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Wavelength-dispersive X-ray Fluorescence Spectrometric Determination of Tantalum in Columbite-tantalite Using TaKα and an LiF 420 Analysing Crystal

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Abstract: The paper proposes a simple, accurate, precise, and rapid method for determining the high atomic number (Z) major-element, tantalum (Z = 73), in the rare mineral, columbite [(Fe,Mn) $(Nb,Ta)_2O_6$] – tantalite [(Fe,Mn) $(Ta,Nb)_2O_6$], by wavelength-dispersive x-ray fluorescence spectrometry (WDXRFS). The other major-element in columbite-tantalite is the lower atomic number niobium (Z = 41). The method uses the characteristic radiation, TaKα, and an LiF 420 analysing crystal, to overcome the problems associated with the serious x-ray spectral-line interference of the second-order NbKα and NbKβ with the first-order $TaL\alpha_1$ and $TaL\beta_1$ respectively.

Samples of columbite-tantalite ground to minus 300 mesh are blended with cellulose in the proportion of 1:1, and pressed powder-pellets are made from 1-g aliquots, with boric acid as a backing. The analytical standards consist of chemically analysed columbite-tantalite containing 5 to 80% by weight of Ta_2O_5. The instrumental parameters include a rhodium x-ray tube (operating voltage = 100 kV; current = 10 mA), air path, fine collimator (150 μm), and scintillation counter. The counting involves fixed time with three readings of 20s each on the peak and three readings of 20s each on one background.

The accuracy achieved is excellent (within 1.6 to 2.2%), as is the precision (within 0.4 to 2.4%). The time taken for determining Ta_2O_5 in a batch of twentyfour samples of columbite-tantalite, for a replication of four analyses per sample, by one operator using a manual WDXRF spectrometer, is only five hours.

Keywords: X-ray spectrometry, WDXRFS, Columbite-tantalite, TaKα radiation, LiF 420 analysing crystal.

INTRODUCTION

The rare mineral, columbite [(Fe,Mn) $(Nb,Ta)_2O_6$] – tantalite [(Fe,Mn) $(Ta,Nb)_2O_6$], is a major source of tantalum which is used in capacitors, tantalum carbide cutting tools, superalloys, chemical reactor vessels, ballistics, chemical processing industry, high-temperature devices, lens glasses, biocompatible agents, and in surgical and dental instruments.

The chemical analysis of tantalum in columbite-tantalite is tedious and time-consuming. Wavelength-dispersive x-ray fluorescence spectrometry (WDXRFS) is an excellent analytical technique for determining tantalum in columbite-tantalite accurately, precisely, and rapidly. However, as the atomic number (Z) of Ta is high (Z = 73), it is necessary to use the L x-ray spectra of Ta for analysis, because, the minimum critical excitation potential (MCEP) of the more intense K-spectra of Ta is high (57.098 keV for TaKα and 65.212 keV for $TaK\beta_1$). As atleast three times the MCEP are to be given for obtaining a measurable x-ray fluorescent yield, and most x-ray spectrometers have x-ray generators with a maximum output of only 60 kV, no x-ray analyst appears to have used the K-spectra of Ta for determining this element in columbite-tantalite.

Using the L x-ray spectra for determining tantalum in columbite-tantalite poses one problem: The lower atomic number niobium (Z = 41) is a major-element in columbite-tantalite. The second-order NbKα and NbKβ seriously interfere with the first-order $TaL\alpha_1$ and $TaL\beta_1$ that are normally used for analysis.

The purpose of this paper is to present the results of a study aimed at determining tantalum in columbite-tantalite using TaKα and an LiF 420 analysing crystal. It is worth pointing out that, of the three LiF analysing crystals – 200, 220, and 420 – LiF 420 has seldom been used in geochemical analysis by WDXRFS. This aspect makes our study all the more important. Also, to the best of our knowledge, a study of this kind has never been attempted before by any x-ray analyst. The paper will also discuss the accuracy and

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precision achieved, x-ray spectral-line interferences, inter-element effects, speed, advantages, and limitations of the method.

EXPERIMENTAL

Sample Preparation

Samples of columbite-tantalite were ground to minus 300 mesh using a hydraulic splitter, laboratory-type jaw crusher, and disc-mill. The powders were blended with cellulose in the proportion of 1:1 and homogenized in a mixer-mill. Smaller representative volumes of the powders were obtained using two-way riffle pattern sample dividers. Aliquots of 1 g weighed from these splits were transferred to cylindrical sample-dies, and with boric acid as a backing, were pelletized at a pressure of 2500 kg/cm^2 in a hydraulic press, to give pellets of 41 mm diameter.

Preparation of Analytical Standards

Natural samples of columbite-tantalite analysed by classical wet-chemical methods, and containing 5 to 80 percent by weight of Ta_2O_5, were used as analytical standards. Powder-pellets were made from 1–g aliquots of the analytical standards, following the same procedure as for the samples.

Instrumentation

The instrument used for WDXRFS consisted of a Philips PW 1410 sequential x-ray spectrometer with a dual sample changer, five-position analysing crystal assembly, fine (150 μm) and coarse (550 μm) collimators, scintillation counter, gas-flow proportional counter, automatic discriminator and crystal attenuator unit (PW 1414), a PW 1140 x-ray generator (100 kV; 80 mA; 3 kW), and a PW 1370 electronic measuring console comprising the PW 4620 h.v. supply-ratemeter-channel, PW 4625 h.v. supply, PW 4630 counter-timer-printer control, PW 1451 goniometer control unit and stepping motor for selecting twentyfive pre-programmed two-theta positions, and a PM 8000 flat-bed chart recorder.

Instrumental Parameters

In order to calibrate the instrument for determining tantalum in columbite-tantalite, pressed powder-pellets of the analytical standards were irradiated in the WDXRF spectrometer. Table 1 gives the instrumental parameters using a rhodium x-ray tube.

Table 1. Instrumental parameters for determining Ta_2O_5 in columbite-tantalite by wavelength-dispersive x-ray fluorescence spectrometry

X-ray tube	Rhodium
Radiation	TaKα
Voltage	100 kV
Current	10 mA
Analysing crystal	LiF 420
Collimator	150 μm
Detector	Scintillation Counter
Path	Air
Peak two-theta	13.83°
Background two-theta	14.53°

Counting: Fixed time. Three readings of 20s each for peak and for the background, involving a total counting time of 120s per powder-pellet.

Data Processing, Calibration, and Computation

The x-ray fluorescence (XRF) spectral intensity data on the samples and analytical standards obtained from the peak of the characteristic radiation, TaKα, and the background, were processed on a desk-top computer with the facility for recording on magnetic cards programmes for data conversion, least-squares linear regression analysis (LSLRA), and statistical evaluation. Calibrations relating the background–corrected net count rates to the Ta_2O_5 contents in the analytical standards were derived by LSLRA. The resultant regression equation of the form

$$y = a + bx$$

where y = net counts per second of the characteristic radiation, TaKá, a = intercept, b = slope, and x = Ta_2O_5 content in the analytical standards, was used to compute the Ta_2O_5 contents in the samples for which values of y were determined experimentally.

RESULTS

Intensity-concentration Relationship

Figure 1 illustrates the calibration graph obtained for determining Ta_2O_5 in columbite-tantalite. A perfect linear relationship between the background-corrected net intensities of TaKα, and the Ta_2O_5 contents in the analytical standards is evident. The correlation coefficient is very high, being 0.9999.

DISCUSSION

Accuracy and Precision

Implicit in the procedure developed by us is the need to prepare two powder-pellets from two splits of each sample, and to analyse them twice using the instrumental parameters listed in Table 1. Such a scheme, after data processing and

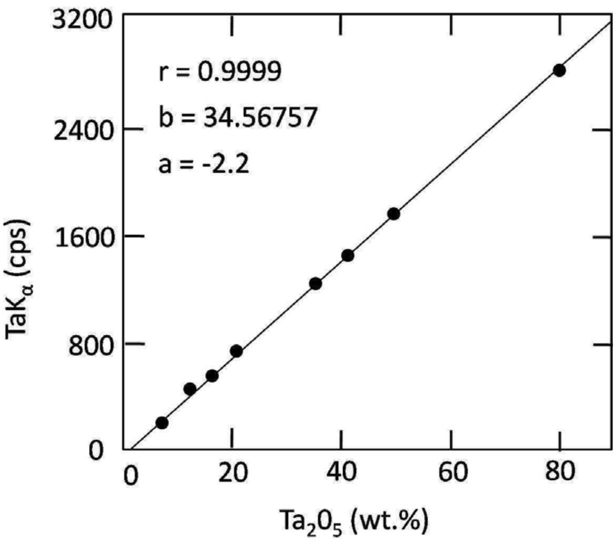

Fig.1. Calibration graph for determining Ta_2O_5 in columbite-tantalite by wavelength-dispersive x-ray fluorescence spectrometry using the instrumental parameters of Table 1.

computation, will yield four separate determinations for Ta_2O_5 per sample, which are then subjected to statistical analysis for determining the arithmetic mean ($\bar{x}$), standard deviation (s), and coefficient of variation (C). Table 2 gives the relevant data for the international columbite-tantalite standards, IGS-33 and IGS-34. The percentage deviation of the arithmetic mean of a set of four values (two each for each of the two powder-pellets), from the corresponding value obtained, can be taken as a measure of the accuracy achieved in the WDXRF spectrometric method proposed here. The coefficient of variation is a measure of the precision achieved.

The accuracy is excellent (within 1.6% for IGS-34 with 49.831% Ta_2O_5 and within 2.2% for IGS-33 with 5.373% Ta_2O_5). The precision is also excellent (within 0.4% for IGS -34 and within 2.4% for IGS-33).

X-ray Spectral-line Interferences

The characteristic radiation, TaKα, used for determining tantalum in columbite-tantalite, and the background position, are not affected by any x-ray spectral-line interferences.

Inter-element Effects

The calibration graph shown in Figure 1 relating the background-corrected net count rates of the characteristic radiation, TaKα, to the Ta_2O_5 contents in the analytical standards, conforms perfectly to the equation of the straight line, $y = a + bx$. This indicates that inter-element effects, also known as absorption-enhancement effects, or as matrix effects, are fully corrected. This has been achieved by totally eliminating the physical and compositional differences, if any, between the samples and the analytical standards, and presenting them as powder-pellets with thin surfaces for x-ray excitation.

Speed of Analysis

The speed of geochemical analysis by WDXRFS is primarily controlled by the time spent on sample processing and pelletization, and the type of instrumental parameters (that is, whether the intensities of the peaks of characteristic radiations are to be measured, or whether background-corrected net intensities of the characteristic radiations are to be measured, and if so, whether one or two background measurements are required to be made). Considering the analytical programme shown in Table 1, the time taken for determining Ta_2O_5 in a batch of twentyfour samples of columbite-tantalite, for a replication of four analyses per element per sample, by one operator using a manual WDXRF spectrometer, is only five hours. With an

Table 2. Data on the accuracy and precision achieved for determining tantalum in columbite-tantalite with the proposed wavelength-dispersive x-ray fluorescence spectrometric method

No.	Component	Standard [(a)]	Recommended Value[(b)] (wt.%)	Results from the proposed method [(c)]				Accuracy [(d)] (percent)
				$\bar{x}$	n	s	C	
1	Ta_2O_5 (wt. %)	IGS – 33	5.373	5.494	4	0.130	2.4	2.2
2	Ta_2O_5 (wt. %)	IGS – 34	49.831	49.008	4	0.176	0.4	1.6

(a) IGS – 33 and IGS – 34 are columbite-tantalites.

(b) Source of values: Lister, B. (1986). Re-evaluation of Reference Materials, IGS 21-39. Geostand. Newslett., v. 10, p. 177-181.

(c) $\bar{x}$ = Arithmetic mean. n = Number of determinations. s = Standard deviation. C = Coefficient of variation, in percent.

(d) Accuracy, as given, is the percentage deviation of the arithmetic mean of a set of four values (two each for each of two powder-pellets), from the recommended value.

automated computer-controlled WDXRF spectrometer system having multiple sample-holders, capable of operating round the clock, the speed of analysis can be increased enormously.

Advantages of the Method

The method proposed here for determining Ta_2O_5 in columbite-tantalite has three main advantages: First, the use of TaKá overcomes the problems associated with the serious x-ray spectral-line interference of the second-order NbKα and NbKβ with the first-order TaLα_1 and TaLβ_1, respectively. Secondly, it involves extremely simple sample processing and pelleting procedures that require only very small amounts of sample. Thirdly, the method is accurate, precise, and rapid.

Limitation of the Method

The use of pressed powder-pellets makes it imperative to replace pellets of the analytical standards with new ones periodically as they deteriorate with analysis over long periods.

CONCLUSIONS

The characteristic radiation, TaKα, with an LiF 420 analysing crystal, can be used to determine the high atomic number (Z) major-element, tantalum (Z = 73), in the rare mineral, columbite [$(Fe,Mn)(Nb,Ta)_2O_6$] – tantalite [$(Fe,Mn)(Ta,Nb)_2O_6$], by wavelength-dispersive x-ray fluorescence spectrometry (WDXRFS). The other major-element in columbite-tantalite is the lower atomic number niobium (Z = 41). The use of TaKα overcomes the problems associated with the serious x-ray spectral-line interference of the second-order NbKα and NbKβ with the first-order TaLα_1 and TaLβ_1, respectively. The method developed by us is simple, accurate, precise, and rapid. The accuracy achieved is excellent (within 1.6 to 2.2%). The precision is also excellent (within 0.4 to 2.4%). The time taken for determining Ta_2O_5 in a batch of twentyfour samples of columbite-tantalite, for a replication of four analyses per sample, by one operator using a manual WDXRF spectrometer, is only five hours. With an automated computer-controlled WDXRF spectrometer system having multiple sample-holders, capable of operating round the clock, the speed of analysis can be increased enormously.

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