

Determination of tungsten in beneficiation products of wolframite bearing granites from Degana area, Rajasthan

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ABSTRACT

Large deposit of wolframite and scheelite become a source of an important strategic metal like tungsten. During XRF analysis of tungsten from low grade tungsten ore from Degana, it was observed that there was marked difference in the analytical values of tungsten estimated by different methods. The problem of matrix in the low grade tungsten ore was found which adversely affects the results even when standards for calibration were selected from the similar origin. In the present study, influence coefficient (α) was calculated using secondary standards. Mathematical correction models proposed by de jongh, Rasberry and Heinrich and Lucas-Tooth-Pyne were applied. It was observed that the results were significantly improved after applying this correction. Experimental condition as well as comparison between the results obtained through these correction models have been computed. Results obtained by this technique were compared with secondary standards and found to be of high accuracy. Out of the three models it was observed that Rasberry and Heinrich model is more suitable for accurate results.

INTRODUCTION

Several low grade tungsten deposits have been located in the different parts of the country e.g., Degana (Rajasthan), Kuhi-Khobna (Maharashtra), Kolar gold field (Karnataka), Bankura (West Bengal), Almora (U.P.) etc.

The mineral processing division of NML had undertaken sustained programme of study on the feasibility of beneficiating those ores. During the progress of these studies a large number of beneficiation products containing widely varying amounts of tungsten from high (concentrates) to very low (tailing) up to 0.01% were required to be analysed. The analyses were required to be

very accurate specially in the lower range so that correct material balance could be computed for planning further tests. The existing methods of analysis of tungsten were found wanting in respect of both these requisites and the necessity of a rapid at the same time sensitive method of analysis was keenly felt.

The chemical analysis of tungsten is difficult compared to many other transition elements specially in ppm level. Various methods for the analysis of tungsten in different ores are available in literature^[1-10]. Apart from the conventional wet chemical methods these include Spectrophotometry, Emission Spectrography, Polarography, Neutron activation analysis, X-ray fluorescence spectrometry etc. A review on various methods used for the analysis of tungsten is given by Topping^[11]. Spectrophotometric methods employing thio-cyanate and dithiol are most commonly used for the tungsten in ores^[11-12]. Separation of tungsten is invariably required for spectrophotometric procedures^[12]. Neutron activation technique has been successfully used for the estimation of low percentage of tungsten^[13-14] and is employed for the low grade ores^[15]. This technique however requires complex radio chemical procedure to minimise interference^[14]. Atomic absorption spectrometry has though been applied to the estimation of high percentage of tungsten^[16-18], it can not be used for lower concentration due to the poor sensitivity^[19]. Plasma emission spectroscopy offers a much higher sensitivity for tungsten and has been employed for its determination in steels and alloys^[20-21] and tungsten ore^[22]. X-ray spectrometry has been in recent years widely used for the estimation of tungsten in low level for its rapid, accurate and reproducible results when a large number of samples are to be analysed. Several workers have suggested various methods for its sample preparation which has a vital importance in the XRF analysis. It is seen that fusion^[23-25] or solution^[26-27] technique are in common use so as to reduce the effect of particle size, heterogeneity and mineralogical compositions. Since sample preparation by fusion or solution is a time consuming process, ultrafine grinding followed by pelletization^[28] was preferred. Pelletization technique and use of secondary standards for the calibration of XRF spectrometer are in common use for the analysis of various ores and concentrates, presuming that matrix effect can be minimised by selecting standards from the same origin having similar mineralogical composition as that of the samples to be analysed. However, during the analysis of tungsten in beneficiation products of wolframite bearing granite from Degana using similar secondary standards it was observed that no linearity could be obtained. This nonlinearity may be due to some inter elemental effect which has to be accounted for (Fig. 1).

In the present paper, correction algorithms proposed by de jongh, Lucaus-Tooth-Pyne, Rasberry and Heinrich have been used to study the matrix effects^[29-30]. Alfa coefficient has been calculated using intensity and concentra-

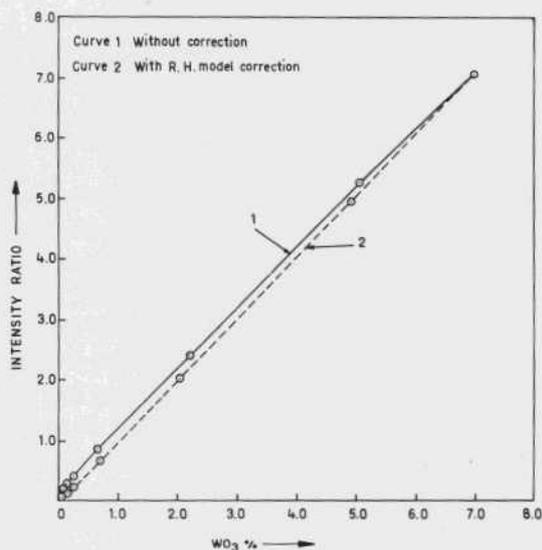


Fig. 1 : Showing the analytical curve.

tion data with the secondary as well as the synthetic standards.

EXPERIMENTAL

Selection and preparation of standards

In the XRF analysis matrix corrections is important for accurate analysis. This can be achieved either by mathematically or by using suitable calibration standards of identical compositions with unknowns. In the present work few samples of the ores from the same origin having the same mineral composition were accurately analysed by conventional wet-chemical methods for a number of times and preserved in a desiccator to be used for the preparation of analytical curves. In addition to these, some synthetic standards were also prepared to provide the intensity data to cover a wide range of analysis. For this, accurately analysed gauge materials containing low amounts of tungsten was used as a basic matrix and wolframite concentration (70% WO₃) were added to make varied WO₃ concentration. The standards used for the analysis covered the range from 0.008 to 8.0% to accommodate some of the beneficiation products. The concentration of the standard used for the calibration and regression analysis are shown in Table 1. Care was taken to ensure that the standards and samples were of the same particle size distribution as far as possible. Any adverse effect in accuracy due to a particle size variation was minimised by high pressure briquetting.

Pelletization

The samples for both the secondary standards as well as synthetic standards were ground to a fine powder of -200# and pressed into briquettes^[31-33] at 12000 Kg/cm² pressure using boric acid as backing material as suggested by Roase *et. al.*^[34]. A double layer briquettes were prepared first by lightly pressing boric acid in the mould and then adding the powder sample on top before final pressure was applied. The size of the briquettes thus formed were 38mm dia. and 10mm thick. During pelletization addition of binder or flux were avoided to prevent further dilution. The pelletization of the unknown samples were also made exactly same as the standards. The conditions are given in the Table 2(A).

Measurements

A Philips sequential type X-ray fluorescence spectrometer (PW 1404) with chrome-Gold target as a source of excitation was used. The full area of the briquettes were exposed to X-ray for a fixed time of 20 seconds with respect to a monitor buffer. Since a number of samples were analysed in one batch, one check sample (reference standard) was always recycled with every set of analysis to ascertain the precision.

LiF 200 ($2d = 0.4027\text{\AA}$) was found to be most suitable crystal analyser which could diffract the characteristic radiation within the goniometer span of the unit. The secondary fluorescence (radiation) were then received by the flow scintillation counter and subsequent pulse counts were recorded for each element subtracting the back ground counts.

The entire measurements were governed by a measuring programme followed by a calculation parameter. Regression analysis and calculations were executed with a computer linked directly to the spectrometer. The experimental conditions and measurement programme used during the entire operation is shown in Table 2(B) and 2(C).

RESULTS AND DISCUSSION

Evaluation of results

X-ray radiation intensity were made on different standards (both secondary and synthetically prepared) and count ratios were calculated with help of reference standards. Analytical curves were constructed by plotting count ratios versus percentage of the elements in the standards. Count ratios of tungsten in the unknown samples were calculated and from the corresponding count ratios, percentage was calculated from the analytical curve (Fig. 1).

Table 1 : Concentration of WO_3 used in calibration and regression

Sl.No.	% WO_3	Sl. No.	% WO_3
1.	0.008	7.	0.430
2.	0.023	8.	0.670
3.	0.056	9.	1.160
4.	0.085	10.	2.100
5.	0.118	11.	4.920
6.	0.240	12.	7.100

Table 2 : Experimental conditions

(A) Sample Preparation

Technique	:	High pressure double layer briquetting
Equipment	:	AMIL Briquetting press
Pressure	:	12000 Kg/cm ²
Backing material	:	Boric acid
Time for pressure applied	:	2 minutes
Diameter	:	38 mm

(B) Instrumental Parameters

Target	:	Chromium - Gold tube
Analysing crystal	:	LiF 200
Detector	:	Flow Scintillation counter
Optical path	:	Vacuum (~ 0.2 torr)
Characteristic radiation	:	La
Operating Voltage and Current	:	60 KV, 50mA
Goniometer setting (2θ)	:	42.98
Pulse height distribution	:	Fine
Order	:	1

(C) i) Measurement Programme

Mask	:	Nil
Measurement	:	w.r.t., monitor buffer
Channel	:	W
Measurement Time	:	20 seconds

ii) Calculation Parameters

a) de jongh's correction algorithms

$$\begin{array}{llll} D = -0.03995 & E = 1.0046 & \text{Alpha(W)} = & 3.7648 \\ K = 0.01205 & \sigma = 0.0145 & & \end{array}$$

b) Lucas-Tooth-Pyne correction algorithm

$$\begin{array}{llll} D = -0.04026 & E = 1.00743 & \text{Alpha(W)} = & 3.55146 \\ K = 0.01158 & \sigma = 0.01520 & & \end{array}$$

c) Lucas-Tooth-Pyne correction algorithm

$$\begin{array}{llll} D = -0.03956 & E = 0.99814 & \text{Alpha(W)} = & 4.37009 \\ K = 0.01158 & \sigma = 0.0140 & & \end{array}$$

Precision and Accuracy

Samples were analysed by this method for tungsten contents for a number of times and the data obtained is shown in Table 3. The coefficient of variation (v) were calculated by the following relation

$$v = \frac{100}{\bar{x}} \sqrt{\frac{\epsilon d^2}{(n-1)}}$$

where \bar{x} = average concentration in percent

d = difference of determination from the mean and

n = number of determinations.

Results obtained by using the described method have been compared with the results obtained by wet chemical methods. In general, the analytical errors (% deviation from chemical values) were obtained with in 6% of the amount present as shown in Table 3. So correction algorithms of the existing three models were applied to achieve reproducible and accurate results.

Discussion

It is well known that, in XRF spectrometry, analysis of an element is affected by the matrix and when there is wide variation in the analyte concentration, the matrix correction also changes accordingly. To minimise the inter elemental effect over the analytical accuracy, different sets of standards were selected judiciously as shown in Table 1, so that the mineralogical compositions of standards and the unknown were almost similar. This avoided the mathematical correction [35-36] for matrix effect. The correlation between the net countrate, or ratio, and

Table 3 : Data on precision of the method

Sl. No.	Chemical value	XRF Values*	% deviation from chemical value	Standard Deviation	Coefficient Variation
1.	0.008	0.0082	2.50	0.0003	3.65
2.	0.056	0.053	5.35	0.0067	12.64
3.	0.118	0.115	2.54	0.0070	6.08
4.	0.430	0.440	2.32	0.0260	5.90
5.	1.160	1.220	5.17	0.0600	4.90
6.	2.100	2.220	5.71	0.1900	8.56
7.	4.920	5.040	2.44	0.2000	3.77
8.	7.100	7.010	1.27	0.1700	2.43

*Average of 8 values

chemical concentration is only linear for a limited concentration range. In most cases the calibration line tends to deviate from linearity due to inter-elemental effects, such as enhancement and absorption. Correction for these effects, commonly termed "MATRIX EFFECT" can be applied in order to "Pull" the calibration line to linearity.

But in actual practice the linearity of the analytical curve so obtained indicates that there is still some absorption or enhancement effect which could give rise to any erroneous results. In such cases, particularly when the analysis is done on sample ranging from raw ores i.e., as received condition, intermediate beneficiation products, i.e., middling to concentrates, as well as tailing, the concentration for the matrix effect over the analysis of each elements is vary important.

The effect due to the particle size and the inhomogeneity were avoided by high pressure briquetting of the samples. The influence coefficient were calculated for individual algorithm. It was observed that results which has been obtained without using the influence coefficient showed marked differences from the standardised values, where as after the application of these equations, the error was drastically reduced in a good number of standards used for the calibration (Table 4). Since there is an enhancement effect occur in this case, Rasberry & Heinrich model is used to provide a better line fit and also found quite suitable for the analysis. The precision and accuracy data is shown in Table 3. However, in the present studies the effect of self absorption or enhancement of tungsten itself on the analysis was carried out since the variation in rest of the matrix

Table 4 : Comparison of the correction algorithm models

Sl. No.	% WO ₃	XRF results without correction		XRF Results after correction					
		(%) WO ₃	(%) Error	dj Model		L.T.P. Model		R.H. Model	
				(%) WO ₃	(%) Error	(%) WO ₃	(%) Error	(%) WO ₃	(%) Error
1.	0.023	0.0245	6.52	0.024	4.35	0.0235	2.17	0.0228	0.86
2.	0.085	0.0875	2.94	0.083	2.35	0.0841	1.05	0.0842	0.94
3.	0.24	0.263	9.58	0.25	4.17	0.235	2.08	0.243	1.25
4.	0.67	0.647	3.43	0.685	2.23	0.682	1.79	0.0676	0.89
5.	2.10	2.22	5.71	2.081	0.90	2.085	0.70	2.086	0.19
6.	4.92	5.04	2.44	4.856	1.30	4.883	0.75	4.901	0.38
7.	7.10	7.01	1.27	7.088	0.17	7.110	0.14	6.995	0.07

concentration is not very significant. The range of tungsten percentage varied only upto 5.0% and the standards were selected upto 7.0%.

CONCLUSIONS

It may be stated that XRF equipment is being acquired by many laboratories and possibly in course of time this would be used to a large extent. The method is to be highly recommended, especially for tungsten bearing material, for which dissolution procedures are not satisfactory. Moreover, the sample once prepared can be preserved indefinitely, for recheck whenever necessary. A major factor is in the preparation of samples and standards which should ideally match each other in the physical and chemical parameters. This is very often not possible so mathematical corrections of the experimentally measured intensity becomes a must. Therefore care has been taken to apply some correction algorithms on XRF analysis of tungsten in low grade tungsten ore of degana and found that a reproducible and accurate results were obtained after applying the Rasberry and Heinrich model for correction.

ACKNOWLEDGEMENT

The authors wish to express their grateful thanks to Prof. P. Ramachandra Rao, Director, National Metallurgical Laboratory, Jamshedpur, for his kind permission to publish this paper.

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