

Short Report

Simultaneous Determination of Thorium and Uranium in Mineral Fertilizers by Inductively Coupled Plasma Optical Emission Spectrometry

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The simultaneous determination of thorium and uranium in mineral fertilizers by inductively coupled plasma optical emission spectrometry (ICP OES) was optimized. The three-level factorial design was applied to optimize the operating conditions of radiofrequency power and nebulizer gas flow rate. The analytical method was specific and selective for both elements.

Keywords: thorium, uranium, simultaneous determination, experimental design, ICP OES

Introduction

In recent decades, food security has become an aspect of great concern regarding environmental safety due to the accumulation of toxic chemicals in the environment, caused by the emission of natural and anthropogenic sources.¹⁻⁹

Among the anthropogenic sources, mineral fertilizers used as supplies to provide chemical elements and needed nutrients for the plants can be highlighted. In recent years, with the expansion of agricultural activities, there has been an increase in the implementation of the same inefficient use of the planting areas that ended up in negative environmental consequences, such as pollution, biodiversity loss, soil nutrients imbalance, salinization, besides economic damage and human and animal health harm, as a result of the introduction of contaminants from various sources used in the manufacturing process of agricultural supplies.^{1-6,10}

Nitrogen, potassium and sulfur-based fertilizers are relatively free of contaminants, but the phosphate fertilizers, derived from phosphate rock, may contain several contaminants, such as As, Be, Cd, Cr, F, Hg, Mn, Pb, Sr, Th, U, V and Zr, and the concentrations of these depend on the geological origin and location of phosphate rock mining.¹¹⁻¹³

The actinide elements thorium and uranium are important from the point of view of technological applications, especially in metallurgy, ceramics and nuclear industry. They occur naturally in the environment at concentrations of 10-15 and 2-4 mg kg⁻¹, respectively.^{14,15} These trace elements are found in soil, rocks, water and other samples, and can be incorporated into the human food chain.¹⁶ Their metal ions are known to cause acute toxicological effects on humans, and their compounds are potential carcinogenics.¹⁷⁻¹⁹

Aiming harmless food production, in recent decades, some countries have established limits for contaminants in mineral fertilizers. In Canada, through the Federal Fertilizers Act, limits for the contents of As, Cd, Pb and Zn were adopted.²⁰ In the United States one federal law controls the content of contaminants in fertilizers, through the regulation published in July 24, 2002 by the United States Environmental Protection Agency (USEPA), which establishes limits for content of As, Cd, Cr, Pb and Hg in zinc-based fertilizer.²¹ Besides each state having its own regulation, in Brazil, the Ministry of Agriculture, Livestock and Food Supply (Ministério da Agricultura, Pecuária e Abastecimento (MAPA)), through the Normative No. 27 (June 5, 2006), established the maximum limits for contaminants, such as As, Cd, Cr, Pb and Hg in mineral fertilizers as well as the percentage of phosphorus pentoxide (P₂O₅) used in the manufacture of fertilizer.²²

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Thorium and uranium determination in various types of matrices and by different techniques and methods has been widely reported in the literature. Krejčova *et al.*²³ carried out the determination of Th, U and other elements in several related river species (fish, insects, benthos) by orthogonal time-of-flight (o-TOF) inductively coupled plasma mass spectrometry (ICP-MS). Avivar *et al.*²⁴ performed the determination of Th and U, at trace level, in environmental samples using solid-phase extraction online connected to ICP-MS. The determination of Th, U and Ra isotopes in samples of water and soil was accomplished by alpha spectroscopy, as described by Hao *et al.*²⁵ According to Zoriy *et al.*,²⁶ Th and U concentrations in plant samples were determined using quadrupole ICP-MS. Abdul-Hadi *et al.*²⁷ used energy dispersive X-ray fluorescence spectrometry (EDXRF) to determine the concentrations of Th, U and K in rock samples. Determination of Th and U by inductively coupled plasma optical emission spectrometry (ICP OES) is described in many studies reporting separation processes of these two elements, in order to avoid spectral interferences caused by emission lines of Th on the lines of the U, as for example, described by Daneshvar *et al.*¹⁸ that determined Th and U in natural water samples by ICP OES after extraction and pre-concentration.

The determination of U by ICP OES may find some drawbacks due to spectral interferences caused by rare earth elements, calcium, iron, vanadium and zirconium. Thorium can also interfere in the determination of U, depending on the choice of the emission line, whose selection for analysis by ICP OES must take into account the following parameters: sensitivity, spectral interferences, sample matrix and the expected concentrations of the elements.²⁸⁻³⁰

Different empirical methods were developed, such as combination of arrays, internal standardization, standard addition and methods based on empirical modeling, to correct matrix effects in ICP OES.²⁹⁻³¹ The current optical spectrometers are equipped with grid echelle and charged-coupled devices (CCD), which improve the measurements of several spectral lines, allowing the separation of emission peaks and minimizing the overlap lines, thus enabling to perform simultaneous measurements.^{28,31-36}

The intensity of a spectral line depends on the experimental parameters of the ICP OES instrument, radiofrequency power, nebulizer gas flow and plasma observation site (axial or radial), which can be optimized. The adjustment of these operating parameters allows a robust condition for analysis, in which the ICP system resists changes in concentration of the concomitants in the matrix with no significant variation in the intensity of the emission line of analytes.^{28,31-34}

This work proposes the optimization of an analytical method for the simultaneous determination of Th and U in mineral fertilizers by ICP OES.

Experimental

Instrumentation

An ICP OES with axial view (View Pro, Varian, Mulgrave, Australia) and solid state detector cooled to -35°C by a Peltier system was employed in all measurements. The echelle polychromator is maintained at 34°C and purged with argon 99.9999% (White Martins, São Paulo, Brazil), allowing measurements in the spectral range of 167-785 nm. The observation zone in the axially viewed system was automatically set by the program supplied with the axial view control software using the Mn II 257.610 nm emission line. The operating conditions established are shown in Table 1.

Table 1. Characteristics and operating conditions used for analysis by ICP OES with axial view

Parameter	Condition
Radiofrequency power / kW	1.0
Plasma gas flow rate / (L min ⁻¹)	15.0
Auxiliary gas flow / (L min ⁻¹)	1.5
Nebulizer gas flow rate / (L min ⁻¹)	0.9
Nebulizer type	concentric, SeaSpray
Spray chamber type	cyclone
Replicates	3
Injector tube diameter / mm	2.4
Signal integration time / s	1.0
Background corrector	automatic mode on
Wavelength / nm	Th II: 401.913; U II: 385.957; Mg I: 285.208; Mg II: 280.265; Ca II: 373.690; Fe II: 259.940

I: Atomic line; II: ionic line.

External calibration was used for the determination of the elements. For Th and U an intermediate solution was prepared by dilution of a 1000 mg L⁻¹ stock solution (Specsol®) to a concentration of 100 mg L⁻¹. Another 1000 mg L⁻¹ stock solution (Specsol®) containing Ca and Fe was diluted according to the calibration range. The calibration curves were prepared in concentrations from 0.4 up to 4.0 mg L⁻¹ for Th and U, and from 5.0 up to 200.0 mg L⁻¹ for Ca and Fe, six solutions including the blank.

Sampling, sample preparation and addition, and recovery test

Mineral fertilizer samples were obtained in the state of Sergipe, Brazil, and analyzed. The procedure employed

in the preparation of the samples had been optimized in another study carried out by our group.³⁷ The first step of the procedure was drying under mild conditions, in an oven with air circulation for 48 h at the temperature of 40 °C, in order to prevent the loss of volatile elements such as mercury. Prior to digestion, the samples were ground in a mortar, and sieved to achieve fine particle size smaller than 150 µm.

A mass of approximately 0.20 g (dry weighed) of the samples was introduced into Teflon pumps, suitable for block digestion, and then, 1.4 mL of concentrated HNO₃ (65% m/m), 1.0 mL of H₂O₂ (30% m/m) and 7.6 mL of deionized water were added to a final volume of 10.0 mL. The system was closed and the samples were heated and kept at 180 °C for 2 h. After digestion the samples were transferred to volumetric flasks, and completed to a final volume of 25.0 mL with deionized water.³⁷

For addition and recovery test 1.0 mg L⁻¹ of Th and U was added to five different samples of commercial fertilizer and standard reference materials (SRMs), Florida Phosphate Rock (National Institute of Standards and Technology (NIST) SRM 120c) and Western Phosphate Rock (NIST SRM 694). The procedure was applied to the samples, blank solutions and SRMs in triplicate.^{38,39}

Results and Discussion

Evaluation of the operating conditions of the ICP OES using three-level full factorial design

The emission intensities of Th and U were measured at different wavelengths available on spectrometer program

software for Th (268.429, 269.242, 274.716, 283.730, 288.505, 318.019 and 401.913 nm) and U (263.553, 294.192, 367.007, 385.464, 385.957 and 409.013 nm). This procedure allowed the selection of the lines considered more sensitive and free of spectral interferences, since the spectrometer has a resolution of 0.002 nm. The lines chosen for subsequent steps of the study were wavelengths of 401.913 nm for Th and 385.957 nm for U.

A three-level factorial design with two variables, in which the central point was quintuplicated, was applied to optimize the operating parameters of the ICP OES. The variables evaluated were radiofrequency power (RFP) and nebulizer gas flow rate (NGF). The matrix of the factorial design is shown in Table 2. The experimental data were treated using Statistica 8.0[®] software.

The response of the factorial design was evaluated through the intensities of Th and U and the ratio of the emission intensities of the atomic and ionic lines of magnesium [Mg II (280.265 nm)/Mg I (285.1213 nm)]. For Mg II/Mg I ratio, a value greater than 8.0 indicates the plasma robust conditions, which minimizes interferences from the ICP system allowing to adapt changes in the concentrations of the major elements, acids, and other components with no significant variation in the intensities of analyte lines.^{32,33}

The normalization of the intensities of Th, U and Mg II/Mg I ratio were performed dividing each value by the highest value of each response according to the concept of multiple response (MR) (equation 1) obtained through the sum of the three individual responses (intensity of Th, intensity of U and Mg II/Mg I ratio):

Table 2. Matrix of the three level factorial design and two variables

Experiment	RFP / kW	NGF / (L min ⁻¹)	Intensity of Th / cps	Intensity of U / cps	Mg II/Mg I ratio	Normalized intensity of Th	Normalized intensity of U	Normalized Mg II/Mg I ratio	Multiple response
1	1.0	0.6	7673	2532	10.0	0.647	0.726	0.762	2.13
2	1.0	0.8	9738	2691	8.4	0.822	0.771	0.639	2.23
3	1.0	1.0	9718	2790	8.4	0.820	0.800	0.639	2.26
4	1.2	0.6	4403	2172	10.2	0.372	0.622	0.777	1.77
5	1.2	0.8	9059	3144	11.7	0.764	0.901	0.890	2.56
6	1.2	1.0	8761	2961	11.4	0.739	0.848	0.870	2.46
7	1.4	0.6	6180	2429	13.1	0.521	0.696	1.000	2.22
8	1.4	0.8	10041	3211	12.2	0.847	0.920	0.927	2.69
9	1.4	1.0	11852	3490	11.6	1.000	1.000	0.880	2.88
10	1.2	0.8	8897	2964	11.4	0.751	0.849	0.864	2.46
11	1.2	0.8	8897	2964	11.6	0.751	0.849	0.879	2.48
12	1.2	0.8	9024	2865	11.7	0.761	0.821	0.887	2.47
13	1.2	0.8	8102	2745	11.4	0.684	0.787	0.868	2.34
14	1.2	0.8	9006	2593	11.3	0.760	0.743	0.862	2.37

RFP: radiofrequency power; NGF: nebulizer gas flow rate.

$$MR = \frac{\text{Intensity of Th}}{\text{Maximum intensity of Th}} + \frac{\text{Intensity of U}}{\text{Maximum intensity of U}} + \frac{(\text{Mg II/Mg I}) \text{ ratio}}{\text{Maximum (Mg II/Mg I) ratio}} \quad (1)$$

wherein intensity of Th is the intensity measured at wavelength 401.913 nm; maximum intensity of Th is the intensity measured at wavelength 401.913 nm in the factorial design proposed; intensity of U is the intensity measured at wavelength 385.957 nm; maximum intensity of U is the intensity measured at wavelength 385.957 nm in factorial design proposed; (Mg II/Mg I) ratio is the value between the intensities of the Mg II (280.265 nm) and Mg I (285.208 nm) emission lines, and maximum (Mg II/Mg I) ratio is the maximum value of the ratio between the intensities of the emission lines found in the experiments.

Observing the Pareto chart with standardized effect estimate (absolute value), shown in Figure 1, it is possible to confirm that all variables were significant for the system, as well as the interactions between them. The most significant variable was the linear NGF since it increases the efficiency of aerosol generation reaching the plasma, i.e., a large

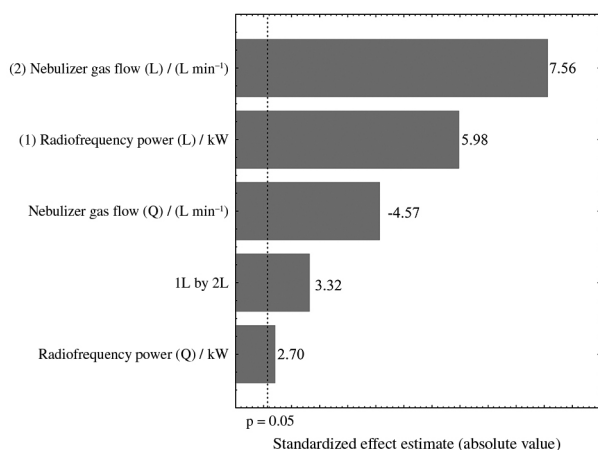


Figure 1. Pareto chart for the three level factorial design for two variables (effects of the RFP and NGF). L: Linear parameter; Q: quadratic parameter.

Table 3. ANOVA results obtained for the 3² factorial design

Parameter	S.S.	d.f.	M.S.	F-value	p-value
(1) RFP (L + Q) / kW	2.75×10^{-1}	2	2.75×10^{-1}	4.30×10^1	4.46×10^{-2}
(2) NGF (L + Q) / (L min ⁻¹)	4.98×10^{-1}	2	4.98×10^{-1}	7.80×10^1	6.67×10^{-3}
1L by 2L	7.00×10^{-2}	1	7.00×10^{-2}	1.10×10^1	2.11×10^{-2}
Lack of fit	7.50×10^{-2}	3	2.50×10^{-2}	3.90	8.84×10^{-2}
Pure error	3.20×10^{-2}	5	6.00×10^{-3}	–	–
Total sum	9.08×10^{-1}	13	–	–	–

S.S.: Sum of squares; d.f.: degrees of freedom; M.S.: mean square; RFP: radiofrequency power; L: linear parameter; Q: quadratic parameter; NGF: nebulizer gas flow.

amount of atoms are excited. The linear RFP is the second most significant variable.

The more RFP is increased, the more the increase in the energy available to excite Th atoms will be and, consequently, the higher the intensity of the emission lines of the analyte will be.²⁸ The interaction between the variables was also positive, showing the direct relation of the RFP and NGF on the increase of the intensity of both elements.

To evaluate the fitting of the model, the data analysis of variance (ANOVA) was applied. A summary of the ANOVA results is given in Table 3. The regression model was significant for a 95% confidence level ($F_{\text{calculated } 2,11} = 10.34$; $F_{\text{tabulated } 2,11} = 3.98$; $p\text{-value} = 2.96 \times 10^{-3}$). The lack of fit was evaluated through the F-test, wherein $F_{\text{calculated}} (3.90)$ was less than $F_{\text{tabulated}} (19.40)$, showing no lack of fit ($p\text{-value} = 8.84 \times 10^{-2}$).^{40,41}

The evaluation of the model was also done by correlation between the predicted values and obtained values and the results (Figure 2) show a good correlation between the proposed experiments by the 3² factorial design with two variables, expressed by correlation coefficient (r) equal to 0.96.

After statistical analysis, it was possible to attest that a better condition is achieved when there is a combination of

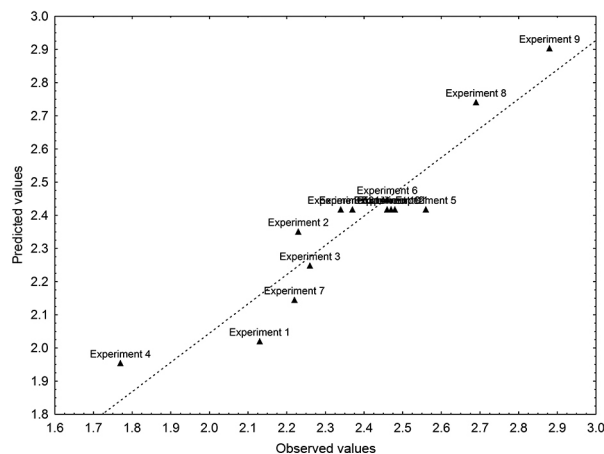


Figure 2. Graph of the predicted values vs. observed values for each experiment of the proposed factorial design ($r = 0.96$).

RFP and NGF in high levels, especially for atoms and ions with high energy excitation, as Th and U.⁴² The operating conditions of the ICP OES were evaluated through the global response calculated from the sum of the responses regarding the intensities of Th and U, and Mg II/Mg I ratio (equation 1). The best overall response obtained was the combination of the RFP of 1.4 kW and NGF of 1.0 L min⁻¹, but at these working conditions, higher power requires more frequent maintenance of the radiofrequency source and it causes an increased wear of the torch.

Therefore, the operating conditions adopted for this work were RFP of 1.0 kW and NGF of 0.9 L min⁻¹ at the critical point, evaluated through the multiple response, since all values obtained were higher than 8.0 (Table 2), a clear indication of the robustness of the plasma because, at these conditions, an effective energy is transferred to analytes running through the central channel of the plasma.^{33,42-44}

Analytical parameters

Limits of detection and quantification

The limits of detection (LOD) and quantification (LOQ) were calculated by the background equivalent concentration (BEC) and the signal-to-background ratio (SBR), according to the International Union of Pure and Applied Chemistry (IUPAC): $BEC = C_{\text{standard}} / SBR$, for $SBR = (I_{\text{standard}} - I_{\text{blank}}) / I_{\text{blank}}$; C_{standard} is the reference element concentration in the standard solution, I_{standard} and I_{blank} are the emission intensities for the reference element and blank solutions, respectively, at the selected wavelength.^{45,46}

The LOD was then calculated as $(3 \times RSD_{\text{blank}} \times BEC) / 100$ and $LOQ = (10 \times RSD_{\text{blank}} \times BEC) / 100$, where RSD_{blank} is the relative standard deviation of ten measurements of the emission intensity of the blank solution at the selected

wavelength.^{45,46} The LOD values were 0.6 to 0.8 $\mu\text{g g}^{-1}$ for Th and U, respectively. The LOQ values were 2.2 and 2.5 $\mu\text{g g}^{-1}$ for Th and U, respectively, as shown in Table 4.

The LOD and LOQ values obtained in this work for simultaneous determination of Th and U are comparable to those reported in the literature using separation and preconcentration techniques.^{17,47-50} The analytical methods using ICP-MS present LOD values better than those by ICP OES technique (ng g^{-1} vs. $\mu\text{g g}^{-1}$, respectively), but ICP-MS is also susceptible to interference and is much more expensive.

Accuracy and precision

The accuracy of the method was evaluated by analysis of NIST SRMs 694 and 120c, and the found values compared with the certified values were in good agreement for U (Table 5), 89 ± 4 and $90 \pm 10\%$ ($n = 3$), respectively, calculated according to equation 2,

$$\text{Agreement (\%)} = \frac{\text{Found value}}{\text{Certified value}} \times 100 \quad (2)$$

in which the found value is the concentration obtained in the determination of the analytes by the method and the certified value is the one reported in the SRMs certification document. The precision, expressed as relative standard deviation (RSD), was better than 4.3% ($n = 3$) for analysis of the SRMs for uranium determination.

For Th, addition and recovery tests, using 125.0 mg kg^{-1} (or 1.0 mg L^{-1}) of the analyte, were performed in NIST SRMs 694 and 120c, and the recoveries were 94 ± 7 and $97 \pm 5\%$ ($n = 3$), respectively. The RSDs for addition and recovery tests for both elements were better than 3.0% for Th and 4.4% for U (Table 6). Recovery tests were performed since SRMs do not contain certified value for

Table 4. Values of background equivalent concentration (BEC), limits of detection (LOD) and quantification (LOQ) for simultaneous determination of Th and U by ICP OES

Parameter	BEC / ($\mu\text{g L}^{-1}$)	LOD ^a / ($\mu\text{g L}^{-1}$)	LOQ ^a / ($\mu\text{g L}^{-1}$)	LOD ^a / (mg kg^{-1})	LOQ ^a / (mg kg^{-1})
Th (401.913 nm)	13.0	5.0	18.0	0.6	2.2
U (385.957 nm)	15.0	6.0	20.0	0.8	2.5

^aLimits established using 0.20 g of sample in a final volume of 25.0 mL. BEC: Background equivalent concentration; LOD: limit of detection; LOQ: limit of quantification.

Table 5. Certified values, found values, RSD and agreement between the values of U in standard reference materials (SRMs)

NIST SRM	Certified value / %	Found value ^a / %	RSD / %	Agreement ^b / %
694 (as U)	0.01414 \pm 0.00006	0.01252 \pm 0.00057	1.8	89 \pm 4
120c (as U ₃ O ₈)	0.0135 \pm 0.0002	0.0122 \pm 0.0013	4.3	90 \pm 10

^aMean \pm confidence interval at 95% ($n = 3$); ^bagreement = [(found value / certified value) \times 100]. NIST standard reference material (SRM) 694: Western Phosphate Rock; NIST SRM 120c: Florida Phosphate Rock; RSD: relative standard deviation.

Table 6. Results of concentration values of the potential interfering elements, added and found, relative standard deviation and recovery for Th and U

Sample	Potential interfering element		Th					U				
	Ca / (mg kg ⁻¹)	Fe / (mg kg ⁻¹)	Found value / (mg kg ⁻¹)	Added concentration / (mg kg ⁻¹)	Found value after added / (mg kg ⁻¹)	RSD / %	Recovery ^a / %	Found value / (mg kg ⁻¹)	Added concentration / (mg kg ⁻¹)	Found value after added / (mg kg ⁻¹)	RSD / %	Recovery ^a / %
NIST 694	25.20 ± 0.59 ^{b,c}	0.47 ± 0.02 ^{b,c}	9.6 ± 0.6	125.0	127.1 ± 4.2	3.0	94 ± 7	125.2 ± 5.7	125.0	248.0 ± 11.0	4.4	98 ± 11
NIST 120c	29.20 ± 2.48 ^{b,c}	0.72 ± 0.07 ^{b,c}	15.7 ± 3.3	125.0	136.5 ± 6.0	2.1	97 ± 5	103.4 ± 11.0	125.0	217.5 ± 5.0	2.1	91 ± 5
N:P:K (1:56:0)	< 72.0	246.7 ± 8.4	< 2.2	125.0	126.6 ± 9.5	3.0	101 ± 8	< 2.5	125.0	124.4 ± 6.6	2.1	99 ± 5
N:P:K (45:2:0)	0.18 ± 0.03 ^b	481.6 ± 108.6	< 2.2	125.0	104.9 ± 2.7	1.0	84 ± 2	< 2.5	125.0	110.5 ± 5.9	2.2	88 ± 5
N:P:K (46:0:0)	< 72.0	< 47.7	< 2.2	125.0	144.3 ± 8.8	2.4	115 ± 7	< 2.5	125.0	143.7 ± 17.1	4.8	115 ± 14
N:P:K (28:0:22)	< 72.0	< 47.7	< 2.2	125.0	145.8 ± 18.5	5.1	117 ± 15	< 2.5	125.0	147.2 ± 6.6	1.8	118 ± 5
N:P:K (10:10:10)	152.8 ± 8.0	< 47.7	< 2.2	125.0	137.6 ± 2.4	0.7	110 ± 2	< 2.5	125.0	131.2 ± 10.6	3.3	105 ± 8

^aRecovery = [(found value after added – found value) / added concentration] × 100; ^bconcentration expressed in % m/m; ^cresults expressed as concentration in % m/m of CaO (NIST 694: found value = 35.3 ± 0.8%, certified value = 43.6 ± 0.4%, agreement = 81 ± 2%; NIST 120c: found value = 40.86 ± 3.47%, certified value = 48.02 ± 0.17%, agreement = 85 ± 7%) and Fe₂O₃ (NIST 694: found value = 0.67 ± 0.03%, certified value = 0.79 ± 0.06%, agreement = 85 ± 4%; NIST 120c: found value = 1.03 ± 0.10%, certified value = 1.08 ± 0.03%, agreement = 95 ± 9%). NIST 694: Western Phosphate Rock; NIST 120c: Florida Phosphate Rock; results expressed as mean ± 95% confidence interval (n = 3).

Th, the sample matrices are highly complex due to the presence of several other elements and their composition is basically phosphate rocks, which are used as raw material in the manufacturing processes of fertilizers.

Application of optimized method

The optimized method was applied to five samples of commercial mineral fertilizers and the found concentrations of Th and U were lower than LOQ values. Thus, addition and recovery tests were also applied to these samples and the results obtained, using equation 3, ranged from 84 ± 2 to 117 ± 15% for Th and 88 ± 5 to 118 ± 5% for U (n = 3). These values are satisfactory considering a range of 80-120%.⁵¹ The RSDs were better than 5.1% for Th and better than 4.8% for U; these values are acceptable for determination of trace elements,⁵¹ indicating the good precision and accuracy of the analytical method (n = 3), as shown in Table 6.

$$\text{Recovery (\%)} = [(\text{found value after added} - \text{found value}) / \text{added value}] \times 100 \quad (3)$$

where found value after added is the measure of the concentration obtained for the analytes after adding them to the samples, the found value is a measure of the concentration obtained for the analytes without adding them to the sample, and the added value is the concentration of the analyte that was added.

In order to verify the presence of possible interferences caused by Ca and Fe, the concentrations of these elements were also determined in the mineral fertilizer samples and in the SRMs. When these elements are present in concentrations from < 72.0 to 29.20 ± 2.48% m/m for Ca and from < 47.7 to 0.72 ± 0.07% m/m for Fe, no significant differences were observed for the analytes when the results are compared with the recovery percentages obtained for the commercial samples and the SRMs. For mineral fertilizer samples, the concentrations of Th and U were below LOQs, as shown in Table 6.

The emission signals were obtained free of interferences. In Figure S1 (Supplementary Information) the uranium emission spectrum and the vicinity of the analytical ionic line at 385.957 nm for NIST SRM 694, which contains iron in the concentration of 0.47 ± 0.02% m/m, are shown. An emission spectrum and the vicinity of uranium at the same analytical ionic line for NIST SRM 694 containing Fe in the concentration of 0.47 ± 0.02% m/m with the addition of 125.0 mg kg⁻¹ (or 1.0 mg L⁻¹) of Th and U were also obtained, as shown in Figure S2. Finally, Figure S3 shows the emission spectrum of U (125.0 mg kg⁻¹ or 1.0 mg L⁻¹) in N:P:K fertilizer (45:2:0) sample and addition of Th (125.0 mg kg⁻¹ or 1.0 mg L⁻¹) and presence of Ca (0.18 ± 0.03% m/m) and Fe (481.6 ± 108.6 mg kg⁻¹).

The results for the determination using the developed method are considered satisfactory and can be attributed to the use of the ionic lines of the elements. According to Scott *et al.*⁵² no atomic line of uranium shows any

appreciable intensity for the determination by ICP OES, but ionic lines may be employed.

The determinations of U were not significantly affected by the presence of possibly interfering elements as Th, Ca and Fe present in mineral fertilizer samples. Fujino *et al.*⁵³ reported that many rare earth elements and thorium may interfere in the determination of U when present in excess of 10× or more, and Ca, Fe, V and Zr also strongly affect the emissions of U. Santos *et al.*²⁹ demonstrated that calcium causes suppression of the emission intensity for the lines 386.952 and 367.007 nm in concentrations of 10 mg L⁻¹, while the other three lines (385.957, 385.494 and 409.13 nm) are free of interferences. The same experiment was carried out to evaluate iron interferences and the results showed that, under the conditions established (for at least 10 mg L⁻¹ of Fe), there is no interference in the emission intensity of U for the five lines. It also evaluated the effect of Al, Ba, Cd, Co, Cr, Fe, Mo, Ni, Sb, Pb, Zn and V on the determination of uranium and no influence was observed on the emission intensity of U under the established conditions for five lines.²⁹

To obtain correct measurements of the intensity of uranium emission, a wavelength suitable to provide good sensitivity and low interference caused by matrix effects was required to be chosen, as well as the spectral interferences caused by the overlapping of the analyte lines by other element lines, and also the presence of species more easily ionizable which can cause decrease of sensitivity. The use of a more adequate wavelength can also be evaluated by the limits of detection and background equivalent concentration values.³⁰ The values obtained for these determinations were satisfactory since the ICP OES instrument used has a resolution of < 9 pm in the region ranging from ultraviolet to < 20 pm in the visible region, resulting in the minimization of the interferences.

Conclusions

The instrumental conditions of ICP OES with axial configuration have been optimized by applying a three-level factorial design with two variables and quintuplicate of central point, establishing a radiofrequency power of 1.0 kW and a nebulizer gas flow of 0.9 L min⁻¹ as optimum conditions for the determination of Th and U.

The optimized analytical method was applied successfully to the simultaneous determination of Th and U in commercial mineral fertilizer samples, where both element concentrations were below the limits of quantification obtained for the method in five samples.

The results for the determination obtained using the developed method are considered to be satisfactory and can be attributed to the use of the ionic lines for determination of

Th and U. Calcium and Fe were determined in the samples and the SRMs, but the concentrations are not significant as to affect the simultaneous determination of Th and U in mineral fertilizers. These determinations were satisfactory since the ICP OES instrument used has an adequate resolution, resulting in the minimization of the interferences.

Supplementary Information

Supplementary data are available free of charge at <http://jbc.sbg.org.br> as PDF file.

Acknowledgements

The study was financially supported by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), Fundação de Apoio à Pesquisa e Inovação Tecnológica do Estado de Sergipe (FAPITEC, Process No. 019.203.01713/2010-4) and Instituto Tecnológico e de Pesquisa do Estado de Sergipe (ITPS), which provided fellowships, financial support and infrastructure.

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Submitted: August 25, 2015

Published online: November 24, 2015

FAPESP has sponsored the publication of this article.