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Potentiometric determination of Tantalum content in ores using an ion selective membrane electrode.

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Abstract

In this paper, a method for determination of tantalum in ores by direct potentiometry using an ion selective membrane electrode sensitive to the ion TaF_6^- *has been proposed. After checking the Nernstian behavior of the electrode in the presence of* TaF_6^-*, the influence of* NbF_6^- *concentration on the determination of tantalum was also investigated. Potentiometric measurements on synthetic solutions of* TaF_6^- *in the concentration range from* 10^{-3} *to* 10^{-5} $mol.l^{-1}$ *were performed in the presence of* 10^{-3} $mol.l^{-1}$ *of* NbF_6^- *as interferering ions. From the results recorded, it appeared that the response of the electrode deviate to the Nernstian behavior when* TaF_6^- *concentration is less or equal to* 5×10^{-5} $mol.l^{-1}$ *corresponding to a concentration of* NbF_6^- *at least twenty times greater than that of* TaF_6^-*. Using the standard addition method, it was observed that the ion* NbF_6^- *is no longer interferering with* TaF_6^- *on the entire range of concentration of* TaF_6^- *investigated. The accuracy of the method conducted on a series of potentiometric measurements was about 1%. The technique developed has then been applied to the determination of tantalum in samples of Colombo-tantalite from various region of Rwanda.*

Key words*: Potentiometry, Nernstian slope, tantalum, niobium, Colombo-tantalite.*

1. Introduction

Tantalum is an element found in nature always associated with niobium (Aubouin et al., 1968). They are widely known to have similar chemical properties, thus for the determination of tantalum in a mixture of tantalum and niobium, it is most often offered to perform a preliminary separation (Cotton et al., 1988). Indeed, these two elements react very similarly with most common titrant reagents and selective masking of niobium is difficult to achieve.

A number of methods has been proposed to separate Tantalum from Niobium such as reversed phase high performance liquid chromatography

(Vachirapatama et al., 2000, Narumol et al., 1999), extraction chromatography and paper chromatogram separation (Yang et al., 2002). Although these techniques are very selective, they suffer from heavy and complicated separation process and need a special instrument. Wang et al (2005) proposed a fast determination of of Nb and Ta with flow injection chemiluminescence method. In this method they could determine trace amounts of Nb and Ta in geological samples with satisfactory results.

Ion-selective electrode for the determination of tantalum have been developed. The response behavior of ions selective electrodes in terms of selectivity, precision, reliability, response time and life time are not well known, hence their applications are limited. Extraction-Spectrophotometric determination of tantalum using Brilliant Green-hexafluorotantalate(V) ion has been tested (Agrawal and John, 1985) but its application is not reported. In 1997, Amare et al., designed a new hexafluorotantalate (V) ion-selective liquid membrane electrode using brilliant green-hexafluorotantalate(V) ion-association complex in nitrobenzene with PVC support. The results showed that the electrode was highly selective and was responding to hexafluorotantalate(V) ion over a wide linear range with Nernstian slope and short response time. However, the same results showed that this electrode had the traditional barrel-type configuration and requires an internal reference electrode system. To overcome this problem, Tewolde et al., (1997) conducted a study on the determination of Tantalum with hexafluorotantalate(V)-selective Coated Graphite Electrode. In fact, it has been found that some of the inherent problems associated with liquid membrane electrodes could be overcome by coating the sensing element on solid conductors such as silver, platinum, and graphite (Du et al., 2002).

Amare et al., (1997) also tried to develop an hexafluorotantalate(V)-selective coated graphite electrode. This electrode was prepared by coating Malachite Green-hexafluorotantalate(V) extract in 1-chloronaphthalene with a PVC matrix on a graphite rod. This electrode was found to be highly selective to hexafluorotantalate(V) and free from interference of niobium which commonly occurs with tantalum. The analytical application of the electrode was extended to the determination of tantalum in tantalite-columbite ores and several synthetic matrices using four potentiometric techniques and the results were in good agreement with the actual or certified values.

In this study Tantalum was determined by potentiometry using an indicator electrode in the ion-sensitive membrane TAF_6^-. Since Niobium also forms a complex with fluoride ions (NbF_6^-), it was proposed to study the influence of the concentration of this element on the determination of tantalum in mixture of tantalum and niobium first. Secondary the concentration of tantalum in the samples provided by Rwanda Metals was determined.

2. Material and methods

2.1. Material

A) Sample preparation

In order to determine tantalum in ores, samples require to be solubilised. This is achieved by use of concentrated sulfuric acid in the presence of $K_2S_2O_7$ as melting agent at high temperature.

B) Experimental setup

During this research, a reference electrode Ag^+ / AgCl double junction filled with KCl 3 mol. / L was used together with an Ion-selective electrode in tantalum as indicative membrane electrode sensitive to the ion TaF_6^- see figure 1.

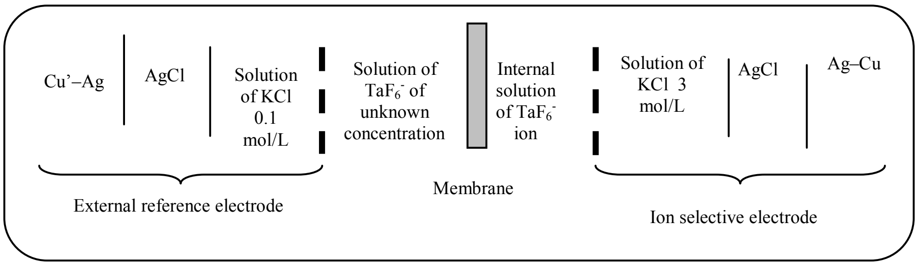

Figure 1: Potentiometric cell.

2.2. Methods

In order to detect a possible influence of niobium on tantalum determination, synthetic solutions of TaF_6^- with concentrations of 10^{-5} mol. / L, 2×10^{-5} mol. / L, 5×10^{-5} mol. / L, 10^{-4} mol. / L, 2×10^{-4} mol. / L, 5×10^{-4} mol. / L and 10^{-3} mol. / L each containing niobium at a concentration of 10^{-3} mol. / L were used.

Two methods (direct potentiometry and standard addition methods) were used for TaF_6^- determination. In the direct potentiometry method, the potential was directly read by putting the ion selective membrane device and the external reference electrode in the solution to be measured. In the standard addition method after thoroughly mixing of the sample solution, the potential E_1 was measured. Then, after addition of 2 ml of a 10^{-4} mol. / L of the standard solution of TaF_6^- the potential E_2 of the ion selective electrode was again measured.

3. Results

3.1. Nernstian slope behavior

To check the Nernstian behavior of the ion selective electrode TaF_6^-, synthetic solutions of respective concentrations of 10^{-5} mol. / L, 10^{-4} mol. / L and 10^{-3} mol. / L of this species were prepared . The variation of potential E measured for standard solutions versus $\log C_{TaF_6^-}$ is shown in figure 2. This figure shows a line whose equation determined by application of the law of least squares has the form: $E = -0,392 - 0,0589 \log C_{TaF_6^-}$ (1). As it can be seen from the equation, the slope determined from this study was 0.0589 V.

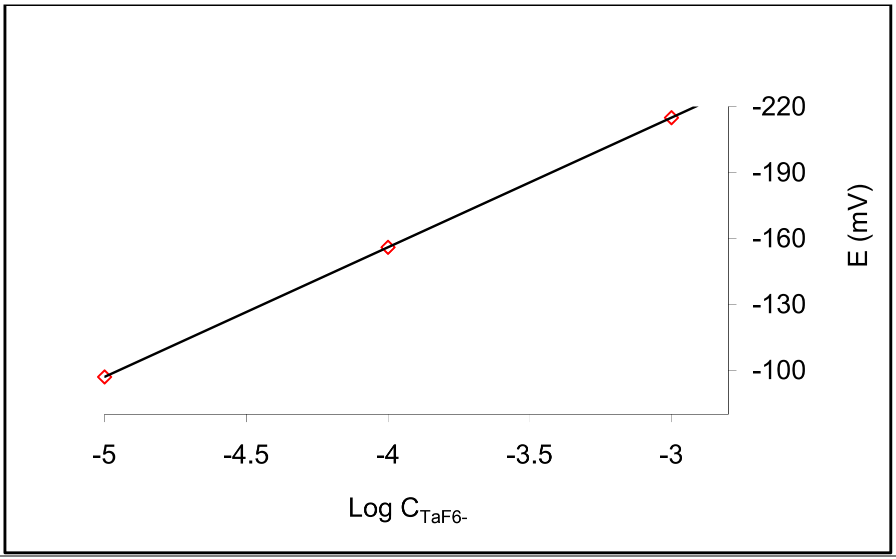

Figure 2: Variation of the electrode potential E versus $\log C_{TaF_6^-}$

3.2. Influence of NbF_6^- concentration on TaF_6^- determination.

From this study, interference of Niobium onto Tantalum determination have been conducted on synthetic solutions of TaF_6^- of concentrations ranging from 10^{-3} mol / L to 10^{-5} mol / L in the presence of 10^{-3} mol / L of NbF_6^-. Results from this study are shown in figure 3. From this figure, the deviation to the Nernstian slope of the ion selective electrode of the TaF_6^- in the presence of the interfering ion NbF_6^-, occurs at a concentration lower to 5×10^{-5} mol / L of TaF_6^- equivalent to twenty times less the concentration of NbF_6^-.

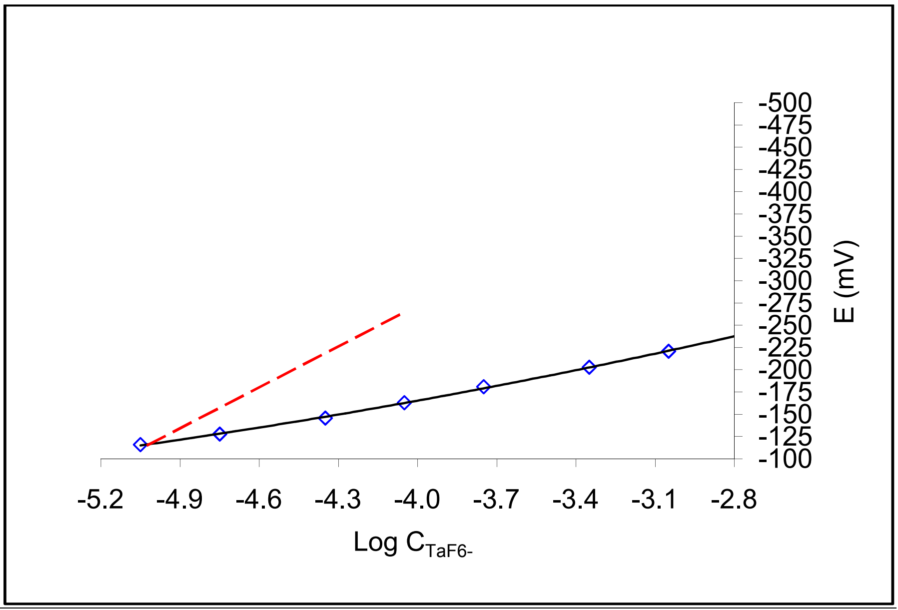

Figure 3: Variation of the electrode potential E versus $\log C_{TaF_6^-}$ at constant NbF_6^-.

3.3. Influence of NbF_6^- concentration by the standard addition method.

To check the validity of this method, two successive standard additions have been conducted to a series of solutions of known concentrations of TaF_6^- in the presence of 10^{-3} mol / L of NbF_6^-. Results from this study in figure 4 are showing a very good agreement between the values of the calculated concentration of TaF_6^- and the series of prepared solutions.

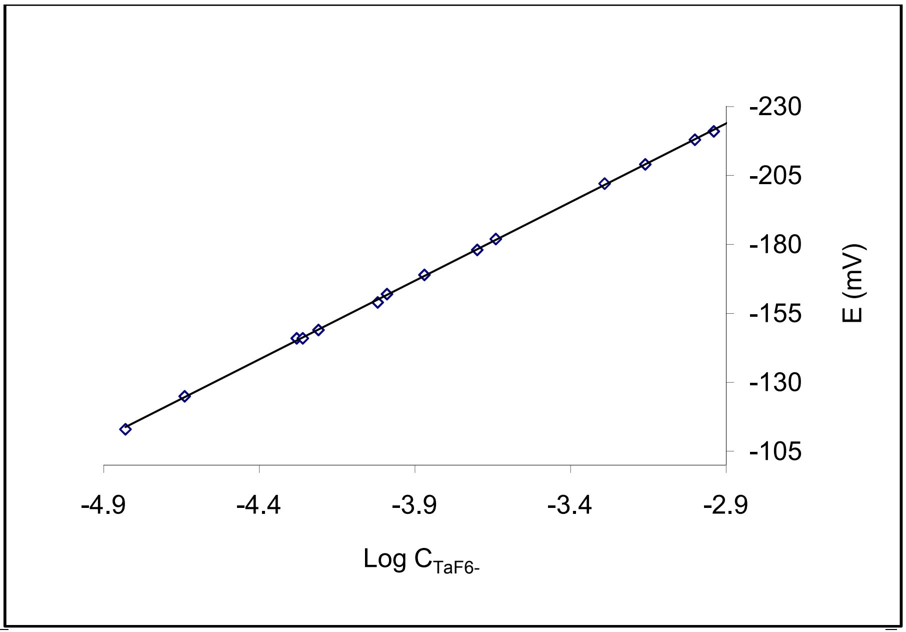

Figure 4: Variation of the electrode potential E determined during the standard addition method versus $\log C_{TaF_6^-}$ at constant NbF_6^-.

3.4. Tantalum determination in various ores from Rwanda

The standard addition method was used for Tantalum determination for various ores from Rwanda. For each series of measurements were carried out not only to calibrate the experimental TaF_6^- ion selective electrode to ensure proper operation but also to determine the tantalum content of a control sample whose content is 24.44 % in Ta_2O_5. To improve the accuracy of the method a blank reading was performed. Tables 1, 2 and 3 are giving results from this study.

Table 1: Ta_2O_5 content in samples from Mushubi, Rusoyo and Kirambo-Rugote

	% Ta_2O_5	
	sample 1	sample 2
Blank sample	-	-
Control sample	24,47	24,47
Mushubi sample	23,42	23,59
Rusoyo sample	32,92	32,92
Kirambo - Rugote sample	11,23	11,53

Table 2: Ta_2O_5 content in samples from Ngara, Kirambo and Kabuye

	% Ta_2O_5	
	sample 1	sample 2
Blank sample	-	-
Control sample	24,72	24,24
Ngara sample	16,99	17,39
Kirambo sample	27,23	27,63
Kabuye sample	8,15	8,48

Table 3: Ta_2O_5 content in samples from Kirambo - Wakiyumba, Kamabuye and Kabaya

	% Ta_2O_5	
	sample 1	sample 2
Blank sample	-	-
Control sample	24,06	23,88
Kirambo - Wakiyumba sample	22,16	22,57
Kamabuye sample	26,66	26,01
Kabaya sample	38,22	38,97

4. Discussion

4.1. Nernstian slope behavior

The measured electrical potential difference E is connected to the activity of the species TaF_6^- by the expression $E = E^o - 2,3\frac{RT}{F}\log a_{TaF_6^-}$ (2) with E^o the standard potential corresponding to $a_{TaF_6^-}$ = 1. At a fixed ionic strength the expression becomes $E = E^o - 2,3\frac{RT}{F}\log C_{TaF_6^-}$ (3). These expressions reflect the potential of a specific ion selective electrode TaF_6^- are identical to the Nernst equation. In fact, the graph representing the potential versus $\log C_{TaF_6^-}$ is then a line with a slope equal to the Nernst coefficient $-2.3\frac{RT}{F}$ (4) in the case of TaF_6^- .

The Nernstian behavior of the ion selective electrode can easily be explained by interpretation of the plot given on figure 1. In fact, the examination of this figure shows a line whose equation (1) was determined by the regression technique and the slope value thus determined was very close to the theoretical value of Nernst coefficient -0.05915 V at 25 °C. Therefore, the electrode used in this study showed a Nernstian behavior in the range of concentrations used for the calibration.

4.2. Influence of NbF_6^- concentration on TaF_6^- determination.

As defined by Barth & Hedin, (1973) an ion selective electrode is a probe with a specific task of determining ion species, if possible independently of the presence of other ion species in the solution. In the case where the electrode is sensitive to other types of ions, it is an interference phenomenon. Under these conditions the response of the ion selective electrode TaF_6^- in the presence of interfering ions NbF_6^- is given by the expression:

$$E = Eo - 2.3\frac{RT}{F}\log C_{TaF_6^-} - 2.3\frac{RT}{F}\log\left(1 + k_{TaF_6^-/NbF_6^-} \times \frac{C_{NbF_6^-}}{C_{TaF_6^-}}\right) \quad (5)$$

The gap between this ideal Nernstian slope to the ion TaF_6^-, difference due to the non-specificity of the membrane is given by the expression:

$$-2.3\frac{RT}{F}\log\left(1+k_{TaF_6^-/NbF_6^-}\times\frac{C_{NbF_6^-}}{C_{TaF_6^-}}\right)(6)$$

This difference depends on both the proportion of the ion NbF_6^- compared to the ion- TaF_6^- and the coefficient $k_{TaF_6^-/NbF_6^-}$ (7), called potentiometric selectivity coefficient of the membrane for the pair of ions TaF_6^- / NbF_6^- . For this study, the limit of the Nernstian behavior for TaF_6^- ions in the presence of the interferering ion NbF_6^- appears at concentration below 5×10^{-5} mol / L.

For concentrations higher than or equal to 5×10^{-5} mol / L, the expression of he potential is:

$$E=-0,394-0,0579\log C_{TaF_6^-}\ (8)$$

The slope is close to theoretical value of -0.058 V at 20 °C. This was also the average value of temperature at which the study was realized.

4.3. Influence of NbF_6^- concentration by the standard addition method.

The standard addition method involves measuring the potential of the ion selective electrode to determine the ion concentration before and after adding a volume of a standard solution to a given volume of the unknown solution. If V_o and v are the respective volumes of the unknown and the standard solutions, Co and C their respective concentrations we may write the following expressions:

$$E=E^o-2.3\frac{RT}{F}\log C_o\quad(9)$$

$$E^{'}=E^o-2.3\frac{RT}{F}\log\frac{V_oC_o+vC}{V_o+v}\quad(10)$$

Where E and $E^{'}$ are the potentials measured before and after addition of the volume of the standard to the volume V_0 of the unknown solution. In solving the above system of equation we get the value of C_o.

In figure 3, shows the linearity recorded over the range of concentrations explored, hence it can be say that the ion selective electrode to the ion TaF_6^- gave an ideal Nernstian response to the ion analyzed. The equation of the graph, calculated by the regression method was as followed:

$$E = -0,391 - 0,0575 \log C_{TaF_6^-} \quad (11)$$

It should be noted that the slope of this regression line was also close to the theoretical value of -0.058 V at 20 °C.

To characterize the precision of the method, relative standard deviation has been calculated assuming that the sources of random error are the same for all measurements. This assumption is generally valid if samples have similar compositions and were analyzed in exactly the same way. For that matter, six determinations have been made from the control sample. The standard deviation of the sample was then calculated from this expression:

$$S = \sqrt{\frac{\sum_{i=1}^{N}\left(X_i - \bar{X}\right)^2}{N-1}} \quad (12)$$

The relative standard deviation was obtained by dividing the standard deviation by the average of the data series. When the relative standard deviation is multiplied by 100% is called variation coefficient VC.

$$VC = \frac{S}{\bar{X}} \times 100\% = \frac{0.31}{24.19} \times 100\% = 1.26\% \quad (13)$$

Therefore, it was clear the analysis method used has a good accuracy.

5. Conclusion

Potentiometric response of an ion selective electrode for a given ionic species implies the presence of that species within the membrane and its exchange between the membrane and the solution in contact. The ideal case is when the exchange between the electrode and the solution can only be happening for the ion for interest. Form this study the response of the ion selective electrode followed the Nernstian behavior between the concentration range from 10^{-3} to 10^{-5} mol. / L. However, when TaF_6^- concentration was below 10^{-5} mol/L, interference from NbF_6^- at 10^{-3} mol. /L was affecting the determination of Tantalum and the slope was deviating from the Nernstian behavior. In order to minimize the matrix effect on Tantalum determination, the standard addition method is recommended instead of the direct potentiometry method. The results obtained show that the electrode response was Nernstian in the range of concentrations from 10^{-3} to 10^{-5} mol / L despite the presence of the interfering ion. The standard addition method was used for determination of Tantalum content in ores from various region of Rwanda. The accuracy of the method conducted on a series of potentiometric measurements was about 1%.

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