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Article

Comparative Evaluation of a Novel Lithium Metaborate Fusion Approach and Phosphate Fusion for Multielement ICP-OES Analysis of Nb–Ta Ores

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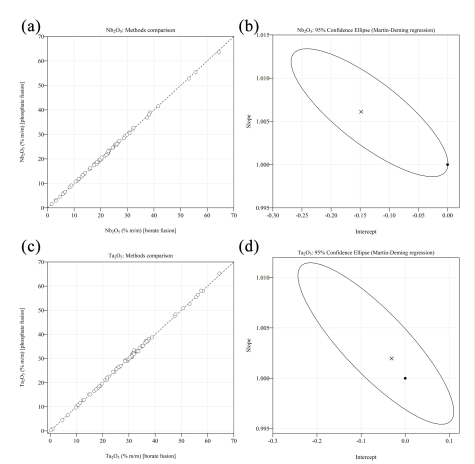
ABSTRACT: Reliable determination of niobium and tantalum in Nb–Ta ores is analytically challenging due to the refractory nature of the matrix and pronounced spectral and matrix effects in ICP-OES. In this study, two chemically distinct fusion procedures – an established phosphate fusion and an optimized lithium metaborate ($LiBO_2$) fusion followed by dissolution in a dilute HF/HNO_3 mixture – were systematically compared. A dataset of 69 natural Nb–Ta mineral concentrates and one industrial synthetic material analyzed over a ten-year period was used for the comparison. Method equivalence was assessed using Deming regression with a heteroscedastic error structure. Trueness was evaluated using the CRM X1808 certified reference material and an in-house reference material characterized by X-ray fluorescence (XRF). Both fusion methods provided analytically equivalent results for Nb_2O_5 and Ta_2O_5 across the entire concentration range. However, borate fusion allowed simultaneous determination of a broader range of elements, including Na_2O, P_2O_5, and SiO_2. Although both approaches can be used to quantify most analytes, their applicability is partly complementary: phosphate digestion does not allow reliable determination of sodium and phosphorus, and SiO_2 determination may be limited at higher concentrations. In addition, while both fusion techniques are considerably more rapid and more robust than conventional acid digestion, borate fusion also allows slightly faster sample preparation. Overall, fusion-based approaches represent an efficient and reliable strategy for the comprehensive analysis of complex Nb–Ta matrices.



INTRODUCTION

Niobium (Nb) and tantalum (Ta) are metals critical for advanced metallurgy and the electronics industry, typically occurring together in nature as columbite–tantalite solid solutions series.[1,2] Their reliable quantitative determination is essential for quality control and the optimization of industrial processing.[3] From an analytical standpoint, Nb-Ta concentrates represent one of the most challenging matrices encountered in ICP-OES due to their refractory nature, extreme spectral richness, and severe matrix effects arising from the complexity of their mineralogical and chemical composition.[4,5]

Wet chemical decomposition typically involves digestion in concentrated mineral acids.[1,4] Although hydrofluoric acid (HF) is required, conventional procedures rely on hot mixtures of concentrated acids that pose significant safety risks and may lead to volatilization losses, including the loss of silicon as SiF_4.[1,6] Moreover, acid dissolution may result in the loss of volatile elements such as Pb, Se, Te, and Sb. In addition, multi-step protocols are often necessary to completely dissolve refractory phases such as zircon or cassiterite.[7,8] Unlike these hazardous hot acid digestion methods, current alternatives reduce risks and improve efficiency.[9]

On the other hand, fusion-based techniques are the most reliable

procedures for the quantitative dissolution of refractory Nb–Ta minerals.[8] Phosphate fusion has been widely applied, as polyphosphates effectively stabilize Nb and Ta in solutions.[8,10] However, this method introduces high sodium and phosphorus loads, precluding the determination of P_2O_5 and Na_2O_5.[8] Furthermore, established phosphate or KOH fusion protocols typically require additional heating during the dissolution of the melt, followed by prolonged cooling before dilution to volume.[3,11]

Complete dissolution using $Li_2B_4O_7$ resulted in recoveries of 98.5 ± 0.2% Nb_2O_5 and 100.4 ± 0.3% Ta_2O_5 was reported by *Nete et al.*.[12] Nevertheless, this approach is characterized by a larger batch of flux and time-consuming dissolution under more drastic conditions in sulfuric acid and 30 ml of methanol at 40 °C.[12]

On the other hand, $LiBO_2$ behaves differently due to its basicity, leading to better dissolution of acidic oxides. The melt also tends to crack during crystallization, making it unsuitable for disc preparation, but it facilitates dissolution. Lithium metaborate ($LiBO_2$) fusion represents a chemically distinct alternative that has been previously successfully applied in silicate analysis.[6] Moreover, the use of borate-based fluxes for the dissolution of high-purity niobium and tantalum oxides has been evaluated; however, challenges with analyte stability and secondary precipitation have been reported on numerous occasions when applied in combination with traditional procedures.[1,2] Although rapid fusion protocols for Nb–Ta minerals have been reported, including phosphate-based methods that take only 10–15 min,[8,10] these procedures often require additional heating steps (e.g., water bath dissolution) to achieve complete dissolution of the melt.

In summary, acid digestion is generally suitable for readily soluble oxides, carbonates, and sulfides; however, complete dissolution of refractory Nb–Ta minerals is always difficult.[1,9]

Alkali fusion significantly improves the decomposition of Nb– and Ta–bearing oxides by converting them into soluble niobate and tantalate species.[3] Nevertheless, large amounts of alkali introduced during fusion may result in high dissolved solids, increased reagent blanks, and severe matrix effects during subsequent ICP-OES analysis. In addition, dissolution of the fusion cake and control of contamination require careful optimization.[4,7]

Phosphate fusion provides a fluoride-free alternative, although its dissolution efficiency for highly refractory Nb-Ta materials is generally lower. However, phosphate-rich solutions are often less suitable for subsequent separation and instrumental analysis due to their high salt content, increased spectral background, and potential matrix interferences.[8,10]

Lithium borate fusion is widely recognized as one of the most effective approaches for the complete decomposition of refractory geological materials. The method provides near-total dissolution of resistant oxide and silicate phases, minimizes mineralogical effects, and is particularly suitable for quantitative recovery of high-field-strength elements.[2,6]

The approach presented in this study is based on an optimized 15-minute metaborate fusion followed by direct dissolution using a dilute HF/HNO_3 mixture under ambient conditions. This eliminates the need for additional heating and improves analytical throughput by avoiding cooling steps typically associated with phosphate fusion procedures. The performance of the proposed method was evaluated using a dataset of 69 Nb–Ta concentrates analyzed over a ten-year period. Method equivalence was assessed using Deming regression,[13] while analytical trueness was evaluated using the CRM X1808 certified reference material and supplementary reference materials.[14]

EXPERIMENTAL

Samples. Samples. A total of 71 materials were analyzed between 2014 and 2025, including 69 natural Nb–Ta concentrates, one certified reference material (CRM X1808), and one industrial synthetic sample (Tables S1 and S2). The Ta_2O_5/ Nb_2O_5 ratio ranged from approximately 1:6 to 11:1 in the natural concentrates and reached 104:1 in the synthetic material, covering a broad compositional range relevant to Nb–Ta ore characterization. All samples were ground to a particle size below 75 μm prior to fusion.

Reagents and standard solutions All solutions were prepared using deionized water. High-purity HNO_3 and HF (Analytika, Czech Republic) were used for sample stabilization and matrix matching. Analytical-grade $NaH_2PO_4 \cdot H_2O$ and Na_2HPO_4 (Merck, Germany) were used for phosphate fusion, while ultrapure $LiBO_2$ (Claisse, Canada) was used for borate fusion. Prior to use, $LiBO_2$ beads were ground to a fine powder to improve sample homogenization.

Calibration standards were prepared from commercial single- and multi-element solutions (Analytika, Czech Republic). All standards were matrix-matched to the corresponding decomposition procedure. Calibration solutions for borate fusion contained $LiBO_2$ and HF/HNO_3, whereas those for phosphate fusion were matched to the sodium phosphate matrix to minimize matrix-related effects during ICP-OES analysis.

CRM and reference materials. Method trueness was evaluated using CRM X1808 and expressed as analyte recovery relative to certified values. Additionally, an in-house reference material (IHRM), characterized by an accredited laboratory using XRF, was used to assess consistency in Ta-rich matrices. Certified values were available for Nb_2O_5 and Ta_2O_5, while concentrations

of other elements were used as indicative reference values.

External validation by XRF analysis. Selected samples were also analyzed in parallel by an independent accredited laboratory. An ISO/IEC 17025-accredited laboratory for the analysis of Ta/Nb-bearing materials, such as tantalite-columbite, used a fused-bead WD-XRF methodology. The instruments employed were a Bruker S8 TIGER, a PANalytical Axios, and a PANalytical Zetium. All three instruments demonstrated equivalent performance. The calibration was validated using commercially available certified reference materials (CRMs), internally produced reference materials, and synthetic spiked beads. Additionally, pressed-pellet scans were used for sample profiling; however, any results obtained using the pressed-pellet method were considered semi-quantitative.

Instrumentations. Elemental analysis was performed using Thermo Scientific iCAP 6500 Duo and iCAP PRO XPS ICP-OES spectrometers. The former was used until 2022, after which analyses were performed using the iCAP PRO XPS. Both instruments employ high-resolution echelle optics and CID detector technology for simultaneous multi-element determination.

ICP-OES method optimization and spectral line selection. Operating parameters were optimized for the highly complex Nb–Ta–Fe–Mn matrix, characterized by extreme spectral richness and pronounced matrix effects.[4,5] Primary importance was placed on signal stability and the minimization of non-spectral interferences. Radial plasma viewing was employed for most analytes to maximize analytical robustness against matrix-induced suppression effects and to handle the high total dissolved solids (TDS) originating from the fusion flux.[15,16] To ensure complete chemical resistance against the hydrofluoric acid (HF) present in the borate decomposition solutions, the sample introduction system was equipped with an HF-resistant DuraMist nebulizer, a PTFE cyclonic spray chamber, and a ceramic alumina injector (2.0 mm i.d.) within the partially demountable torch assembly.[1,6] Axial viewing was selectively used only for elements present at low concentrations (Na, K, W). Detailed instrumental operating parameters of both the iCAP 6500 and the iCAP PRO XPS spectrometers are summarized in Table 1.

Due to the extreme spectral complexity of Nb–Ta matrices, no internal standard was applied. Preliminary tests demonstrated that the high background levels characteristic of these refractory ores precluded the effective use of common internal standards.[4,5] Instead, matrix-matched calibration solutions containing acid and flux compositions identical to the sample digests were used to compensate for easily ionizable element (EIE) effects and matrix-related transport phenomena.[8,16,17]

Spectral line selection was guided by the simultaneous monitoring of multiple emission lines and by the individual assessment of matrix effects. Recommended primary and alternative wavelengths for each element are summarized in Table 2. For final quantification, niobium was determined using the Nb (II) line at 316.340 nm and tantalum was determined using the Ta (II) line at 240.063 nm.[4,8] These wavelengths provided an optimal compromise between sensitivity and resistance to spectral interferences in real concentrates.[4,7] Alternative lines were monitored for verification to ensure the consistency of analytical results over the ten-year study period. The selection of other analytical wavelengths was based on a comprehensive review of the literature and further validated using interference tables and spectral scans provided by the instrument control software.

Due to the mineralogical variability of the samples, spectral lines were assessed individually to identify potential overlaps. For example, determination of tantalum using the Ta (II) line at 268.517 nm was found to be susceptible to interference from vanadium and titanium.[7,8]

Inter-instrument comparability of the two ICP-OES instruments used during the ten-year study period was verified by CRM analyses. Welch's t-test showed no statistically significant difference between the results ($p = 0.288$), indicating the absence of instrument-related bias and confirming equivalence of results at $\alpha = 0.05$.

For minor and trace elements, interferences from flux

Table 1. Instrumental ICP-OES operating parameters

Parameter	Setting	
	iCAP 6500 Duo	iCAP PRO XPS
RF Power (W)	1150	1050
Plasma gas flow (L min^{-1})	12	11.5
Nebulizer flow (L min^{-1})	0.7	0.6
Viewing height (mm)	12	10
Integration time (s)	5	5
Repeats	3	3

Table 2. Recommended primary and alternative atomic (I) and ionic (II) emission lines for multi-element ICP-OES analysis of refractory Nb–Ta ores

Element	Primary line (nm)	Alternative lines (nm)
Nb*	316.340 (II)	309.418 (II); 319.498 (II)
Ta*	240.063 (II)	263.558 (II); 268.517 (II)
Al	396.152 (I)	394.401 (I); 309.271 (I)
Ca	315.887 (II)	317.933 (II;) 393.366 (II)
Fe	238.204 (II)	259.837 (II)
K	769.896 (I)	766.490 (I)
Mn	257.610 (II)	260.569 (II)
Na	589.592 (I)	588.995 (I)
P	177.495 (I)	178.284 (I)
Si	251.611 (I)	250.690 (I); 212.412 (I)
Ti	336.121 (II)	323.452 (II); 337.280 (II)
W	239.709 (II)	224.875 (II); 207.911 (II)
Zr	339.198 (II)	343.823 (II)

* For final quantification, Nb was determined using the Nb (II) line at 316.340 nm, and Ta was determined using the Ta (II) line at 240.063 nm.

components or internal standards were carefully evaluated, including the effect of scandium on sodium determination using the Na (I) line at 588.995 nm. When phosphorus was determined using the P (I) line at 178.221 nm, a direct spectral interference from sodium was identified; furthermore, in this spectral region, emission intensity can be influenced by the presence of (EIE), which can affect plasma ionization equilibrium. [6,18]

During the analysis, multiple emission lines were monitored for each element, and the final selection for quantification was always individually evaluated with respect to the specific sample matrix. Emission lines for selected elements (Na, K, P) were measured in axial viewing mode to improve sensitivity.[6,18]

Experimental design and statistical methods. A total of 69 Nb–Ta concentrates were used to evaluate the agreement between the optimized borate fusion and the reference phosphate procedure. All samples, including the certified reference material (CRM X1808), were analyzed in triplicate to ensure robust precision estimates. Analytical signals were processed and calibrated using the manufacturer's software (iTEVA and Qtegra), and the resulting concentration data were subsequently exported to Microsoft Excel for final data reduction.

The agreement of results for Nb_2O_5 and Ta_2O_5 was assessed using iteratively reweighted general Deming regression.[13] The standard deviations (SD) derived from triplicate measurements (as estimates of measurement error) provided the necessary weighting factors for the regression, ensuring that the estimation of systematic bias accounted for the heteroscedastic nature of measurement uncertainties across the entire concentration range. The heteroscedasticity of regression residuals was tested using the studentized Breusch-Pagan test[19] and orthogonal regression residual plots. To provide a robust estimate of potential methodological bias, 95% confidence intervals and a 95% confidence ellipse were calculated using bias-corrected and accelerated bootstrap resampling.

Confidence intervals can only be used to assess the slope or the intercept separately. To assess both the slope and the intercept at the same time, a confidence ellipse must be used.[20] All significance tests were conducted at a level of $\alpha = 0.05$.

All calculations were made with the freely available R software (*https://cran.r-project.org/*). The R library *boot* was used for bootstrap implementation, and the R library *car* was used for confidence ellipse visualization. The studentized test for heteroscedasticity was computed using the R lmtest library. The iteratively reweighted generalized Deming regression script was programmed in R (see the supporting information – Text S1).

RESULTS AND DISCUSSION

Fusion procedures. The chemical characterization of Nb–Ta concentrates was performed using two independent fusion-based procedures.[1,4] The first one of these was the well-established and validated phosphate fusion method.[8,10] This procedure utilizes linear and cyclic polyphosphates that act as powerful complexing agents, effectively stabilizing Nb and Ta in acidic media.[10,21] However, the massive contamination of the resulting solution with sodium and phosphorus from the flux precludes their determination.[8]

The second procedure was an optimized borate fusion using pure $LiBO_2$, which served as a complementary technique to obtain a comprehensive multi-element profile, including Na_2O and P_2O_5. The melt was dissolved in a mixture of HNO_3 and HF, which ensures the stabilization of Si, Nb, and Ta through the formation of stable fluoride complexes.[1,4]

Phosphate fusion (reference method). The benchmark procedure followed the established phosphate-based fluxing protocols described by Mahanta et al. and Radhamani et al.[8,10] To prepare the flux, 2.00 ± 0.1 g of Na_2HPO_4 and 2.00 ± 0.1 g of $NaH_2PO_4 \cdot H_2O$ were combined in a platinum crucible and melted to form a homogeneous polyphosphate glass. After cooling, a precisely weighed portion (0.25 g) of the dried, finely ground concentrate was added to the melt. Decomposition was performed over a Meker burner for 15 min, providing the intensive heating required to ensure the complete dissolution of refractory minerals into the phosphate matrix.[10]

In a significant modification of the traditional protocol, which typically relies on passive dissolution in a water bath[8,10], the subsequent disintegration of the melt was optimized for modern laboratory throughput. Following fusion, the cooled crucible was placed in a glass beaker containing approximately 75 mL of deionized water. To ensure rapid and uniform dissolution, a cross-shaped magnetic PTFE stir was used and the entire assembly was placed on a multi-position magnetic stirrer with integrated heating. This modified approach enabled the simultaneous, controlled processing of multiple sample melts. Once the solutions reached ambient temperature, they were transferred to 100-mL volumetric flasks and diluted to the mark. The final dilution factor was optimized to 25-fold to enable the simultaneous determination of all analytes in a single measurement run. This optimized dilution provided an ideal balance between ensuring sufficient sensitivity for the detection of trace impurities and maintaining the major constituents within the linear calibration range.

Optimized lithium metaborate fusion. The newly developed decomposition protocol was adapted from conventional silicate

rock fusion procedures[6] with significant modifications specifically tailored to meet the analytical requirements of high-grade refractory Nb–Ta concentrates. A precisely weighed portion (0.1 g) of the finely ground sample was thoroughly mixed with 1.0 ± 0.05 g of pre-ground $LiBO_2$ powder in a platinum crucible, maintaining a sample-to-flux ratio of 1:10.[2,6] The mixture was fused over a Meker burner for 15 min, resulting in the formation of a homogeneous, glassy melt (If a homogeneous glass bead fails to form, the addition of a small amount (~20 mg) of a glass-forming component, such as Al_2O_3 or SiO_2, can facilitate melt formation). After it was removed from the flame, the crucible was allowed to cool partially before being submerged in a PTFE beaker containing 70 mL of deionized water, 3 mL of concentrated HF, and 4 mL of concentrated HNO_3.

A cross-shaped magnetic PTFE stir bar was added to the crucible, and the disintegration of the melt was performed on a multi-position magnetic stirrer under ambient conditions without external heating (Fig. S9). Once the melt was fully dissolved, the solution was transferred to a 100-mL volumetric flask and diluted to the mark. Before the final ICP-OES analysis, the solutions were diluted 10-fold. This modified approach offers a distinct operational advantage by eliminating the secondary heating and subsequent cooling cycles required in conventional fusion protocols.[8,10] In the final ICP-OES analysis, this approach thereby increased laboratory throughput while preserving the stability of fluoride complexes in the HF/HNO_3 medium.

To ensure the precision and statistical reproducibility of the results, the samples were prepared and analyzed in triplicate for both fusion methods.

Comparison of fusion methods for Nb_2O_5 and Ta_2O_5. Accurate quantification of Nb and Ta is essential for Nb–Ta ore concentrates, given their strategic importance and significant economic value in high-tech sectors.[9,22] Given the refractory nature of these materials, the use of two chemically independent decomposition procedures**,** the established phosphate benchmark and the proposed optimized borate fusion method essentially served as an internal validation approach.[8,21] Matrix-matched ICP-OES calibration was found to be essential, as fusion procedures introduce high concentrations of dissolved flux components. Matching the acid and flux compositions of calibration standards to those of the sample solutions minimized matrix-related transport effects and EIE-induced signal variations, thereby contributing to the good agreement observed between the two decomposition methods over a wide concentration range. While tantalum (Ta_2O_5) was determined in all the 71 materials, niobium (Nb_2O_5) quantification was performed for a subset of 68 samples due to minor technical constraints encountered during the analytical runs. This slight discrepancy did not affect the statistical power of the comparison, as both datasets remained sufficiently large to ensure robust regression parameters and an accurate estimate of methodological bias.

The inherent mineralogical diversity of Nb–Ta concentrates requires such analytical redundancy, as variable concentrations of major or minor constituents can lead to the failure of a specific fusion protocol.[5,8] For instance, an elevated silica (SiO_2) content is a documented limitation for phosphate-based procedures, as these melts are primarily optimized for refractory oxide matrices.[5,8] Simultaneously, the use of alternative fluxing agents, such as the borate mixture proposed here, ensures total decomposition even in samples rich in refractory impurities that often resist traditional fluxes.[2,6]

To rigorously assess the performance of the proposed borate fusion against the established phosphate protocol, the following sections provide a detailed statistical comparison for each analyte, beginning with the evaluation of niobium.

Niobium oxide. Results of the Nb_2O_5 and Ta_2O_5 determination for all analyzed samples after phosphate and borate fusion, including standard deviations, can be found in Tables S1 and S2. The relationship between the measurement error (expressed as standard deviation) and the mean measured values for both fusion methods (Fig. S1 and Fig. S2) exhibits a statistically significant slope ($p < 10^{-7}$), confirming the presence of a proportional error term. In both cases, the intercept is not significant, indicating that the multiplicative component predominates in the measurement error (i.e., the measurement error increases systematically with the signal amplitude).

The iteratively reweighted Deming regression (IRGDR) method[20] was used to accurately estimate systematic errors in the results of both methods (Fig. 1a). Bootstrap confidence intervals yielded an intercept of -0.1510 (-0.2624, -0.0683) and a slope of 1.005826 (1.0002, 1.0121).

The slope is statistically different from unity (slope of the identity line), albeit only marginally, indicating the presence of a proportional systematic error. Similarly, the intercept is significantly different from zero (intercept of the identity line), suggesting a constant bias, likely related to background signals or sample preparation effects.

However, these deviations are analytically negligible in the context of ore-concentrate analysis. For a material containing approximately 56 wt.% Nb_2O_5, an intercept of -0.15 wt.% corresponds to a relative deviation of only about 0.27%, which is well below the typical analytical precision of ICP-OES (RSD ≈ 1–3%) for such complex refractory matrices.[7,8]

These results confirm very good, although not complete, agreement between the two methods. A more appropriate representation using confidence ellipse analysis further indicates boundary agreement (Fig. 1b). Therefore, for rigorous method-to-method conversion, it is appropriate to correct for both slope and intercept.

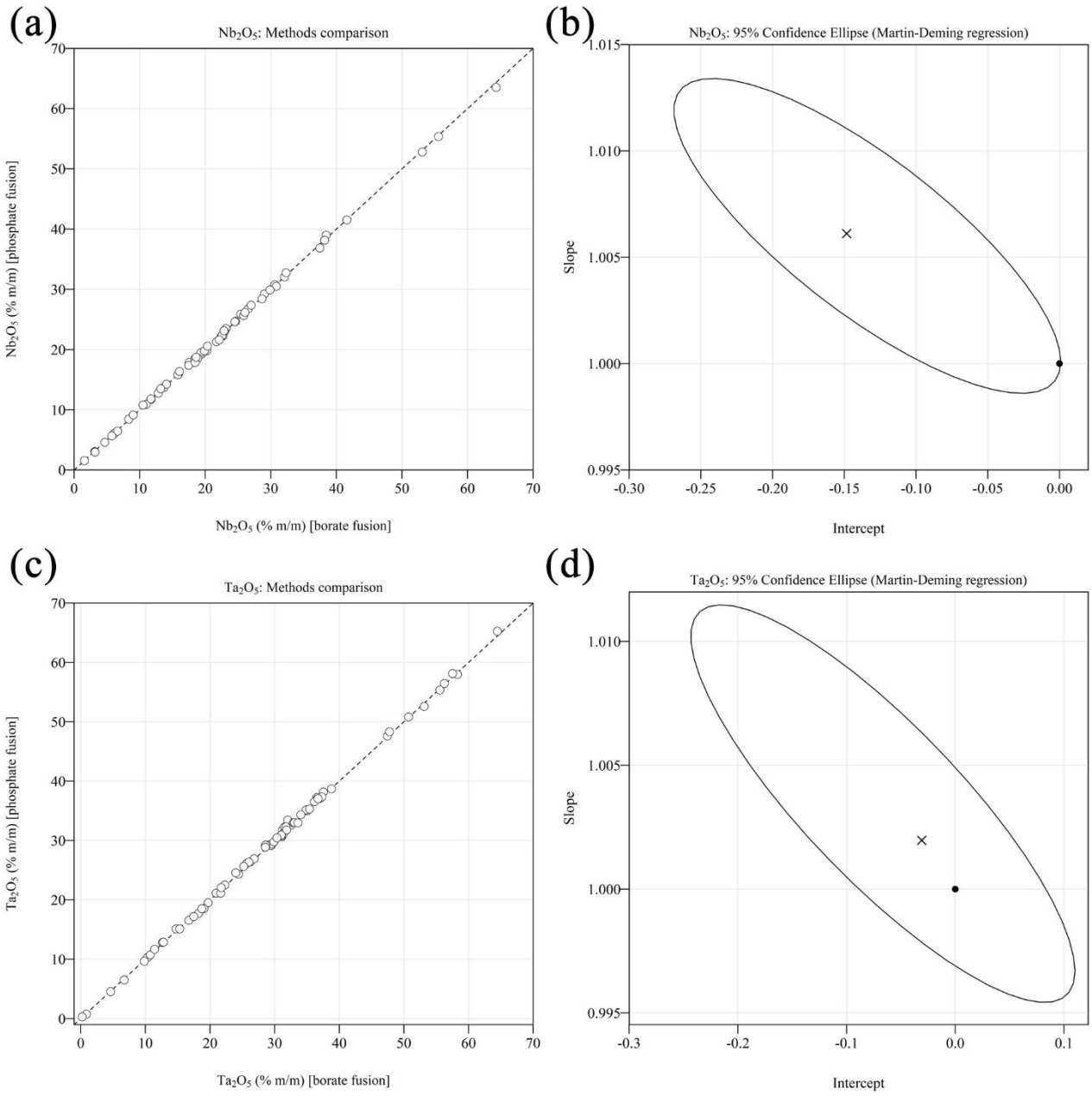


Fig. 1 Scatter plot comparing the methods used to determine Nb_2O_5 (a) and Ta_2O_5 (c). The dashed line has a y-intercept of zero and a slope of one, marking the identity line, which corresponds to complete agreement between the results of the two methods. Confidence ellipse comparing the methods used to determine Nb_2O_5 (b) and Ta_2O_5 (d). The black dot corresponds to the intercept of 0 and the slope of 1. The cross corresponds to the calculated intercept and slope. The ellipse is the joint confidence region for both estimates.

The studentized Breusch–Pagan test was used to evaluate the heteroscedasticity of the regression residuals (see supporting information). Analysis of classical orthogonal residuals (Fig. S3) indicates statistically significant heteroscedasticity ($p < 0.001$). However, after normalization by measurement standard deviations (Fig. S4), the heteroscedasticity disappears ($p = 0.80$). This indicates that the observed heteroscedasticity arises solely from measurement uncertainty, not from the regression model.

Given the large sample size ($n = 68$), the statistical tests have high power to detect even minute differences that do not affect practical validity. The minor bias observed for niobium, which was not observed for tantalum, is likely related to its higher sensitivity to variations in plasma excitation conditions induced by the matrix.[2,8]

Tantalum oxide. The relationship between the measurement error

(as standard deviation) and the average values measured for both fusion methods (Figs. S5 and S6) exhibits a statistically significant slope ($p < 10^{-6}$ to 10^{-9}), confirming the presence of a proportional error term. In both cases, the intercept is not significant, which again indicates the predominance of the multiplicative component in the measurement error (the measurement error increases systematically with the signal amplitude). While tantalum exhibits a clear proportionality of error, the overall heteroscedasticity is less pronounced than that observed for niobium (see the supporting information).

The iteratively reweighted Deming regression method was used to accurately estimate the systematic errors in the results of both methods (Fig. 1c). The bootstrap confidence intervals yielded an intercept estimate of -0.0308 (-0.1747, 0.1495) and a slope of 1.0020 (0.9936, 1.0076).[13] Neither the intercept nor the slope is statistically different from the reference values of 0 and 1, confirming that the methods are statistically equivalent (Fig. 1d). For Ta, no correction of the slope or intercept is necessary when converting results between the two procedures, and the methods are therefore interchangeable.

According to the studentized Breusch-Pagan test,[19] the classical orthogonal residuals (Fig. S7) do not exhibit heteroscedasticity ($p = 0.70$). For residuals weighted by measurement standard deviations (Fig. S8), the degree of heteroscedasticity increases slightly but remains statistically insignificant ($p < 0.078$). This indicates that for tantalum, heteroscedasticity is less pronounced, and although weighted models are not strictly necessary, they may be used for methodological consistency across the study.

The statistical significance of the bias observed for niobium ($n = 68$) is primarily a consequence of the high power of the statistical tests, which are capable of detecting even minute physical differences that do not affect practical analytical validity.[13]

Although matrix composition was nominally matched between calibration standards and samples, small variations in flux mass may lead to minor differences in total dissolved solids (TDS) and the solution's physical properties.[6,16] Such variations are known to influence aerosol formation and analyte transport to the plasma, as well as plasma conditions, including excitation efficiency and the spatial distribution of emitting species.[16,18] Matrix effects in ICP-OES are generally attributed to changes in plasma conditions, particularly variations in the thermal characteristics of the plasma, electron number density, and the population of emitting species, all of which directly affect analyte excitation and emission intensity.[15,16]

Individual elements differ in their sensitivity to such matrix-induced variations, with niobium being more susceptible than tantalum. Tantalum's greater robustness can be attributed to the higher stability of its fluoride complexes in fluoride-rich environments.[1,17] Furthermore, the more covalent character of the Ta–O bond compared to the more ionic nature of the Nb–O bond may contribute to differences in the reactivity of their respective oxides in acidic media.[2] Consequently, these factors likely contribute to the small but statistically significant bias observed for niobium, while the overall agreement between the methods remains analytically acceptable.

Nb_2O_5 and Ta_2O_5 Inter-laboratory Validation and Method Accuracy. The method bias of the optimized borate fusion was evaluated through an inter-laboratory comparison involving seven Nb–Ta concentrates, including the internal benchmark IHRM. These samples were analyzed independently by our laboratory and an external accredited laboratory using XRF. Importantly, the comparison was conducted as a double-blind study, in which analyses were performed independently in our laboratory and in an accredited laboratory, without prior information about the samples' composition. Results were subsequently compared; therefore, this procedural independence ensured that the data remained fully objective and unbiased.[1,10]

As shown in Table 3, the results for both Nb_2O_5 and Ta_2O_5 demonstrate excellent agreement between the two methods. The bias of the optimized borate fusion relative to the accredited laboratory results ranged from -1.07% to +0.82% for Nb_2O_5 and -0.84% to +1.01% for Ta_2O_5.

Regarding the reference phosphate fusion method, a maximum bias of -2.20% was observed for Ta_2O_5 in a single sample (Sample 5), whereas all other samples exhibited significantly lower deviations. For all other samples, the phosphate fusion method exhibited significantly lower deviations. The fact that the borate fusion method maintained a narrow bias range, even for this outlier sample, highlights its robustness to matrix variability and the potential instability of tantalum in phosphate media.[8,10] The consistent performance achieved under independent conditions confirms that the optimized borate fusion is a highly reliable and robust method for the commercial grading of Nb–Ta concentrates.[7,8]

This independent inter-laboratory comparison validates the conclusions drawn from the previous parts of the study. The results obtained by both digestion methods demonstrate good agreement with the values determined by the external laboratory. Given that the external laboratory did not provide standard deviations or other measurement uncertainties, our findings fall well within the acceptable analytical range. This verification confirms that the observed differences are analytically negligible for the practical evaluation of niobium-tantalum concentrates. The statistically significant bias identified for niobium in the large dataset ($n = 68$) is primarily a mathematical artifact of the high power of the statistical tests used and remains analytically negligible for the practical evaluation of niobium-tantalum ore concentrates.[13]

Table 3. Inter-laboratory comparison of Nb_2O_5 and Ta_2O_5 determination: optimized borate fusion and phosphate fusion versus external XRF values

Sample ID		XRF value (wt.%)	Borate fusion		Phosphate fusion	
			Measured value (wt.%)	Bias (%)	Measured value (wt.%)	Bias (%)
IHRM	Nb_2O_5	26.69	26.91	+ 0.82	26.78	+ 0.33
	Ta_2O_5	18.55	18.74	+ 1.01	18.50	- 0.28
Sample 5	Nb_2O_5	15.82	15.90	+ 0.53	15.90	+ 0.48
	Ta_2O_5	31.32	31.10	- 0.71	30.63	- 2.20
Sample 14	Nb_2O_5	30.74	30.85	+ 0.36	30.52	- 0.73
	Ta_2O_5	36.90	37.06	+ 0.42	37.10	+ 0.54
Sample 20	Nb_2O_5	17.60	17.50	- 0.59	17.39	- 1.20
	Ta_2O_5	28.79	28.85	+ 0.55	29.20	+ 1.44
Sample 35	Nb_2O_5	25.70	25.43	- 1.07	25.88	+ 0.70
	Ta_2O_5	37.43	37.32	- 0.30	37.35	- 0.21
Sample 36	Nb_2O_5	22.99	22.94	- 0.21	23.00	+ 0.06
	Ta_2O_5	32.66	32.92	+ 0.80	32.98	+ 0.98
Sample 37	Nb_2O_5	26.08	25.86	- 0.84	25.66	- 1.61
	Ta_2O_5	33.37	33.09	- 0.84	33.03	- 1.03

Note: (1) The inter-laboratory comparison was conducted as a blinded study; all internal measurements were finalized and reported before receiving the external XRF results; (2) Bias (%) – relative bias calculated as: $bias = \frac{internal\ mean - XRF\ value}{\text{XRF value}} \times 100$ [16]

Table 4. Comparison of borate and phosphate fusion results with certified values for CRM X1808

Oxide	CRM X1808		Borate fusion method			Phosphate fusion method		
	Certified values (wt.%)	SD (wt.%)	Measured value (wt.%)	SD (wt.%)	Recovery (%)	Measured value (wt.%)	SD (wt.%)	Recovery (%)
Nb_2O_5	56.71	0.05	57.2	0.6	100.86	57.3	0.7	101.10
Ta_2O_5	0.265	0.003	0.26	0.01	98.11	0.263	0.003	99.25
SiO_2	3.52	0.02	3.5	0.1	97.98	3.4	0.1	97.77
Al_2O_3	0.614	0.007	0.63	0.01	102.48	0.609	0.007	99.19
CaO	11.67	0.01	11.8	0.2	100.86	11.9	0.2	101.97
Fe_2O_3	7.74	0.04	7.70	0.09	99.48	7.8	0.1	100.39
K_2O	0.463	0.002	0.43	0.01	92.67	0.45	0.04	96.32
MnO	0.383	0.002	0.369	0.005	96.34	0.375	0.004	97.91
Na_2O	4.73	0.06	4.83	0.03	102.11	-	-	-
P_2O_5	0.134	0.004	0.138	0.004	102.99	-	-	-
TiO_2	3.92	0.01	3.87	0.05	98.72	4.03	0.07	102.81
ZrO_2	0.837	0.002	0.85	0.02	101.43	0.83	0.01	99.04

Note: (1) SD (wt %) - standard deviations calculated from triplicate fusion; (2) Recovery (%) – relative recovery calculated as: $R = \frac{Cfound}{Creference} \times 100$ [17]

Assessment of analytical trueness using reference materials. The analytical trueness of the compared dissolution procedures was evaluated using the certified reference material (CRM X1808) and IHRM. The agreement between measured and reference values was used to assess method performance under realistic matrix conditions. This combined approach provides a more comprehensive evaluation by accounting for potential matrix effects and non-spectral interferences inherent in high-TDS geological concentrates.

Analysis of certified reference material. The concentrations determined by both the optimized borate fusion and the reference phosphate fusion method, along with their comparison to certified values, are summarized in Table 4. Good agreement was observed for most elements, confirming the overall reliability of both dissolution procedures. These estimated values are very close to the standard deviation values mentioned in the text and thus provide a reliable measure of the accuracy of this method. The evaluation of trueness is based primarily on the magnitude of the bias, which reflects systematic deviation from certified values and provides a direct measure of method performance.

For the major component of the analyzed matrix, Nb_2O_5 (56.71%), the borate fusion method showed excellent agreement with the certified value (recovery of 100.86%). This result confirms that the statistically significant bias previously identified in the large-scale method comparison (n = 71) is attributable to the high power of the statistical tests and does not represent an analytically meaningful difference.[13] Such minor deviations fall well within the performance limits expected for high-grade refractory niobium-tantalum matrices.[4,7]

In contrast, Ta_2O_5 is present as a minor component (0.265 wt.%) in the matrix dominated by niobium. The observed recovery (98.11%) reflects the expected variability at low analyte concentrations, where reduced signal-to-background (S/B) ratios increase sensitivity to matrix effects and signal fluctuations.[4,16] Na_2O and P_2O_5 were determined only using borate fusion. Both elements show

Table 5. Comparison of borate fusion and phosphate fusion results with indicative external laboratory values for the IHRM

Oxide	XRF value (wt.%) *	Borate fusion		Phosphate fusion	
		Measured value (wt.%)	SD (wt.%)	Measured value (wt.%)	SD (wt.%)
Al_2O_3	1	1.68	0.05	1.67	0.002
CaO	0.2	0.25	0.03	0.234	0.008
Fe_2O_3	16.7	17.0	0.4	17.1	0.1
K_2O	< 0.1	0.026	0.007	0.021	0.002
MnO	2	2.62	0.05	2.51	0.02
Na_2O	< 0.1	0.07	0.01	-	-
P_2O_5	0.5	0.477	0.007	-	-
TiO_2	29	29.9	0.3	29.8	0.3
SiO_2	2	2.26	0.08	2.09	0.03
WO_3	1	0.820	0.008	0.824	0.005
ZrO_2	0.4	0.375	0.02	0.337	0.007

Note: (1) SD (wt %) - standard deviations calculated from triplicate fusion; (2) * Values for elements other than Nb and Ta are only indicative.

good agreement with certified values (recovery of Na_2O: 102.11%, P_2O_5: +102.99%), consistent with the expected uncertainty at low concentrations. The bias observed for sodium may be related to matrix effects associated with its behavior as EIE, which can influence plasma conditions and the stability of emission signals[16,18]. For phosphorus, the observed deviations may be due to its lower emission sensitivity and greater dependence on background correction[4]. In this study, Na, K, and P were measured in axial view, which increases sensitivity but also enhances the influence of matrix effects and non-spectral interferences.[15] Although the sodium concentration is relatively high in this CRM, it is often significantly lower in real samples, where these effects are more pronounced.

Biases observed for minor components are consistent with the expected performance of ICP-OES. At low analyte concentrations, deteriorating S/B ratios increase the influence of noise, background correction, and memory effects.[1] These effects are further intensified by high total dissolved solids (TDS), which impact aerosol generation, analyte transport, and plasma excitation conditions.[6,16] The negative bias observed for SiO_2 is attributed to background and matrix-related effects in complex solutions.[8] The bias observed for K_2O reflects both its generally low concentration and its nature as an easily ionizable element, which modifies plasma ionization equilibrium.[18] In axial observation mode, such elements are particularly sensitive to variations in plasma conditions and total dissolved solids due to the extended optical path length.[15] In addition, trace contamination from flux components increases the blank level, further reducing the effective S/B ratio and affecting measurement reliability at low concentrations.[1,18]

Moderate biases observed for Al_2O_3, TiO_2, and MnO can be attributed to differences in excitation efficiency and line sensitivity to variations in plasma conditions and matrix composition.[4,8]

A comparison of the results obtained from the two fusion methods (borate and phosphate) was also performed using a paired t-test with Welch's modification. Its application is appropriate only in the absence of proportional systematic error, i.e., when the slope of the orthogonal regression line is very close to 1.[23] This condition was met for both Nb_2O_5 and Ta_2O_5. For these analytes, the paired t-test did not reveal a statistically significant difference ($\alpha = 0.05$) between the results obtained by the two fusion methods.

A very small but statistically significant difference between the reference and measured values was observed for K_2O and MnO in the borate fusion data. All results from paired t-tests are available in Tables S3 -S4.

From a practical perspective, the primary objective is to ensure that concentration does not exceed technological limits. Within this context, the observed biases are acceptable. At higher concentrations (e.g., Nb_2O_5), relative errors decrease due to improved S/B ratios.

Using a single dilution represents a deliberate compromise between analytical accuracy and throughput. Although lower dilution factors would increase the signal intensities of minor elements, they would require calibration solutions matched to higher concentrations of dissolved flux components. This would increase TDS, enhance non-spectral interferences, and accelerate contamination of the sample introduction system and plasma.[6,16]

Overall, both dissolution methods provide analytically comparable results within the uncertainty associated with ICP-OES analysis of these complex matrices. Borate fusion extends analytical capabilities to a broader range of elements, while phosphate digestion remains a reliable approach for established Nb and Ta determination.[8] The observed biases, particularly for minor components, are consistent with the expected ICP-OES performance for complex refractory matrices.

In-house reference material (multi-element comparison). The evaluation using the IHRM supports the conclusions drawn from the CRM-based assessment, as summarized in Table 5. The material is representative of typical Nb–Ta concentrates, allowing assessment of method performance under realistic matrix conditions.

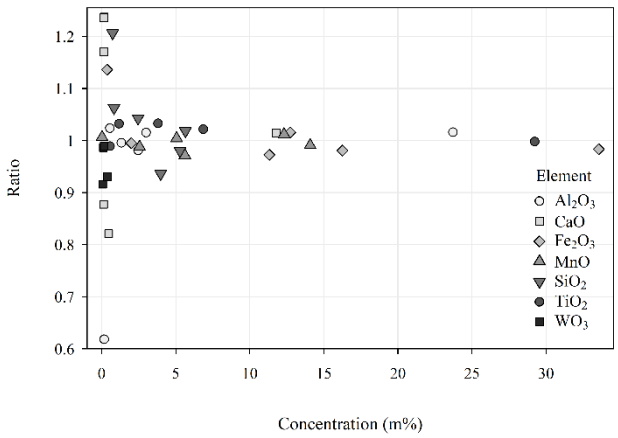


Fig. 2 Relationship between analyte concentration and agreement between the borate fusion and phosphate fusion methods expressed as borate-to-phosphate ratios plotted on a concentration scale. Larger deviations are observed at lower concentrations due to lower S/B ratios.

The accredited laboratory supplied validated reference values for Nb_2O_5 and Ta_2O_5. The XRF results for the remaining elements should be regarded as indicative only, as they were not subject to full multi-element validation.

For Nb_2O_5 and Ta_2O_5, the agreement between the two methods is discussed separately; this section therefore focuses on additional elements. For these elements, externally obtained values serve only as qualitative references, and agreement should be interpreted in terms of consistency rather than accuracy.

Very good agreement was observed between the borate fusion and phosphate fusion methods for major components, with consistent trends also evident in the indicative external data. This confirms that both dissolution methods provide comparable analytical information under realistic sample conditions.

Most results obtained by borate fusion and phosphate fusion show very good agreement. A more pronounced difference is observed for SiO_2, for which values obtained by both methods are slightly higher than the indicative data supplied by the external laboratory. Considering the low silicon content in this material, this discrepancy is more apparent than in the CRM. It is consistent with the generally increased sensitivity to background effects at low concentrations.[5] A contribution of memory effects in silicon determination cannot be excluded.[1]

For P_2O_5, the values obtained by borate fusion are close to the indicative external data. Sodium was reported below the detection limit in the external analysis, whereas it remained detectable after borate fusion at concentrations below the detection limit of the XRF method. A similar trend was observed for K_2O, where ICP-OES enabled determination at lower concentrations than XRF. This difference reflects the generally lower detection limits of ICP-OES compared to XRF and confirms its greater sensitivity for trace-level analysis.[4,8]

With phosphate fusion, slightly lower potassium values were obtained, possibly due to the influence of the flux-derived blank. Potassium commonly occurs as an accompanying element of sodium, and even trace contamination can have a significant effect at low concentration levels.

Overall, very good agreement between the two dissolution methods was also observed for minor components, with differences being consistent with the expected performance of ICP-OES at low analyte concentrations. The results confirm that the two methods are complementary and together provide comprehensive quantitative information on the composition of Nb–Ta concentrates with variable matrices.

Comparison of the two dissolution methods using additional samples. The applicability of both dissolution methods was further evaluated using six samples representing a wider compositional range of Nb–Ta concentrates. The concentrations of the analyzed components covered broad ranges, including Al_2O_3 (0.17–23.7 wt.%), CaO (0.11–11.8 wt.%), Fe_2O_3 (0.31–34 wt.%), SiO_2 (0.60–5.6 wt.%), TiO_2 (0.56–29.3 wt.%), and WO_3 (0.058–1.2 wt.%). Elements present at lower concentrations exhibited correspondingly low levels, for example, K_2O (~0.02–0.13 wt.%). In the case of phosphate fusion, potassium concentrations were partially below the limit of quantification (LOQ), which can be attributed to the influence of the flux-derived blank and reduced sensitivity at low concentration levels. Sodium and phosphorus were determined only after borate fusion, with Na_2O ranging from 0.03 to 12.3 wt.% and P_2O_5 ranging from 0.025 to 3.28 wt.%; P_2O_5 was below the LOQ in two samples. The sets of determined elements varied among samples depending on specific analytical requirements; consequently, the number of available data points differed slightly among analytes. To enable comparison across analytes present at widely different concentration levels, the results are expressed as borate-to-phosphate ratios and summarized in Fig. 2 and Table S5. Only elements determined by both methods are included in the graphical and tabular comparison; analytes with a higher proportion of results below the quantification limit, such as K_2O after phosphate fusion, were therefore excluded.

A clear dependence of agreement between the two dissolution methods on analyte concentration is evident in Fig. 2. Most data points at higher concentrations cluster near unity, confirming very good agreement between the borate fusion and phosphate fusion methods.[8,13] In contrast, a larger spread is observed at lower concentration levels, which can be attributed to reduced S/B ratios and increased sensitivity to matrix effects.[4,16] This trend is consistent with the results of the CRM and IHRM evaluations, in which larger deviations were observed for minor components due

to the same analytical limitations.[13] The differences observed between the methods therefore do not indicate systematic bias but rather reflect the expected performance of ICP-OES in multi-element analysis across a wide concentration range.

The results further demonstrate that both dissolution methods provide reliable and mutually comparable analytical data for major components, as well as for accompanying elements over concentration ranges spanning several orders of magnitude. Moreover, borate fusion extends the analytical capabilities of the method by enabling the determination of sodium and phosphorus, which cannot be reliably quantified after phosphate digestion.

CONCLUSION

This study compares an optimized $LiBO_2$ fusion method with the established phosphate fusion procedure for the analysis of high-grade Nb–Ta concentrates by ICP-OES. Both methods showed comparable performance in determining Nb_2O_5 and Ta_2O_5. Although statistical analysis indicated a small but significant deviation for Nb_2O_5, the difference remained within typical analytical uncertainty and was not analytically relevant. CRM results confirmed excellent agreement with certified values, while Ta_2O_5 results showed no evidence of systematic bias. Assessment using CRMs, in-house reference materials, and real samples demonstrated that deviations for minor elements are consistent with expected ICP-OES limitations at low concentrations and in complex matrices. Dispersion between methods increased as analyte concentrations decreased, particularly for SiO_2, suggesting additional influences such as matrix effects, blank contributions, and memory effects.

These effects are consistent across all evaluated datasets and do not indicate a systematic difference between the dissolution methods. Overall, both dissolution methods are reliable, robust, and suitable for practical application in the analysis of Nb–Ta concentrates. Phosphate fusion remains a benchmark method for the routine determination of the major components Nb and Ta. At the same time, borate fusion extends the analytical capability to comprehensive multi-element determination, including sodium and phosphorus. The two methods should therefore be considered complementary, enabling detailed characterization of samples with complex and variable mineralogical compositions.

The proposed method introduces two key innovations. First, $LiBO_2$ fusion is followed by ambient dissolution of the fusion melt in a dilute HF/HNO_3 medium, eliminating the additional heating and cooling steps required in conventional fusion procedures and improving sample throughput. Second, method performance was evaluated using advanced statistical tools, including iteratively reweighted Deming regression, bootstrap confidence intervals, and heteroscedastic error modeling, providing a rigorous assessment of method equivalence, bias, and analytical reliability across a large set of Nb-Ta concentrates.

ASSOCIATED CONTENT

The supporting information (Text S1, Figs S1−S9, and Tables S1−S5) is available at https://www.at-spectrose.com

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Notes

The authors declare no competing financial interest.

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