

CHARACTERISATION OF COLUMBITE-TANTALITE (COLTAN) ORE FROM CONGO. ELEMENTAL COMPOSITION BY TOTAL REFLECTION X-RAY FLUORESCENCE ANALYSIS

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Abstract

The paper describes the analysis of a columbite-tantalite (coltan) mineral ore from Congo by using total reflection X-ray fluorescence (TRXRF) analysis. The sample was mineralised with lithium tetraborate and lithium metaborate flux mixture. TRXRF allows multi-element analysis in a wide range of concentrations. The results were in good agreement with those obtained using another alkaline fusion with sodium peroxide.

Keywords: TRXRF; Alkaline Fusion; Elemental Composition; Columbite-Tantalite;

1. Introduction

Columbite-tantalite ore is known as Coltan in some African countries. It occurs mainly as an accessory mineral disseminated in granitic rocks or in pegmatites associated with granites where columbium (niobium, Nb, is the actual name) and tantalum are present in the form of mixed oxides corresponding to the general formula $(Fe,Mn)(Ta,Nb)_2O_6$ (1) with widely varying ratios of Nb to Ta. When niobium predominates over tantalum the mineral is known as columbite; when the reverse is true the proper name is tantalite. Coltan ore exists in all continents but most deposits with relatively high niobium or tantalum content are small and erratically distributed. Most of the niobium and tantalum metal produced today is extracted from columbite-tantalite ore and is obtained from Africa, Brazil, Australia and India. For niobium alone, pyrochlore and barochlore is another important source mineral found in countries like Canada, Brazil and Norway (2-5).

Niobium as ferroniobium is used extensively in the steel industry as an additive in the manufacture of high strength, low alloy and carbon steels. Niobium and many of its alloys exhibit superconductivity, thus they are of great interest for propulsion devices, electronic devices and other applications. Tantalum is used in chemical industry equipment for reaction vessels and heat exchangers in corrosive environments. In 1994 over 72% of the tantalum produced in the world went into the manufacturing of solid tantalum capacitors

for use in the most demanding electronic applications. The very low corrosion rate and inertness of tantalum make it attractive for many biomedical applications (2).

The elemental composition of mineral ores is of great importance in the classification and grading of the ores. Qualitative and quantitative data on ore samples are of great interest to mineral prospectors and investors because it is very important to be sure of the quality/grade of the ores they are dealing with. There is, therefore, a need for a multi-elemental analytical technique for the analysis of the solid mineral samples. Usually inductively coupled plasma atomic emission spectrometry (ICP-AES) or atomic absorption spectrometry (AAS), energy dispersive X-ray fluorescence (EDXRF) spectrometry and total reflection X-ray fluorescence (TRXRF) spectrometry were used (6-9).

In this paper we have employed a TRXRF technique in the analysis of a sample of coltan from Congo, previous an alkaline fusion with lithium tetraborate and lithium metaborate flux mixture. The results were compared with those obtained with another alkaline fusion utilizing sodium peroxide (10-11).

2. Experimental

2.1. Standards and Reagents

All glassware was rinsed with 5% (v/v) pure nitric acid (C. Erba, Milan, Italy). High-quality water (18.2 M Ω) obtained from a Milli-Q water purification system (Millipore, Milford, MA, USA) was used exclusively. Ultra-pure and certified hydrofluoric acid (C. Erba), pure lithium tetraborate (BDH, Poole, UK), pure lithium metaborate (BDH), pure sodium peroxide (BDH), scandium (III) standard solution containing 1,000 mg L⁻¹ of scandium (J. T. Baker, Deventer, The Netherlands) and gallium (II) standard solution containing 1,000 mg L⁻¹ of gallium (J. T. Baker) were used.

2.2. Instrumentation and Software

TRXRF analysis was performed on TX2000 spectrometer (Ital Structures, Riva del Garda, Italy) that consists of a x-ray tube with an alloy anode of Molybdenum/tungsten, a monochromator of the X-ray beam that use a highly reflective multilayer made of Si/W, a solid state lithium-drifted silicon detector Si(Li) that is cooled with liquid nitrogen (resolution energy range 135 eV to 5.9 keV and 1000 cps). The equipment runs under TXRFACQ32 program that includes facilities for data acquisition, spectrum analysis and interpretation and quantitative analysis. Both Mo-tube and W-tube excitation were used for analysis with tube setting of 40 kV and 20 mA. Live time was 600 s.

2.3. Analytical Procedure

2.3.1. Preliminary Sample Processing

A coltan ore sample was ground finely on a vibratory disc mill. A 0.15-g coltan ore sample so obtained was fused with 10 g of lithium tetraborate and lithium metaborate mixture (1:3, w/w) in a platinum crucible and kept in the muffle furnace for half hour at 900 °C. The cooled melt was dissolved adding 90 mL of ultrapure water acidified with 4 % (v/v) hydrofluoric and 6% (v/v) nitric acid.

Another aliquot of 0.12-g was fused with 1.2 g of sodium peroxide in a graphite crucible and kept in the muffle furnace for half hour at 550 °C. The cooled melt was treated first with 90 mL of ultrapure water at 80 °C for 15 min and then with 1 mL of hydrofluoric acid and 4 mL of nitric acid heating until obtaining a clear solution.

2.3.2. Determination of elemental composition

A 10- μ L of the sample solution obtained in the preceding section was transferred on to quartz sample carrier. 1 mL of scandium (III) solution as internal standard and 1 mL of gallium (II) solution to control the matrix effect were added. The sample was evaporated at 100 °C and the analysis was carried out with Mo- K α and W-L α . The conversion of the signals in concentrations occurs by operations of fitting in order to minimise the deviations between the fit/background and the spectrum.

3. Results and Discussion

Multi-element analysis by total reflection X-ray fluorescence spectrometry has evolved during two decades. At the present there are commercial equipments available for the chemical analysis in all kind of biological and mineral samples. The technique of analysis in TRXRF is founded on the same principles of conventional X-ray fluorescence measurements. When radiation passes from a medium of lower density to one of higher density it is totally reflected if the angle of incidence is below a certain critical angle, typically a few milliradians of X-ray. By illuminating the sample with a beam that is being totally reflected, the absorption of the beam in the supporting substrate is largely avoided and the associated scattering is greatly reduced. So the background noise is reduced. A further contribution to the reduction of background noise is obtained by minimising the thickness of the sample; minimal quantity of sample (10-100 μ L) is required for the analysis, the solvent is evaporated and a thin film a few nanometers thick remains and the matrix effect is eliminated. In this work TRXRF analysis was used for the qualitative and quantitative determination of most elements in a coltan mineral ore. In Figure 1 a TRXRF spectrum of the mineral ore was reported and as may be seen accurate multi-element analysis was obtained.

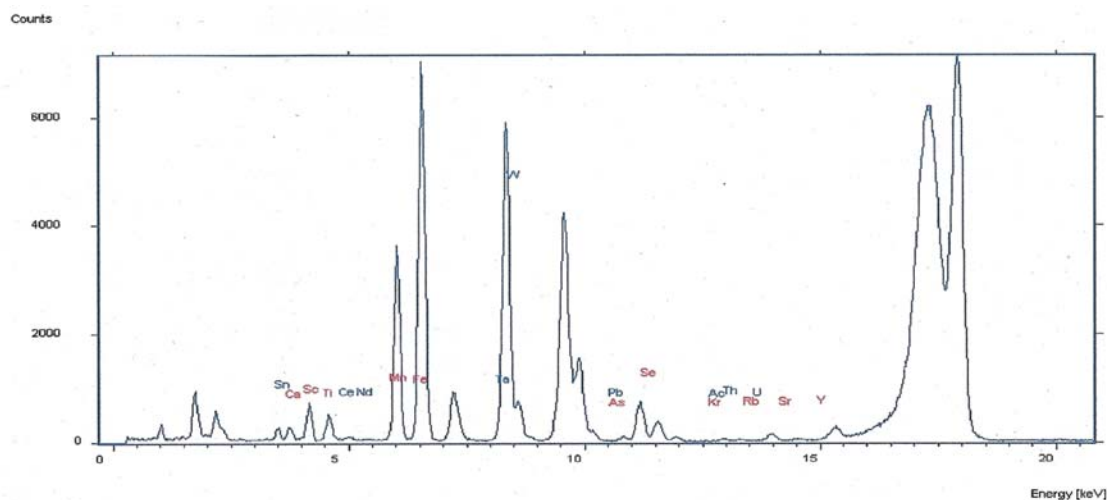


Figure 1. TRXRF Mo-K α spectrum of a coltan sample from Congo. Scandium (III) was added as internal standard. For conditions of analysis see Experimental.

To estimate the matrix effect a solution of gallium (II) was added at the sample obtaining a recovery ranging from 95% to 110%. Quantitative analysis was carried out utilising scandium (III) as internal standard because of its lack in the sample. The results obtained are reported in table 1.

Table 1. Elemental composition of a coltan mineral ore.

MAJORS	% w/w	SD	RSD%	LOD %	SOURCE
Nb	24	2	7	0,3	W-La
Ta	11,7	0,6	5	0,015	Mo-Ka
Fe	8,2	0,4	5	0,01	Mo-Ka
Mn	5,4	0,4	8	0,015	Mo-Ka
Sn	3,39	0,04	1	0,06	W-La
W	1,18	0,09	8	0,015	Mo-Ka
Ti	1,12	0,06	6	0,015	W-La
TRACES	PPM	SD	RSD%	LOD (PPM)	SOURCE
Ca	4705	256	5	300	W-La
V	<200			200	Mo-Ka
Cr	<200			200	Mo-Ka
Se	<30			30	Mo-Ka
Y	1071	72	7	20	Mo-Ka
K	<500			500	Mo-Ka
Rb	<20			20	Mo-Ka
Sr	152	40	26	20	Mo-Ka
Pb	488	147	30	70	Mo-Ka
Th	221	87	39	40	Mo-Ka
U	1094	126	12	40	Mo-Ka
Ce	968	196	20	280	W-La
Nd	608	23	4	250	W-La

The table 1 reportes major elements in percent in weight and trace metals in mg kg⁻¹ (ppm). All data are the results of two independent measurements and relative standard deviation is less than 8% for major elements. Table 1 relate also the detection limits (LOD) calculated by the following equation $LOD = 3 C (I_{peak})^{-1}$ square root I_{back} were C, I_{peak} , I_{back} represent the amount of the element, net intensity (cps) of the peak of the element and background intensity (cps) respectively (12). Table 2 compares the obtained results analysing the samples with two distinct alkaline fusions. The correlation parameters between the two alkaline fusions are given by the straight line (reported in Figure 2) equation $Y = 0.99487 (\pm 0.01984) + 197.2 (\pm 1239.3)$ (n = 14). A paired t-test showed that no significant differences exist between the two alkaline fusions.

Figure1. Straight line obtained plotting results analysing a coltan mineral ore with two distinct alkaline fusion.

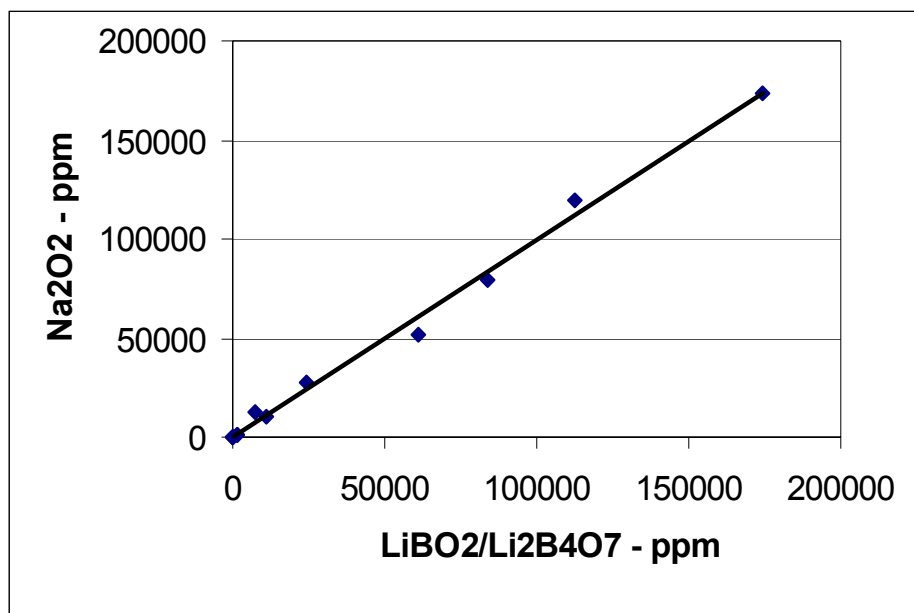


Table 2. Elemental composition (mg Kg^{-1}) of a coltan mineral ore analysed with two distinct alkaline fusion.

Element	$\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$	Na_2O_2
Ti	11093	10765
V	200	200
Cr	200	200
Mn	61221	52282
Fe	83874	79772
Y	1117	1007
Nb	174558	173569
Ta	112179	119155
Sn	24615	27099
W	7151	12545
Sr	129	189
Pb	308	539
Th	215	138
U	1269	979

4. Conclusion

The TRXRF technique was employed in the analysis of a columbite-tantalite mineral ore. Due to its multi-element capability and high sensitivity TRXRF is a valuable tool for elemental composition of mineral ores.

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References

- 1) H.H. Read, Rutley's Elements of Mineralogy, George Allen & Unwin, London, **1976**.
- 2) Kirk-Othmer Encyclopedia of Chemical Technology (4th ed.) New York, Wiley, **1997**.
- 3) R.L. Parker, J.W. Adams, Niobium and Tantalum, U.S. Mineral Resources, U.S. Geological Survey Professional Paper 820, **1973**, 443.
- 4) Cunningham, U.S. Bureau of Mines Bulletin **1985**, 675, 185.
- 5) F.W. Miller, R.J. Fantel, D.A. Buckingham, U.S. Bureau of Mines Information **1986**, Circular 9085, 20.
- 6) G. Amil, M. Ramanaji, M.R.P. Reddy, Arbind Kumar, T.L. Prakash, V.C. Sethi, *Atomic Spectroscopy* **2002**, 23, 32.
- 7) S.M. Pyle, J.M. Nocerino, S.N. Deming, J.A. Palasota, *Environ. Sci. Technol.* **1996**, 30, 204.
- 8) A. Johnson, G.C. Lalor, H. Robotham, M.K. Vutchkor, *J. Radioanal. Nucl. Chem.* **1996**, 209, 101.
- 9) E.I. Obiajunwa, *Nuclear Instrum. Methods in Physics Research B* **2001**, 184, 437.
- 10) T.T. Chao, R.F. Scanzolono, *J. Geochemical Exploration* **1992**, 44, 65.
- 11) Z.Sulcek, P. Povondra, C.R.C., Inc. **1989**.
- 12) R. Klockenkamper, Total reflection X-Ray Fluorescence Analysis, Wiley Inc. **1997**.