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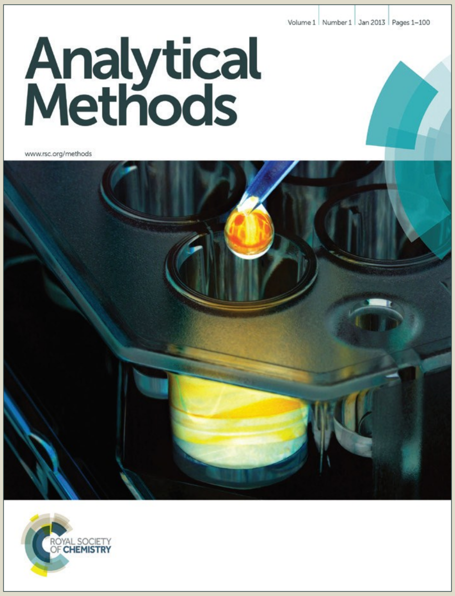

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ARTICLE

Straightforward determination of U, Th, and Hf at trace levels using ultrasonic nebulization and axial view ICP OES

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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Inductively coupled plasma optical emission spectrometry (ICP OES) is applied for direct determination of U, Th and Hf in environmental and geological samples (phosphate rock, soil, sediment, bush branches and leaves, and natural water). Several spectral lines and sample decomposition procedures were investigated with respect to spectral and non-spectral interferences. For U and Hf determination, the geological samples treatment required hydrofluoridric acid, whereas Th could be accurately determined in the samples decomposed by *aqua regia* solely. Ultrasonic nebulization (USN) and pneumatic nebulization with aerosol desolvation (PN-DES), with and without a microporous membrane, were evaluated for introducing the sample solution into the ICP. Better results were obtained by using USN; the limits of detection of U (U II 409. 014 nm), Th (Th II 401.913 nm) and Hf (Hf II 264.141 nm) were 0.03, 0.01, and 0.01 µg g^{-1}, respectively. Uranium, Th and Hf were precisely and acurately determined without matrix separation/analyte pre concentration; the relative standard deviation (RSD) was typically < 7% and the recovery of the analytes in the certified reference materials (phosphate rock, soil, sediment, vegetal, and natural water) ranged from 83 to 112%. These results were linked to careful selection of spectral lines, which depended on the sample matrix and reagents used for sample decomposition.

1 Introduction

Uranium and Th have been used as fuel in nuclear power plants, for electricity generation. Hafnium is a good absorbent of neutrons; therefore, this element has been used in the manufacture of nuclear reactor control rods. Thin films of HfO have been used in modern semiconductor devices by the semi conductor industry, replacing polysilicon. Hafnium is considered non toxic to humans. On the other hand, U and Th are very toxic and can induce the development of cancer.[1-4]

Inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS) are quite convenient for the determination of U, Th Hf. The main advantages of such techniques are the good sensitivity (higher for ICP-MS), wide linear dynamic range and multielement feature. However, despite the great progress of resolution and sensitivity of ICP OES instruments, many spectral inferences have yet to be resolved. Spectral interference is prone to occur in the determination of several elements particularly for U, Th and Hf in light of the rich emission spectra collected from the ICP source. This is more severe when the determination of very low concentrations of these elements in complex matrices is intended - the prominent spectral lines of the analytes cannot be monitored and there is significant emission background of concomitant matrix elements. The situation does not improve by measuring the analyte signal in radially viewed ICP instead of axially viewed ICP because the sensitivity of the former is about one order of magnitude worst.

Prominent spectral lines of U, Th and Hf are coincident with others, depending on the sample matrix. Iron and Ca, major elements present in the environment, are usually responsible for interference in the determination of U, Th and Hf by ICP OES.[5] The effect of Fe on the determination of U and Th was evaluated by Fujino *et al*.[6] They observed that Fe interferes on U(II) 385.96, U(II) 367.01 and U(II) 263.55 nm. However, spectral interference of Fe on U(I) 409.01 and U(II) 393.20 nm was not observed in the determination of U in iron-rich matrices.[2] They also observed that the spectral lines Th(II) 256.56, Th(II) 269.26, Th(II) 283.73, Th(II) 318.02 and Th(II) 401.01 nm were not affected by Fe. The same authors reported that rare earth elements and Th interfered on U determination in apatite mineral if the concentration of the interfering elements was 10 times higher than that of U, depending on the spectral line. In addition, bands are observed in the 175 - 475 nm interval of the emission spectrum of the Ar-ICP operated at atmospheric pressure. These bands correspond to emission of NO, OH and N_2, as a consequence of the rotational energy of these molecules. Thus, it is not possible to monitor the most sensitive spectral line of the analytes because the background is high, worsening the limit of detection (LOD).

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Matrix separation/analyte pre-concentration have been conducted to avoid spectral interference and improve the LOD of U, Hf and Th.[2-4,6-17] Nevertheless, the use of organic solvent should be avoided in this step since it may extinguish the ICP and/or increase spectral and non spectral interferences by carbon. Zaror *et al.*[13] employed anion exchange chromatography for Ca separation in order to avoid interference caused by Ca on U determination by ICP OES. They had observed that Ca caused non-spectral interference on U - the U signal was 30% lower in the presence of Ca, which can be related with ion-to-atom equilibrium shifts in the ICP.

The ICP-MS technique is very suitable for the determination of U, Th and Hf due to the high sensitivity and low spectral interference. However, ICP OES could alternatively be employed when the dissolved solids content in the sample solution is very high and severe matrix effects tend to occur in ICP-MS. It is worth citing that low LOD can be achieved when axial view ICP OES is combined with a high-efficiency nebulizer to introduce the sample solution into the ICP.[18] Ultrasonic nebulization (USN) and pneumatic nebulization with aerosol desolvation (PN-DES) are very useful when the determination of lanthanides and/or actinides elements is intended. The USN and PN-DES systems can be associated with a desolvation membrane, which assists the removal of residual solvent, *i.e.*, the solvent that still remains present after the condensation step. In this way, the additional desolvation may increase the sensitivity and reduce the formation of molecules containing O and/or H, as observed for ICP-MS.[19-24] Molecules such as MO, MOH, XO, XO_2, XOH (M is a metal and X a non- metal) are reduced due to water removal (H and O are removed as a consequence). The oxide formation rate has been reduced at least in one order of magnitude and the limits of detection (LODs, in ng L^{-1}) for PN/DES were 2 - 10 better than those for pneumatic nebulization.[19] Aerosol desolvation led to reduction of U hydride formation by two orders of magnitude.[20]

Straightforward determination of U, Th and Hf at trace levels in real sample using ICP OES has not yet been investigated. The main reason is the occurrence of spectral interference as discussed above. However, such determination might be possible by a systematic wavelength selection.

The determination of U, Th e Hf in environmental and geological samples by means of axial view ICP OES is proposed here. To this end, several spectral lines, different samples preparation procedures and high efficiency nebulizers are evaluated. Thereby, the analytes determination can be possible without laborious matrix separation, which may be analyte-specific and matrix-dependent.

2 Experimental

2.1 Instrumentation

An Optima 2000 DV ICP OES spectrometer (Perkin Elmer, MA, USA) was employed throughout the work. High purity argon (99.996%, White Martins/Praxair, SP, Brazil) was used as plasma gas, auxiliary gas and carrier/nebulizer gas. Nitrogen (99.999%, White Martins/Praxair, SP, Brazil) was used for purging the optical system of the ICP OES instrument. Air was used (as shear gas) to remove the unstable plasma tip. A CETAC U5000AT$^+$ (Ohama, Nebraska, USA) ultrasonic nebulizer and a pneumatic neubulizer/dessolvation system (APEX-Q, ACM, ESI, Omaha, NE, USA) were employed for introducing the solutions into the ICP. The heater and cooler temperature in the USN system were 140 ºC and 3 ºC while those in pneumatic nebulization (PN) were 140 ºC and 2 ºC, respectively. The operational conditions and accessories employed are summarized in Table 1 while the spectral lines monitored are cited in Table 2. The most sensitive spectral lines given in the software of the ICP OES instrument were monitored. A microwave oven (Berghof, Speedwave 4) equipped with PTFE-PFA (polytetrafluoroethylene-perfluoroalkoxy) flasks (for 60 mL and supporting 40 bar) was employed for sample decomposition.

Table 1 Operating conditions of ICP OES and respective accessories

Parameters and accessories	Setting
Plasma power (W)	1300 - 1500
Plasma gas flow rate (L min^{-1})	15
Auxiliary gas flow rate (L min^{-1})	0.2
Nebulizer gas flow rate (L min^{-1})	0.6 for USN and 0.8 for PN
Purging gas (mL min^{-1})	2.5
Injector tube	Alumina (2.0 mm i.d.)
Signal processing mode	Peak area (7 points per peak)
Integration time	Auto (1 - 5 s)
Sample uptake rate (mL min^{-1})	2.5 for USN and 1.0 for PN
Plasma view	Axial

Table 2 Spectral lines monitored and potentially interfering elements

Analyte	State	Wavelength (nm)	Relative[a] Intensity	Potential Interfering
U	I	385.958	7900	Ca, Fe, Th, Sc, Nd, Dy
U	II	367.007	7300	Ca, Fe, Th
U	II	409.014	5700	Fe
U	II	393.203	5200	Th, Fe, Dy
U	II	424.167	2600	Na
Th	II	283.730	20000	Fe
Th	II	283.231	b	
Th	II	274.716	b	Si
Th	II	401.913	21000	
Th	II	339.204	b	Fe, Cu
Hf	II	277.336	46000	Cr
Hf	II	273.876	b	Cr
Hf	II	264.141	51000	
Hf	II	232.247	27000	Fe

I: atomic; II: ionic; a: informed by the manufacturer of the OPTIMA 2000 DV instrument; b: not informed

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2.2 Reagents, standards and solutions

Water (resistivity of 18.2 MΩcm) purified in a Milli-Q system (Milliprore, Billerica, MA, USA) was used to prepare all solutions and samples. Nitric acid (65% m/m), HCl (37% m/m), HF (48% m/m), H_2O_2 (30%), and H_3BO_3 (all from Merck - Darmstadt, Germany) were used for sample preparation. Calibration solutions containing U, Th and HF were prepared in 5% (v/v) HNO_3 (Merck), by serial dilution of monoelement stock solutions of U, Th and Hf containing 1000 mg L^{-1} of the analyte (from Spex Certiprep (Metuchen, NJ USA). The concentration of the calibration solutions ranged from 0.1 to 100 μg L^{-1}. Calibration curves with 5 calibration points were obtained.

2.3 Samples and sample preparation

To following certified reference materials were analyzed: phosphate rock (NIST 694), Montana soil (NIST 2710A) and trace elements in natural water (NIST 1640) from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA); Tibet sediment (NCS DC70319) from National Sciences Foundation of China; and bush branches and leaves (NIM-GBW07602) from National Research Centre for Certified Reference Material (China). Three procedures were investigated for decomposition of the sediment, phosphate rock and soil as is following detailed.

(A) 150 mg of sample were weighed and transferred to the PTFE-PFA flask accompanying the microwave oven; 4 mL HNO_3 + 1 mL HF + 1 mL HCl + 1 mL H_2O_2 were added to the sample in the flask; the flask was closed, placed in the rotor and then transferred to the microwave oven; the mixture was irradiated for 5 minutes at 1015 W - 140 °C, 25 minutes at 1160 W - 175 °C and then cooled for 5 minutes. Subsequently, the flask was opened and 4 ml of 20% (m/v) H_3BO_3 were added to the solution in the flask. The flask was closed again and the mixture was heated at 200 °C for 10 min at 1160 W and then cooled for 5 minutes.

(B) 150 mg of sample were weighed and transferred to the PTFE-PFA flask; 9 mL of *aqua regia* (3 mL HCl + 1 mL de HNO_3) were added to the sample in the flask of the microwave oven, which was subsequently closed; in the microwave oven the mixture was irradiated for 5 minutes at 1015 W – 140 °C, 25 minutes at 1160 W - 200 °C and then cooled for 5 minutes.

(C) 150 mg of sample were weighed and transferred to the PTFE-PFA flask of the microwave oven; 9 mL of *aqua regia* + 1 mL HF were added to the sample in the flask, which was subsequently closed; in the microwave oven the mixture was irradiated for 25 minutes at 1015 W - 140 ^{o}C, 5 minutes a 1160 W - 200 °C and then cooled for 5 minutes.

The solutions obtained in procedures (A), (B), and (C) were transferred to graduated polypropylene vials and the volume elevated to 20 mL by adding water.

The certified bush branches and leaves sample was decomposed as follow: 500 mg of sample were weighed and transferred to PTFE-PFA flask accompanying the microwave oven; 6 mL HNO_3 + 2 mL H_2O_2 were added to the sample in the flask, which was subsequently closed and placed in the microwave oven where the mixture was irradiated for 2 minutes at 1160 W - 170 °C, 2 minutes at 1305 W - 190 °C and then cooled for 20 minutes. The solution obtained was transferred to graduated polypropylene vial and the volume elevated to 20 mL by adding water.

The only treatment given to the certified water (NIST 1640) was matching the HNO_3 concentration in the sample with that of the acid in the calibration solutions

3 Results and discussion

3.1 Sensitivity and LOD

The LODs for the spectral lines and nebulization systems investigated are given in Table 3. The LODs were calculated according to the equation “3s + b”, where b is the average concentration of 10 consecutive analyte determinations in the blank (5% v/v HNO_3) and s is the standard deviation of them. According to Table 3, the LODs are almost similar for the systems employed. By comparing the LODs for PN-DES and PN/DES-MD, one can conclude that the membrane does not improve the LOD. The precision improved by using the membrane, but the sensitivity worsened. This must be a consequence of the water effect in the ICP; the species originating from water, mostly hydrogen, oxygen and OH radicals improve energy transfer in the ICP. Thus, water present at a certain amount in the ICP enhances the sensitivity. In addition, the analyte is probably partially retained in the microporous membrane, reducing the final emission signal.

Table 3 Spectral lines of U, Th and Hf monitored and respective limits of detection as a function of the nebulization systems

Spectral Line	Limit of Detection (μg L^{-1})		
	PN/DES-MD	PN-DES	USN
U (I) 385.958	0.13	0.04	0.07
U (II) 367.007	0.20	0.15	0.06
U (II) 409.014	0.09	0.05	0.03
U (II) 393.203	0.13	0.09	0.10
U (II) 424.167	0.27	0.04	0.17
Th (II) 283.730	0.11	0.08	0.05
Th (II) 283.231	0.10	0.05	0.01
Th (II) 274.716	0.09	0.04	0.01
Th (II) 401.913	0.04	0.01	0.01
Th (II) 339.204	0.04	0.01	0.02
Hf (II) 277.336	0.05	0.02	0.02
Hf (II) 273.876	0.14	0.02	0.02
Hf (II) 264.141	0.03	0.02	0.01
Hf (II) 232.247	0.02	0.02	0.01

USN: ultrasonic nebulization; PN-/DES: pneumatic nebulization/aerossol desolvation; PN/DES-MD: pneumatic nebulization/aerossol desolvation - dessolvation membrane

3.2 Samples analysis

Different reagents were evaluated for decomposition of soil, phophate rock and sediment. Hydrofluoric acid was added to the sample by considering the presence of silicon compounds in the

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analyzed materials, which are solubilized with HF. On the other hand, the investigated elements may form insoluble fluorides,[25] but they can be solubilized with H_3BO_3.

Figure 1 reveals the influence of sample preparation on the precision and accuracy for the wavelengths investigated. By monitoring the spectral line U(II) 393 203 nm, the element was not detected in any sample due to the low intensity of the signal for all sample preparation procedures. Zaror *et al*.[13] used HF and HNO_3 to decompose phosphate rocks and marine sediments to determine U by ICP OES. They observed the U signal was suppressed by Ca, a very easily ionizable element. The concentration of Ca in the samples analyzed in the present work is high (31.1 ± 0.4% Ca in phosphate rock; 0.964 ± 0.045% Ca in Montana soil; 1.00 ± 0.03% Ca in Tibet sediment). Thus, Ca may have suppressed the U 393.203 nm signal. For other spectral lines of U it is seen that the concentration found is higher than the certified one, possibly due to spectral interference caused by Fe.[2,6] The Fe concentration in the analyzed samples is also high - 0.55 ± 0.06% Fe in phosphate rock; 2.89 ± 0.06 % Fe in Montana soil, and 4.11 ± 0.10% Fe in Tibet sediment. Rare earth elements and Th are also interferent of U, causing spectral interference.[6] Sert [26] observed that the spectral lines U(II) 367.007 nm and U(II) 409.014 nm were more appropriate in the determination of U in minerals by ICP OES. The author cited that Fe 385.991 nm interferes on U 385.958 nm. The results obtained in the present work corroborate with those of Sert [26], with the exception of the soil sample. When U was measured by monitoring the U(II) 367.007 nm line, the U concentration found in the soil was higher than that certified, regardless the sample decomposition procedure. As illustrated in Figure 1, procedure C is appropriate for decomposition of samples of the three matrices when the U determination is intended. *Aqua regia* and HF were used in procedure C, improving the sample decomposition. However, the concentration of the interfering elements also increases and, therefore, a judicious selection of the spectral lines is mandatory. For U determination in soil and sediment, the U(II) 409.014 nm line is recommended whereas U(II) 367.007 nm and U(II) 424.167 are for U in phosphate rock, depending on the sample preparation procedure.

With respect to Th, the element is detected at 283.231 nm and 274.716 nm only for procedure C. However, the concentration found is higher than that certified, revealing the existence of spectral interference, probably by Fe (283.310 nm) and Si (274.72 nm), respectively. Spectral interference must also occur at 339.204 nm for Th in soil decomposed according to procedures A and B, and for sediment decomposed according to procedure A. In this case, Fe (339.201 nm) and Cu (339.202 nm) probably interfere. The results for Th in Figure 1 demonstrate that the spectral line 283.730 nm is appropriate. For Th measurement at this wavelength, procedures B and C could be monitored for soil and sediment. Procedure C is only recommended for soil if the spectral line Th(II) 339.204 nm is monitored. Regardless the wavelength, it can be stated that HF and/or *aqua regia* (procedures B and C) are essential for decomposition of soil and sediment with the end of Th quantification.

Method C is also appropriate for Hf. This can be explained by the fact that Hf becomes a passive metal in presence of HNO_3 (used in procedures A and B), producing insoluble oxides. These oxides should be soluble in the solution obtained according to procedure A, but H_3BO_3 may have interfered. It is important to remark that H_3BO_3 was added in order to improve the solubility of fluoride compounds of the actinide elements. In Figure 1 it can be seen that interference has occurred at 273.876 nm for procedures A B, and C. The Hf signal was probably overlapped by Cr (273.938 nm). In contrast, Hf was not detected at 232.247 nm for any sample preparation procedure investigated. Figure 1 indicates that Hf in soil should be measured in 264.141 nm while in sediment it should be at 277.336 nm in order to obtain more accurate results.

Table 4 summarizes the spectral lines and sample preparation procedures recommended for each analyte and matrix investigated. In Table 4 it can be seen that procedure C allows obtaining accurate results for soil, sediment and phosphate rock, which is dependent of the spectral line monitored. Hydrofluoric acid or *aqua regia* is necessary for Th (procedures B and C) and Hf (procedure C). Unlike U, H_3BO_3 is not recommended for Th and Hf. However, for U determination in the investigated matrices by means of ICP OES it is not necessary H_3BO_3 (procedure A) to prepare the sample because accurate results can be obtained using procedures B and C solely.

Table 4 Spectral lines and sample decomposition procedures (A, B, C - detailed on section 2.3) recommended for U, Th and Hf determination in soil, sediment and phosphate rock.

Spectral Line (nm)	Decomposition Procedure		
	Soil	Sediment	Phosphate Rock
U (II) 409.014	C	C	A
U (II) 367.007	-	-	A, C
U (II) 424.167	A, B	-	B
Th (II) 283.730	B	B	-
Th (II) 339.204	C	-	-
Hf (II) 277.336	C	C	-
Hf (II) 264.141	C	-	-

In a subsequent step, the investigated elements were determined in the certified samples. The analyte concentrations found in the samples are given in Tables 5 and 6 where one can note that accurate results were obtained; the concentrations determined were in agreement with those certified or expected for the spiked sample. By considering the mean uncertainty, the concentrations found agree with those certified with 95% of confidence, with the exception of Hf in Montana soil. However, the Hf concentration in this material is not certified; only an informative value is given on the respective certificate.

All nebulization systems employed contribute for reduction of oxides and molecules in the ICP[27] because of water removal. They could, in principle, be employed for introducing the solution into the ICP in order to determine U, Th and Hf by ICP OES.[27] The PN/DES system was also employed, but most results were not accurate (only the Th concentration in Tibet sediment was in agreement with that certified). When comparing the performances of USN and PN-DES in the determination of U, Th and Hf, the superiority of USN was evident. The better performance of the USN can be explained by the quality of the aerosol produced; the diameter of 90% of the droplets

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that constitute the aerosol range from 4 µm to 30 µm. This way, a greater amount of sample is transported to the ICP by means of USN, increasing the sensitivity. [28,29] The high density of the aerosol produced also facilitates the analyte conversion to atomic and ionic species in the ICP, improving the accuracy of the results.

Two other samples (bush branches and leaves and natural water) were analyzed (Table 6). By comparing Tables 5 and 6 it is seem that several spectral lines selected for soil, sediment and phosphate rock are not appropriate for bush branches and leaves. In this sample there are 0:20% Al, 1.68% Ca, 0:48% Mg, 0.1% P, 0.92% K, 0.60% Si, 1.96% Na, and 0.73% S. The higher concentrations found of U 385.958 nm, U 367.007 nm, U 409.014 nm, and U 424.167 nm can be explained by interference of Ca, Fe and Na, respectively (Table 2). In the case of Th 283.730 nm, Th 274.716 nm and Th 339.204 nm, interference of Fe, Si and Cu may have occurred (Table 2). Iron may have also interfered on Hf 232.247 nm. As indicated in Table 2, Cr interferes on Hf 273.876 nm. Although the concentration of Cr is low (2.6 µg g^{-1}) in the certified sample, the Hf concentration found is compatible with that of Cr. Thus, the highest concentration of Hf may be due to interference of Cr. Changes in the ICP atmosphere, which are dependent of the sample matrix and reagents used for sample treatment[27] can also contribute to inaccuracy. Such non spectral interference led to signal suppression of Th 283.231 nm and Hf 277.336 nm in bush branch and leaves. With respect to natural water, whose matrix is 5% (v/v) HNO_3 (the acid concentration was similar in the calibration solutions) and where only trace elements are present, signal suppression is observed for several spectral lines monitored. In this case, additional studies must be conducted for drawing more concrete conclusions about the signal suppression observed,

Table 5 Concentrations (average ± standard deviation, n = 3) of U, Th and Hf determined in the certified reference materials. USN was used for introducing the solution into the ICP

Analyte	Certified (µg g^{-1})	Found (µg g^{-1})
	Phosphate Rock (NIST 694)	
U(II) 424.167	141.14 ± 0.0036	138.28 ± 5.12 [B]
Th(II) 283.730	33.33[a]	33.20 ± 0.16 [C]
Hf(II) 273.876	33.33[a]	33.33 ± 0.67 [B]
	Montana Soil (NIST 2710[a])	
U(II) 409.014	9.11 ± 0.30	9.48 ± 0.19[C]
Th(II) 339.204	18.1 ± 0.30	18.0 ± 1.0[C]
Hf(II) 264.141	7	9.77 ± 0.15[C]
	Tibet Sediment (NCS DC70319)	
U(II) 367.007	4.8 ± 0.4	5.4 ± 1.6[C]
Th(II) 283.730	25.5 ± 1.2	26.1 ± 0.4[B]
Hf (II) 277.336	9.5 ± 1.0	7.84 ± 0.76[C]

[a] Sample spiked with the analyte before decomposition;
B, C: decomposition procedure (see section 2.3)

Table 6 Concentrations (average ± standard deviation, n = 3.) of U, Th and Hf determined in the certified samples; USN was used for introducing the solution into the ICP

Analyte	Bush Branches and Leaves (NIM-GBW07602)		Natural Water (NIST 1640)	
	Certified (µg g^{-1})	Found (µg g^{-1})	Certified (µg L^{-1})	Found (µg L^{-1})
U 385.958	(0.11)[a]	36.08 ± 1.73	25.35 ± 0.27	18.66 ± 0.71
U 367.007	(0.11) [a]	8.22 ± 0.05	25.35 ± 0.27	24.23 ± 1.06
U 409.014	(0.11) [a]	0.82 ± 0.08	25.35 ± 0.27	26.71 ± 1.57
U 393.203	(0.11) [a]	< 0.10	25.35 ± 0.27	< 0.10
U 424.167	(0.11)	4.04 ± 0.14	25.35 ± 0.27	25.10 ± 1.61
Th 283.730	0.37 ± 0.02	2.32 ± 0.01	1.619 ± 0.016	< 0.05
Th 283.231	0.37 ± 0.02	< 0.01	1.619 ± 0.016	< 0.01
Th 274.716	0.37 ± 0.02	27.77 ± 0.57	1.619 ± 0.016	1.29 ± 0.54
Th 401.913	0.37 ± 0.02	0.42 ± 0.03	1.619 ± 0.016	< 0.01
Th 339.204	0.37 ± 0.02	1.94 ± 0.06	1.619 ± 0.016	< 0.02
Hf 277.336	0.14 ± 0.02	< 0.02	-	< 0.02
Hf 273.876	0.14 ± 0.02	1.70 ± 0.05	-	< 0.02
Hf 264.141	0.14 ± 0.02	0.14 ± 0.04	-	0.32 ± 0.08
Hf 232.247	0.14 ± 0.02	7.93 ± 0.16	-	< 0.01

[a:] non certified, only informative value.

4 Conclusions

It has been demonstrated that direct determination (without matrix separation/analyte pre concentration) of U, Th and Hf in geological and environmental samples is possible using axially viewed ICP OES and USN. Accurate results were found by using USN for introduction the sample solution into the ICP instead of PN-DES. In order to obtain accurate results, the wavelengths were carefully selected, which depended on the sample matrix and reagents used for sample decomposition. In general, the use of HF is mandatory for obtaining accurate results in geological samples. In the case of Hf, *aqua regia* must also be added to the sample in view of insoluble compounds generated during sample decomposition.

Acknowledgements

The authors thank CAPES, CNPq and FAPERGS for financial support and scholarships provided.

References

1 V. K. Jain, R. A. Pandya, S. G. Pillai and P. S. Shrivastav, *Talanta,* 2006, **70**, 257.
2 O. Fujino, S. Umetani, E. Uenoa, K. Shigeta and T. Matsuda, *Anal. Chim. Acta,* 2000, **420**, 65.
3 S. R. Yousefi, S. J. Ahmadi, F. Shemirani, M. R. Jamali and M. Salavati-Niasari, *Talanta,* 2009, **80**, 212.
4 S. Shariati, Y. Yamini and M. K. Zanjani, *J. Hazard. Mater.,* 2008, 156, 583.
5 A. A. Ghazi, S. Qamar and M. A. Atta, *Spectrochim. Acta B,* 1994, **49**, 527.

Analytical Methods Accepted Manuscript

6 O. Fujino, S. Umetani and M. Matsui, *Anal. Chim. Acta,* 1994, **296**, 63.

7 G. Daneshvar, A. Jabbari, Y. Yamini and D. Paki, *J. Anal. Chem.*, 2009, **64**, 602.

8 F. A. Aydin and M. Soylak, *Talanta*, 2007, **72**, 187.

9 E. R. Unsworth, J. M. Cook and S. J. Hill, *Anal. Chim. Acta*, 2001, **442**, 141.

10 G. V. Britsom, B. Slowikowski and M. Bickel, *Sci. Total Environ.* 1995, **173**, 83.

11 A. Sabarudin, O. Noguchi, M. Oshima, K. Higuchi, and S. Motomizu, *Microchim. Acta*, 2007, **159**, 341V. K. Jain, R. A. Pandya, S. G. Pillai and P. S. Shrivastav, *Talanta,* 2006, **70**, 257.

12 E. Kamata, R. Nakashima and M. Furukawa, *J. Anal. At. Spectrom.*, 1987, **2**, 321.

13 O. A. Zaror, R. S. Juarez, E. Zeiller and R. Zeisler, *Fresenius J. Anal. Chem.,*1996*,* **355**, 694.

14 N. Bahramifar and Y. Yamini, *Anal. Chim. Acta,* 2005, **540**, 325.

15 M. Ayranov, J. Cobos, K. Popa and V. V. Rondinella, *J. Rare Earths*, 2009, **27**, 123.

16 M. R. Jamali, Y. Assadi, F. Shemirani, M. R. M. Hosseini, R. R. Kozani, M. Masteri-Farahaniand M. Salavati-Niasari, *Anal. Chim. Acta,* 2006, **579**, 68.

17 J. S. Santos, L. S. G. Teixeira, R. G.O. Araújo, A. P. Fernandes, M. G. A. Korn and S. L.C. Ferreira, *Microchem. J.*, 2011, **97,** 113.

18 F.R.S. Bentlin, D. Pozebon, J. *Braz. Chem. Soc*. 2010, **21**, 626.

19 V. L. Dressler, D. Pozebon, A. Matusch and J. S. Becker, *Inter. J. Mass Spectrom*., 2007, **266,** 25.

20 C. S. F. Boulyga, J. L. Matusevich, V. P. Mironov, V. P. Kudrjashov, L. Halicz, I. Segal, J. A. McLean, A. Montaser and J. S. Becker, *J. Anal. At. Spectrom*. 2002, **17**, 958.

21 S. Yousefi J. Ahmadi, F. Shemirani, M. R. Jamali and M. Salavati-Niasari, *Talanta,* 2009, **80**, 212.

22 M. E. Wieser, D. Buhl, C. Boumanand J. Schwieters, J. *Anal. At. Spectrom.*, 2004, **19**, 844.

23 S. D'Ilio, N. Violante, S. Caimi, M. Di Gregorio, F. Petrucciand O. Senofonte, *Anal. Chim. Acta*, 2006, **573**, 432.

24 M. P. Aliaga-Campuzano, J. P. Bernal, S. B. Briceño-Prieto, O. Pérez-Arvizuand E. Lounejeva, *J. Anal. At. Spectrom.*, 2013, **28**, 1102.

25 M. F. L'Annunziata, *Handbook of Radioactivity Analysis*, Academic Press, 3rd edn., 2012.

26 S. Sert, *Appl. Spectrosc.,* 2013, **67**, 731.

27 M. Grotti, C. Lagomarsino and J. M. Mermet, *J. Anal. At. Spectrom,* 2006, **21**, 963.

28 M. A. Tarr, G. Zhu, and R. F. Browner, *Appl. Spectrosc.,* 1991, **45**, 1424.

29 T. M. Castillano, N. P. Vela and J. A. Caruso, *J. Anal. At. Spectrom.,* 1992, **7**, 807.

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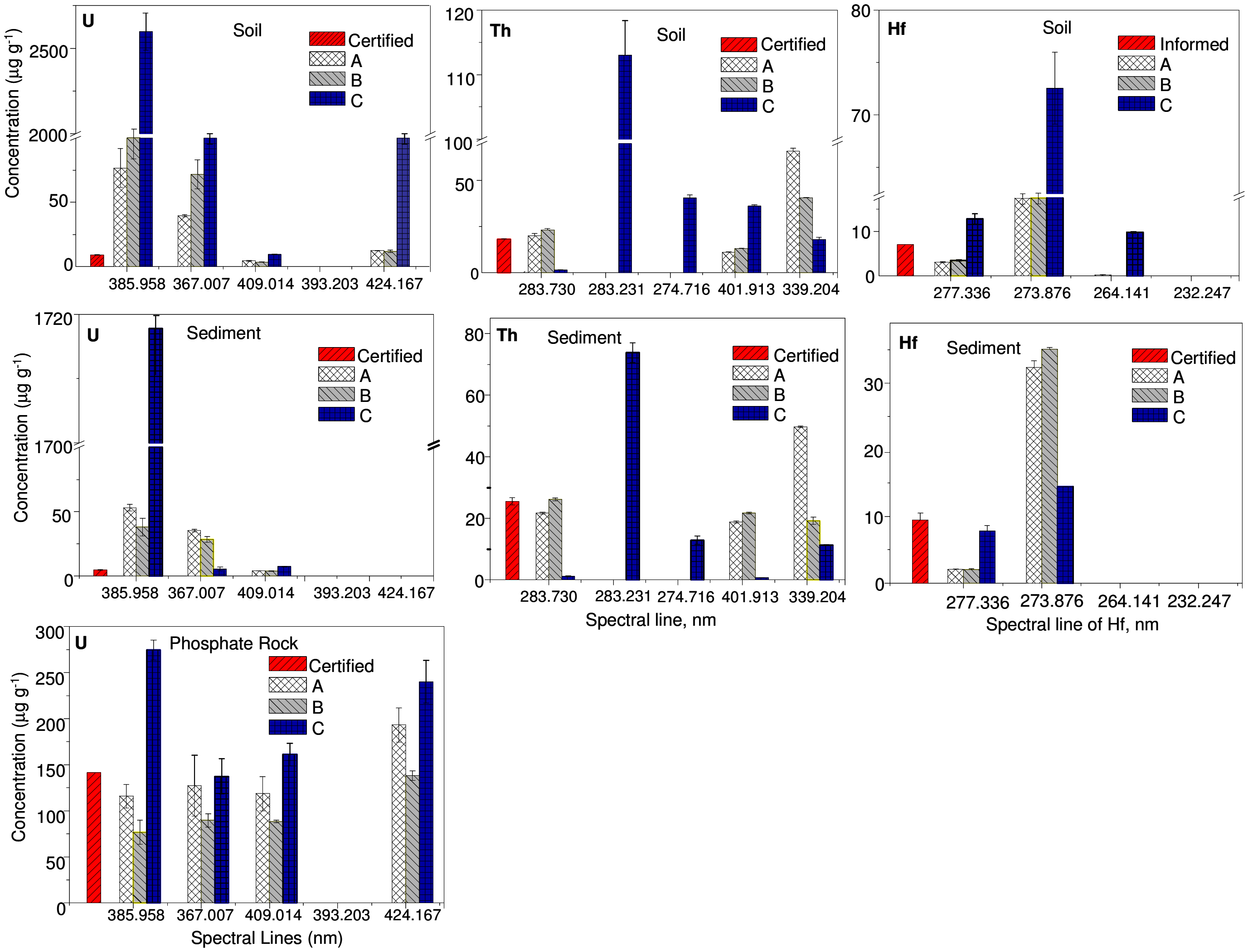
Figure 1 Element concentrations found in certified soil, sediment and phosphate rock as a function of sample preparation procedures (A, B, and C - described on section 2.3) and wavelength monitored. USN was employed for introducing the sample solution into the ICP. The LOD for each spectral line is given in Table 3. Th and Hf in phosphate rock (not shown) are not certified.



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Low concentrations of U, Hf, and Th were quantified using USN and axial view ICP OES, without matrix separation/analyte precontration.

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