

Method development and validation for simultaneous determination of IEA-R1 reactor's pool water U and Si content by ICP OES

João Cristiano Ulrich¹, Sabine Neusatz Guilhen¹, Marycel Elena Barboza Cotrim¹, Maria Aparecida Faustino Pires¹

¹Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN/SP - Av. Prof. Lineu Prestes, 2242 - Cidade Universitária - CEP: 05508-000 - São Paulo/SP.

E-mail: jculrich@ipen.br

Abstract: IPEN's research reactor, IEA-R1, an open pool type research reactor moderated and cooled by light water. High quality water is a key factor in preventing the corrosion of the spent fuel stored in the pool. As a safety management policy, IPEN has adopted a water chemistry control which periodically monitors the levels of uranium (U) and silicon (Si) in the pool's reactor. An analytical method was developed and validated for the determination of U and Si by ICP OES. This work describes the validation process including the parameters selectivity, linearity, quantification limit, precision and recovery.

Keywords: validation, uranium, silicon

1. INTRODUCTION

IEA-R1, an open pool type research reactor moderated and cooled by light water, was commissioned 1957 and is located at the Instituto de Pesquisas Energéticas e Nucleares, IPEN-CNEN-SP, a Brazilian agency managed by the National Nuclear Energy Commission. The reactor's fuel elements use low enriched uranium (LEU) targets, i.e., up to 20% enriched uranium (²³⁵U isotope), assembled as fuel plates of U₃Si₂ dispersed in Al [1].

Spent fuel is provisionally stored in the pool until relocation to a final disposal site or until the decay heat is low enough to allow migration to a dry storage facility. Systematic treatment and purification of the pool water is required to its quality assurance, a key factor in preventing corrosion of aluminum clad fuel elements and other structural components in water [2-4].

Also, dispersed impurities in the water may become activated by neutron flux as the water circulates through the reactor core, impairing radiological shielding and, consequently, the attenuation of the radiation emitted by the reaction in the core.

This way, specifying requirements and operational limits for water treatment and purifications systems is essential for the management of water quality in research reactors. Therefore, the Research Reactor Center (CRPq/IPEN) has established sampling procedures and physical-chemical parameters to periodically monitor the water quality. The Chemistry and Environment Center (CQMA/IPEN) provides assistance concerning the water chemistry control, in which the levels of silicon and uranium in the pool's reactor are determined. This way, the detection of either of these elements in the water may indicate a possible leakage of the fuel to the reactor's pool.

However, carbon steels, usually employed in pipelines and valves of the reactor, may also respond for the silicon presence in the water, since carbon steels are essentially alloys of iron and carbon with small additions of elements such as manganese and silicon to provide the desired mechanical properties [5]. Also, silicon in water may also be accounted for its leaching from the concrete.

That's why, more permissible limits for silicon are allowed, given that the amount of silicon determined in the water would only be derived from the fuel leaching process if the equivalent amount of uranium was also determined. When silicon is found in water in the absence of uranium, one can assume that the source is less worrisome and that the water quality is satisfactory, since no corrosion products are being detected in the water. Therefore, uranium is the key parameter.

Naturally, corrosion products are greatly diluted, given that 273 m³ of water is used to fill the pool. This way, when uranium is detected, immediate attention should be directed to remediate and isolate the fuel element.

An applicable technique for uranium and silicon quantification in water is inductively coupled plasma optical emission spectrometry (ICP OES).

Validation is defined by the International Vocabulary of Metrology (VIM) [6] as "verification, where the specified requirements are adequate for an intended use". Method validation has an important role in analytical laboratories to ensure the quality and to demonstrate the method's performance. This paper describes the validation of a method developed for simultaneous determination of uranium (U) and silicon (Si) in the IEA-R1 reactor's pool water.

The method was evaluated for selectivity, linearity, quantification limit, precision and recovery in order to verify each of these parameters'

acceptance to INMETRO protocol for validation of analytical methods [7].

2. EXPERIMENTAL

2.1. Reagents and standards

Uranium (U) and silicon (Si) single element standard solutions (1000 µg mL⁻¹, Inorganic Ventures, USA) were appropriately diluted to prepare standard calibration solutions ranging from 0.05 to 10 µg g⁻¹ in a 1% (v v⁻¹) nitric acid (HNO₃, 65%, Merck, Darmstadt, Germany) aqueous solution. Ultrapure water with a resistivity of 18 MΩ cm was obtained using a Master system (Gehaka, São Paulo, Brazil).

2.2. Instrumentation

A Spectro ARCOS ICP optical emission spectrometer (Spectro Analytical Instruments Co, Kleve, Germany), equipped with an axially viewed plasma, was used for the determination of U and Si in water. Sample introduction system was composed by a cross flow nebulizer and a Scott double-pass spray chamber. Instrumental parameters selected for U and Si determination were: 1400 W RF power, 12 L min⁻¹ plasma flow, 1 L min⁻¹ auxiliary flow, 1 L min⁻¹ nebulizer flow, 3 replicates, wavelengths: U = 409,014 nm and Si = 251,612 nm.

2.3. Method validation

The first step in method validation was to prepare a written protocol with detailed instructions in the form of analytical procedures and statistical treatment of the obtained data. This protocol assumed that the instrument was previously selected for sensitivity and that the analysts were experienced in analytical methods validation. The second step involved experimental tasks as to prepare and analyze the solutions for each specific parameter defined in the protocol. The following step was the evaluation of the method's performance and to establish the degree of acceptability that is required for each specific

parameter. Finally, the appropriate filing of the method's documentation, containing procedures, calculations and the all records, was conducted.

The evaluation of the matrix effect, or selectivity, was investigated comparing two calibration curves obtained from matrix blank solution spiked with U and Si standard solutions and spiked public supply water. Student's t-test was applied for the comparison of the two curves and the (1) was used to calculate experimental t (t_{exp}), which is then compared with the critical (theoretical) t.

$$t_{exp} = \frac{|\bar{X}_A - \bar{X}_B|}{\sqrt{S_{AB} \left(\frac{1}{n_A} + \frac{1}{n_B} \right)}} \quad (1)$$

Where \bar{X}_A , \bar{X}_B = average of groups A,B; n_A, n_B = number of values each group and S_{AB} = weighted variance.

Linearity was evaluated by the determination of the working range and then, the calibration solutions were prepared and measured. ANOVA statistical test was applied. The total variability of the responses was decomposed into the sum of squares due to regression and the residual (about regression) sum of squares and then later is decomposed into lack-to-fit and pure error sums of square.

The method's precision was evaluated as the coefficients of variation for the recovery tests on the measured concentration of elements in two spiked samples.

Accuracy was estimated through recovery tests using two spiked solutions and the results calculated by (2).

$$Recovery (\%) = \left[\frac{(C_1 - C_2)}{C_3} \right] \times 100 \quad (2)$$

Where:

C_1 = concentration of the analyte in the fortified sample

C_2 = concentration of the analyte in the unfortified sample

C_3 = concentration of the analyte added to the fortified sample

3. RESULTS AND DISCUSSION

3.1. Selectivity

As cited in 2.3 section, the t-test was applied to compare the two calibration curves. For U, $t_{exp} = 0.04$ and $t_{critical} = 2.23$ and for Si, $t_{exp} = 0.39$ and $t_{critical} = 2.23$. The criterion is if $t_{exp} < t_{critical}$ the H_0 is "accept", i.e. both samples (and calibration curves) contain the analytes and exhibit no matrix effect.

Therefore, for both analytes, the selectivity is proved.

3.2. Linearity

As cited in 2.3, the calibration experiment was started with the choice of a preliminary linear working range from 0.05 to 10.0 $\mu\text{g g}^{-1}$ of both analytes. Six calibration solutions (concentrations of 0.05, 0.25, 0.5, 2.5, 5.0 and 10.0 $\mu\text{g g}^{-1}$) were prepared and analyzed. Three replicates of each concentration were prepared and the calibration curves were measured three times, independently. Table 1 summarizes the analysis of variance. Homogeneity of variances and linearity were verified by a statistical significant test. Table 2 shows the results of linearity and regression efficiency tests for the U and Si.

Table 1. Analysis of variance – uranium (U) and silicon (Si) calibration curves

Uranium				
Sources of Variability	Sum of Squares (SQ)	Degrees of Freedom	Mean Sum of Squares (MQ)	
Totals	1.59x10 ¹¹	17	9.35 x10 ⁹	MQT
Regression	1.59x10 ¹¹	1	1.59x10 ¹¹	MQR
Residual	3.22 x10 ⁸	16	2.01 x10 ⁷	MQE
Pure Error	2.98 x10 ⁸	13	2.29 x10 ⁷	MQEP
Lack-of-Fit	2.41 x10 ⁷	4	6.02 x10 ⁶	MQL
Silicon				
Sources of Variability	Sum of Squares (SQ)	Degrees of Freedom	Mean Sum of Squares (MQ)	
Totals	9.13 x10 ¹¹	17	5.37 x10 ¹⁰	MQT
Regression	9.08 x10 ¹¹	1	9.08 x10 ¹¹	MQR
Residual	5.52 x10 ⁹	16	3.45 x10 ⁸	MQE
Pure Error	5.27 x10 ⁹	13	4.06 x10 ⁸	MQEP
Lack-of-Fit	2.45 x10 ⁸	4	6.13 x10 ⁷	MQL

Table 2. Results of linearity and regression efficiency tests

Uranium calibration curve	
Linearity (lack-of-fit)	Regression validity
$F_{\text{calculated}} = \text{MQL}/\text{MQEP} = 0.26$	$F_{\text{calculated}} = \text{MQR}/\text{MQE} = 7875.1$
$F_{0.025;4;12} = 4.12$	$F_{0.025;1;16} = 6.12$
$F_{\text{calculated}} < F_{0.025;4;12}$: Linearity is accepted	$F_{\text{calculated}} > F_{0.025;1;16}$: Regression validity accepted
Efficiency: $R^2 = \text{SQR}/\text{SQC} = 0.998$: $R^2 > 0.95$ regression accepted	
Silicon calibration curve	
Linearity (lack-of-fit)	Regression validity
$F_{\text{calculated}} = \text{MQL}/\text{MQEP} = 0.15$	$F_{\text{calculated}} = \text{MQR}/\text{MQE} = 2631.4$
$F_{0.025;4;12} = 4.12$	$F_{0.025;1;16} = 6.12$
$F_{\text{calculated}} < F_{0.025;4;12}$: Linearity is accepted	$F_{\text{calculated}} < F_{0.025;1;16}$: Regression validity accepted
Efficiency: $R^2 = \text{SQR}/\text{SQC} = 0.994$: $R^2 > 0.95$ regression accepted	

It was observed, in table 2, that $R^2 = 0.99$ for both analytes. As $R^2 > 0.95$ was the adopted criterion to accept the regression, the linearity for U and Si was accepted.

A significant MQR/MQE ratio confirms that there is regression. If the ratio MQL/MQEP is higher than the critical level, the linear model appears to be inadequate.

3.3. Quantification limit

As mentioned in INMETRO document [7], quantification limit was defined as the first point

of calibration curve, i.e. for both analytes the quantification limit is $0.05 \mu\text{g g}^{-1}$.

3.4. Precision

Coefficients of variation (CV) ranged from 0.02 % to 1.2 % and 0.1 % to 1.6 % ($n = 9$) for U and Si, respectively. These results demonstrated that the method has good precision.

3.5. Recovery

A satisfactory accuracy for the proposed method was achieved, since recovery values, for U, varied from 90.4 ± 0.2 % ($5.0 \mu\text{g g}^{-1}$) to 100.4 ± 0.8 % ($2.5 \mu\text{g g}^{-1}$) and for Si the values

from $83.6 \pm 0.1 \%$ ($5.0 \mu\text{g g}^{-1}$) to $98.4 \pm 0.8 \%$ ($2.5 \mu\text{g g}^{-1}$).

4. CONCLUSION

The method development in this work was suitable for the determination of U and Si with good precision and accuracy. The validation process proved the absence of matrix effects and the linearity was suitable since $R^2 > 0.95$ for both analytes, with acceptable regression.

5. REFERENCES

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