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Improved Reliability in TIMS Isotopic Analysis of NUSIMEP-7 Microparticles using an Optimized Data Integration Method

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Abstract : Isotopic analysis of ultra-trace uranium particles for nuclear safeguards requires the highest level of accuracy and reliability. Previously, uranium isotope ratios in NUSIMEP-7 (the 7th Nuclear Signatures Interlaboratory Measurement Evaluation Programme; an interlaboratory comparison/proficiency-test exercise for uranium microparticles) particles were determined using thermal ionization mass spectrometry (TIMS) with an optimized static detection method, yielding satisfactory results. However, the data integration procedure can also significantly influence the final analytical results, especially for ultra-trace level samples analyzed by the continuous heating method. In this study, raw data from the original NUSIMEP-7 particle analysis were retrospectively re-processed using a recently optimized data integration protocol: 'Method I' (Summed Intensity Ratio), with an 'over 25%' signal integration range. The results showed improvements in accuracy for all isotope ratios. Most notably, the z-scores and zeta-scores, which are critical for interlaboratory comparison programs, were significantly improved, moving from 'acceptable' or 'warning' levels to 'excellent'. For the key n(^{235}U)/n(^{238}U) ratio, the z-score improved from 1.9 to -0.66, and the zeta-score improved from 1.3 to -0.12. This study demonstrates that applying optimized data processing protocols, even retrospectively, can significantly enhance the fidelity and reliability of ultra-trace isotopic analyses.

Keywords : Uranium, TIMS, Particle Analysis, Data Integration, NUSIMEP-7, Safeguards

Introduction

The isotopic analysis of nuclear materials in environmental samples plays a key role of the nuclear safeguards, providing an important tool to monitor nuclear activities.[1] Swipe samples collected from nuclear facilities are subjected to two main types of analysis: bulk analysis and particle analysis. Bulk analysis determines the total amount and average isotopic composition of nuclear material, which shows a general overview of a nuclear history.[2-4] In contrast, particle analysis provides detailed information by determining the isotopic ratios of individual particles.[5-11] This allows to trace the nuclear history of a facility and the origin of specific materials, disclosing undeclared activities.

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Thermal Ionization Mass Spectrometry (TIMS) is a powerful technique for this purpose thanks to its high sensitivity, accuracy, and precision, as well as its negligible matrix effects and spectral interference.[5] However, analyzing individual particles, which often contain only picogram (pg) or femtogram (fg) quantities of uranium, often makes the analysis difficult.

Two major challenges arise in ultra-trace TIMS analysis. The first is ion detection. The previous study experimentally evaluated three TIMS detection methods (dynamic, multi-dynamic, and static) for samples ranging from 1 ng down to 1 pg.[12] This concluded that for pg-level particle analysis, the static detection method—which uses multiple ion counters for simultaneous measurement of all isotopes—provides the best accuracy, precision, and the lowest uncertainty. This method was successfully applied to the analysis of NUSIMEP-7 particles of which uranium amounts were in pg-levels. NUSIMEP-7 is an interlaboratory comparison programme in which uranium isotope amount ratios in microparticles are benchmarked against certified reference values, and participating laboratories are evaluated using z- and zeta-scores.

The second challenge, which is the focus of this letter, is data processing. TIMS analysis is easily influenced by mass fractionation, where lighter isotopes evaporate preferentially at lower temperatures. The total evaporation tech-

Table 1. Summary of TIMS isotopic measurements of individual NUSIMEP-7 particles (Before optimized integration method applied).

	$n(^{234}U)/n(^{238}U)$ ($\times 10^{-4}$)	$n(^{235}U)/n(^{238}U)$ ($\times 10^{-2}$)	$n(^{236}U)/n(^{238}U)$ ($\times 10^{-4}$)
Certified Value	3.451[±0.002]	3.415[±0.002]	1.0327[±0.0007]
NU7-3	3.4[±1.1][a]	3.343[±0.083]	1.09[±0.48]
NU7-5	3.78[±0.45]	3.361[±0.056]	1.24[±0.35]
NU7-6	3.57[±0.28]	3.403[±0.032]	1.23[±0.19]
NU7-7	3.38[±0.25]	3.425[±0.025]	1.21[±0.12]
Average	3.54[±0.18]	3.383[±0.038]	1.192[±0.068]
Accuracy (%)	2.47	-0.931	15.4
z score	1.0	1.9	0.3
zeta score	0.3	1.3	1.1

[a] Expanded uncertainty $U = k \cdot u_c$ with $k = 2$ at approximately 95 % of confidence level

nique is used to correct for this.[13] For ultra-trace samples, this is modified into a 'continuous heating method', where the sample is gradually heated until the entire U content is totally consumed, and data is collected throughout the entire evaporation profile.[14] This profile does not produce stable signal intensities, but consists of a signal rise, a peak, and a decay back to background. How these data points are integrated significantly impacts the final result. The previous study reported in 2022 specifically addressed this problem.[15] It evaluated three data integration methods: 1) Summing all ion intensities for each isotope before calculating the final ratio (Method I), 2) Calculating a ratio for each data set, then taking a simple average of all ratios (Method II), 3) Calculating a ratio for each data set, then applying a weighting factor based on the ^{238}U signal intensity before averaging (Method III). This study concluded that Method III, combined with an integration range of 'over 25%' (using only data sets with above 25% of the maximum ^{238}U signal), provides the best performance for pg-level samples. This protocol effectively minimizes distortions from low-signal, high-noise data points in the tails of the evaporation profile.

The original NUSIMEP-7 analysis in the previous study was performed using the optimized static detection method, but before this data integration method was optimized.[15] The scores, while satisfactory, showed room for improvement. This letter reports the results of retrospectively applying the optimized data integration method to the original NUSIMEP-7 dataset, with the hypothesis that this re-processing would enhance the analytical reliability and improve the interlaboratory comparison tests.

Methodology

No new experimental measurements were performed for this study. The work consists entirely of the re-processing of previously acquired raw data.

Original Data Source

The raw data were sourced from the particle analysis of the samples for NUSIMEP-7 performed in the previous study.[15] In this study, individual particles from a NUSIMEP-7 sample planchet were identified by an Energy Dispersive Spectroscopy (EDS) equipped in a Scanning Electron Microscopy (SEM) and transferred to zone-refined rhenium filaments using a micromanipulator system within the SEM. The particles were approximately 0.8 μm in diameter, corresponding to an estimated uranium mass of ~1 pg or less.

Isotopic measurements were performed using TIMS (TRITON Plus, Thermo Fisher Scientific). The optimized static detection method was used, with a detector configuration employing three Secondary Electron Multipliers (SEMs) and one Compact Discrete Dynode (CDD) to simultaneously detect $^{234}U^+$, $^{235}U^+$, $^{236}U^+$, and $^{238}U^+$. The continuous heating method was applied. The original dataset forms the basis for the 'Before' results presented in Table 1.

Data Re-processing Protocol

The raw data for the four particles identified as NU7-3, NU7-5, NU7-6, and NU7-7 were re-processed. This new process, designated 'After' (Table 2), followed the optimized method.

· Integration Range: Only data sets where the $^{238}U^+$ signal intensity was greater than 25% of the maximum observed $^{238}U^+$ intensity were included in the calculation. This excludes the data from the initial heating ramp and final tail-off, which are more susceptible to background noise and distortion. Figure 1 shows a representative $^{238}U^+$ intensity (cps) profile under continuous heating with the integration range of over 25%. The optimized integration range focuses on the central high-intensity portion, where the signal-to-noise ratio (S/N) is maximized and short-term fluctuations are minimized.

· Integration Method: The calculation of isotope ratios was performed using Method I (Summed Intensity Ratio), in which the final isotope ratio (R) was determined from the

Table 2. Summary of TIMS isotopic measurements of individual NUSIMEP-7 particles (**After** optimized integration method applied).

	$n(^{234}U)/n(^{238}U)$ ($\times 10^{-4}$)	$n(^{235}U)/n(^{238}U)$ ($\times 10^{-2}$)	$n(^{236}U)/n(^{238}U)$ ($\times 10^{-4}$)
NU7-3	3.4[±1.6][a]	3.41[±0.11]	1.13[±0.70]
NU7-5	3.73[±0.69]	3.363[±0.084]	1.12[±0.45]
NU7-6	3.55[±0.42]	3.420[±0.034]	1.20[±0.29]
NU7-7	3.31[±0.85]	3.43[±0.12]	1.22[±0.63]
Average	3.51[±0.18]	3.404[±0.028]	1.178[±0.043]
Accuracy (%)	1.62	-0.33	14.0
z score	0.64	-0.66	0.28
zeta score	0.06	-0.12	0.28

[a] Expanded uncertainty $U = k \cdot u_c$ with $k = 2$ at approximately 95 % of confidence level

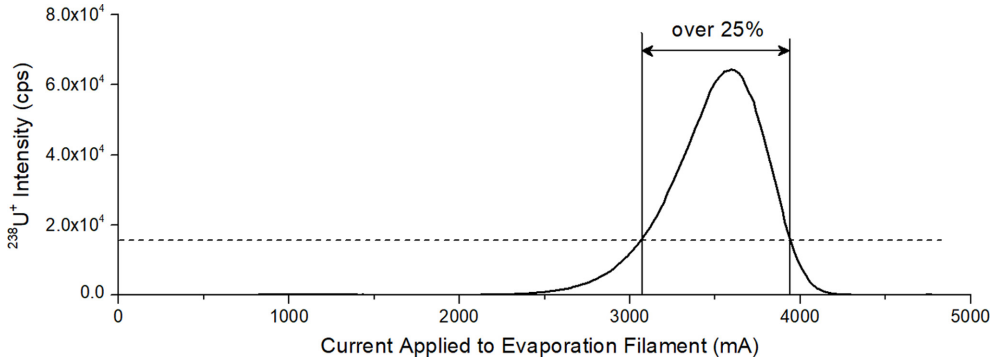

Figure 1. The profile of $^{238}U^+$ intensity and the integration range of 'over 25%'.

ratio of the summed ion signal intensities of the numerator and denominator isotopes within the integration range. Rather than averaging individual ratios of a data set, the total integrated intensities of each isotope were first obtained, and then the final isotope ratio was calculated. The following is an example of a calculation of $n(^{235}U)/n(^{238}U)$.

$$R = \frac{\sum I_i^{235}}{\sum I_i^{238}} \quad (1)$$

where I_i^{235} and I_i^{238} are the individual $^{235}U^+$ and $^{238}U^+$ signal intensities of *i*-the data set.

Performance Evaluation

The 'Before' and 'After' results were compared using three metrics:

· Accuracy (%): The relative deviation of the measured average value from the certified reference value.

· z-score: A measure of agreement, calculated as follows:

$$z = \frac{X_{\text{lab}} - X_{\text{ref}}}{\sigma} \quad (2)$$

where X_{lab} is the laboratory's result, X_{ref} is the certified value, and σ is the standard deviation for proficiency assessment. $|z| < 2$ is considered 'satisfactory'.

· zeta-score: A measure of agreement that accounts for uncertainties, calculated as follows:

$$\text{zeta} = \frac{X_{\text{lab}} - X_{\text{ref}}}{\sqrt{u_{\text{lab}}^2 - u_{\text{ref}}^2}} \quad (3)$$

where u_{lab} and u_{ref} represents the standard uncertainties of the lab and reference values, respectively. The uncertainty was estimated according to GUM (Guide to the expression of Uncertainty in Measurement).[16] $|zeta| < 2$ is considered 'satisfactory'.

Results and discussion

The comparative results of the re-processing are presented in Table 1 (Before) and Table 2 (After) for the four NUSIMEP-7 particles. Figure 2 summarizes the re-processed isotope ratios for the particles. A direct comparison of the average performance metrics clearly indicates a consistent improvement in both accuracy and interlaboratory performance parameters across all ratios, especially for $n(^{235}U)/n(^{238}U)$.

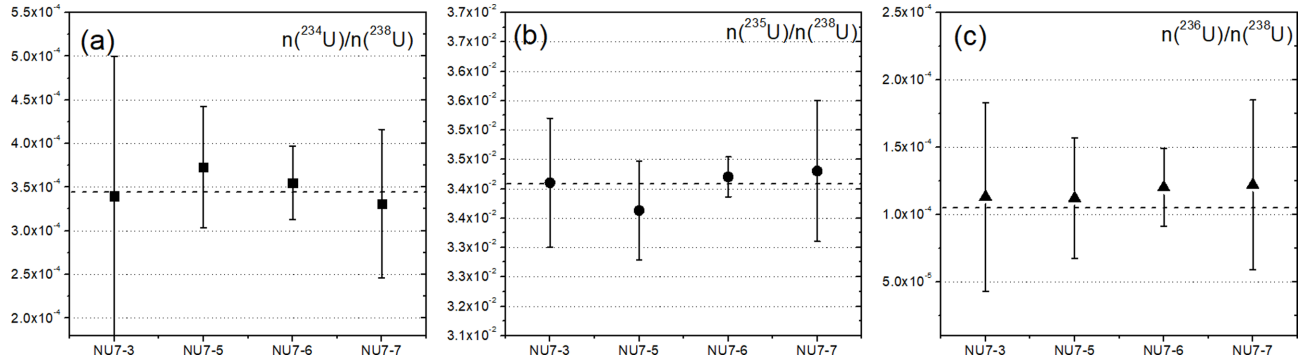

Figure 2. The isotope ratios of uranium in NUSIMEP-7 microparticles. (a) n(^{234}U)/n(^{238}U), (b) n(^{235}U)/n(^{238}U), and (c) n(^{236}U)/n(^{238}U).

Improvement in Accuracy

The accuracy, or relative bias, improved for all three isotope ratios. For n(^{234}U)/n(^{238}U), the accuracy of the averaged ratio improved from 2.47% to 1.62%. This indicates that the optimized integration range preferentially removed noise-dominated signals without significantly change in the central tendency of the dataset. The n(^{234}U)/n(^{238}U) bias, while still high, improved from 15.4% to 14.0. The persistence of a high positive bias for ^{236}U is expected and attributed to peak tailing from the abundant ^{238}U isotope, an instrumental artifact when no RPQ (retarded potential quadrupole) or explicit peak-tail correction is applied, not correctable by this data integration method.[17]

The most clear improvement was for the main n(^{235}U)/n(^{238}U) ratio, where the accuracy improved from -0.931% to -0.33%, and the mean value shifted from 3.383×10^{-2} to 3.404×10^{-2}, much closer to the certified value (3.415×10^{-2}). This implies that the original integration method, which likely included more of the low-signal data, was introducing a negative bias to the mean. The previous study showed that including data below the 25% threshold can distort the final ratio.[15] By applying the over 25% range and summed intensity ratio (Method I), this bias was effectively reduced, bringing the measured value closer to the certified reference value.

It is also noted that the average expanded uncertainty for n(^{235}U)/n(^{238}U) and n(^{236}U)/n(^{238}U) decreased from 3.8×10^{-4} to 2.8×10^{-4}, and from 6.8×10^{-6} to 4.3×10^{-6}, respectively, by applying optimization. This indicates an improvement in precision. These trends show that the optimized integration simultaneously enhances accuracy and precision.

Improvement in Interlaboratory Scores (z and zeta)

The practical benefit of this enhanced accuracy is most evident in the interlaboratory comparison scores. For (^{235}U)/n(^{238}U), the z-score improved dramatically from 1.9 to -0.66. A z-score of 1.9, while technically 'satisfactory' ($|z| < 2$), is on the edge of the 'warning' threshold. A score of -0.66, however, is firmly in the 'excellent' category.

Similarly, the zeta-score for this ratio improved from 1.3 to -0.12. The zeta-score compares the deviation $X_{\text{lab}} - X_{\text{ref}}$ to the combined uncertainties ($\sqrt{u_{\text{lab}}^2 - u_{\text{ref}}^2}$). A score of 1.3 suggests that the deviation between the lab value and the reference value is 1.3 times the combined standard uncertainty, indicating a potential underestimation of uncertainty or a systematic bias. The new score of -0.12 shows that the deviation is now much smaller than the combined uncertainty, indicating excellent statistical agreement between the measured value and the certified value.

The scores for (^{234}U)/n(^{238}U) (zeta: 0.3 → 0.06) and (^{236}U)/n(^{238}U) (zeta: 1.1 → 0.28) also showed significant improvement, demonstrating that the re-processed data is in much better statistical agreement with the certified values.

This analysis confirms that the original experimental data, acquired using the optimized static detection method, was of high quality. The sub-optimal performance scores (z=1.9, zeta=1.3) were not due to poor experimental work, but rather to a data processing protocol that was not fully optimized for the unique challenges of pg-level continuous heating profiles.

Analytical implications

This has important implications for uranium microparticle analysis in safeguards. Laboratories that have archived raw cycle-by-cycle data can retrospectively re-process past measurements to optimize them with current best practices, thereby enhancing long-term comparability and traceability of results. In addition, the improved z and zeta scores obtained here suggest that similar post-acquisition optimization strategies could be beneficially applied to other U- or Pu-bearing microparticle intercomparisons, contributing to more robust qualification and performance assessment within the NWAL.

Summary

This study successfully demonstrates that the reliability and accuracy of TIMS isotopic analysis coupled with the continuous heating method for ultra-trace uranium parti-

cles can be significantly enhanced by applying the optimized data integration method. By retrospectively applying the 'Method I' (summed intensity ratio) and 'over 25% integration range' protocol to the previous NUSIMEP-7 particle dataset, the analytical accuracy was improved, and systematic bias was reduced.

Most importantly, the interlaboratory comparison scores (z and zeta) were dramatically improved, moving from 'borderline' or 'warning' levels to 'excellent'. This work confirms that a robust data integration strategy is not merely a final step but a critical component of the analytical method, as important as the instrumental setup (e.g., the static detection mode). This finding implies that laboratories performing ultra-trace particle analysis should review not only their instrumentation but also their data integration methods to ensure the highest possible fidelity and reliability in their results.

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