check controls. These errors are the lowest compare to the values obtained with the standard method and the cold plasma condition, showing that the use of the collision reaction cell is the most suitable to measure iron with Q-ICP-MS.

3.4. Implementation to iron measurement in the CRM Morille

For the measurement of iron in CRM "Morille", we chose to measure iron with He, even if CH_4 slightly improved the detection limit. Indeed, we observed that Mn, present as an impurity, weakly reacts with CH_4 to form MnH^+ at mass 56 and interfere with the iron analysis. Therefore, using gas to improve sensitivity must be study in terms of sensitivity but also in terms of new interferences that can be formed with other impurities.

In the medium resolution of the SF-ICP-MS, an improvement of both the accuracy and the repeatability was observed for iron (certified value 211.6 ± 6.5 mg kg^{-1} U): a 207.4 ± 13.6 mg kg^{-1} U was obtained with a 3% repeatability in medium resolution by SF-ICP-MS; compared to 189.1 ± 23 mg kg^{-1} U with a 6% repeatability at using of the Octopole Reaction System (ORS) of the Q-ICP-MS. The $^{40}Ar^{16}O^+$ interference was properly resolved on SF-ICP-MS in medium resolution and the measurement of iron could be easily performed at mass 56. However, the measurement values are consistent with both ICP-MS.

4. Conclusion

This study presents a complete analytical procedure from the sample digestion to the concentration determination of 25 impurities in a nuclear grade uranium oxide. After mineralization, the separation procedure allows for a total elimination of the uranium matrix and the subsequent impurities measurement. It limits the pollution and increases the productivity of the instrument. Moreover, this separative step improves the detection limits values compared to the ones obtained with a sample

dilution step. The analytical results are in perfect agreement with the CRM values, except for six elements whose values are slightly underestimated, allowing us to validate our entire procedure.

The polyatomic interference ($^{40}Ar^{16}O^+$), which hinders the analysis of iron ($^{56}Fe^+$) at low level concentration, was significantly reduced following three different ways: cold plasma conditions, medium resolution and ORS mode.

In the standard mode, the SF-ICP-MS presented systematically a better sensitivity that allowed to reach lower concentration level than the Q-ICP-MS (44 vs. 215 ng L^{-1} at mass 57).

With cold plasma conditions, the iron measurement could be made at mass 56 as the formation of $^{40}Ar^{16}O^+$ was drastically reduced. Consequently, the Q-ICP-MS detection limit was improved to 15 ng L^{-1}, compared to 215 ng L^{-1} at mass 57 in the standard mode. Q-ICP-MS showed also better results than the SF-ICP-MS (132 ng L^{-1}).

The lowest detection limits with Q-ICP-MS were achieved using collision/reaction cell. Indeed, a 8 ng L^{-1} detection limits was obtained using CH_4 as a reaction gas and 12 ng L^{-1} with He in a collision process, thus improving the detection limits by a 25 fold factor compare to the standard mode. Similarly, using medium resolution with the SF-ICP-MS allowed to properly reduce the ArO^+ interference and to measure iron at mass 56 with 10 ng L^{-1} detection limit. Finally, iron was measured with a good accuracy (less than 5%) with He as collision gas and with the use of the medium resolution.

The interferences are significantly reduced with the use of the collision/reaction cell, but are not completely removed. Nevertheless, Q-ICP-MS, equipped with the latest generation of collision/reaction cell, have become a key technique for multi-elementary analysis at trace and ultra-trace levels: they are reasonable cost, relatively easy to use and with short time set-up.

Currently, isotopic dilution is investigated to overcome potential problem of separation yield and to improve the measurement accuracy. So far, it has been successfully tested on a round-robin test solution: for all of the seven elements of interest (Ce, Cu, La, Mo, Th, Cd and Mn), results are in perfect agreement with the certified value and with an accuracy better than 5%. In a near future, CRMs with lower certified concentration will be investigated to test the separation yield for elements from different groups.

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