

Chapter 2

Analysis of Non-Conducting Tantalite Minerals by Glow Discharge Optical Emission Spectrometry

M. Nete, W. Purcell, and J.T. Nel

Abstract Capabilities of the radio frequency glow discharge optical emission spectroscopy (RF-GD-OES) for analysis of Ta₂O₅/Nb₂O₅ and tantalum and niobium in electrically non-conducting geological samples were investigated. The metal pentoxides (Ta₂O₅ and Nb₂O₅) and the tantalite mineral powders were mixed with a thermally conductive copper powder in ratios of up to 1:10 sample: copper and pressed into a disc sample for glow discharge sputtering. Studies were carried out to determine and optimize all the parameters affecting the analyses by the RF-GD-OES technique. This included the determination of the ability of the methodology to generate usable analytical curves for the target elements. Good calibration curves which were used for analyses of Ta and Nb in the tantalite minerals were obtained at optimized experimental conditions. Respective tantalum and niobium recoveries were in the order of 99.78–104.91% and 98.34–102.03% from the mineral analyses.

Keywords Tantalite • Tantalum oxide • Niobium oxide • Glow discharge • Analysis

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2.1 Introduction

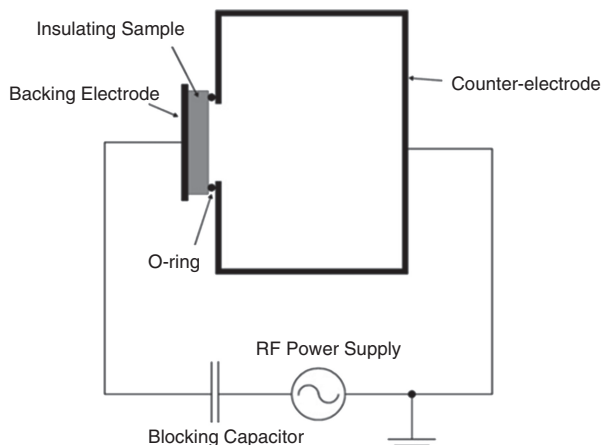
Tantalum and niobium are group VB elements with very similar chemical properties and as such they are always found together in nature. These elements have recently been found to have a great potential for use in strategic energy technologies such as nuclear, solar, carbon capture and capacitor manufacturing [1]. Tantalum is used for manufacturing of capacitors [2, 3], which offer high capacitance density needed in the smallest possible size. Niobium oxide is used in the manufacturing of high refractive index lenses as well as high dielectric and multilayer ceramic capacitors [3, 4]. Niobium oxide powder material has many desirable properties as a solid electrolyte capacitor. These properties include a better load resistance, reduced costs and significant reduction in ignition failure [5].

The demand for highly precise quantitative methods for accurate characterization of niobium and tantalum in various sample matrices has increased significantly due to their importance in the production of modern industrial products [1]. Conventional wet analytical methods such as inductively coupled plasma spectroscopy (ICPS) and flames which require complete sample dissolution are the most successful and commonly used techniques. However, the different sets of impurities in natural samples such as tantalite mineral can alter the performance of the dissolution method and thereby require a modification of the already existing methods or even developing a new alternative dissolution method.

The use of glow discharge spectrometry (GDS) for bulk analysis of mineral samples has been relatively poorly explored. The general challenge in using solid analysis techniques such as GDS and X-ray fluorescence (XRF) is the sample preparation, especially for powder samples which require homogenization of the sample prior to analysis. In addition, the most limiting factor is the requirement that the samples be electrically conductive for successful measurements using GDS analysis. Challenging as the sample preparation may be, the direct analysis of solid samples is important for the reduction of acidic liquid waste which in turn ensures a safe environment free of chemical contamination. Compared to XRF, glow discharge optical emission spectroscopy (GD-OES) has a higher sensitivity for the light metals such as B, Be and Li (ppm range), better precisions and lower %RSD values [6].

Compared to wet spectrometric methods, such as AAS and ICPS, GDS has advantages of being partially non-destructive, multi-elemental, fast and requiring simpler sample preparation [7]. Moreover, the GD-OES analysis is non-destructive; hence the samples can be stored and reused for other investigations at a later stage or be kept as archival samples [8]. GDS is superior for rapid depth profiling [9], surface, interface and bulk qualitative and quantitative analyses of solids [10]. Metallic bar or disc samples can be analyzed directly without any preparation or slightly polished to ensure that they are vacuum-tight when pressed against a silicone O-ring. Powdered conductive samples on the other hand need to be pressed into discs for analysis by GDS. Non-conductive powders such as metal oxides and minerals are either pressed into very thin discs that can be analyzed using the radio

Fig. 2.1 Diagrammatic representation of a radio frequency glow discharge (RF GD) sample introduction system [11]



frequency GD lamp or mixed with conductive host material such as copper powder (to make them electrically conductive) and then pressed into a disc [7]. The main challenge in this method of sample preparation is obtaining a homogenous mixture. The accuracy of analysis depends strongly on the even distribution of the particles of the analyte. These requirements cannot always be fulfilled, especially when the amount of sample is very small.

The sample introduction into the GD-OES instrument involves mounting of the sample over an O-ring at the lamp opening (Fig. 2.1) where it is held in place by vacuum. This method of sample introduction into the system requires preparation of non-porous and flat polished sample surfaces. Once the sample is properly mounted the next requirement is the production of sufficiently energetic ions by the lamp to sputter the atoms on the sample surface.

The aim of this study was to investigate the capability of the GD-OES in quantitative and accurate determination of Ta and Nb in tantalite minerals. Samples were prepared for analysis by mixing the non-conductive metal oxide and mineral samples with the conductive copper powder. Optimum experimental conditions were investigated extensively during the developments to obtain a good calibration curve. These included the determination of an optimum sample:host material ratio, preburn times as well as optimal voltage and current.

2.2 Experimental

2.2.1 Reagents and Equipment

Tantalite samples (manganotantalite (Tan A) and ferrocolumbite (Tan C)) were sourced from Mozambique. High purity Ta_2O_5 , Nb_2O_5 and 99.5% copper powder (particle size $<425 \mu\text{m}$) were purchased from Sigma Aldrich South Africa.

Powdered samples were mixed using a Retsch mixer mill MM 200 and the mixtures were pressed into discs using an Altech hydraulic press. Sample discs were analyzed by a LECO GDS850A glow discharge optical emission spectrometer (GD-OES).

2.2.2 Sample Preparation

Calibration samples were prepared by mixing the non-conducting $(\text{Ta/Nb})_2\text{O}_5$ mixture with the host (conductive) copper powder. Samples were mixed in ratios ranging between 1:99 and 1:1 m/m (sample to host) with copper powder. The mixture was shaken for 10 min using a Retsch mixer mill MM 200. Samples were pressed into 2.0 mm \times 25 mm discs at a pressure of at least 10 MPa for 30 s with a hydraulic press (Fig. 2.2). The mineral samples (maximum particle sizes = 250 μm) were prepared in a similar manner to the calibration samples. The sample discs were analyzed using GD-OES. Experimental factors which were investigated include the influence of sample to host material ratio, power effects and pre-burn time.

2.3 Results and Discussion

2.3.1 Optimization of the Sample Preparation

The development of the sample preparation method was begun by investigation of the niobium/tantalum pentoxide:copper mixtures at ratios ranging between 1:99 and 1:1. The experimental results indicated that at higher relative metal pentoxide concentrations sample discs were not vacuum-tight. The results indicated that the porosity of the discs increased as the sample content was above the 15% concentration. Another observation which was made was the obvious segregation between the metal oxide particles and those of the copper metal at 10% metal oxide and above. Lastly, metal oxide concentrations between 10 and 15% were not sputtered even though they were vacuum-tight on the instrument (Fig. 2.3). The observed particle separation between the oxide materials and the copper metals could be due to the difference in the densities and/or the particle sizes of these samples. This could also be due to the diffusional migration of the non-conducting metal oxide and copper particles [12] which may occur during the pressing of the samples. This separation may be occurring even at lower metal pentoxide concentrations but only become visible at relatively higher metal pentoxide concentration which would imply potentially poor homogeneity of the discs.



Fig. 2.2 Hydraulic press for preparation of pellets for analysis by GD-OES

2.3.2 Calibration Curves

The limit of detection (LOD) estimates of 0.0024% for Nb and 0.0028% for Ta (which were comparable and in the same magnitude to those of inductively coupled plasma optical emission spectroscopy (ICP-OES)) were obtained by using a copper powder sample (~7 g) as blank in this study. The copper powder (host matrix), which is responsible for the spectral background has a different sputtering rate from the oxide materials to be analyzed. The analytical calibration curve was investigated for the metal pentoxide with concentrations of less than 10%. Measurements were initially performed under default instrument conditions of 700 V, 20 mA and 1 min pre-burn time at three different positions (to determine the reproducibility of intensities) of each standard and a plot of intensities against concentrations was

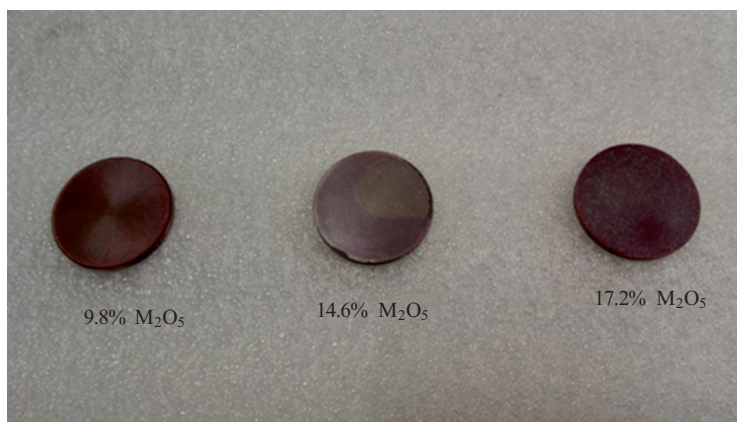


Fig. 2.3 Influence of sample concentration on the homogeneity and porosity of the sample/copper powder mixture

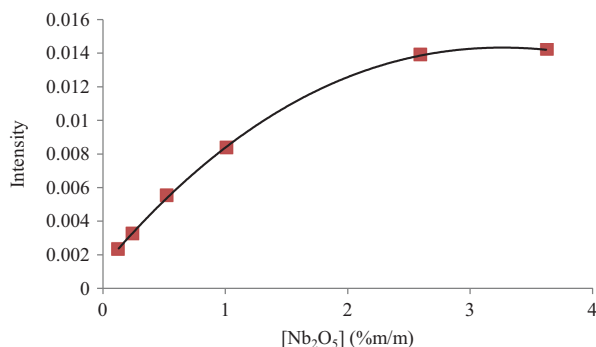


Fig. 2.4 Standard curve for intensity versus concentration for analysis of Nb₂O₅ by RF-GD-OES under default instrument conditions

established. The calibration curves (Figs. 2.4 and 2.5) exhibited good linearity in the ranges of 0.13–1.01% of niobium and 0.15–4.20% of tantalum. At these lower concentrations correlation coefficient values (R^2) for Ta and Nb linear curves were 0.988 and 0.990 respectively. Above the 1.01% Nb₂O₅ concentration there is a clear loss of linearity in the calibration curve but generally good reproducibility of the signal intensities for all the standard samples.

Literature study has indicated that this loss of linearity with the Nb₂O₅ concentration increase could be due to the slow sputtering rate of the oxide material [13]. Another literature study has shown that the increase in oxide concentration leads to decrease in discharge voltage and subsequently to decreased sputter yields [14]. The stronger molecular bonding in oxide material is responsible for the slower sputtering of these materials compared to metals. The Ta₂O₅ calibration curve on the other hand displayed less or no loss of linearity over a concentration of 0.15–4.20% Ta₂O₅. The linear calibration curves (0.13–1.01% Nb₂O₅ and

Fig. 2.5 Standard curve for intensity versus concentration for analysis of Ta₂O₅ by RF-GD-OES under default instrument conditions

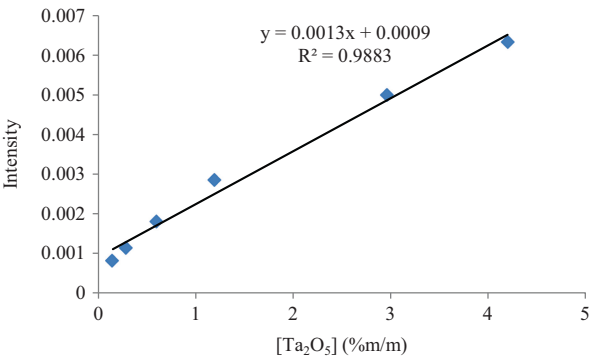


Table 2.1 Quantities and %RSD values of Ta₂O₅ and Nb₂O₅ in tantalite minerals determined by RF-GD-OES under default instrument conditions and comparison to ICP-OES results

Sample ID	ICP-OES [15]		RF-GD-OES		Average % recovery	
	Ta ₂ O ₅	Nb ₂ O ₅	Ta ₂ O ₅	Nb ₂ O ₅	Ta ₂ O ₅	Nb ₂ O ₅
Tan A	27.8(3)	27.0(2)	23(1)	9(1)	82.73	34.02
%RSD			4.94	13.34		
Tan C	33.0(2)	13.7(2)	29(2)	6(1)	87.88	46.50
%RSD			6.94	20.96		

0.15–4.20% Ta₂O₅) were used for quantification of Ta and Nb in the tantalite minerals, under the default instrument conditions. The results were compared to the previous ICP-OES analysis results [15] and unsatisfactory recoveries of less than 90% Ta₂O₅ and 50% Nb₂O₅ were obtained (Table 2.1) in this study. In addition to the poor analyte recoveries were the high %RSD values (up to 20.96%) which indicated poor reproducibility of the data points.

In the next step, it was decided to investigate the effect of the pre-burn time to try and improve the recovery of the analytes during the mineral analysis. The influence of the pre-burn time was studied at the current of 23 mA, voltage of 700 V and the pre-burn times of 1, 2 and 5 min (Fig. 2.6). Experimental results obtained in this part of the study indicated a significant improvement of Nb₂O₅ recoveries from 34.02 to 76.40% when the pre-burn time was increased from 1 to 5 min. The Ta₂O₅ recoveries also increased from 82.73 to 98.17% during the same pre-burn time increase. The %RSD of Nb₂O₅ analysis improved from 13.34 to 2.52% and 4.94 to 3.44% for Ta₂O₅ for the 1 to 5 min pre-sputtering times during analysis of Tan A. The longer pre-sputtering maximizes the sputtering of the oxide material thereby improving the stability of the RF power discharge which results in achievement of reproducible intensities.

The influence of power was studied to improve both the linear range of the standard curves as well as the recovery of the analytes. The influence of power on the intensities obtained was studied by analyzing three Nb₂O₅ standard samples (each sample disc was sputtered at three different positions) at a current of 23 mA and 5 min pre-burn time while changing the discharge voltage from 600 to 900 V (Fig. 2.7). The results obtained in this part of the study indicated an increase in the

Fig. 2.6 Elemental recoveries versus pre-burn time for analysis of tantalite A mineral by RF-GD-OES at 23 mA and 700 V

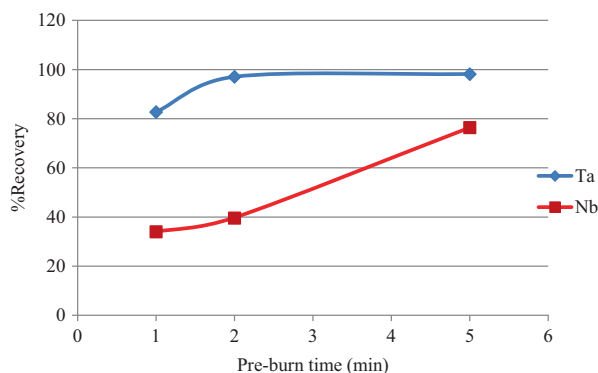
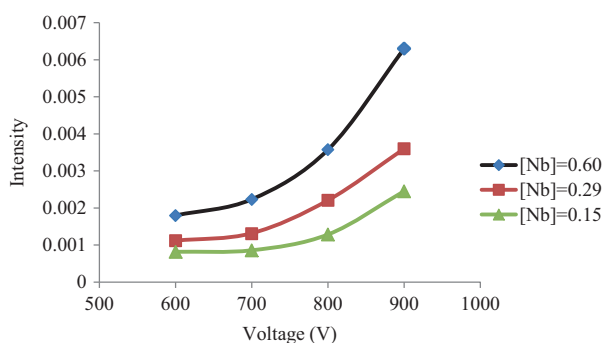


Fig. 2.7 Intensities versus voltage for analysis of Nb_2O_5 standard samples by RF-GD-OES at 23 mA and 5 min pre-burn time



intensities of the standard samples with increasing discharge voltage. Similar results were also obtained for Ta_2O_5 standard samples under the same experimental conditions. It is clear from these results that more power and pre-sputtering time are essential for better sputter rates of the oxide materials. A higher power is mainly required to break the stronger molecular bonds of the oxide material while longer pre-burn times are important for stable RF power discharge and steady sputter rates and excitations.

The combination of longer pre-burn times and a higher discharge voltage was used to establish the calibration curves of both Ta and Nb (Figs. 2.8 and 2.9). As previously, measurements were performed in triplicate for each standard and the lowest and highest data values are indicated by vertical error bars. These calibration curves (Figs. 2.8 and 2.9) exhibit improved linear range (0.13–2.6%) and good linear regression (R^2 value = 0.9992) for Nb_2O_5 . The Ta_2O_5 calibration curve was not studied beyond the 0.15–4.20% range due to the fear of particle segregation and poor sputtering, which were previously observed for higher oxide concentrations. However, the new experimental conditions greatly improved the linear regression of the standard curve (R^2 = 0.9995).

Percentage recoveries of the analytes in the two minerals also improved significantly (Table 2.2) under these new set of experimental conditions (23 mA, 900 V and 5 min pre-burn time). The %RSD values of the analytes' recoveries were less than 5%.

Fig. 2.8 Standard curve for intensity versus concentration for analysis of Nb₂O₅ by RF-GD-OES at optimum conditions

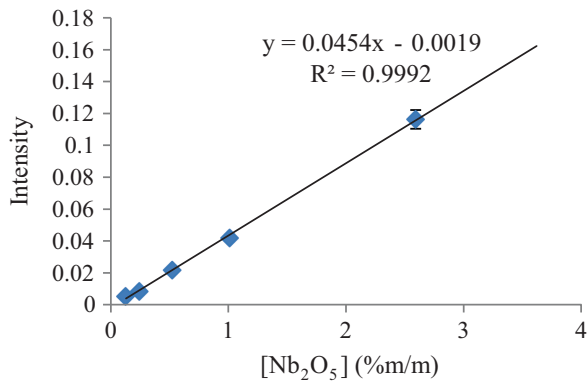


Fig. 2.9 Standard curve for intensity versus concentration for analysis of Ta₂O₅ by RF-GD-OES at optimum conditions

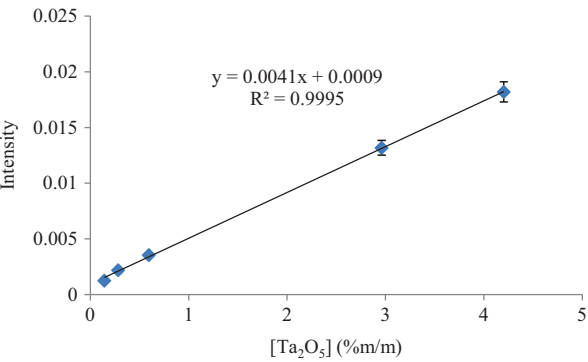


Table 2.2 Quantities and %RSD values of Ta₂O₅ and Nb₂O₅ in tantalite minerals determined by RF-GD-OES under optimized experimental conditions and comparison to ICP-OES results

Sample ID	ICP-OES [15]		RF-GD-OES		Average % recovery	
	Ta ₂ O ₅	Nb ₂ O ₅	Ta ₂ O ₅	Nb ₂ O ₅	Ta ₂ O ₅	Nb ₂ O ₅
Tan A	27.8(3)	27.0(2)	28.1(9)	26.8(5)	101.08	99.26
%RSD			1.55	1.99		
Tan C	33.0(2)	13.7(2)	32.7(9)	12.9(8)	99.09	94.16
%RSD			3.19	1.65		

2.4 Conclusion

The analytical capabilities of RF-GD-OES for tantalum and niobium analyses in powdered tantalite minerals were investigated. Studies were carried out to develop a sample preparation method for successful analysis of non-conducting (Ta/Nb)₂O₅ and Ta/Nb in tantalite samples. Optimization of sample preparation and analytical parameters was successfully achieved for satisfactory determination of Ta/Nb in

non-conducting tantalite samples. Good calibration curves were obtained using a RF lamp at lower sample:copper ratios. The figures of merit (R^2 and standard deviations indicated by error bars) obtained for the standard curves were highly satisfactory. Studies were carried out to investigate the influence of operating parameters such as the applied voltage and the pre-sputtering time. At optimal conditions the respective tantalum and niobium recoveries from the mineral analyses were in the order of 99.78–104.91% and 98.34–102.03% respectively. The %RSD values were decreased from 13.34 to 1.99% for Nb_2O_5 and 4.94 to 1.55% for Ta_2O_5 by increasing both the pre-burn time and the applied voltage during analysis of Tan A sample. Comparison of the mean results obtained in this study to those recorded using ICP-OES analysis indicated high comparable values. The Student t-test gave t values which ranged from 0.391 and 2.191 and which were all below the tabulated value of 2.447 at the 95% confidence level.

Acknowledgements The authors thank the Research Fund of the University of the Free State, the National Research Foundation of SA, the South African Nuclear Energy Corporation Ltd (Necsa) and the New Metals Development Network (NMDN) of the Advanced Metals Initiative (AMI) of the Department of Science and Technology of South Africa (DST) for financial support. The authors also wish to thank Dr Steven Lötter for his assistance on the operation of the GD-OES instrument.

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Emerging Trends in Chemical Sciences

Ramasami, P.; Gupta Bhowon, M.; Jhaumeer Laulloo, S.;

Li Kam Wah, H. (Eds.)

2018, IX, 420 p., Hardcover

ISBN: 978-3-319-60407-7