Determination of Sn, Nb, and Ta in Tin Concentrates Using Wavelength Dispersive X-Ray Fluorescence Spectrometry

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INTRODUCTION

Tin (Sn), tantalum (Ta), and niobium (Nb) are extensively used in many modern high-tech industrial applications, such as for super-alloys and in the electronics industry (1, 2). Nb and Ta have strategic utility in the aero-space industry (missiles, air-planes, etc.), nuclear technology, and in the development of super-conducting technologies (3). Granite and pegmatites are by and large the common host rocks for both magmatic and hydrothermal tin ore deposits in which the major tin-bearing mineral is cassiterite (SnO_2). Varying contents of Nb and Ta (up to ~10 wt.% of Nb_2O_5 and Ta_2O_5) generally reported from such ores can be effectively recovered as by-products (4, 5). Sub-microscopic inclusions (exsolved phases) of columbite-tantalite within cassiterite mainly account for the Nb-Ta content in tin ore. Other Nb-Ta oxide minerals found associated in minor amounts with cassiterite-bearing ores are tapiolite, wodginite, ixiolite, and pyrochlore (6).

Systematic and rapid analysis of Sn, Nb, and Ta in such ores and their panned concentrates/beneficiation products are routinely required for ore-grade monitoring and for regulating process parameters for optimum recovery. Several techniques are employed for the determination of Sn, Nb, and Ta such as gravimetry (7), UV-Vis spectrophotometry (8), and inductively coupled plasma optical emission spectrometry (ICP-OES) (9). How-

ABSTRACT

An analytical methodology has been developed for the quantification of tin, niobium, and tantalum in tin concentrate samples using wavelength dispersive X-ray fluorescence spectrometry (WDXRFS). A series of synthetic standards were prepared by blending variable but precisely weighed quantities of Specpure[®] oxides of Sn, Nb, Ta, Fe, and Mn to obtain a mixture of SnO_2 and stoichiometric composition of columbite-tantalite [$(\text{Fe}_{0.8}\text{Mn}_{0.2})(\text{Nb}, \text{Ta})_2\text{O}_6$]. The analytical data obtained by application of this method to tin concentrate samples were compared with those obtained by ICP-OES, and the experimental results are in good agreement.

ever, analysis of tin concentrates containing variable quantities of SnO_2 , Nb_2O_5 , and Ta_2O_5 by conventional wet chemical techniques is often laborious and involves multiple steps essentially due to the refractory nature of the minerals involved (7, 10, 11). In this context, the suitability of wavelength dispersive X-ray fluorescence spectrometry (WDXRFS) as a cost-effective, rapid, and eco-friendly technique for the analysis of tin concentrates (>60 wt.%) containing up to 15 wt.% of Nb_2O_5 and 25 wt.% Ta_2O_5 has been examined, and the method developed is presented here.

EXPERIMENTAL

Instrumentation

The XRF measurements were performed on a sequential wave-

length dispersive X-ray fluorescence spectrometer (MagiX PRO: PW 2440, PANalytical, The Netherlands), equipped with an end-window Rh-anode having a rated capacity of 4 kW (66 kV/125 mA). The spectrometer consists of two primary collimators (150 and 300 μm), five analyzing crystals (PX 1, PE 002, Ge 111, LiF 200, and LiF 220) with a wide range of 2d spacings, and four detectors (Gas Flow Proportional Counter, Scintillation Counter, Xe-sealed and Duplex detector). The spectrometer was interfaced to a personal computer with the SuperQ software from PANalytical. The instrumental operating conditions are listed in Table I.

Sample Preparation

The unknown samples were ground to about 45 μm size using a jaw crusher/pestle and mortar, followed by high speed impact and swing mills. A smaller representative volume of the homogenized powder of each sample was obtained by coning and quartering. The representative powdered samples/standards of 1 g were weighed and spread uniformly over a 20 g boric acid bed in a cylindrical sample die, and finally pelletized in a semi-automatic pelletizer at a pressure of 20,000 kg/cm^2 , resulting in a solid pellet of 41 mm in diameter.

METHODOLOGY

Preparation of Analytical Standards

The WDXRFS technique is a comparative method wherein close matrix matching of certified reference materials (CRMs) are highly essential, and are analyzed along with the samples. Since CRMs con-

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taining the intended range of Sn, Nb, and Ta are not commercially available, a series of eight synthetic standards were prepared by blending variable but precisely weighed quantities of Specpure[®] oxides of Sn, Nb, Ta, Fe, and Mn. For this purpose, a synthetic mixture of columbite-tantalite of stoichiometric composition of $[(Fe_{0.8}Mn_{0.2})(Nb, Ta)_2O_6]$ (12) was initially prepared and mixed with a pure SnO_2 base in varying carefully measured proportions. The standard addition and dilution approach was adopted for mixing the oxides. The blended products were further ground in an agate mortar over 30 minutes for homogenization at the particle size of about 45 μm . The pressed pellet sample preparation method was adopted for WDXRFS analysis. The calculated values of the synthetically prepared standards are given in Table II.

Calibration and Application

The X-ray fluorescence spectral intensity data on analytical standards obtained from the peaks of characteristic radiations and backgrounds were processed using the SuperQ analytical software (M/s PANalytical Ltd., The Netherlands) using linear regression of the net intensities versus concentrations. The matrix effects were corrected using empirical coefficients, more specifically alphas, based on count rate. The SuperQ analytical software facilitates data conversion, least-squares linear regression analysis (LSLRA), and statistical evaluation. Calibrations relating either to background corrected net count rates or peak count rates to element concentrations in the analytical standards are derived by LSLRA as per regression equation (Eq. 1).

$$y = mx + c \quad (\text{Eq. 1})$$

where y = counts per second of $SnK\alpha$, $NbK\alpha$, $TaL\beta$, $FeK\alpha$, and $MnK\alpha$, C = intercept, m = slope, and x = concentration of the element in the standard. These are used to compute the concentrations of Sn, Nb, Ta, Fe, and Mn in the samples.

The instrument was calibrated using the corrected net peak intensity (kilocounts/second) against the concentration of each element in synthetically prepared in-house standards. The calibration curves of Sn, Nb, Ta, Fe, and Mn are given in Figure 1 (a-e).

X-Ray Spectral Line Interferences

The line interferences were minimized by using analytical lines free of line overlaps and line coincidences from other elements and by selecting interference-free background positions. Table III lists the general spectral line interferences such as $AgK\beta$ on $SnK\alpha$, $UL\beta_2$ on $NbK\alpha$, $HfL\beta_2$ on $TaL\beta_1$, $ThL\alpha_2$ on $FeK\alpha$, and $3AmL\beta_2$ on $MnK\alpha$. However, the relative intensities of $AgK\beta$ (5%), $UL\beta_2$ (23.6%), $HfL\beta_2$ (20.48%), $ThL\alpha_2$ (11.41%), and $3AmL\beta_2$ (23.6%) are minimum, and also the concentrations of these elements in the tin concentrate samples and standards are negligible. The $L\beta$ line was chosen in the case of estimation of Ta, as instrumental power (4KW) was a constraint in the selection of $TaK\alpha$ (57.098 KeV) line. Besides, the $NbK\alpha$ and β lines interfere with $TaL\alpha$ and β lines, respectively. Therefore, low voltage (kV) and current (mA) were used for the selective excitation of the $L\beta$ line (13, 14).

RESULTS AND DISCUSSION

Evaluation of Precision, Accuracy, and Limit of Detection

The accuracy and precision of the method was evaluated using the three different synthetic standards

TABLE I
Instrumental Parameters for the Determination of Sn, Nb, Ta, Fe, and Mn by WDXRFS

Parameters	Sn	Nb	Ta	Fe	Mn
Line	$K\alpha$	$K\alpha$	$L\beta$	$K\alpha$	$K\alpha$
Potential (kV)	60	40	40	50	50
Current (mA)	16	20	20	40	40
Collimator (μm)	150	150	150	150	300
Crystal	LiF 220	LiF 220	LiF 220	LiF 200	LiF 200
Angle (2θ)	19.8556	30.3904	55.5052	57.5010	62.9660
Detector	Scintillation	Scintillation	Scintillation	Duplex	Duplex
Time (seconds)	20	30	30	20	20

TABLE II
Calculated Values of Synthetically Prepared Standards

Standard No.	SnO_2 (wt.%)	Nb_2O_5 (wt.%)	Ta_2O_5 (wt.%)	$Fe_2O_3(T)$ (wt.%)	MnO_2 (wt.%)
Syn-1	50.00	15.27	25.39	7.34	2.00
Syn-2	57.00	13.13	21.84	6.31	1.72
Syn-3	64.00	11.00	18.28	5.28	1.44
Syn-4	75.00	7.64	12.70	3.67	1.00
Syn-5	81.00	5.80	9.65	2.79	0.76
Syn-6	87.50	3.82	6.35	1.83	0.50
Syn-7	93.75	1.91	3.17	0.92	0.25
Syn-8	96.88	0.95	1.59	0.46	0.12

Fig. 1. Calibration curves for (a) SnO_2 , (b) Nb_2O_5 , (c) Ta_2O_5 , (d) $\text{Fe}_2\text{O}_3(\text{T})$, and (e) MnO_2 analysis.

(Syn-1, Syn-4, and Syn-7). In order to evaluate precision, triplicate pellets of each standard were prepared and six measurements for each pellet were carried out. The experimental fluorescent intensities were interpolated in the calibration curve for their determination. The precision was evaluated in terms of relative standard deviation (% RSD), and accuracy in terms of percent-

TABLE III
Spectral Line Interferences on Sn, Nb, and Ta by WDXRFS

Element	Line	Angle $2(\Theta)$	Relative Intensity (%)
Sn	$\text{SnK}\alpha_1$	19.8382	100
	$\text{AgK}\beta_2$	19.6908	5
Nb	$\text{NbK}\alpha_1$	30.3744	100
	$\text{UL}\beta_2$	30.7297	23.6
Ta	$\text{TaL}\beta_1$	55.5468	57.81
	$\text{HfL}\beta_2$	55.5286	20.48
Fe	$\text{FeK}\alpha_1$	57.4636	100
	$\text{ThL}\alpha_2$	57.4603	11.41
Mn	$\text{MnK}\alpha_1$	62.9158	100
	$3\text{AmL}\beta_2$	62.9869	23.6

age relative error (% RE), and standard error (En).

The relative standard deviation (%RSD; $n=6$) of analysis on the synthetically prepared standards by the newly developed WDXRFS method was 0.07–0.17% for SnO_2 , 0.20–0.43% for Nb_2O_5 , 0.68–2.35% for Ta_2O_5 , 0.16–0.89% for $\text{Fe}_2\text{O}_3(\text{T})$, and <0.01–0.41% for MnO_2 . The error of the analysis by WDXRFS technique was found to be ± 0.79 –2.56% for SnO_2 , $\pm <0.01$ –0.77% for Nb_2O_5 ,

± 0.39 –1.14% for Ta_2O_5 , ± 0.50 –2.17% for $\text{Fe}_2\text{O}_3(\text{T})$, and $\pm <0.01$ –1.00% for MnO_2 (Tables IV–VI).

The limit of detection (LOD) of SnO_2 , Nb_2O_5 , Ta_2O_5 , $\text{Fe}_2\text{O}_3(\text{T})$, and MnO_2 concentration was at 95 percent confident level and can be calculated using the following equation:

$$\text{LOD} = \frac{3}{m} \sqrt{I_B / T_B} \quad (\text{Eq. 2})$$

where m = net counts per second per parts per million (ppm), I_B = counts per second of the background and T_B = counting time for the background measurement. The lower limits of determination (LOD) were determined and found to be 0.007 wt.% for SnO_2 and 0.020 wt.% for Nb_2O_5 , 0.20 wt.% for Ta_2O_5 , 0.02 wt.% for $\text{Fe}_2\text{O}_3(\text{T})$, and 0.050 wt.% for MnO_2 .

Application to Nb-Ta Bearing Tin Ore Samples

In order to evaluate the quality of the WDXRFS analysis of the Nb-Ta bearing tin ore samples, three unknown samples were characterized for SnO_2 , Nb_2O_5 , Ta_2O_5 , $\text{Fe}_2\text{O}_3(\text{T})$, and MnO_2 using the present method, and an alternative method based on ICP-OES determination. The data obtained by WDXRFS were found to be in good agreement with those obtained by ICP-OES (Table VII), thus confirm-

TABLE IV
Accuracy and Precision Using Synthetic Standard (Syn-1) by WDXRFS

Element	Assigned Values (wt.%)	Mean (n=6)	SD	RSD (%)	Uncertainty of the Analysis (%)
SnO_2	50.00	49.07	0.08	0.17	± 1.87
Nb_2O_5	15.27	15.29	0.03	0.20	± 0.12
Ta_2O_5	25.39	25.68	0.17	0.68	± 1.14
$\text{Fe}_2\text{O}_3(\text{T})$	7.34	7.38	0.01	0.16	± 0.50
MnO_2	2.00	1.99	<0.01	0.26	± 0.67

n: number of determinations.

SD: standard deviation.

RSD: relative standard deviation.

TABLE V
Accuracy and Precision Using Synthetic Standard (Syn-4) by WDXRFS

Element	Assigned Values (wt.%)	Mean (n=6)	SD	RSD (%)	Uncertainty of the Analysis (%)
SnO ₂	75.00	74.41	0.06	0.08	± 0.79
Nb ₂ O ₅	7.64	7.61	0.02	0.21	± 0.77
Ta ₂ O ₅	12.70	12.65	0.01	0.80	± 0.39
Fe ₂ O ₃ (T)	3.67	3.64	0.01	0.21	± 0.82
MnO ₂	1.00	0.99	<0.01	0.41	± 1.00

n: number of determination, SD: standard deviation, RSD: relative standard deviation.

TABLE VI
Accuracy and Precision Using Synthetic Standard (Syn-8) by WDXRFS

Element	Assigned Values (wt.%)	Mean (n=6)	SD	RSD (%)	Uncertainty of the Analysis (%)
SnO ₂	96.88	94.40	0.07	0.07	± 2.56
Nb ₂ O ₅	0.95	0.95	<0.01	0.43	<0.01
Ta ₂ O ₅	1.59	1.58	0.04	2.35	± 0.63
Fe ₂ O ₃ (T)	0.46	0.47	<0.01	0.87	± 2.17
MnO ₂	0.12	0.12	<0.01	<0.01	<0.01

n: number of determination, SD: standard deviation, RSD: relative standard deviation.

TABLE VII
Comparison of Analytical Results by WDXRFS and ICP-OES

Oxides	Sample 1		Sample 2		Sample 3	
	WDXRFS (wt.%)	ICP-OES	WDXRFS (wt.%)	ICP-OES	WDXRFS (wt.%)	ICP-OES
SnO ₂	65.65	65.00	66.63	66.53	66.77	64.50
Nb ₂ O ₅	4.42	4.40	4.70	4.10	4.74	4.10
Ta ₂ O ₅	7.60	7.30	7.37	6.80	7.42	6.90
Fe ₂ O ₃ (T)	10.97	8.69	10.08	9.30	9.66	9.55
MnO	1.45	1.20	1.66	1.43	1.59	1.43

ing the accuracy of the results obtained by the WDXRFS method.

CONCLUSION

An analytical methodology was developed for the quantification of tin, niobium, and tantalum in tin concentrate samples using wavelength dispersive X-ray fluorescence spectrometry (WDXRFS). A series of synthetic standards were prepared by blending variable but precisely weighed quantities of Specpure[®] oxides of Sn, Nb, Ta, Fe, and Mn to obtain a mixture of SnO₂ and

stoichiometric composition of columbite-tantalite [(Fe_{0.8}Mn_{0.2})(Nb, Ta)₂O₆]. The data obtained by WDXRFS for the tin ore samples were found to be in good agreement with the results obtained by ICP-OES. The proposed WDXRFS method is useful for the determination of a wide range of SnO₂ (50–100 wt.%), Nb₂O₅ (0.5–15.27 wt.%), and Ta₂O₅ (1.5–25.39 wt.%) in tin-rich concentrate samples.

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