

X-RAY FLUORESCENCE ANALYTICAL METHODOLOGY FOR THE DETERMINATION OF Nb, Ta, Fe AND Mn EXTRACTED IN HYDROMETALLURGIC PROCESSES

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Abstract— Analytical methodologies were developed for the quantification of niobium, tantalum, iron and manganese in samples of minerals and solid residues coming from ore pressure leaching, using different acids. The adopted instrumental technique was X-ray fluorescence on pelleted solid samples. The analysis of the experimental data obtained by the different assayed methods showed that the direct technique using calibration curves built from pure oxide patterns and the method of standard addition were those giving statistically acceptable results. Comparison of the analytical data obtained by application to ore and leaching residue samples of these methods with a reference method showed that the experimental results were satisfactory.

Keywords— X-ray fluorescence, niobium, tantalum, iron, manganese, determination, leaching process.

I. INTRODUCTION

Niobium and tantalum compounds are used in several high technology industrial activities such as electronics, superconductors, superalloys, aerospace, and nuclear, among others. (Tolley, 1992; Gupta and Suri, 1994). These elements are not abundant on the earth surface and the major ores containing them are pyrochloro, microlite, columbite, tantalite and tantalocolumbite (Habashi, 1997). In Argentina, there are deposits of Nb and Ta containing ores in pegmatitic rocks in the provinces of Salta, Catamarca, La Rioja, Córdoba and San Luis. Several studies of the geochemical and geological features of these deposits have been performed (Arcidiácono, 1974; Gallisky, 1983 and Angelelli, 1984). Also, various chemical treatments have been developed for Nb and Ta extraction from ores, among them reduction, chlorination, alkaline fusion and acid dissolution (Gupta and Suri, 1994; Habashi, 1997). At the same time, several methodologies have been designed for the determination of these metals in the products of the above mentioned treatments. (Habashi, 1997). Among

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these are gravimetry (Gibalo, 1970) together with UV-Visible absorptiometry (Charlot, 1961), inductively coupled plasma optical emission spectrometry (ICP-OES) (Kubová et al., 1993; Roychowdhury et al., 1995) and X-ray fluorescence (XRF) (Parker and Brocchi, 1981; Ruiz et al., 1993 and 1996; Balaes et al., 1987).

The determination of Nb and Ta constitutes one of the most complex tasks in analytical chemistry, since they occur together in nature and also they exhibit similar physicochemical characteristics (Gibalo, 1970). Therefore, analytical methodologies by wet processes are particularly difficult. Studies performed by Atkinson et al. (1952) have demonstrated that the results obtained in quantitative determinations of these elements may be unsatisfactory and that they not only depend on the method used but may also vary if the same method is performed by different analysts. Our research group is carrying out studies on the extraction of niobium and tantalum from local ores by means of pressure leaching in acid medium. The need to perform an adequate follow-up of the recovery obtained after each assay makes it indispensable to use a rapid and reliable technique for the quantitative determination of the metals present in columbo-tantalites and in the residues of extractive metallurgy. The purpose of this work was to develop suitable methods for the quantitative determination of niobium, tantalum, iron and manganese in the reactants, products and residues of columbo-tantalites pressure leaching, using hydrofluoric and carboxylic acids. After optimizing the sample preparation procedure, the technique of X-ray fluorescence was selected as the method giving the most reproducible and accurate results. The results were compared to those obtained by the gravimetric method of classical analysis for Nb and Ta as well as to those obtained by means of ICP-OES.

II. EXPERIMENTAL

II.1. Reactants

The columbo-tantalite samples came from mineral ores in the province of San Luis, Argentina. Characterization by XRD showed that besides columbo-tantalite, the ore

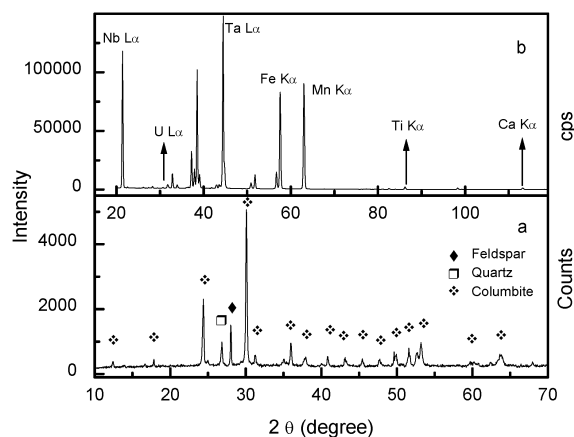


Fig. 1. Characterization of the ore a: XRD; b: XRF.

also contained quartz, feldspar and mica (Fig. 1a). The results of the ore characterization by XRF, shown in Fig. 1b, indicate that the ore stoichiometry is $(\text{Mn}_{0.53}\text{Fe}_{0.47})(\text{Nb}_{0.66}\text{Ta}_{0.34})$. The standards were prepared from Ta_2O_5 , Nb_2O_5 , MnO_2 (Fluka A G, Switzerland), Fe_2O_3 prepared from $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (Cicarelli) (Kodama, 1963), boric acid (Analar, U.K.) and high purity natural quartz. All the remaining reagents (carboxylic acids, HF, KHSO_4 , etc.) were of "pro analysi" quality.

II.2. Equipment

The ore was ground in a N.V. TEMA vibratory disc mill with chromium-nickel steel tray and separated into fractions of different particle size (between $-10 +20 \mu\text{m}$ - 325 mesh ASTM) in a Fritsch Analysette 03-502 lab sieve. The solid samples were pelleted at 15,000 kPa with a hydraulic press. The characterization of starting materials and residues by XRD was performed on a Rigaku D-MAX-III C diffractometer (30 kV and 20 mA, with Ni filter and Cu K_{α} radiation). The measurements using the XRF technique were performed on a Philips PW 1400 spectrometer, equipped with a chromium tube. The measurements by ICP-OES were conducted on a Baird ICP 2070 equipment, with a nebulizer suitable to work in HF medium. The Nb and Ta extraction assays were carried out on a Parr reactor of 450 ml capacity, built in Monel, using HF and mixtures of HF and carboxylic acids as leaching agents.

II.3. Work methodologies

Measurements by ICP-OES were carried out using a calibration curve obtained from standards of known concentration, in 10% (v/v) HF medium. The XRF measurements on solid and liquid samples were performed by two different methodologies: the calibration curve method and the standard addition method. The liquid samples presented to the equipment had an HF concentration of approximately 10% (v/v). A known mass of the solid samples, previously conditioned, was pelleted on a previously prepared boric acid support (Perino and Gasquez, 2000).

II.4. Preparation of standards and samples

A. ICP-OES technique

The stock solutions for the preparation of standards were separately prepared for each of the elements to be investigated. In the case of Nb and Ta, the technique described by Ruiz et al. (1996) was used. The Fe and Mn solutions were obtained as follows: approximately 100 mg of the metal were placed into a Teflon flask and 2 ml of distilled water and 3 ml of concentrated HNO_3 were added. This mixture was then heated in sand bath until almost dry and 10 ml of concentrated HF were added. Finally, the solution was taken to a volume of 100 ml with distilled water. Adequate aliquots of these solution were used to prepare the different standards, using 10% (v/v) HF as diluent. The concentration range of the standards was varied according to the probable content of the element to be measured in the sample. The samples presented to the ICP-OES equipment were the solutions obtained from the fusion of the ore with KHSO_4 and subsequent dissolution with tartaric acid (Ruiz et al. 1996), as well as those obtained from the filtrate after ore leaching in the Parr reactor. These solutions were conveniently diluted with 10% (v/v) HF so that their concentration was within the linear range of the calibration curve.

B. XRF technique

The measurements using X-ray fluorescence were performed on liquid and solid samples. The liquid samples were prepared following a procedure similar to the one describe in Section A. The analyzed solid samples came from the untreated ore in some cases and from the residues of the leaching process in others.

B.1. Liquids

B.1.1) Standard addition method

The stock solutions for each element were obtained as described in Section A. Increasing amounts of the element to be determined were separately added to equal aliquots of the sample so that the concentration of the sample was within the concentration ranges of the additions. Appropriate volumes of these solutions were placed in the measurement cells (Chemplex, covered with $6.3 \mu\text{m}$ - thick Mylar), and radiation was measured at the peak and at both of it sides. The net intensity was obtained by subtracting the average value of the background intensity to the peak intensity.

B.1.2) Use of the calibration curve

The standards and samples were prepared in a similar fashion to that described in Section A. The XRF measurements were performed as indicated in Section B.1.1).

B.2. Solids

B.2.1) Standard addition method

The standard addition method was investigated using two diluents: boric acid and quartz. At this stage, and with the purpose of determining the method reliability,

Table 1. Standards of Nb, Ta, Fe and Mn for the measurements on pelleted samples.

Standard	Composition			
	Nb ₂ O ₅ (mg)	Ta ₂ O ₅ (mg)	FeO (mg)	MnO (mg)
1	40.5	120.2	27.26	8.02
2	80.0	80.0	18.16	16.32
3	59.8	59.8	36.38	32.76
4	120.4	41.4	8.92	24.14
5	142.2	40.3	9.22	8.32

Note: The composition in FeO and in MnO was calculated from the Fe₂O₃ y MnO₂ oxides used for preparation of the standards.

only samples coming from unleached ore were used. The standards used were pure Nb, Ta, Fe and Mn oxides.

B.2.1.a) Adequate constant masses of the ore were mixed with increasing amounts of the corresponding oxide and variable amounts of boric acid, separately for each element, until a total mass of 100 mg was obtained. The used granulometry was -325 mesh. The solids were mixed in a manual agate mortar up to homogeneity and the sample was subsequently pelleted. Measurements were carried out by reading the radiation of the peak and both sides of the peak. The net intensity was calculated as described above.

B.2.1.b) In a first stage, a procedure similar to that described in the above section was used, but using quartz as diluent. Since the results obtained up to this point had not been totally satisfactory, a study was performed in order to optimize the sample method preparation. The investigated variables and the procedure used are described in the following section.

Ore-diluent ratio

Pellets were prepared by mixing, first manually and then in agate mechanical mortar, 100 mg of the ore with different quartz amounts to cover a concentration range (w/w) of the ore in the pellet between 0.5 (1:1 ratio) and 0.050 (1:20 ratio). The mixing time was three hours, and particle size was -270 +325 mesh. The measurements in the XRF equipment were performed as described in previous sections.

Mixing time

Pellets were prepared following a similar procedure to that described above. The ore-quartz ratio was 1:15, particle size was -270 +325 mesh and the mixing time varied between 1 and 12 hours.

Particle size

The study of the effect of granulometry was performed using three fractions of different particle size: -140 +200; -270 +325 and -325 mesh. The ore-quartz ratio was 1:15 and the mixing time was 1 hour. After selecting the working variables for each of the elements to be determined, 200 mg aliquots of the ore were mixed with 3000 mg of quartz and with increasing amounts of the respective oxides. Once the different mixtures were obtained, 100 mg pellets were prepared

with each one of them. The measurements of fluorescence radiation were performed following a procedure similar to that described above.

B.2.2) Use of the calibration curve

The standards for obtaining the calibration curves of each elements were prepared by mixing different masses of the oxides, as shown in Table 1.

The mixing methods and conditions used were those that were considered optimum regarding to the mixing time and particle size; 100 mg pellets were used.

III. RESULTS AND DISCUSSION

The study was performed using the above described ore samples, whose composition was determined using six replicates, by gravimetry and UV-visible absorptiometry, for Nb and Ta (Ruiz et al., 1993). Fe and Mn were determined by redox volumetry (Kodama, 1963).

This validation method was considered the most adequate, since standard materials with similar composition to the samples subjected to leaching assays were not available. The percent composition (w/w), n=6 and $\alpha = 0.05$, was: Nb₂O₅: 39.94 (s = 0.1855); Ta₂O₅: 34.07 (s = 0.1115); FeO: 7.71 (s = 0.1198) y MnO: 8.40 (s = 0.12848). Results obtained by a prestigious international laboratory using different methods matched ours by $\pm 3\%$.

A. ICP-OES technique

ICP-OES had the advantage of offering a rapid procedure for the analysis of the ore sample and the solutions coming from the ore leaching. However, the results obtained by this technique were not accurate enough to be considered satisfactory. Errors were usually above 10%, and were probably caused by difficulties in the nebulization process of the samples. For this reason, ICP-OES was only used in those leaching process situations which required the quantification of very low concentrations.

B. XRF technique

The measurements of X-ray fluorescence were carried out under the following working conditions:

- Gas flow detector and scintillation detector in tandem
- First order spectral lines
- Tube anode: Cr, operated at 60 kV and 40 mA
- Analyzing crystal: LiF 200
- Nb line: L _{α} (2 θ = 21.360); Ta line: L _{α} (2 θ = 44.420); Fe line: K _{α} (2 θ = 57.52); Mn line: K _{α} (2 θ = 62.97)
- Exposition conditions: in air
- 40 s counting time for all the analyzed elements

B.1. Liquids

The results obtained with liquid samples in HF medium were not totally satisfactory, either for those coming from ore dissolution or from leaching in the reactor. The important dispersion observed in the results was proba-

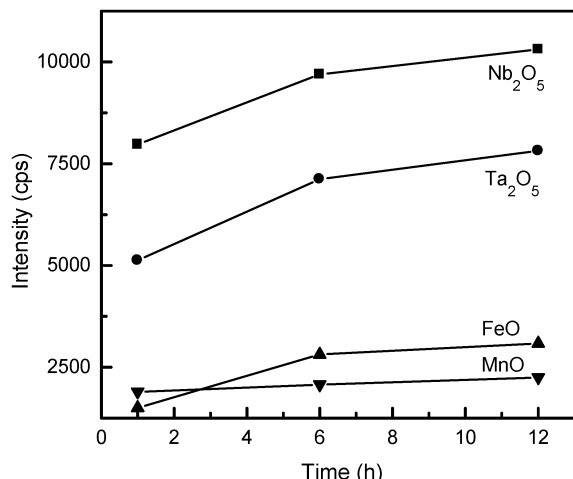


Fig. 2. Effect of mixing time of the solids on fluorescent intensity.

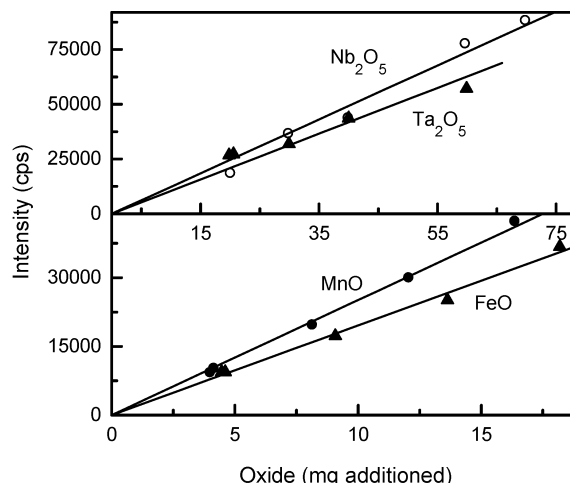


Fig. 4. Calibration curves using standards prepared with mixture of pure oxides.

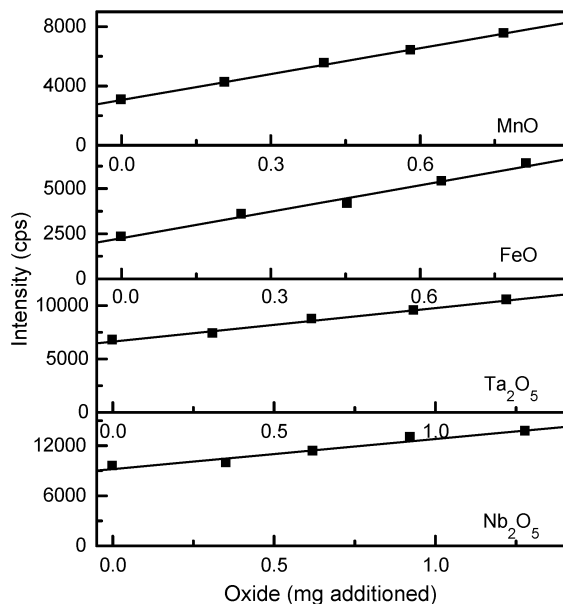


Fig. 3. Application of standard addition method for Nb, Ta, Fe and Mn oxides.

bly caused to the formation of a solid film on the Mylar, favored by the action of the X radiation.

B.2. Solids

Comparison of the results obtained by standard addition using boric acid and quartz as diluents demonstrated that dilution with quartz yields more accurate results. For this reason, the study of the variables for the preparation of the samples and standards (ore-diluent ratio; mixing time and particle size) was done using quartz as diluent and an univariate methodology. The recommended values, i.e., those giving the maximum fluorescent intensity for each variable were the following: ore-quartz ratio, 1:15; mixing time, 6 h (30 min manually and 5.30 h in mechanical mortar); particle size, -325 mesh. Figure 2 shows that after a mixing time of 6 hours the X-ray intensity did not increase significantly.

Table 2. Determination of Nb, Ta, Fe and Mn in ores.

Component (% w/w)	Ore		
	Method 1	Method 2	Method 3
Nb ₂ O ₅	40.92 s=0.48	40.70 s=0.31	39.94 s=0.19
Ta ₂ O ₅	33.74 s=0.42	34.45 s=0.42	34.07 s=0.11
FeO	7.76 s=0.20	7.45 s=0.25	7.71 s=0.12
MnO	8.22 s=0.10	8.53 s=0.07	8.40 s=0.13

Note: 1: Standard addition method; **2:** Calibration with standards prepared with pure oxides; **3:** Reference method.

Figure 3 shows the results obtained in the application of standard addition for the Nb, Ta, Fe and Mn oxides

The degree of linearity is acceptable for all the analyzed elements in the concentration range used. Also, the ore composition obtained by this method differs by 3 % from that obtained using the reference method.

Although the standard addition method is relevant for the comparison and validation of experimental results, this technique is not suitable for determining the composition of residues coming from leaching process, since relatively large amounts of sample are needed. Therefore, we investigated the possibility of performing calibration curves using standards prepared with pure oxides (Section B.2.2). Figure 4 shows the calibration curves obtained for Nb, Ta, Fe and Mn.

Tables 2 and 3 inform the results obtained by application of standard addition and calibration with pure oxides for an ore sample and a leaching residue sample, compared to those obtained by the reference method.

From Tables 2 and 3, it can be seen that the results agreement between ± 4%, for all the elements studied, both in the ore sample and in the residue of acid leaching.

Table 3. Determination of Nb, Ta, Fe and Mn in residues.

Component (w/w)	Residue		
	Method 1	Method 2	Method 3
Nb ₂ O ₅	33.40	35.40	33.38
	s=0.46	s= 0.53	s=0.22
Ta ₂ O ₅	36.82	36.64	36.75
	s=0.60	s= 0.18	s=0.13
FeO	45.05	43.28	44.80
	s=0.79	s= 0.58	s=0.11
MnO	33.36	32.19	33.23
	s=0.18	s= 0.45	s=0.21

IV. CONCLUSIONS

The analytical methodologies developed for niobium, tantalum, iron and manganese are satisfactory for a wide range of concentrations and are applicable to ore and leaching residue samples. The calibration by means of standards prepared with pure oxides has proved to be useful due to its simplicity, versatility and analytical performance.

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