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Preparation of Uranium Silicon Standards for XRF

N. H. C. Ribeiro[1], and R. H. L. Garcia[2]

[1] *nathan.holanda@usp.br, SECON/IPEN, Av. Prof. Lineu Prestes, 2242 São Paulo – SP - 05508-000*
[2] *rlgarcia@ipen.br*

1. Introduction

In uranium silicide synthesis for research reactors, elemental heterogeneity compromises chemical uniformity and batch quality. Quantifying these variations is crucial, as compositional deviations directly affect the thermomechanical performance and safety of the final material. Despite the higher uranium density of U_3Si, U_3Si_2 is the preferred fission material because it exhibits smaller, less distributed fission gas bubbles during irradiation, maintaining better post-irradiation mechanical characteristics [1,2]. X-Ray Fluorescence (XRF) enables the elemental quantification of U, Si and impurities. As a fast, non-destructive technique that minimizes waste generation, XRF can replace traditional quality control methods like gravimetry and potentiometry. However, accurate XRF quantitative analysis requires a specific calibration curve built from reference samples with similar elemental proportions. Since commercial uranium silicide reference samples are unavailable, this work aims to synthesize these samples and validate a computational method to establish an XRF calibration curve.

2. Methodology

This metrological study focuses on synthesizing reference materials and establishing an XRF calibration curve by correlating known U and Si proportions with their respective photon emission intensities. The experimental setup comprises two main stages: (1) sample design and physical preparation, and (2) instrumental chemical characterization with adaptive chemometric modeling. The XRF analysis was performed using a ThermoFisher QuantX Spectrometer (Fig. 1), correlating photon intensities with nominal stoichiometries. Raw spectral data acquired under specific instrumental conditions were utilized. Twelve distinct spectra were processed computationally using Python libraries (Pandas and NumPy) to efficiently convert raw outputs into manageable matrices.



Figure 1 – ThermoScientific QuantX XRF Spectrometer.

Sampling Design and Physical Preparation

Samples were produced by melting natural uranium (99.9% purity) and analytical silicon (99.8% purity) in a magnetic induction furnace at different stoichiometries (Table I)[1]. Samples were coded by their Si molar percentage. To prevent textural variables from compromising the calibration curve, the ingots were comminuted to the desired particle size [1,3]. For XRF analysis, powder samples were pressed into ~40 mm pellets using a 15-ton hydraulic press and analytical wax as a binder to ensure mechanical integrity.

Table I: Composition and fusion temperature of samples.

Sample Code	%mass U	%mass Si	%mol U	%mol Si	Temperature (ºC)
33Si	94.47	5.53	66.86	33.14	1703
40Si	92.7	7.3	59.96	40.04	1702
41Si	92.38	7.62	58.85	41.15	1700
42Si	91.96	8.04	57.45	42.55	1699
50Si	89.56	10.44	50.3	49.7	1707
67Si	80.91	19.09	33.34	66.66	1769

Instrumental chemical characterization and application of adaptive chemometric modeling

XRF quantified the mass fraction (wt.%) of U, Si, and metallic impurities using parameters optimized for nuclear fuels. Following Scapin et al. [4], the equipment evaluated the U/Si ratio to address heavy material absorption challenges. Instead of a full-spectrum approach, this study proposes a targeted multivariate calibration workflow driven by an adaptive chemometric architecture. The methodology computationally extracts specific Regions of Interest (ROIs) for the analytes. For >20 kV excitations, it applies trapezoidal background subtraction, mitigating severe Bremsstrahlung radiation from the dense uranium matrix to isolate the net peak area [5].

To circumvent the uranium Matrix Effect and quantify sample constituents, instrumental data interpretation employed an Automated Machine Learning (Auto-ML) strategy. Auto-ML automates the selection of the best predictive model by contrasting univariate and multivariate algorithms to elect the most precise option. To formalize this dynamic, the framework pits the available regression algorithms against each other in a computational competition. During validation, the algorithm achieving the highest predictive accuracy is designated the **winner model**, a term adopted throughout this study to denote the most robust calibration architecture per analyte.

Multivariate calibration is well-attested for U_3Si_2 matrices [6]. The two evaluated models were:

- **Mode 1 (Multivariate Internal Standard):** Employs Partial Least Squares (PLS) regression [7] on a matrix including the Si/U intensity ratio and net analyte area, linearizing the auto-absorption matrix effect [8].
- **Mode 2 (Univariate OLS):** Applies Ordinary Least Squares regression solely on the isolated analyte photon intensity, serving as a baseline diagnostic tool for matrix susceptibility.

Built upon the *scikit-learn* architecture [9], the framework evaluates both models via Leave-One-Out Cross-Validation (LOOCV). LOOCV iteratively trains the model on *N-1* samples and tests on the single excluded sample until all have been tested. This rigorous technique prevents statistical overfitting in limited sample sizes [10], electing the winner model by maximizing the coefficient of determination (R^2) and minimizing Root Mean Square Error (RMSE).

Because the models are trained directly on instrumental raw data, their native coefficients inherently carry physical meaning. The algorithm seamlessly extracts the deterministic polynomial coefficients (β_n) and the intercept (β_0), from the winner model, translating the regression results directly into a physical machine equation ready for quality control applications. Fig. 2 illustrates this adaptive chemometric pipeline, from raw spectra ingestion to the extraction of the deterministic equation.

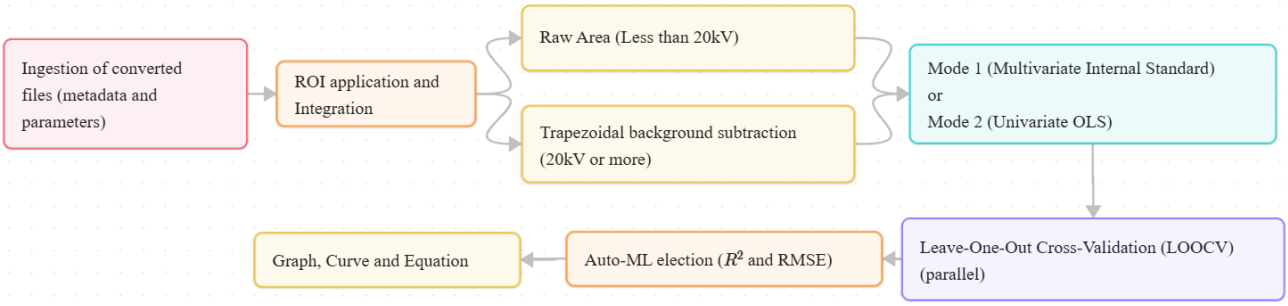


Figure 2 - Adaptive chemometric workflow and Auto-ML data pipeline for XRF spectral analysis.

3. Results and Discussion

Computational Validation and Data Treatment

The computational workflow was successfully validated across all synthesized standards (33Si to 67Si). Automated treatment organized the high-density XRF data, preventing formatting inconsistencies. Dynamic extraction successfully isolated the Si and U quantum jumps, and conditional logic expunged continuous background noise while preserving fragile low-energy analytical signals.

Proof of Concept for Multivariate Calibration

Rather than characterizing unknown samples, this stage aimed to construct a robust regression model by validating the full pipeline across the 12 empirical spectra. The Auto-ML competition provided empirical proof of the severe matrix effect in U_3Si_2 alloys. The univariate approach (Mode 2) collapsed, exhibiting negative R^2 values due to non-linear auto-absorption. Conversely, the Internal Standard approach (Mode 1) successfully mitigated the matrix effect by stabilizing the predictive matrix via the Si/U fractional ratio, reconstructing a robust calibration curve.

Furthermore, following LOOCV validation, the algorithm successfully extracted the deterministic polynomial equation (Equation 1) directly in photon counts:

$$Y_{nominal} = (\beta_1 \times Ratio) + (\beta_2 \times Net_Area) + \beta_0 \qquad \textit{(Equation 1)}$$

This delivers a straightforward, non-destructive quality control formula ready for direct laboratory deployment.

Calibration Results and *Winner* models Analysis

Evaluation yielded distinct winner models depending on extraction parameters and analytes. As predicted, multivariate and univariate performances contrasted starkly. Under initial batch parameters, Si defaulted to Univariate OLS (Mode 2), but its trend line severely deviated from the ideal 1:1 proportionality, confirming its inadequacy without matrix corrections. Conversely, optimized parameters utilizing trapezoidal background subtraction established optimal performance. In this definitive batch, the Multivariate Internal Standard (Mode 1) was elected the winner model for both Si and U, proving its capability to neutralize heavy matrix auto-absorption.

4. Conclusions

While the automated X-ray spectrometry pipeline yielded promising preliminary results, the software is being structurally modified into a generalist analytical tool with improved interfaces to ensure statistical viability for laboratory routines. Regarding nuclear applications, a current limitation is the restricted standard batch size (N=6), which mathematically confines trend analysis to first-degree linear models to

prevent statistical overfitting. Therefore, a long-term objective is expanding the U_3Si_2 standard library, safely enabling higher-order polynomial modeling of the auto-absorption curvature to establish a definitive calibration curve.

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References

[1] R. H. L. GARCIA, "Caracterização e quantificação de fases em ligas de urânio-silício para aplicação como combustível nuclear". *Dissertation (Ph.D. in Nuclear Technology - Materials)*. Instituto de Pesquisas Energéticas e Nucleares. Universidade de São Paulo. São Paulo (2019).

[2] M. R. Finlay, G. L. Hofman, J. L. SNELGROVE, "Irradiation behaviour of uranium silicide compounds.". *Journal of Nuclear Materials*. vol. 325, n. 2–3, pp.118–128 (2004).

[3] R. E. VAN GRIEKEN, A. A. MARKOWICZ. (Eds.). *Handbook of X-Ray Spectrometry. 2.ed*. Marcel Dekker. New York. United States of America (2002).

[4] M. A. SCAPIN et al. "Uncertainty measurement evaluation of WDXRF and EDXRF techniques for the Si and U_{total} determination in U_3Si_2 nuclear fuel.". *Journal of Radioanalytical and Nuclear Chemistry*. vol. 287, n. 2, pp. 453-459 (2011).

[5] M. WEST et al. "Atomic Spectrometry Update – a review of advances in X-ray fluorescence spectrometry and their applications.". *Journal of Analytical Atomic Spectrometry*. vol. 30, n. 9, pp. 1839-1884 (2015).

[6] M. A. SCAPIN, C. A. COTRIM, M. A. F. PIRES, "Application of multivariate calibration for simultaneous determination of major and minor constituents in U_3Si_2 by WDXRF technique.". *Journal of Radioanalytical and Nuclear Chemistry*. vol. 302, n. 1, pp. 441-447 (2014).

[7] P. GELADI, B. R. KOWALSKI, "Partial least-squares regression: a tutorial". *Analytica Chimica Acta*. vol. 185, pp. 1-17. (1986).

[8] R. TERTIAN, F. CLAISSE, *Principles of Quantitative X-Ray Fluorescence Analysis*. Heyden. London. United Kingdom (1982).

[9] T. HASTIE, R. TIBSHIRANI, J. FRIEDMAN, *The Elements of Statistical Learning: Data Mining. Inference. and Prediction. 2. ed.* Springer. New York. United States of America (2009).

[10] F. PEDREGOSA et al. "Scikit-learn: Machine Learning in Python". *Journal of Machine Learning Research*. vol. 12, pp. 2825-2830 (2011).