Evaluation of Standard Measurement Uncertainty From Method Validation Data for the ICP-OES Determination of Nb, Ta, Fe, Mn, Ti, Sn, Zr, and W in Niobite-Tantalite Samples

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ABSTRACT

A procedure is described for the evaluation of standard measurement uncertainty from validation data by the GUM “bottom-up” approach for the determination of Nb, Ta, Fe, Mn, Ti, Sn, Zr, and W in niobite-tantalite (columbite-tantalite) mineral samples by inductively coupled plasma optical emission spectrometry (ICP-OES). Sample preparation was carried out by fusion using a phosphate salt mixture. The method was validated using a single laboratory approach by assessing analytical performance characteristics like specificity, linearity, range, accuracy, and precision. The method showed good specificity and no spectral interferences were observed for all elements determined. Relative standard deviation (RSD) values ranging from 0.9 to 8.3% were obtained for the repeatability studies with values

ranging from 2.5 to 14.3% for the intra-lab reproducibility studies. Accuracy was established by application of the method to two niobite-tantalite certified reference materials (CRMs) and also by comparison of the results obtained for a niobite-tantalite sample by the present method with those obtained by an alternate method. The validated method was applied to the determination of Nb, Ta, Fe, Mn, Al, Ti, Sn, Zr, and W in selected niobite-tantalite samples from India. The measurement uncertainty (MU) associated with the quantitative determination of Nb, Ta, Fe, Mn, Ti, Sn, Zr, and W in a typical niobite-tantalite sample was evaluated using the GUM “bottom-up” modelling approach. The MU results were compared with those obtained using the Horwitz equation and an uncertainty budget presented in this paper.

emerged as the most important techniques employed in geochemical exploration programs, where reliable quantitative measurement of several elements in a large number of samples needs to be carried out with speed and cost-effectiveness. Geological sample analyses are further compounded by the presence of a complex range of matrices and the potential for widely different compositions within an analytical batch of samples.

Further, both ICP-OES and ICP-MS being solution-based techniques, wet chemical procedures for complete sample breakdown become unavoidable and imperative. Analytical methodologies involving wet procedures are particularly difficult for the analysis of niobite-tantalite minerals since these elements do not form simple soluble compounds in aqueous solutions (2). In neutral and acid solutions, they hydrolyze with the formation of hydrophilic colloidal systems. Tartaric acid, oxalic acid, citric acid, fluoride, and a mixture of hydrogen peroxide and sulfuric acid are used to prevent hydrolysis. Owing to their easily hydrolyzable nature in the presence of mineral acids, fusion digestions are preferred for the dissolution of these mineral samples. Several fusion digestion methods have been reported for these samples. Potassium bisulfate fusion, followed by dissolution of the fused melt in tartaric acid solution prior to determination by AAS and ICP-OES, has been reported (3, 4). Sodium peroxide fusion, followed by acid hydrolysis separation, has also been

INTRODUCTION

Niobium (older name: Columbium) and tantalum compounds are used in several high technology fields, such as the aerospace, nuclear, and electronic industries, and in the manufacturing of superconductors, cutting tools, thermocouples, dielectrics, cryotrons, and super alloys (1). “Niobite-tantalites” are refractory

minerals of niobium and tantalum which occur in nature along with other minerals like samarskite, euxenite, fergusonite, and cassiterite. In view of the economic importance of Nb and Ta, there exists a need to develop and validate analytical methods for the chemical characterization of their ores and minerals for use in geochemical exploration for these metals and evaluation of their potential resources.

Over the past few decades, inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) have

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utilized (5). Lithium metaborate (6), fluoride salt mixture (7), and phosphate salt mixture (8) have been employed for fusion digestion of niobite-tantalite samples prior to multi-element determination by ICP-OES. Among all fusion digestion methods developed by our laboratory, the one employing a phosphate salt mixture is simple, reliable, fast, and eco-friendly (8). Hence, this method was selected for inclusion under the scope of accreditation of our laboratory as per ISO/IEC: 17025(2005) standard (9).

It is mandatory for laboratories seeking accreditation as per the ISO/IEC: 17025 (2005) standard to validate all non-standard methods and laboratory-developed methods placed under their scope of accreditation (9). Although, ICP-OES has become a routine analytical technique for metal determination in diverse samples and several papers have been published, there is a paucity of information related to method validation and evaluation of measurement uncertainty (10). Therefore, an intra-laboratory validation of the analytical method for the determination of the main constituent elements in niobite-tantalite samples by ICP-OES after fusion digestion using a phosphate salt mixture (8) was carried out and the results are presented in this paper. The method was validated according to the guidelines cited in several publications (11-13) and applied to the determination of Nb, Ta, Fe, Mn, Ti, Sn, Zr, and W in niobite-tantalite samples from India. Besides common method performance characteristics obtained in the validation process, it is also mandatory for testing laboratories seeking accreditation as per the ISO/IEC: 17025 (2005) standard to have and apply procedures for estimating the uncertainty of measurements.

When reporting the result of a measurement of a physical quan-

tity, it is obligatory that some quantitative indication of the quality of the result be given, so that those who use it can assess its reliability. One useful measure of this is measurement uncertainty (MU). The publication of the "Guide to the Expression of Uncertainty in Measurement" (the GUM) by ISO formally established the general rules for evaluating and expressing uncertainty in measurement across a broad spectrum of measurements (14). The EURACHEM/CITAC document shows how the concepts in the ISO guide may be applied in chemical measurement (16). Different approaches are reported for the estimation of total standard MU (14-16). In this study, a simple procedure has been described for evaluation of the MU by GUM "bottom-up" modelling approach using the validation data, and the results are compared with those obtained using the Horwitz equation (17, 18).

EXPERIMENTAL

Reagents and Standards

All reagents used were of analytical grade or better. All solutions were made using ultrapure (resistivity 18 M Ω -cm) water. Analytical grade mineral acids were procured and purified further prior to use by sub-boiling distillation. Class A grade volumetric glassware was used for the studies and calibration was carried out by accredited agencies.

Traceable elemental standard stock solutions (1 mg/mL) were procured from M/s Inorganic Ventures (USA) for all elements determined. Matrix-matched mixed multi-element working standard solutions in the range of 0.1 to 50.0 μ g mL⁻¹ were prepared from the above stock solutions by appropriate dilution, and doping them with matching equivalent amounts of process blank as that of the sample.

Instrumentation

An ICP-OES Model Ultima-2 (Jobin Yvon Ltd., France) was used. The optimum parameters employed in the present study are given in Table I.

Analytical Test Procedure

Step 1- Sample Dissolution by Mixed Phosphate Fusion

A 4 g portion of a mixture of disodium hydrogen phosphate (anhydrous) and sodium di-hydrogen phosphate monohydrate salts (weight ratio 1:1) was weighed and transferred into a clean platinum crucible. The crucible was heated on a low flame until the mixture melted and formed a fused mass of condensed phosphate. A sample portion in the range of 0.1g to 0.2 g (-200 mesh size) was weighed accurately and transferred into the crucible, fused over a low flame for 2-3 minutes, and continued heating over a high flame until a clear melt was obtained. The melt after cooling was dissolved in ultra-pure water, taken into a beaker, and transferred into a 100 mL standard

TABLE I
ICP-OES Operational
Parameters

Instrumentation	Ultima-2 ICP-OES
Mounting	Czerny-Turner
Focal length	1 m
Dual Grating	4320 grooves mm ⁻¹ 2400 grooves mm ⁻¹
Order of measurement	1st
1st order resolution	0.005 nm
Type of generator	Solid state
Observation	Radial View
Frequency of generator	40.68 MHz
Power	1000 W
Plasma gas flow rate	12 L min ⁻¹
Sheath Gas flow rate	0.2 L min ⁻¹
Nebulizer gas flow rate	0.8 L min ⁻¹
Nebulizer type	Meinhard
Type of spray chamber	Cyclonic
Injector tube diameter	1.8 mm

flask. The beaker was washed with ultra-pure water, and the washings were added into the flask, then made up to volume with ultra-pure water. A process blank was prepared in the same way without taking any sample.

Step 2- Determination of Nb, Ta, Fe, Ti, Sn, Zr, Mn and W by ICP-OES

The sample solution was diluted appropriately with ultra-pure water. A 3-point external calibration of the ICP-OES was carried out using the matrix-matched traceable elemental standards. The intensities of the sample solution were measured, and the concentration of the elements in the measured solution was determined after blank correction from the calibration curve. From those results, the concentrations of the elements in the samples were calculated using the dilution factor, initial sample volume and weight taken.

Alternate Test Procedure

Step 1 - Sample Dissolution by Fluoride Fusion

A sample portion in the range 0.1-0.2 g (-200 mesh size) was accurately weighed into a clean platinum crucible. A 2 g portion of a mixture of KHF₂ and NaF salts (3:1 weight ratio) was added to the sample, heated over a low flame initially until the mixture melted; further heating continued over a high flame until a clear melt was obtained, and cooled. Then, 5 mL of 18N H₂SO₄ acid was added and heated on a hot plate until the evolution of dense white fumes of sulfuric acid ceased. An amount of 3 g of citric acid was dissolved in about 25 mL ultra-pure water taken in a 250 mL beaker, and heated. The platinum crucible with the fused mass was transferred into the beaker containing the citric acid solution, and boiled until the fused mass detached from the crucible and dissolved fully to give a clear

solution. The crucible was removed, washed with ultra-pure water, and the washings were added to the solution. A few drops of H₂O₂ were added to the solution and boiled in case the solution was not clear. The solution was then allowed to cool, transferred into a 100 mL volumetric flask, and made up to volume with ultra-pure water. A process blank was prepared in the same way without taking any sample.

Step 2 - Determination of Nb, Ta, Fe, Ti, Sn, Zr, Mn and W by ICP-OES

The concentrations of Nb, Ta, Fe, Ti, Sn, Zr, Mn, and W in the sample solutions were determined by ICP-OES after appropriate dilution, after a 3-point external calibration using the matrix-matched traceable elemental standards. From those results, the concentrations of the elements in the samples were calculated using the dilution factor, initial sample volume, and weight taken.

RESULTS AND DISCUSSION

Method Validation

Method validation is basically the process of defining an analytical requirement, and confirming that the method under consideration has capabilities consistent with what the application requires. In order to evaluate the present method's performance, specificity (selectivity), trueness (accuracy), precision (repeatability and intermediate precision), and working range including linearity were evaluated (11). For this, a single-laboratory approach was adopted. The data pertaining to performance characteristics were assimilated and checked whether the acceptance criteria were fulfilled. As a first step, critical instrumental parameters were optimized for achieving maximum sensitivity and precision (see Table I).

Specificity (Selectivity)

Different wavelengths were studied for the elements determined and wavelengths with optimum sensitivity were selected. The specificity was investigated by recording the emission profile of the specific element at its emission wavelength, both in the absence and presence of the suspected interfering elements using spiked synthetic solutions. All elements were spiked in appropriate amounts representative of a typical sample composition. The results showed absence of spectral interferences in all cases. The sample solutions also contain high levels of easily ionizable elements (due to the sodium and potassium salts used for fusion digestion) which lead to ionization interferences. In the case of elements, which occur in high concentrations in the sample (Nb, Ta, Ti, Fe, Mn), the ionization effects are negligible as the sodium concentration in the measuring solution is about 0.8 mg mL⁻¹ which is well within the reported tolerance limits (19). In the case of elements which occur in low concentrations in the sample (Sn, W, Zr), the ionization effects were corrected by using matrix-matched calibration standards.

Limit of Quantification (LOQ)

The limit of quantification for the different elements at respective wavelengths used was calculated by multiplying background equivalent concentrations (BEC) by 10 times of the (%)RSD of the blank.

$$LOQ = BEC * 10 * RSD_{BL}$$

The wavelengths used and LOQ values obtained for the different elements are given in Table II. The LOQ values for different elements were in the range of 0.0005 µg mL⁻¹ to 0.016 µg mL⁻¹.

Linearity (Instrumental Working Range)

In order to assess the instrumental working range and to confirm its

fitness for purpose, emission intensities were recorded for a series of six calibration standards. The relationship between concentration and instrument response was plotted using a linear regression equation. The results are presented in Table II. The ICP-OES response for all elements was found to be linear in the range of 0 to 150% of a typical sample concentration, as is evident from the linear calibration curve with $R^2 \geq 0.999$ (Table II), and also from the random distribution of residuals around zero concentration.

Range

In order to assess the method working range, since natural samples covering the entire concentration range were not available,

spiked materials were used. IGS-33 is a niobite certified reference material (CRM) and IGS-34 is a tantalite CRM, supplied by the British Geological Survey, U.K. For samples in the lower range of various elements, spiked materials were prepared by mixing appropriate portions of Specpure[®] alumina powder (obtained from Alfa Aesar) with the above CRMs. For samples in the higher range of elements, the following procedure was used. Appropriate aliquots of standard solutions were taken in a crucible and dried. Accurately weighed portions of Specpure alumina powder were added to the residue; the solutions were prepared and analyzed as per test procedure. Each measurement was replicated three times, and an average was used for

calculation of the result. The obtained concentrations of the elements were compared to the actual concentrations taken. The results are presented in Table III. Random distribution of residuals about zero was obtained confirming the absence of systematic error. The RSD values obtained were within 10% for the entire concentration range, and the coefficient of determination was also greater than 0.99, thus indicating good accuracy and precision over the tested range for all elements.

Accuracy

The IGS-33 Niobite and IGS-34 Tantalite CRMs were analyzed by the test method in 10 replicates, and the values obtained were checked against the accepted values (19, 20, 21). The results are presented in Table IV and V. The results obtained by the present method are within acceptable uncertainty limits about the certified/accepted values for the CRMs, thereby confirming the accuracy of the method.

For further assessment of accuracy, a niobite-tantalite sample was analyzed by the present method and an alternate method using fusion digestion with a fluoride salt mixture coupled to the ICP-OES for analysis (7), and the results compared.

The percent recovery (R,%) of the elements in the samples was calculated, using the following equation:

$$R(\%) = \frac{\text{Value obtained by alternate test procedure}}{\text{Value obtained by present test procedure}} \times 100$$

The recoveries obtained are presented in Table V. The values obtained by both methods were in good agreement with each other, with recovery ratios found to be in the range of 94 to 116%.

TABLE II
Analytical Wavelengths, Limit of Quantification (LOQ),
Instrumental Linearity

Element	Wavelength (nm)	LOQ ($\mu\text{g mL}^{-1}$)	b_1 [Slope]	b_0 [Y intercept]	R^2	Residual sum of squares (RSS)
Nb	316.340	0.006	146,581.84	13,375.65	0.9999	0.2198
Ta	240.063	0.016	19,223.52	6,538.93	0.9997	0.7500
Ti	334.941	0.003	562,499.42	34,714.78	0.9994	0.3880
Fe	238.204	0.006	121,166.00	- 465.89	0.9996	1.0890
Mn	257.610	0.0005	869,502.42	45,293.93	0.9997	0.1931
W	207.911	0.008	6,642.82	- 159.72	0.9997	0.0341
Sn	189.930	0.006	7,614.65	- 1,055.98	0.9995	0.0610
Zr	343.823	0.004	555,121.99	21,259.32	0.9996	0.0099

TABLE III
Results for Method Range

Element	b_1 [Slope]	b_0 [Y intercept]	R^2	Range of (%)RSD	Concentration Range (% w/w)
Nb	1.0068	- 0.4107	0.9997	0.85-1.90	1.0-63.0
Ta	0.9861	- 0.6306	0.9991	1.00-4.55	1.0-74.0
Ti	1.0252	0.0052	0.9999	0.74-3.25	0.1-10.0
Fe	1.0169	- 0.0015	0.9998	0.28-2.30	1.0-20.0
Mn	1.0266	- 0.3234	0.9984	0.02-2.53	0.5-20.0
W	1.0694	- 0.0558	0.9989	0.42-5.10	0.01-10.0
Sn	0.9754	0.0621	0.9998	0.40-3.26	0.05-20.0
Zr	0.9863	0.0103	1.0000	0.89-4.07	0.05-10.0

Short-term Precision (Repeatability)

Repeatability measurements were carried out with a natural niobite-tantalite sample. Ten replicate measurements were made on the same sample in the same laboratory using the same equipment by the same analyst on the same day. The mean and the relative standard deviation "RSD_R" were evaluated for all elements. The Horwitz ratio was employed as acceptance criteria (17, 18). Horwitz Ratio (HorRat) is the ratio of RSD_R calculated from the data of laboratory, to the RSD

predicted from the Horwitz equation (PRSD_R):

$$\text{HorRat}(r) = \text{RSD}_R / \text{PRSD}_R$$

The average concentration of 10 values obtained for every element was used for calculating PRSD_R (%) = $2C^{-0.15}$ where C is the concentration expressed as the dimensionless mass fraction. For single-laboratory validation studies, under repeatability conditions, acceptable values for HorRat(r) are between 0.3 and 1.3. The results are given in Table VI. The HorRat(r) ratio of all the elements were well within the range

of 0.3 to 1.3 for their respective mass concentrations ranges and hence, acceptable.

Intermediate Precision (Intra-lab Reproducibility)

For assessing intermediate precision, replicate measurements were made on two niobite-tantalite samples in the same laboratory using the same equipment by different analysts on different days. The Horwitz ratio was employed as acceptance criteria (17, 18). For validation studies, under reproducibility conditions, acceptable values for HorRat(r) are between 0.5 and 2.0. The HorRat(r) ratio of all the elements was found well within the range of 0.5 to 2.0 for their respective mass concentration ranges and hence, acceptable (Table VII).

Application to Samples

The validated method was applied to some selected samples for the determination of Nb, Ta, Fe, Mn, Ti, Sn, Zr, and W, and results are presented in Table VIII. The method shows good accuracy and precision over the entire method range. The %RSD for all of the estimated elements varied from 1 to 5% at the mg g⁻¹ level and from 5 to 15% at the µg g⁻¹ levels of concentration.

TABLE IV
Results for Accuracy Using CRMs

Element	Accepted Value* (AV) (%)	IGS 33 Present Value (PV) (n=10) (%)	(%)RSD	Accepted Value* (AV) (%)	IGS 34 Present Value (PV) (n=10) (%)	(%)RSD
Nb	47.93	49.03	0.86	18.83	19.16	1.09
Ta	4.37	4.52	1.44	40.88	42.58	1.14
Ti	1.04	0.87	1.95	0.69	0.62	1.86
Fe	13.92	13.82	1.56	4.47	4.30	1.18
Mn	1.64	1.84	1.29	6.82	7.62	0.99
W	0.21	0.20	2.13	0.44	0.40	1.67
Sn	1.42	1.15	1.19	0.08	0.08	6.80
Zr	0.24	0.22	0.93	0.26	0.25	2.51

*References: (19), (20), (21)

TABLE V
Accuracy Results of Sample "AMD-NbTa-2" by Test Method and Alternate Method

Element	Concentration Present Method (n=3) (%)	Concentration Alternate Method** (n=3) (%)	Recovery (%)
Nb	47.80	47.80	100
Ta	6.29	6.21	99
Ti	1.06	1.07	101
Fe	9.37	9.37	100
Mn	5.03	5.19	103
W	0.82	0.77	94
Sn	0.05	0.05	100
Zr	0.24	0.28	116

**Sample solution preparation by fluoride fusion followed by ICP-OES determination.

TABLE VI
Results for Repeatability of Sample "AMD-NbTa-1" (n=10)

Element	Mean Value (%)	RSD _R (%)	Horwitz PRSD _R (%)	HorRat(r)	Acceptable Range: (0.3-1.3)
Nb	49.46	1.68	2.22	0.8	Yes
Ta	5.57	1.93	3.08	0.6	Yes
Ti	0.92	2.26	4.04	0.6	Yes
Fe	11.37	1.30	2.77	0.5	Yes
Mn	4.28	1.02	3.21	0.3	Yes
W	0.93	1.69	4.04	0.4	Yes
Sn	0.05	8.29	6.37	1.3	Yes
Zr	0.30	1.85	4.79	0.4	Yes

Evaluation of Uncertainty Using the GUM “bottom-up” Approach

The measurement uncertainty is estimated mainly either by the bottom-up approaches (14) or the top-down approaches (15). The GUM approach is known as the “bottom-up approach” where all conceivable sources of uncertainty are systematically evaluated using a model equation, and are combined into total uncertainty using the law of propagation of uncertainty. In the “top-down” approach, the methodology is considered as a whole, and the uncertainty is evaluated based on inter-laboratory comparison exercise or proficiency testing data. This latter approach has the advantage of being easier to implement in routine laboratories

which sometimes do not have the time or the resources to develop a strict GUM estimation. In the present work, measurement uncertainty was estimated using the GUM approach as per the following procedure.

In the first step, the test method was summarized step-wise to identify the sources of uncertainty. In the second step, a mathematical model equation for arriving at the test results as per test method was set up as follows:

$$C_{x\text{-sample}} = \frac{C_{x\text{-anal}} * D.F * V_x * 10^{-4}}{(M_x * R_x)}$$

where

- M_x is mass of the sample taken in grams

- V_x is the volume of the made-up sample solution in mL

- D.F is the dilution factor of sample solution (i.e 5, 10, etc.)

- R_x is the recovery factor of element “X” from sample into solution (maximum of 1)

- $C_{x\text{-anal}}$ is the concentration of element “X” in measured solution in $\mu\text{g mL}^{-1}$ obtained from calibration graph and intensity of measured solution

- $C_{x\text{-sample}}$ is the concentration of element “X” in sample in % g/g

- M_x , V_x , D.F, R_x and $C_{x\text{-anal}}$ constitute the inputs, while $C_{x\text{-sample}}$ constitutes the output in the above equation

TABLE VII
Results for Intra-lab Reproducibility of Samples (n=10)

Element	Mean Value	(%RSD _R)	AMD-NbTa-5			Mean Value	(%RSD _R)	AMD-NbTa-7		
			Horwitz (%)PRSD _R	HorRat(r)	Acceptable (Range: 0.5-2.0)			Horwitz (%)PRSD _R	HorRat(r)	Acceptable (Range: 0.5-2.0)
Nb	34.13	2.48	2.35	1.1	Yes	17.18	2.58	2.61	1.0	Yes
Ta	19.01	4.96	2.57	1.9	Yes	5.10	5.41	3.11	1.7	Yes
Ti	7.43	4.56	2.95	1.5	Yes	17.18	3.68	2.61	1.4	Yes
Fe	6.04	5.90	3.04	1.9	Yes	21.58	4.71	2.51	1.9	Yes
Mn	7.31	3.60	2.96	1.2	Yes	4.11	3.85	3.23	1.2	Yes
W	0.08	5.79	5.64	1.0	Yes	0.46	6.40	4.46	1.4	Yes
Sn	<0.05	-	-	-	-	2.44	6.77	3.49	1.9	Yes
Zr	0.22	9.41	4.97	1.9	Yes	0.05	11.02	6.14	1.8	Yes

TABLE VIII
Application to Niobite-Tantalite Samples

Sample		Nb (%)	Ta (%)	Ti (%)	Fe (%)	Mn (%)	W (%)	Sn (%)	Zr (%)
1	AMD-NbTa-1	49.46	5.59	0.92	11.37	4.28	0.93	0.05	0.30
2	AMD-NbTa-2	47.80	6.29	1.06	9.37	5.03	0.82	<0.05	0.24
3	AMD-NbTa-3	47.24	6.85	1.01	10.97	4.31	0.76	<0.05	0.23
4	AMD-NbTa-4	46.94	5.60	0.77	10.74	4.59	0.94	<0.05	0.32
5	AMD-NbTa-5	34.13	19.01	7.43	6.04	7.31	0.08	<0.05	0.22
6	AMD-NbTa-6	20.10	45.58	0.19	3.99	7.89	0.14	0.06	0.17
7	AMD-NbTa-7	17.18	5.10	17.18	21.58	4.10	0.46	2.44	0.05
8	AMD-NbTa-8	14.03	52.94	0.17	3.07	7.86	0.13	0.19	0.18

*Values are the mean of 3 replicate measurements.

In the third step, the different sources of all possible uncertainties associated with the inputs in the model equation were identified. The cause and effect (fish-bone) diagram depicting the various significant sources of uncertainty are shown in Figure 1. Only the sources of uncertainty considered significant were evaluated. A sample was taken as representative and homogenous. Uncertainty in mass of the sample due to balance calibration was included. Uncertainty in sample solution volume associated with volumetric glassware calibration was also included. Recovery uncertainty was evaluated using replicate analyses of CRM IGS-33 Niobite. Uncertainty associated with the dilution factor of the sample solution was evaluated from the uncertainty associated with the volumetric glassware calibration. Calibration uncertainty emanating from uncertainty with the concentration of the calibration stock standard solution and the volumetric glassware calibration was included. The contribution of repeatability to different sources of measurement uncertainty was combined into one

contribution and obtained from repeatability studies by two analysts.

In the fourth step, the evaluation of uncertainties associated with inputs was carried out. The uncertainty estimates were categorized into “Type A” or “Type B” and were evaluated accordingly. The standard uncertainties associated with gravimetric, volumetric operations, and certified standard stock solutions are “Type B” estimates and were evaluated from the calibration certificates. The repeatability uncertainty associated with the concentration of the element in the sample was evaluated from repeatability results which is a “Type A” estimate. A niobite-tantalite sample was analyzed under repeatability condition and repeatability data obtained was used to evaluate repeatability uncertainty as “Type A” estimate. A sample was analyzed by two analysts in five replicates independently for repeatability as per test method and outputs in the model equation are evaluated using the input values. The results were compiled to get the repeatability uncertainty.

In the next step, the output estimate was calculated by substituting the input estimates in the model equation. The input and output estimates evaluated are listed in the Table IX.

In the final step, evaluation of combined total standard uncertainty in output estimate, i.e., test result, was carried out using the relative uncertainties associated with the input estimates (Table IX). An expanded uncertainty in measurement (U) is obtained by multiplying the combined standard uncertainty ($u_c(y)$) of the output estimate (y) by a coverage factor (k) of $U = k u_c(y)$. Since, a normal (Gaussian) distribution can be attributed to the measurement and the standard uncertainty associated with the output estimate has sufficient reliability, the standard coverage factor $k = 2$ was used for 95% coverage probability. The results for measurement uncertainty obtained for a typical niobite-tantalite sample analysis are listed in Table X. Relative measurement uncertainty values at a coverage factor of 2 varied from (U_{rel} ($k=2$)) and ranged from 2.1% for niobium to 10.0% for tin. The uncertainty budget depicting individual contributions to the total uncertainty by the different sources is presented in Table XI. The results show that the contribution to total uncertainty from sample weight, sample solution volume, and dilution factor were negligible. The maximum contribution to total measurement uncertainty was from repeatability uncertainty and recovery uncertainty (Table XI), indicating that they form the key contributors to total MU.

Comparison of MU Results by GUM “bottom-up” Approach and Horwitz Equation

MU was also evaluated by applying the Horwitz formula relating the relative standard deviation to concentration, as a mass fraction, $RSD_R = 2 C^{(-0.15)}$, and multiplying it

Fig. 1. Cause and Effect diagram depicting sources of uncertainty.

by 2 to obtain the expanded uncertainty (17, 18). It was observed that the MU results by the GUM approach compared well with those obtained using Horwitz equation for Nb, Ta, Fe, Mn, and Ti, which occur at high concentrations in the sample. But for Sn, W, and Zr, which occur at low concentrations, MU estimates by GUM were much higher compared to the estimates using the Horwitz equation.

CONCLUSION

The present ICP-OES method is fast, reliable, and enables the quantification of all of the key constituent elements (Nb, Ta, Ti, Fe, Mn, W, Zr and Sn) in niobite-tantalite samples with a single sample preparation step involving fusion with a phosphate salt mixture. The method shows good specificity. The accuracy of the method was verified by recovery estimation using certified reference materials. A simple procedure for evaluation of the total standard measurement uncertainty by the GUM "bottom-up" modelling

approach has been described. The methodology can be used for such multi-element determinations by ICP-OES. MU was evaluated for a typical niobite-tantalite sample and an uncertainty budget presented. The uncertainty estimates compared well with those obtained using the Horwitz equation for elements occurring at high concentrations. The results demonstrate that the method is suitable for application in laboratories rendering analytical support to geochemical exploration programs which are tasked with multi-element analyses of a large number of these types of samples.

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TABLE IX
Uncertainty Sources

Source of Uncertainty	Input / Output	Notation in Model Equation	Estimate	Standard Uncertainty	Probability Type A or B
X ₁	Mass of sample in g	M _x	Input, x ₁	u(x ₁)	Normal, Type B
X ₂	Volume of sample solution in mL	V _x	Input, x ₂	u(x ₂)	Normal, Type B
X ₃	Dilution factor of sample solution	D.F	Input, x ₃	u(x ₃)	Normal, Type B
X ₄	Concentration of element in measured solution in µg/mL	C _{x-anal}	Input, x ₄	u(x ₄)	Normal, Type B
X ₅	Repeatability - Analyst 1 in % g/g		Input, x ₅	u(x ₅)	Normal, Type A
X ₆	Repeatability - Analyst 2 in % g/g		Input, x ₆	u(x ₆)	Normal, Type A
X ₇	Recovery uncertainty (CRM study)	R _x	Input, x ₇	u(x ₇)	Normal, Type A
Y	Concentration in element "X" in sample in % g/g	C _{x-sample}	Output,y	u _c (y)*	

$$u_c(y) = y \cdot \sqrt{\left(\frac{u(x_1)}{x_1}\right)^2 + \left(\frac{u(x_2)}{x_2}\right)^2 + \left(\frac{u(x_3)}{x_3}\right)^2 + \left(\frac{u(x_4)}{x_4}\right)^2 + \left(\frac{u(x_5)}{x_5}\right)^2 + \left(\frac{u(x_6)}{x_6}\right)^2 + \left(\frac{u(x_7)}{x_7}\right)^2}$$

*u_c(y) is the total standard measurement uncertainty.

TABLE X
Evaluation of Standard Uncertainty, Combined Standard Uncertainty, Expanded Uncertainty
for Nb, Ta, Fe, Mn, Ti, Sn, Zr and W in Niobite-Tantalite by ICP-OES for Sample "AMD-NbTa-1"

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Ele-	X ₁	u(x ₁)	X ₂	u(x ₂)	X ₃	u(x ₃)	X ₄	u(x ₄)	X ₅ (%)	u(x ₅)	X ₆	u(x ₆)	X ₇	u(x ₇)	Y	u _c (y)	U	U _{rel}
	(g)		(mL)		(No)		(μg mL ⁻¹)				(g g ⁻¹ %)		(No)		(g g ⁻¹ %)		(k=2)	(k=2)
																	(g g ⁻¹ %)	(%)
Nb	0.100	0.0001	100.0	0.0018	25.0	0.0225	19.785	0.050	49.818	0.357	49.106	0.323	1.022	0.003	49.46	0.53	1.06	2.1
Ta	„	0.0001	„	0.0018	„	„	2.236	0.007	5.644	0.020	5.534	0.032	1.034	0.013	5.59	0.08	0.16	2.9
Fe	„	0.0001	„	0.0018	„	„	4.548	0.009	11.382	0.059	11.358	0.094	0.992	0.018	11.37	0.23	0.47	4.1
Mn	„	0.0001	„	0.0018	5.0	0.0018	8.566	0.017	4.274	0.015	4.292	0.028	1.121	0.033	4.28	0.15	0.29	6.8
Ti	„	0.0001	„	0.0018	5.0	„	1.838	0.005	0.902	0.004	0.9360	0.007	0.836	0.015	0.92	0.02	0.04	3.6
Sn	„	0.0001	„	0.0018	„	„	0.089	0.001	0.042	0.001	0.0470	0.001	0.809	0.023	0.05	0.002	0.005	10.0
Zr	„	0.0001	„	0.0018	„	„	0.596	0.002	0.295	0.003	0.3010	0.001	0.916	0.044	0.30	0.014	0.027	9.2
W	„	0.0001	„	0.0018	„	„	1.854	0.006	0.924	0.003	0.9360	0.008	0.970	0.041	0.93	0.04	0.08	8.5

Note: The notations in columns 2 to 16 are defined in Table VIII. U_c(y) is the combined standard uncertainty;
U (k=2) is the expanded uncertainty at a coverage factor of 2; U_{rel} (k=2) is the relative expanded uncertainty.

TABLE XI
Uncertainty Budget for sample no."AMD-Nb Ta-1" by GUM Approach and Horwitz Equation

Element	Uncertainty due to sample mass u(x ₁)	Uncertainty due to sample solution volume u(x ₂)	Uncertainty due to dilution factor u(x ₃)	Uncertainty due to measured concentration u(x ₄)	Uncertainty due to repeatability of analyst 1 u(x ₅)	Uncertainty due to repeatability of analyst 2 u(x ₆)	Uncertainty due to recovery u(x ₇)	Total standard uncertainty u _c (y)	%U (k=2) by GUM	%U (k=2) by Horwitz equation
										(%)
Nb	0.27	<0.1	0.72	5.6	45.6	38.4	9.4	100	2.1	2.2
Ta	0.14	<0.1	0.38	4.2	5.6	15.5	74.2	100	3.4	2.9
Fe	<0.1	<0.1	0.19	0.9	6.3	16.5	76.0	100	4.1	2.8
Mn	<0.1	<0.1	<0.1	0.4	3.8	3.8	92.1	100	6.8	3.2
Ti	0.1	<0.1	<0.1	2.0	6.8	16.3	74.8	100	3.6	4.0
Sn	<0.1	<0.1	<0.1	0.5	42.9	34.2	22.4	100	10.0	6.3
Zr	<0.1	<0.1	<0.1	0.3	5.5	1.1	93.1	100	9.2	4.8
W	<0.1	<0.1	<0.1	0.5	0.5	3.7	95.3	100	8.5	4.0

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