



The Application of Derivative Spectrophotometric Determination of Tantalum and Niobium in their Leach Liquors using Chromogenic Dye

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Abstract A sensitive and selective derivative spectrophotometric method was described for the determination of niobium and tantalum using Brilliant Green dye in their bearing leach liquors. The calibration working curve was linear between 1 and 15 $\mu\text{g ml}^{-1}$ for Nb and from 1 to 20 $\mu\text{g ml}^{-1}$ for Ta metal ions. The influence of various parameters and reaction conditions for optimum complex development was investigated (effect of different values of acidic pH media, using proper buffer solution, dye concentration, duration time for the stability of complex and the molar ratio of dye). Beer's law was obeyed from 0.25 to 15 ppm for Nb and from 0.25 to 21 ppm for Ta. The relative standard deviations between (0.821, 5.587), percentage errors between (0.474, 3.226) %, for tantalum and the relative standard deviations between (0.252, 5.989), percentage errors between (0.146, 3.458) % for niobium respectively. The optimized method for determination of both elements were applied on several forms of leach liquors with different media.

Keywords derivative, spectrophotometric determination, Nb, Ta, leach liquors and brilliant green.

1. Introduction

This article is mainly considering the precise and accurate quantitative colorimetric analysis of Nb and Ta in different leach liquors, so a stress of the survey on their industrial and geochemical importance, hence there must be several accurate methods for determination one of which include the spectrophotometric determination using various chromogenic dyes.

A great variety of reagents are known for determination tantalum and niobium (Gibalo I. M. and Vinogradov A. P., 1967). However, the studies aiming to find and investigate new reagents with different functional groups are still going on.

Niobium pentoxide (Nb_2O_5) is the most thermodynamically stable among niobium oxides. (Varghese B., Haur S. C. and Lim C. T., 2008).

A number of ion-selective electrodes have been proposed for the potentiometric determination of tantalum (Yuan Q., et al., 1982, Zhang G., et al., 1982, Zhang G., et al., 1983, Feng D., et al., 1982, Xu S., et al., 1984, Semenova I. N., et al., 1986, Zhang G., et al., 1986 and Feng D., et al., 1987).

Recently a new hexafluorotantalate(V) ion-selective liquid membrane electrode has been designed using brilliant green-hexafluorotantalate(V) ion-association complex in nitrobenzene with PVC support (Megersa N., Chandravanshi B. S. and Moges G., 1995). The electrode is highly selective and responds to hexafluorotantalate(V) ion over a wide linear range with Nernstian slope and short response time. However, this electrode has the traditional barrel-type configuration and requires an internal reference electrode system. In



general, the large size of this type of ion- selective electrode along with the requirement that it should be used in a nearly upright position renders it somewhat cumbersome to use and unnecessarily expensive (Freiser H. and Chem J., 1986). 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 (Freiser H. and Chem J., 1986, Moges G. and Kenya J., 1987, Covington A. K., 1980). It is, therefore, worthwhile to undertake the development of a coated conductor electrode based on brilliant green- hexafluorotantalate(V) ion-association complex for the determination of tantalum by ion-selective electrode potentiometry

Spectrophotometric determining 0.001% or more of tantalum in ores and mill products is described. After fusion of the sample with sodium carbonate, the cooled melt is dissolved in dilute sulphuric-hydrofluoric acid mixture and tantalum is separated from niobium and other matrix elements by methyl isobutyl ketone extraction of its fluoride from 1M hydrofluoric acid-0.5M sulphuric acid. The extract is washed with a hydrofluoric-sulphuric acid solution of the same composition to remove co-extracted niobium, and tantalum is stripped with dilute hydrogen peroxide. This solution is acidified with sulphuric and hydrofluoric acids and evaporated to dryness, and the residue is dissolved in oxalic-hydrofluoric acid solution. Tantalum is ultimately determined spectrophotometrically after extraction of the blue hexafluorotantalate-Brilliant Green ion-association complex into benzene from a 0.05M sulphuric acid-0.5M hydrofluoric acid-0.2M oxalic acid medium. The molar absorptivity of the complex is $1.19 \times 10^4 \text{ l. mole}^{-1} \text{ mm}^{-1}$ at 640 nm, the wavelength of maximum absorption. Common ions, including iron, aluminium, manganese, zirconium, titanium, molybdenum, tungsten, vanadium, tin, arsenic and antimony, do not interfere (Donaldson E. M., 1982).

Micro amounts of tantalum can be determined directly by spectrophotometry with 4, 5-dibromo-o-nitrophenylfluorone, citric acid, hydrogen peroxide and Triton X-100 in 0.5–5 mol L⁻¹ sulphuric acid (Wu Z., Hu Z. and Jia X.,1990). A rapid and sensitive method for the extraction and spectrophotometric determination of tantalum in presence of niobium with N-p-chlorophenylbenzohydroxamic acid, where the tantalum-N-p-chlorophenylbenzohydroxamic acid complex is extractable into toluene or benzene in HCl media (Agrawal Y. K. and Patel S. A., 1981). Tantalum (V)-2-(2-thiazolylazo)-5-dimethylaminophenol chelate anion is extracted quantitatively into benzyl alcohol with 1, 3-diphenylguanidine to form a ternary complex (Tsurumi C., Furuya K. and Kamada H., 1981). Mixed-ligand complexes of Tantalum (V) with dithiolphenol and its derivatives in the presence of hydrophobic amines have been studied by spectrophotometry (Kuliyev K. A. and Allahverdiev M.,2016). An extraction-spectrophotometric method for the determination of microgram amounts of tantalum (V) based on the extraction of tantalum-N-4-chlorophenyl-3, 4, 5- trimethoxycinnamohydroxamic acid complex from HCl medium into toluene was described. Brilliant Green was added to the organic phase containing the binary complex and the absorbance of the ternary system was measured. The method has been applied to the determination of tantalum in the presence of niobium (V) and tantalum in standard samples (Agrawal Y. K. and John K. T., 1985). A method for determining ~ 0.001% or more tantalum in ores and mill products was, after fusion of the sample with sodium carbonate, was dissolved in dilute sulphuric-hydrofluoric acid mixture and tantalum was separated from niobium and other matrix elements by methyl isobutyl ketone extraction of its fluoride from 1M hydrofluoric acid- 0.5M sulphuric acid (Donaldson E. M., 1983). The real work was devoted in studying of reaction of a complex formation of Tantalum (V) with thiocatecholic compounds (TCs) {2-hydroxythiophenol (HTP), (2,4-dihydroxythiophenol (DHTP), 2-hydroxy-5-chlorothiophenol (HCTP), 2-hydroxy-5-bromothiophenol (HBTP) and 2-hydroxy-5-iodothiophenol (HITP)} in the presence of hydrophobic amines. As amine aniline (An), N-methylaniline (MAn), N, N-dimethylaniline (DAn), aminopyridine (APy), dipyrindyl (DiPy), guanidine (Gu), diphenylguanidine (DPG), and triphenylguanidine (TPG).

In the present work, a sensitive and selective derivative spectrophotometric method was described for the determination of niobium and tantalum with Brilliant Green dye in ores was studied. Optimum factors affecting the formation and measuring of the complexes such as optimum wavelength, pH, initial concentration of dye, effect of duration time, molar ratios and calibration curves were investigated. The method was accurately applied on several leach liquors bearing Nb and Ta in different media.



2. Experimental

Instrumentation

A double beam UV-Visible spectrophotometer model Shimadzu (UV-11601) from Japan was used, The spectrophotometer ranges from 190 to 1100 nm, with a resolution of 2 nm and a wavelength accuracy of ± 0.5 nm were conducted.

A NEL 980 pH meter was used for recording the pH of the studied solutions. This was calibrated daily with three successive buffer solutions (4, 7 and 10).

Reagents

The chemicals and reagents used through the experiments carried out in the present study were analytical grade quality. Double distilled water was used for preparing all solutions.

Hydrochloric acid, sulphuric acid, nitric acid, perchloric acid, sodium chloride, sodium hydroxide, brilliant green dye, niobium pentoxide Nb_2O_5 powder (Sigma-Aldrich), tantalum pentoxide Ta_2O_5 powder (Sigma-Aldrich).

A solution of 10^{-3} M dye was prepared by dissolving 0.048 g of brilliant green dye with double distilled water in a 100 ml volumetric flask and completed to the mark.

Buffer solution for HCl medium was prepared by mixing 8.3 ml of 0.1 M HCl, 10 ml of 0.5 M NaOH and 4.17 ml of 1 M NaCl with double distilled water in 100ml volumetric flask and completed to the mark.

The buffer solution for HNO_3 medium was prepared by mixing 6.8 ml of 0.1 M HCl, 10 ml of 0.5 M NaOH and 4.32 ml of 1 M NaCl with double distilled water in 100ml volumetric flask and completed to the mark.

Different concentrations of HF (0.5, 1, 3, 4.5, 6 and 8 M) were prepared.

3. Results and Discussions

Mechanism of Brilliant Green dye and complexes

Absorption spectrum of Brilliant Green dye was measured against water as a blank where in figure (1) the absorption spectrum of Brilliant Green dye as well as the absorption spectra of Ta and Nb -dye complexes against water as a blank in the visible regions between 300 nm- 650 nm. Inspection of the data revealed that the maximum absorbance value for the dye was at 625 nm while for the two complexes was at 461 nm.

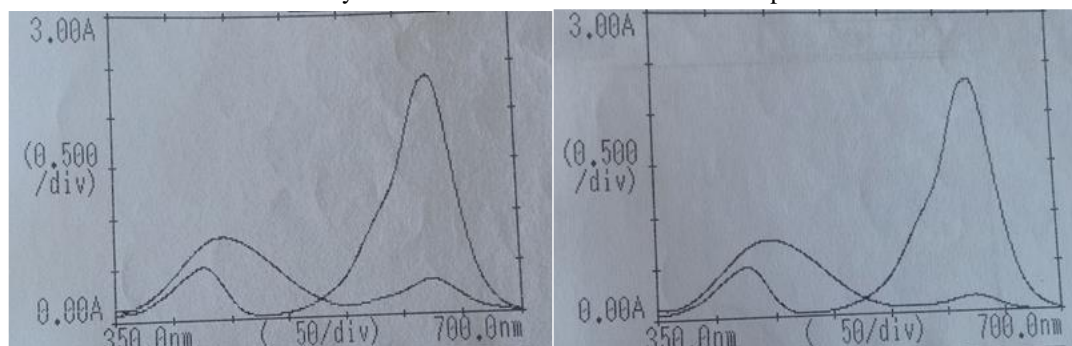


Figure 1: Absorption spectra of dye against water and Ta and Nb -dye complexes against reagent blank

Effect of different acidic media on Ta and Nb-Brilliant green dye complexes

The effect of different acid media concentrations (pH) on complex formation was studied, where different pH values from perchloric acid, hydrochloric acid, nitric acid and sulfuric acid with concentrations 1N were studied. To determine the optimum acidic pH medium, in 10ml volumetric flask an aliquot of 1ml from each of Ta (10^{-3} M), and Nb (10^{-3} M) with 1 ml brilliant green dye (10^{-3} M) were kept constant, while different pH concentrations and the contents were completed to the mark. The absorbance was measured in the range from 300 nm to 500 nm.

Tables (1, 2) summarized the obtained data for the effect of different pH values of acidic media on the absorbance of the complexes. The data gathered established that Ta complex was formed in perchloric acid, hydrochloric acid, nitric acid and sulfuric acid media with high absorbance values recorded at pH 0.69, 0.82,



0.69 and 0.6 respectively. On the other hand, Nb complex was formed in hydrochloric acid and nitric acid media recorded maximum absorbance values at pH 0.69 and 0.82 respectively.

Table 1: Effect of different pH values in different acidic media on the absorbance of Ta complex.

pH values	Absorbance			
	HClO ₄ media	HCl media	HNO ₃ media	H ₂ SO ₄ media
2	0.251	0.396	0.319	0.249
1.3	0.508	0.609	0.742	0.392
1	0.684	0.658	0.779	0.492
0.82	0.698	0.776	0.809	0.502
0.69	0.702	0.709	0.864	0.618
0.6	0.684	0.665	0.797	0.777
0.52	0.435	0.439	0.476	0.754
0.3	0.215	0.129	0.207	0.631

Table 2: Effect of different pH values in different acidic media on the absorbance of Nb complex.

pH values	Absorbance	
	HCl media	HNO ₃ media
2	0.103	0.042
1.3	0.177	0.081
1	0.222	0.102
0.82	0.292	0.623
0.69	0.854	0.310
0.6	0.352	0.252
0.52	0.187	0.100
0.3	0.115	0.089

Effect of buffer pH for optimum formation of Ta and Nb-brilliant green dye complexes

It was necessary to study the effect of buffer pH on the formation of both metal complexes. Different buffer solutions were prepared to study this effect. It was found that the optimum buffer with the highest absorbance values of the Ta and Nb- dye complexes result from using a mixture of 0.1M hydrochloric acid, 0.5M sodium hydroxide and 1 M sodium chloride buffer solutions in a manner to optimize the pH values studied in different media 0.69, 0.82, 0.69 and 0.6 for HClO₄, HNO₃, HCl and H₂SO₄ for Ta and 0.69 and 0.82 for HCl and HNO₃ for Nb respectively.

Optimum buffer which gives the highest absorbance values of both metal- dye complexes result from using a mixture of 0.1M hydrochloric acid, 0.5M sodium hydroxide and 1 M sodium chloride solutions in a manner to have a range of pH values (pH 0.69, 0.82, 0.69 and 0.6 for HCl, HNO₃, HClO₄ and H₂SO₄ respectively) for Ta-dye complex on the other hand pH values of 0.69 and 0.82 for HCl and HNO₃ respectively are used for Nb- dye complex. Table (3, 4) summarized the effect of changing pH on the absorbance of Nb and Ta- dye complexes respectively at maximum wavelength λ_{max} 461nm.

Table 3: Effect of buffer (pH 0.69, 0.82, 0.69 and 0.6) on the absorbance of Ta-brilliant green dye complex

Volume of buffer (ml)	Absorbance			
	pH 0.69 HClO ₄ media	pH 0.82 HCl media	pH 0.69 HNO ₃ media	pH 0.6 H ₂ SO ₄ media
0.1	0.558	0.583	0.411	0.579
0.2	0.685	0.795	0.711	0.695
0.3	0.774	0.820	0.753	0.784
0.5	0.862	0.807	0.802	0.877
0.7	0.803	0.760	0.892	0.808
1	0.658	0.679	0.793	0.632
1.5	0.646	0.512	0.580	0.622
2	0.542	0.260	0.290	0.521
2.5	0.319	0.125	0.261	0.300



Table 4: Effect of acid medium on the absorbance of Nb-brilliant green dye complex.

Volume of buffer (ml)	Absorbance	
	pH 0.69	pH 0.82
	HCl media	HNO ₃ media
0.1	0.160	0.105
0.2	0.229	0.220
0.3	0.439	0.323
0.5	0.777	0.650
0.7	0.770	0.665
1	0.782	0.671
1.5	0.893	0.850
2	0.863	0.801
2.5	0.405	0.520

Effect of different concentrations of HF on the formation of the complexes

The effect of different HF concentrations on complexes formation was studied.

To determine the optimum HF concentration used in the preparation of samples, weight from each aliquot 0.1 g Ta, and 0.1 g Nb each of them in different concentrations of HF, studying their effect on the sensitivity and molar absorptivity of the produced complexes.

Tables (5,6) summarized the obtained data for the effect of different HF acid concentrations on the absorbance of the complexes. The data gathered established that the maximum absorbance values were recorded for 4.56 M of HF.

Table (5): Effect of HF acid concentration on the absorbance of Ta complex.

Concentration of HF acid (M)	Absorbance			
	pH 0.69	pH 0.82	pH 0.69	pH 0.6
	HClO ₄ media	HCl media	HNO ₃ media	H ₂ SO ₄ media
0.5	0.357	0.119	0.328	0.223
1	0.502	0.542	0.582	0.405
3	0.811	0.774	0.749	0.856
4	0.851	0.698	0.790	0.831
4.5	0.960	0.910	0.920	0.961
5	0.699	0.800	0.832	0.712
6	0.602	0.851	0.602	0.740
8	0.480	0.530	0.493	0.404

Table 6: Effect of HF acid concentration on the absorbance of Nb complex.

Concentration of HF acid (M)	Absorbance	
	pH 0.69	pH 0.82
	HCl media	HNO ₃ media
0.5	0.238	0.191
1	0.282	0.452
3	0.294	0.568
4.56	0.998	0.951
6	0.502	0.674
8	0.393	0.589

Effect of brilliant green dye concentration on the absorbance of the complexes

The brilliant green dye concentration should be optimized since lesser or higher amount than necessary, would cause deviation from Beer's law in the construction of calibration curve. For this purpose, different volumes of



10^{-3} M brilliant green dye were added to a series of 10 ml volumetric flasks volume containing 1 ml of 10^{-3} M (Ta and Nb) where at pH was adjusted at the optimized value. The volume was completed to 10 ml and the absorbance of each solution was then measured.

Figures (2,3) show that, the maximum absorbance of the complexes occurs at a concentration of 1×10^{-3} M brilliant green dye at all pH values except for Ta complex at pH 0.69.

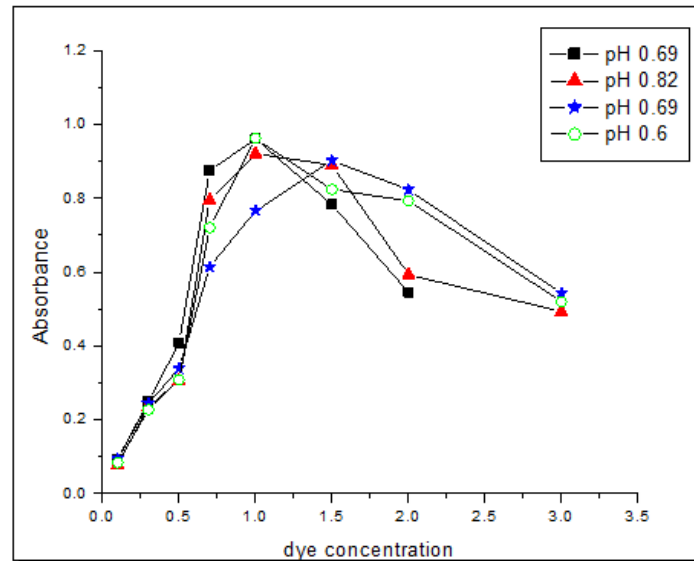


Figure 2: Effect of brilliant green dye concentration on the absorbance of Ta complex

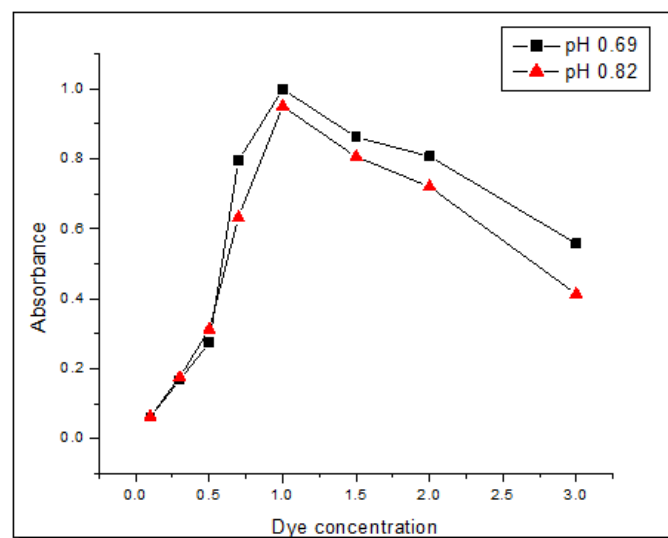


Figure 3: Effect of brilliant green dye concentration on the absorbance of Nb complex

Effect of duration time on the stability of the complexes

After optimizing the formation of Nb and Ta- dye complexes, duration of the stability of complexes was studied. All optimized additions were added. The absorbance was measured instantly and after a period of time, where it was measured periodically.

The data was recorded in Tables (7,8) where it was observed that the complexes were formed instantly and stable for 3 minutes.

Table 7: Effect of duration time on the stability of the Ta complex.

Time (min)	Absorbance			
	pH 0.69	pH 0.82	pH 0.69	pH 0.6
	HClO ₄ media	HCl media	HNO ₃ media	H ₂ SO ₄ media
Zero	0.960	0.920	0.900	0.960
1	0.962	0.920	0.902	0.961
2	0.962	0.921	0.901	0.960
3	0.960	0.921	0.902	0.960
4	0.856	0.900	0.805	0.814
5	0.878	0.844	0.829	0.846

Table 8: Effect of duration time on the stability of the Nb complex.

Time (min)	Absorbance	
	pH 0.69	pH 0.82
	HCl media	HNO ₃ media
Zero	1.405	1.051
1	1.404	1.052
2	1.405	1.051
3	1.404	1.051
4	0.956	0.978
5	0.856	0.870

Composition of the complex

In the present work, continuous variation method was used to investigate the ratios between dye and metal. In continuous variation method the molarities of both components (metal-dye) was changed while keeping the total number of moles of both components constant. Figures (4, 5) indicated that, the optimum molar ratio of the complexes Ta and Nb-brilliant green dye was 1:1 from 10^{-3} M dye and elements.

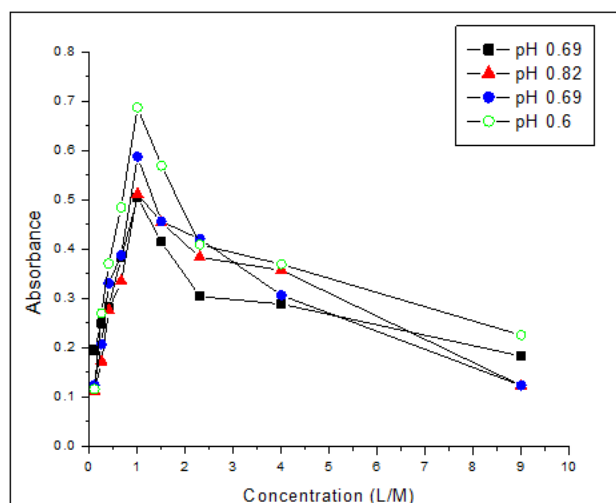


Figure 4: Continuous variation method for estimating the molar ratio between Ta and brilliant green dye complex



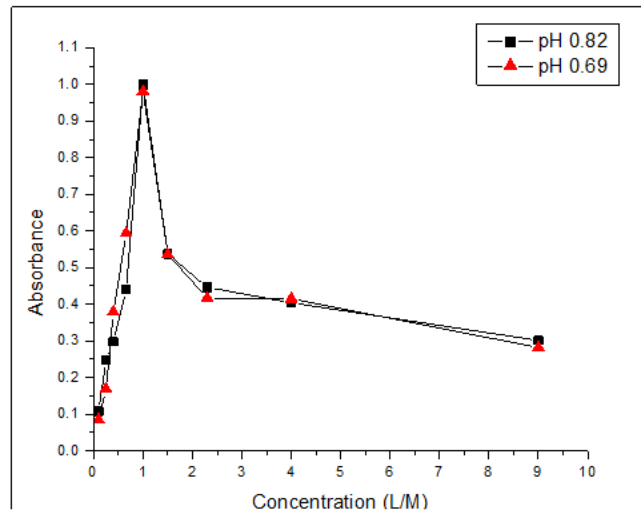


Figure 5: Continuous variation method for estimating the molar ratio between Nb and brilliant green dye complex

Construction of calibration curves

After the detailed study of the relevant factors affecting the brilliant green spectrophotometric determination of Tantalum and Niobium, it was necessary to determine the concentration ranges of Tantalum and Niobium above or below which no further complexes were formed and hence determined.

These two limits could be identified through the construction of calibration curves for the complexes.

The spectra provide linear calibration graphs in the range from 0.1 to 1.1 $\mu\text{g ml}^{-1}$ for Ta and Nb respectively as shown in Figures (6,7,8,9,10,11).

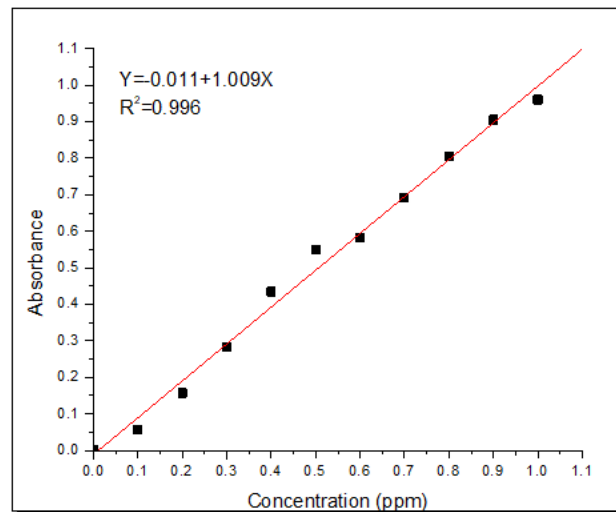


Figure 6: Calibration curve for spectrophotometric determination of Tantalum at pH 0.69 (HClO_4 media)



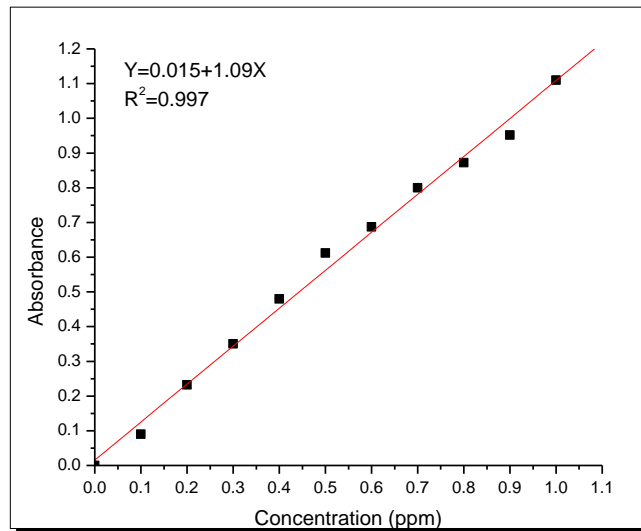


Figure 7: Calibration curve for spectrophotometric determination of Tantalum at pH 0.82

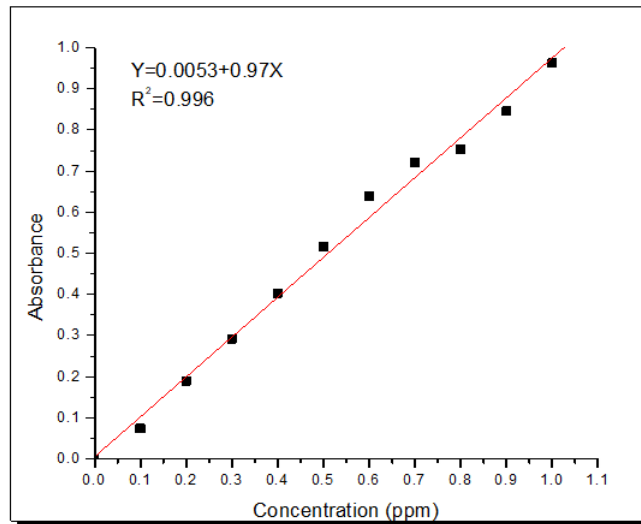


Figure 8: Calibration curve for spectrophotometric determination of Tantalum at pH 0.69 (HCl media)

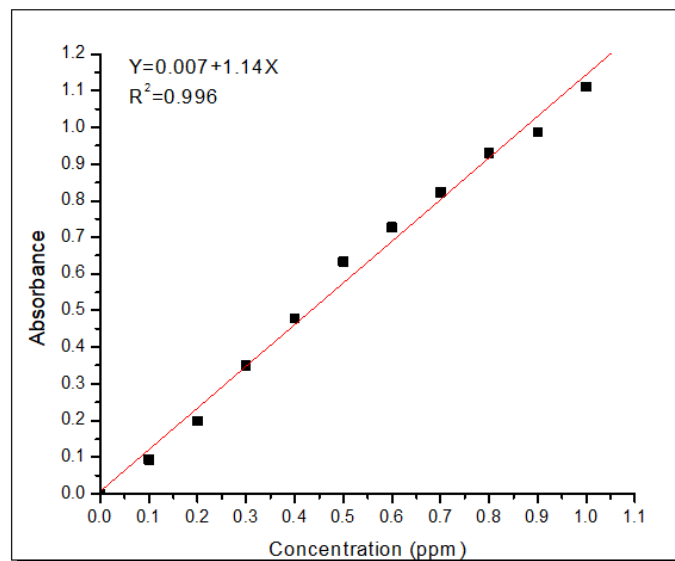


Figure 9: Calibration curve for spectrophotometric determination of Tantalum at pH 0.6



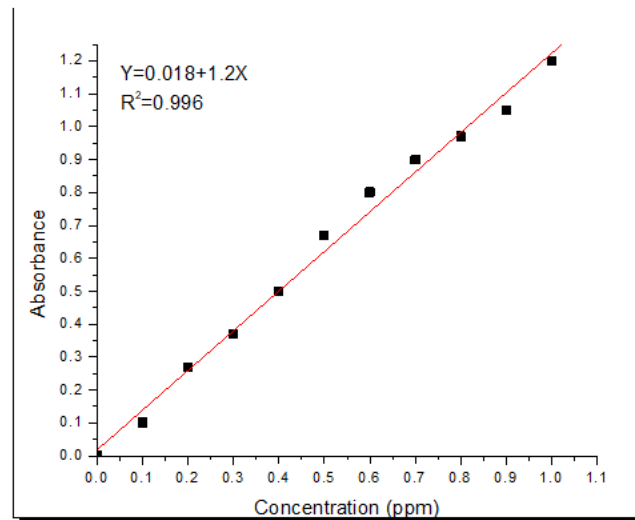


Figure 10: Calibration curve for spectrophotometric determination of Niobium at pH 0.69

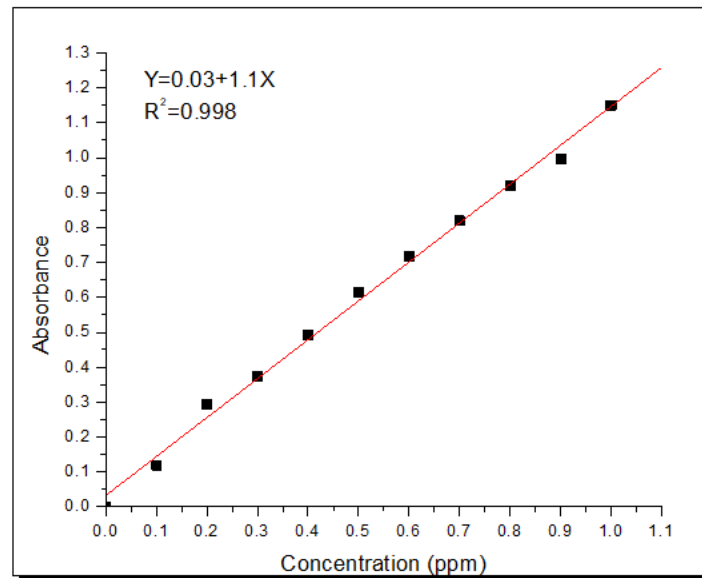


Figure 11: Calibration curve for spectrophotometric determination of Niobium at pH 0.82

Studies of the interference effect

It was necessary to study the tolerance limits of interference effect of the accompanying elements with Ta and Nb.

Table 9: Tolerance limits of Fe concentrations on the determination of Ta and Nb-brilliant green dye complex.

Conc. of Fe (ppm)	Absorbance	
	Ta	Nb
0	0.920	0.845
0.25	0.920	0.845
0.5	0.920	0.845
1	0.920	0.845
1.5	0.920	0.845
2	0.920	0.845
2.5	0.920	0.845
3	0.920	0.845
4	0.920	0.845



5	0.920	0.845
5.5	0.920	1.138
6	0.920	1.201
6.5	0.920	1.200
7	0.993	1.301
7.5	1.100	1.305
8	1.310	1.301

Table 10: Tolerance limits of Ca concentrations on the determination of Ta and Nb-brilliant green dye complex

Conc. of Ca (ppm)	Absorbance	
	Ta	Nb
0	0.922	0.846
0.25	0.922	0.846
0.5	0.922	0.846
1	0.922	0.846
1.5	0.922	0.846
2	0.922	0.846
2.5	0.922	0.846
3	0.922	0.846
4	0.922	0.846
5	0.922	0.846
6	0.922	0.846
7	0.922	0.846
7.5	0.922	0.846
8	0.922	1.029
9	0.922	1.200
9.5	0.922	1.320
10	0.990	1.322
10.5	0.999	1.320
11	1.124	1.321

Table 11: Tolerance limits of Mn concentrations on the determination of Ta and Nb-brilliant green dye complex

Conc. of Mn (ppm)	Absorbance	
	Ta	Nb
0	0.921	0.846
0.25	0.921	0.846
0.5	0.921	0.846
1	0.921	0.846
1.5	0.921	0.846
2	0.921	0.846
2.5	0.921	0.846
3	0.921	0.846
4	0.921	0.846
5	0.921	0.846
6	0.921	0.846
7	0.921	0.846
8	0.921	0.846
9	0.921	0.846
9.5	0.921	0.846
10	0.993	1.043
10.5	0.997	1.012
11	0.995	1.121



Table 12: Tolerance limits of Cd concentrations on the determination of Ta and Nb-brilliant green dye complex.

Conc. of Cd (ppm)	Absorbance	
	Ta	Nb
0	0.921	0.845
0.25	0.921	0.845
0.5	0.921	0.845
1	0.921	0.845
1.5	0.921	0.845
2	0.921	0.845
2.5	0.921	0.845
3	0.921	0.845
4	0.921	0.845
5	0.921	0.845
6	0.921	0.845
7	0.921	0.845
8	0.921	0.845
9	0.921	0.845
10	0.921	0.845
13	0.921	0.845
14.5	0.921	0.845
15	0.991	1.029
15.5	0.999	1.011
16	0.995	1.230

Table 13: Tolerance limits of Co concentrations on the determination of Ta and Nb-brilliant green dye complex.

Conc. of Co (ppm)	Absorbance	
	Ta	Nb
0	0.921	0.847
0.25	0.921	0.847
0.5	0.921	0.847
1	0.921	0.847
1.5	0.921	0.847
2	0.921	0.847
2.5	0.921	0.847
3	0.921	0.847
4	0.921	0.847
5	0.921	0.847
6	0.921	0.847
7	0.921	0.847
8	0.921	0.847
9	0.921	0.847
10	0.921	0.847
13	0.921	0.847
14.5	0.921	0.847
15	0.981	1.083
16	0.989	1.102
17	0.998	1.213



Table 14: Tolerance limits of Mg concentrations on the determination of Ta and Nb-brilliant green dye complex.

Conc. of Mg (ppm)	Absorbance	
	Ta	Nb
0	0.922	0.846
0.25	0.922	0.846
0.5	0.922	0.846
1	0.921	0.846
1.5	0.921	0.846
2	0.921	0.846
2.5	0.922	0.846
3	0.921	0.846
4	0.921	0.846
5	0.921	0.846
6	0.921	0.846
7	0.922	0.846
8	0.921	0.846
9	0.921	0.846
9.5	0.922	0.846
10	0.983	1.003
10.5	0.998	1.010
11	0.978	1.011

Table 15: Tolerance limits of Na and K concentrations on the determination of Ta-brilliant green dye complex.

Conc. of Na and K (ppm)	Absorbance			
	Ta (for Na)	Ta (for K)	Nb (for Na)	Nb (for K)
0	0.911	0.910	0.847	0.845
0.25	0.911	0.910	0.847	0.845
0.5	0.911	0.910	0.847	0.845
1	0.911	0.910	0.847	0.845
1.5	0.911	0.910	0.847	0.845
2	0.911	0.910	0.847	0.845
2.5	0.911	0.910	0.847	0.845
5	0.911	0.910	0.847	0.845
7	0.911	0.910	0.847	0.845
9	0.911	0.910	0.847	0.845
11	0.911	0.910	0.847	0.845
13	0.911	0.910	0.847	0.845
15	0.911	0.910	0.847	0.845
17	0.911	0.910	0.847	0.845
19	0.911	0.910	0.847	0.845
21	0.911	0.910	0.847	0.845
23	0.911	0.910	0.847	0.845
24.5	0.911	0.910	0.847	0.845
25	0.981	0.989	1.027	1.091
25.5	0.989	0.999	1.012	1.121
26	0.998	0.979	1.103	1.100



Table 16: Tolerance limits of Al concentrations on the determination of Ta and Nb-brilliant green dye complex.

Conc. of Al (ppm)	Absorbance	
	Ta	Nb
0	0.911	0.846
0.25	0.911	0.846
0.5	0.911	0.846
1	0.911	0.846
1.5	0.911	0.846
2	0.911	0.846
2.5	0.911	0.846
3	0.911	0.846
5	0.911	0.846
7	0.911	0.846
11	0.911	0.846
13	0.911	0.846
15	0.911	0.846
16.5	0.911	0.846
17	0.996	1.027
17.5	0.999	1.123
18	0.989	1.200

Table 17: Tolerance limits of U concentrations on the determination of Ta and Nb-brilliant green dye complex.

Conc. of U (ppm)	Absorbance of Ta	Absorbance of Nb
0	0.912	0.846
0.25	0.912	0.846
0.5	0.912	0.846
1	0.912	0.846
1.5	0.912	0.846
2	0.912	0.846
2.5	0.912	0.846
3	0.912	0.846
3.5	0.912	0.846
4	0.912	0.846
4.5	0.912	0.846
5	0.990	1.052
5.5	0.998	1.102
6	0.992	1.320

Table 18: Tolerance limits of Th concentrations on the determination of Ta and Nb-brilliant green dye complex.

Conc. of Th (ppm)	Absorbance	
	Ta	Nb
0	0.910	0.846
0.25	0.910	0.846
0.5	0.910	0.846
1	0.910	0.846
1.5	0.910	0.846
2	0.910	0.846
3	0.910	0.846
4	0.910	0.846
5	0.910	0.846
6	0.910	0.846
6.5	0.910	0.846
7	0.982	1.303
7.5	0.987	1.324
8	0.995	1.320



Table 19: Tolerance limits of REE concentrations on the determination of Ta and Nb-brilliant green dye complex.

Conc. of REE (ppm)	Absorbance	
	Ta	Nb
0	0.910	0.847
0.25	0.910	0.847
0.5	0.910	0.847
1	0.910	0.847
1.5	0.910	0.847
2	0.910	0.847
2.5	0.910	0.847
3	0.910	0.847
3.5	0.910	0.847
4	0.910	0.847
4.5	0.910	0.847
5	0.910	0.847
5.5	0.981	1.301
6	0.987	1.342
7	0.995	1.421

From studying the interference effect (Tables from 9 to 19), it was shown clearly that conventional spectrophotometry method is inapplicable for determination of Ta and Nb in presence of other elements. It was found that first order derivative is the suitable one for the determination of Ta and Nb in presence of other elements.

According to the composition of the concentrates of the investigated samples, the interference effect of accompanying elements on determining Ta and Nb with brilliant green dye were studied. Then a series of known concentration mixture of Ta and Nb were prepared with a series of different concentrations for each interfering element, with a constant concentration of Ta and Nb ($1 \mu\text{g ml}^{-1}$). The concentrations of Ta and Nb standard solution only were measured at the optimized conditions against reagent blank at λ_{max} 461 nm. The prepared solutions of Ta and Nb with a series of different concentrations studied of the interfering elements were measured at the same optimized conditions. The obtained results indicated that the tolerance concentrations of other elements mixed with Ta and Nb should not exceed above certain concentration values otherwise it causes a systematic error on their determination using conventional spectrophotometry.

Accordingly, it was found necessary to apply derivative spectrophotometry technique to try to overcome this interference on their precise and accurate quantitative determination of Ta and Nb. It was found that first order derivative was the most suitable one for the determination of Ta and Nb-brilliant green dye complexes in presence of other concentrations of accompanying (interfering) elements.

Selection of the type of derivative for the spectrophotometric determination of the complexes

Derivatisation of spectra is the simplest method for increasing the selectivity, this operation allows to overcome spectral interferences and as a consequence leads to increase the selectivity of assay. Derivatisation of digital data is well known method of separation useful signals from noised data, and by tested first, second, third and fourth derivative it is found that, the selectivity increased using first derivative.

Construction of calibration curves using derivative spectrophotometry

After the detailed study of the relevant factors affecting the optimization of complex formation of Nb and Ta with brilliant green dye, it was found necessary to determine the working concentration ranges of Ta and Nb above and below which no further complexes could be formed and hence determined.

These two limits could be identified through the construction of calibration curves for the complexes. This spectrophotometric determination must be carried out within the concentration range which obeys Beer's law.

The first derivative spectra provide linear calibration graphs in the range from 0.25 to $20 \mu\text{g ml}^{-1}$ for Ta and Nb respectively as shown in figures (12, 13).



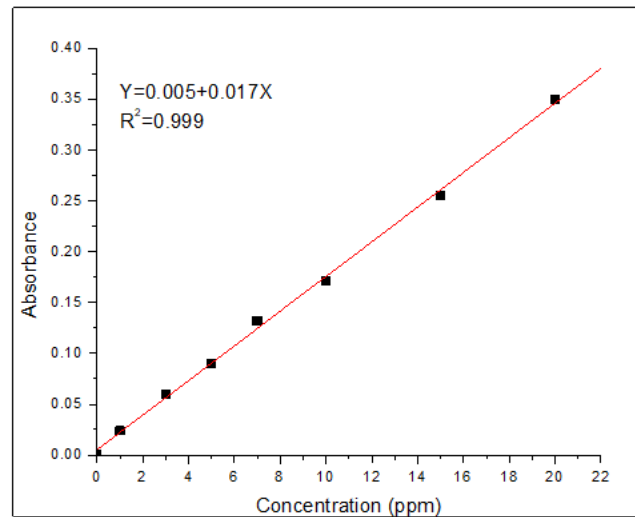


Figure 12: Calibration curve using 1st. Order spectrophotometric determination of Ta

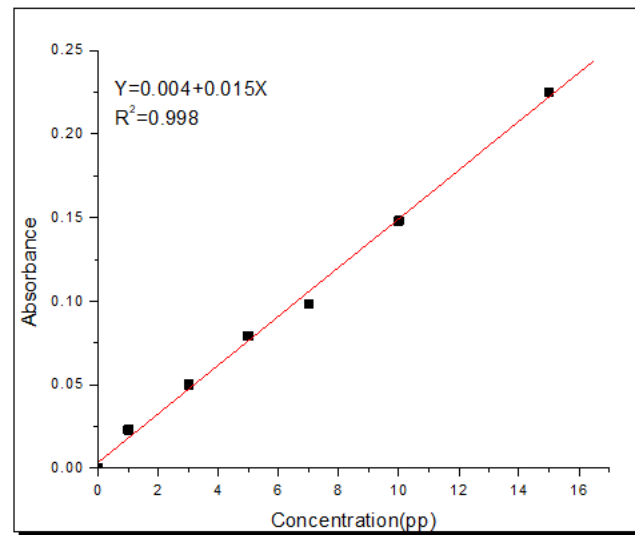


Figure 13: Calibration curve using 1st. Order spectrophotometric determination of Nb

Application

The method was accurately applied on several leach liquors bearing Nb and Ta in different media

Table 20: Analytical results of Ta (ppm) in samples by the present developed method in comparison to ICP-OES

Sample no.	The present developed method	ICP-OES method
1	5	3.3
2	0.3	0.36
3	0.5	0.6
4	7	7.4
5	3	3.2
6	0.5	0.5
7	0.5	0.6
8	5.5	6.5
9	3	2.7
10	0.3	0.1



Table 21: Analytical results of Nb (ppm) in samples by the present developed method in comparison to ICP-OES

Sample no.	The present developed method	ICP-OES method
1	30	33
2	0.5	0.3
3	3	2.5
4	99.8	100.8
5	0.5	0.3
6	0.5	0.3
7	3	2.9
8	78.5	80
9	42	45.3
10	0.4	0.2

4. Statistical Evaluation of the results

Statistical analysis by using appropriate statistical parameters is attempted to cast some light on the accuracy and precision of the results, obtained using the present studied method.

Standard error

Calculation of standard error is very important in the field of applied analytical chemistry. It is used for determination of error percentage for any developed method according to the following successive equations:

$$\text{Standard deviation (S)} = [(\sum X_1 - \bar{X})^2 / N - 1]^{1/2}$$

$$\text{Standard error (S.E.)} = S / N^{1/2}$$

$$\text{Error \%} = 100 (S.E. / \bar{X})$$

$$\text{RSD \%} = 100 (S / \bar{X})$$

Where: X_1 measurement value.

\bar{X} mean of the measurement values.

N number of samples (number of measurements).

Ta							
Sample No.	Concentration	Mean \bar{X}	S	S ²	SE	Error %	RSD %
1	5	5.067	0.058	0.003	0.033	0.658	1.139
	5.1						
	0.3						
2	0.32	0.31	0.01	0.0001	0.0058	1.862	3.226
	0.31						
	0.5						
3	0.52	0.507	0.012	0.0001	0.007	1.316	2.279
	0.5						
	7						
4	7.1	7.033	0.058	0.003	0.033	0.474	0.821
	7						
	3						
5	3	3.1	0.173	0.03	0.1	3.226	5.587
	3.3						
6	0.5	0.527	0.025	0.0006	0.015	2.759	4.778



	0.55						
	0.53						
	0.5						
7	0.51	0.513	0.015	0.0002	0.009	1.718	2.976
	0.53						
	5.5						
8	5.7	5.567	0.115	0.013	0.067	1.198	2.074
	5.5						
	3						
9	3	3.1	0.173	0.03	0.1	3.226	5.587
	3.3						
	0.3						
10	0.32	0.317	0.016	0.0002	0.009	2.785	4.827
	0.33						

Nb	Sample	Concentration	Mean \bar{X}	S	S²	SE	Error %	RSD %
		30						
1		30.5	30.233	0.252	0.063	0.146	0.481	0.832
		30.2						
		0.5						
2		0.55	0.537	0.032	0.001	0.019	3.458	5.989
		0.56						
		3						
3		3.3	3.133	0.153	0.023	0.088	2.815	4.875
		3.1						
		99.8						
4		99.5	99.767	0.252	0.063	0.145	0.146	0.252
		100						
		0.5						
5		0.51	0.517	0.021	0.0004	0.012	2.326	4.029
		0.54						
		0.5						
6		0.51	0.513	0.015	0.0002	0.009	1.718	2.976
		0.53						
		3						
7		3.2	3.167	0.153	0.023	0.088	2.785	4.823
		3.3						
		78.5						
8		79	78.8	0.265	0.07	0.153	0.194	0.336



	78.9						
	42						
9	45	43.333	1.528	2.333	0.882	2.035	3.525
	43						
	0.4						
10	0.4	0.407	0.012	0.0001	0.007	1.639	2.839
	0.42						

In addition, the reference sample JG-2 (from Brammer Standard Company, Inc., USA) was also analysed. The result is given in (Table 23), from which it can be seen that the accuracy and precision of the method are reasonably satisfactory.

Table 23: Analytical results of Ta and Nb (ppm) in reference sample by the present developed method in comparison to ICP-OES

Reference sample	The present developed method	ICP-OES method
Ta	2.65	2.76
Nb	14.5	14.7

Reference sample	Concentration	Mean \bar{X}	S	S ²	SE	Error %	RSD %
Ta	2.7						
	2.65	2.68	0.026	0.0007	0.015	0.569	0.98
	2.69						
Nb	14.5						
	14.56	14.55	0.05	0.0025	0.029	0.199	0.35
	14.6						

5. Conclusion

The proposed method involves the use of first derivative spectra for the determination of tantalum and niobium complexes with brilliant green dye. The method is sensitive and selective in the presence of other elements and successfully used.

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