



Mean centering of ratio spectra as a new spectrophotometric method for the analysis of binary mixtures of Vanadium and Lead in water samples and alloys

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Abstract

A new micelle-mediated extraction method for ultra-trace quantities of V(V) and Pb(II) as a prior step to their simultaneous spectrophotometric determination has been developed. Alizarin red S (ARS), was used as chelating agent in presence of Tween-80 micellar media at pH 5.5, respectively. Mean centering (MC) of ratio spectra has been used for the simultaneous analysis of these metal ions. The analytical characteristics of the method such as (Beer's law, detection limit and relative standard error (R.S.E.) were calculated. Linearity was obeyed in the concentration range 0.255-4.58 μg/ml of V(V) and 0.345-6.14 μg/ml of Pb(II). The detection limit of the method is 0.60 and 0.51 μg/ml for V(V) and Pb(II) respectively. The interference effect of some anions and cations were also tested. The method was applied to the simultaneous determination V(V) and Pb(II) in water samples and alloys.

Keywords: Vanadium, lead, alizarin red S, tween-80, mean centering of ratio spectra.

Introduction

Toxic metals have always been present in the ecosystem, but since due to the industrial revolution there has been a massive redistribution of metals on the surface of the earth. Many metals in certain very small quantities are needed to play their roles to sustain life, and it is when the concentrations are too high that they contaminate soil and water and exert toxic effect. The heavy metals have a great tendency of bioaccumulation through which they enter the food chain and bring about adverse effects on human beings and other living organisms and plants. The key factor for metals is that no metal is degradable, as they stay for a long time, this stability lets them be carried long distances through air and

Lead is counted as one of the heavy metals. Lead is a poisonous metal that can damage nervous connections (especially in young children) and cause blood and brain disorders. Lead is a metabolic poison and a neurotoxin that binds to essential enzymes and several other cellular components and inactivates them.

Vanadium is also an essential element for normal cell growth and essential component of some enzymes, particularly the vanadium - nitrogenase used by some nitrogen fixing microorganisms. Vanadium complexes can reduce growth of cancer cells and improve human diabetes but can be toxic when present at higher concentrations. The toxicity of vanadium depends upon its oxidation state. The vanadate ion is strong inhibitor of the enzyme Na- and K-ATPase, while V(IV) appeared to be a weaker inhibitor. Therefore, it is very important from the analytical point of view to develop sensitive, selective, rapid and economical methods for their simultaneous determination even when present in trace amounts.

A new spectrophotometric method for the analysis of binary and ternary mixtures, without prior separation steps called "mean centering of ratio spectra" method was developed¹⁻⁶. This method is based on the successive derivatives of ratio spectra in two steps⁷⁻¹⁰.

Micelles possess a high potential for multicomponent analysis, which can be used as special reaction media because they alter the rate, equilibrium position, products and stereochemistry of many reactions. However, micelles also change the effective microenvironment around dissolved solutes and their physicochemical properties, such as absorptivity, equilibrium constant and spectral profile¹¹. The addition of surfactant-active substances improves the selectivity and sensitivity of the metal determinations.

Mean centering of ratio spectra: Theoretical background:

Consider a mixture of two compounds X, Y. If there is no interaction among the compounds and Beer's law is obeyed for each compound, it can be written as;

$$A_m = \alpha_x C_X + \alpha_y C_Y \quad (1)$$

Where; A_m = the vector of the absorbance of the mixture, α_x , α_y , = molar absorptivity vectors of X and Y, C_X , C_Y = concentrations of X and Y respectively.

If equation 1 is divided by α_y corresponding to the spectrum of a standard solution of Y in binary mixture, the first ratio spectrum is obtained in the form of equation 2.

$$B = \frac{A_m}{\alpha_y} = \frac{\alpha_x C_X}{\alpha_y} + C_Y \quad (2)$$

If the equation 2 is mean centred (MC), since the mean centering of constant (C_Y) is zero, equation 3 will be obtained

$$MC(B) = MC \left[\frac{\alpha_x C_X}{\alpha_Y} \right] \quad (3)$$

Equation (3) is the mathematical foundation of multi-component analysis that permits the determination of concentration of each of the active compound in the solution (X in the solution) without interfering from the other compounds of the binary system (Y in these equation). As equation 3 shows, there is a linear relation between the amount of MC (B) and the concentration of X in the solution.

A calibration curve could be constructed by plotting MC(B) against concentration of X in the standard solution of X or in the standard binary mixtures. For more sensitivity the amount of MC(B) corresponding to maximum or minimum wavelength should be measured. Calibration graphs for Y could also be constructed as described for X .

Material and Methods

Apparatus: UV-visible absorbance spectra were recorded on a Shimadzu UV-1800 scanning spectrophotometer. Digital century pH-meter CP 901 with a combined glass electrode was used for pH measurements.

Reagents: All the reagents used were of analytical reagent grade unless otherwise stated and double distilled water was used throughout the experiment. A 0.01% (w/v) solution of Alizarin Red S (s d fine) in doubly distilled water was prepared. Stock solution of Pb(II) and V(V) were prepared. Working standard solutions were obtained by appropriate dilution of the stock solution. A buffer solution of pH 5.5 was prepared from 0.2M sodium acetate and 0.2M acetic acid at appropriate concentration and 1.0 % Tween-80 (v/v) solution was prepared in hot double distilled water.

Individual Calibration: An aliquot of the solution containing 0.255-4.58µg/ml V(V) ion or 0.345-6.14 µg/ml of Pb(II) ion, 1.0 ml of 0.01% (v/v) Alizarin red S solution , 2.0 mL of pH 5.5 acetate buffer solution, and 2ml of 1% (v/v) Tween -80 solution was transferred into a 10 mL tube. The solution was taken up to the mark with triply distilled water. The absorbance spectrum of both V(V) and Pb(II) was recorded and stored in the range of 400–600 nm against reagent blank solution.

Mean centering of ratio spectra: A calibration graph for V(V) was obtained by recording and storing the spectra of standard solutions containing different concentrations of V(V). The stored spectra of the solution of V(V) were divided by standard spectrum of Pb(II) according to equation 2. Then mean centering of these vectors with respect to wavelength were obtained according to equation 3.

The minimum or maximum of these vectors with respect to wavelength was used for the construction of calibration graph for V(V). For the prediction of concentration of V(V) in synthetic binary mixtures and real samples the same procedure

was used except that the spectra of the mixture were used instead of the spectra of standard solution of V(V). The construction of calibration curves for Pb(II) and also its prediction step was performed as described for V(V).

Results and Discussion

Alizarin red S (ARS) is used as chromogenic reagents for the determination of a large number of metals. The addition of surfactant-active substances improves the selectivity and sensitivity of the metal determinations. The absorption spectra for V(V) and Pb(II) complexes with ARS against blank solution are shown in figure 1. As figure 1 shows, the spectra of the complexes overlap with each other, and therefore each compound interferes in the spectrophotometric determination of the other. So simultaneous determination of V(V) and Pb(II) is possible by using mean centering of ratio spectra.

Optimization of the system: To take full advantage of the procedure, the reagent concentrations and reaction conditions must be optimised. These parameters were optimised by setting all parameters to be constant and optimizing one each time.

Effect of pH: Absorbance for both complexes was studied over a wide range of pH from 3.0 - 8.0. The studies showed that the absorbance was maximum in the pH range 5.0-6.0 for both V(V) and Pb(II) complexes (figure 2). Hence, further studies were carried out at pH 5.5.

Nature of surfactant: The effect of nature and concentration of different surfactants such as Sodium lauryl sulphate (SLS), cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPB), Triton X-100, Tween-80, and Tween-20 on the absorbance of Pb (II) and V(V)-ARS complexes was studied and it was observed that complex formation is faster, stable and maximum in presence of Tween-80, so it was selected as micellizing agent for further studies. The effect of concentration of Tween-80 on sensitivity of the method was studied by varying its percent concentration from 0.5-3.0 % (w/v) and its volume from 0.5-3.5 mL. The maximum absorbance was found with 2.0-2.5 mL of 1% Tween-80. Hence 2.0 mL of 1% Tween-80 was used for further studies

Effect of reagent concentration: The effect of different amounts of reagent on the absorbance of V(V)-ARS and Pb (II)- ARS complexes was studied at optimum pH value of 5.5 and 2.0 mL of 1.0 % Tween-80. The maximum absorbance was observed when 1.0 - 1.0 mL of 0.01% ARS was used for individual calibration of V(V) and Pb(II) as shown in figure 3. It was expected that increasing ARS concentration causes an increase in absorbance because increase in ARS concentration caused an increase in V(V) and Pb(II) complexes concentration. At higher concentrations of ARS, the concentration of complex did not change significantly but the concentration of uncomplexed ARS increased significantly. Therefore, much probably decrease in absorbance at higher concentrations of ARS. To ensure the

complete complexation for simultaneous determination of V(V) and Pb(II), 2.0 mL of 0.01% ARS was selected as the optimum

Mean centering of ratio spectra: The absorption spectra of the standard solutions of V(V) with different concentrations were recorded in the wavelength range of 400.0–600.0 nm (figure 5) and divided by the normalised spectrum of the Pb(II) and the ratio spectra were obtained (figure 6). Mean centering (MC) of the ratio spectra were obtained in the range 500.0–540.0 nm according to equation 3 (figure 7).

The amount of V(V) was determined by measuring the amplitude at 500.0 nm corresponding to a maximum in the MC of ratio spectra. For the prediction of concentration of V(V) in synthetic binary mixtures and real samples the same procedure was used except that the spectra of the mixture were used instead of the spectra of standard solution of V(V).

In the same way, the absorption spectra of the standard solutions of Pb(II) with different concentrations were recorded in the wavelength range 400.0–600.0 nm (figure 8) and divided by the normalized spectrum of the V(V) and the ratio spectra were obtained (figure 9). Mean centering (MC) of the ratio spectra was obtained in the wavelength range 520.0–560.0 nm according to equation 3 (figure 10).

The amount of Pb(II) was determined by measuring the amplitude at 520.0 nm corresponding to a maximum in the MC of ratio spectra. For the prediction of concentration of Pb(II) in synthetic binary mixtures and real samples the same procedure was used except that the spectra of the mixture were used instead of the spectra of standard solution of Pb(II)

Analytical characteristics: In the proposed method Beer's law was obeyed in the concentration range 0.255 to 4.580 µg/ mL for V(V) and 0.345 to 6.14 µg/ mL for Pb(II). Table 1 shows the linear regression parameters for calibration data for simultaneous determination of V(V) and Pb(II) in their binary mixtures. Limit of detection of the method for determination of V(V) and Pb(II) are also shown in table 1.

The effect of divisor concentration on the analytical parameters such as detection limit, slope, intercept and correlation coefficient of the calibration graphs was also tested. It was observed that changing the concentration of divisors in their linear calibration range had no significant effect on the analytical parameters. Therefore, a normalized spectrum of each of the V(V) and Pb (II) was used as divisor profile in the proposed method.

Accuracy and Precision: In order to obtain the accuracy and precision of the method, several synthetic mixtures with different concentration ratios of V(V) and Pb(II) were analyzed using the proposed method. The results are given in table 2. The prediction error of a single component in the mixtures was calculated as the relative standard error (R.S.E) of the prediction concentration:

$$R.S.E. (\%) = \left(\frac{\sum_{j=1}^N (\hat{C}_j - C_j)^2}{\sum_{j=1}^N (C_j)^2} \right)^{1/2} \times 100 \quad (4)$$

where N is the number of samples, C_j the concentration of the component in the j th mixture and \hat{C}_j the estimated concentration. The total prediction error of N samples is calculated as follows:

$$R.S.E._t (\%) = \left(\frac{\sum_{i=1}^M \sum_{j=1}^N (\hat{C}_{ij} - C_{ij})^2}{\sum_{i=1}^M \sum_{j=1}^N (C_{ij})^2} \right)^{1/2} \times 100 \quad (5)$$

where C_{ij} is the concentration of the component in the j th samples and \hat{C}_{ij} its estimation. Table 2 also shows the reasonable single and total relative errors for such system.

Interference analysis: The effect of various diverse ions on the absorbance of a solution containing 1.0 µg/mL each of V(V) and Pb(II) was studied. An ion was considered to interfere when its presence produced a variation in the absorbance of the sample greater than ±5%. Among the interfering anions examined F^- , I^- , Br^- , Cl^- , CO_3^{2-} , SO_3^{2-} , SO_4^{2-} , NO_3^- , IO_3^- , NO_2^- , $S_2O_3^{2-}$, CH_3COO^- did not interfere at concentrations 1000 times higher than those of the analytes. The most interfering effect was observed in presence of ethylenediamine tetraacetate and oxalate ion. Among the cations interference is observed from presence of Hg^{2+} , Cd^{2+} , Bi^{3+} in the sample solution.

Applications of the method: Determination of vanadium (V) and lead (II) in water samples: Water samples were spiked with known amounts of vanadium (V) and lead (II) and analyzed by the proposed general procedure. Results are shown in table 3 (a).

Determination of vanadium (V) and lead (II) in alloys: Accurately weighted amount of the alloy sample was dissolved in a mixture of 2 ml of concentrated hydrochloric acid and 10 ml of concentrated nitric acid. The solution was evaporated to a small volume, 1:1 sulphuric acid was added and the solution was then evaporated to dryness. The residue was dissolved in 15 ml of distilled water and filtered. The filtrate was transferred into a 100 ml standard flask and diluted to the mark with distilled water. This serves as stock solution. The stock solution was appropriately diluted to obtain the metal ion solution in the required concentration range and analyzed by the proposed general procedure. Results are given in table 3(b).

Table- 1

Analytical Characteristics for Analysis of V(V) and Pb(II) in Binary Mixtures by Mean Centering of Ratio Spectra Method

Analyte	λ (nm)	Regression Equation	r^2	Linear range (µg/mL)	LOD (µg/mL)
V(V)	499.0	$Y=0.108x-0.911$	0.9930	0.255-4.580	0.60
Pb(II)	512.0	$Y=0.016x+0.002$	0.9954	0.690-8.288	0.51

Table-2
Results for analysis of V(V) and Pb(II) in Binary mixtures in different concentration ratios by Mean Centering of Ratio Spectra Method

Taken ($\mu\text{g}/\text{mL}$)		Found ($\mu\text{g}/\text{mL}$)		Recovery (%)	
V(V)	Pb(II)	V(V)	Pb(II)	V(V)	Pb(II)
0.72	0.26	0.71	0.27	98.6	103.8
0.81	0.31	0.79	0.30	97.5	96.7
0.86	0.38	0.85	0.37	98.8	97.3
0.92	0.46	0.93	0.45	101.0	97.8
1.12	0.58	1.11	0.57	99.1	98.2
1.26	0.65	1.25	0.66	99.2	101.2
1.35	0.84	1.33	0.83	98.51	98.8
Mean Recovery				98.95	99.1
R.S.E(%)single				1.323	1.878
R.S.E(%)total					1.456

Table-3
Determination of V(V) and Pb(II) in various samples
 (a) water

Sample	Added($\mu\text{g}/\text{mL}$)		Found($\mu\text{g}/\text{mL}$)		Recovery(%)	
	V(V)	Pb(II)	V(V)	Pb(II)	V(V)	Pb(II)
Tap water (our lab)	00	00	00	2.46	-----	-----
	1.0	1.0	0.98	1.02	98.0	102.0
Ganga River or (Ganga jal)	00	00	00	1.97	-----	-----
	1.50	2.5	1.48	2.52	98.66	100.8

(b) alloys

Alloy Sample	Composition	Present ($\mu\text{g}/\text{mL}$)		Found($\mu\text{g}/\text{mL}$)		Recovery (%)	
		V(V)	Pb(II)	V(V)	Pb(II)	V(V)	Pb(II)
Brass alloy	Zn=24.11%;Sn=1.85%;Cu=70.80%; Pb =2.52%; Fe=0.31%; Pb = 0.06%; Mn = 0.12%; Ni=0.17%.	00	0.84	00	0.83	00	98.80
Aluminium alloy	Al=95.6%,Si=0.78%,Fe=0.72%,Zn=0.8%,Mg=0.465,Ni=0.29%,Cr=0.27%,V=0.15%,Ti=0.15%,Sn=0.2%,Mn=0.2%,Co=0.1%, Pb=0.1%,Sb=0.1%, Bi = 0.06%, Ga = 0.035	1.50	0.4	1.49	0.39	99.33	97.5

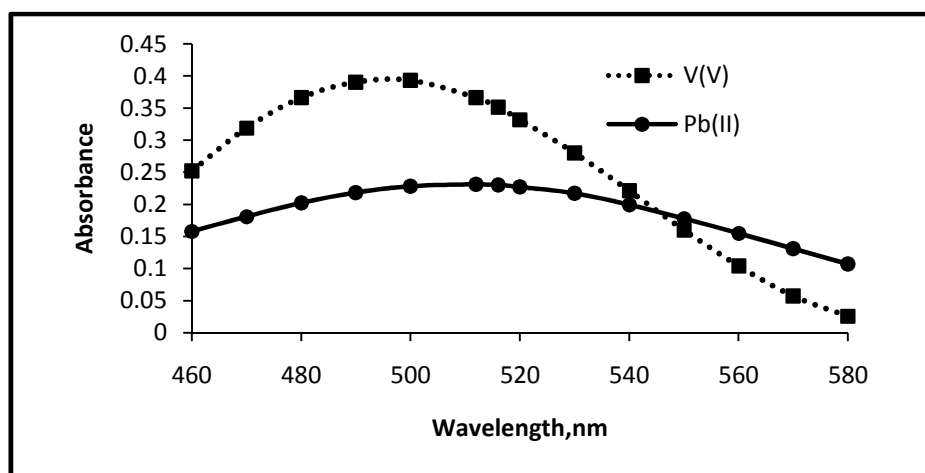


Figure-1

Absorption spectra of Pb (II) and V(V) with 1.0 mL ARS (0.01%) solution and 2.0 mL Tween-80 (1%) at pH 5.5

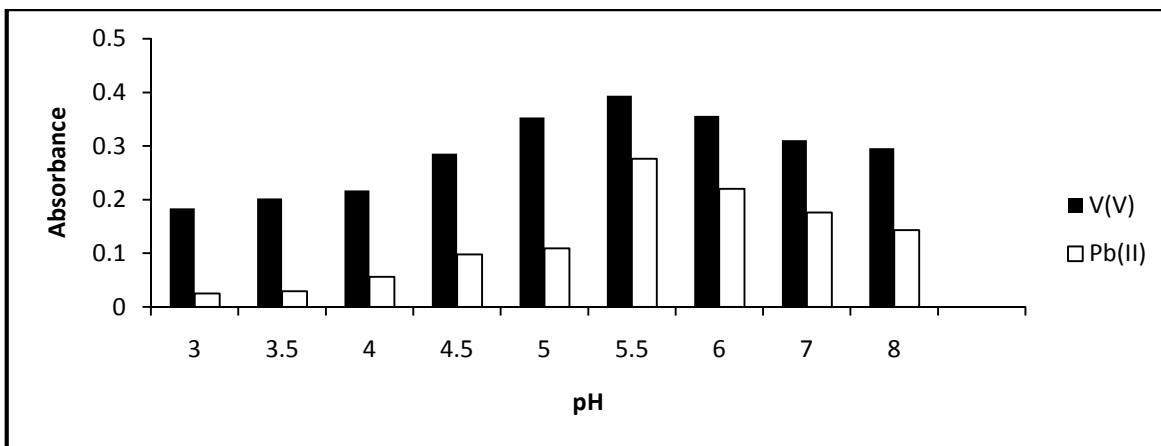


Figure-2
Effect of pH on the change in the absorbance of Pb (II) and V(V)-ARS complexes

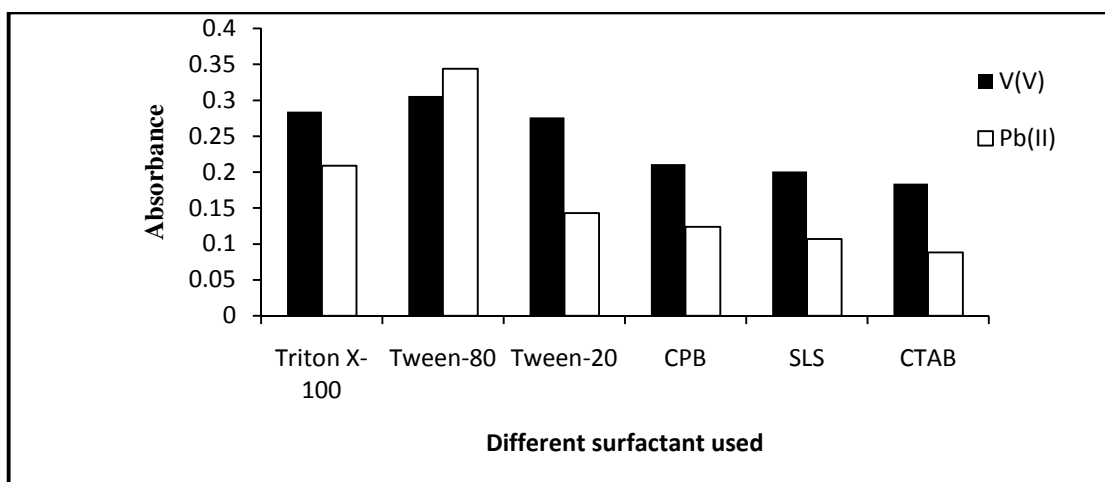


Figure-3
Effect of surfactants on complex formation of Pb (II) and V(V)-ARS

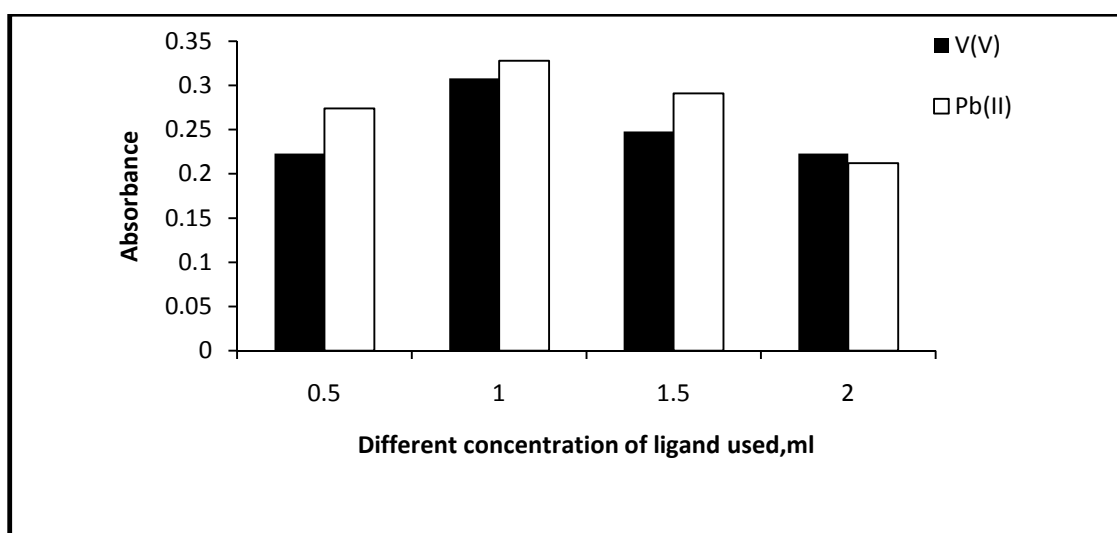


Figure-4
Effect of reagent concentration on the change in the absorbance of Pb (II) and V(V)-ARS complexes

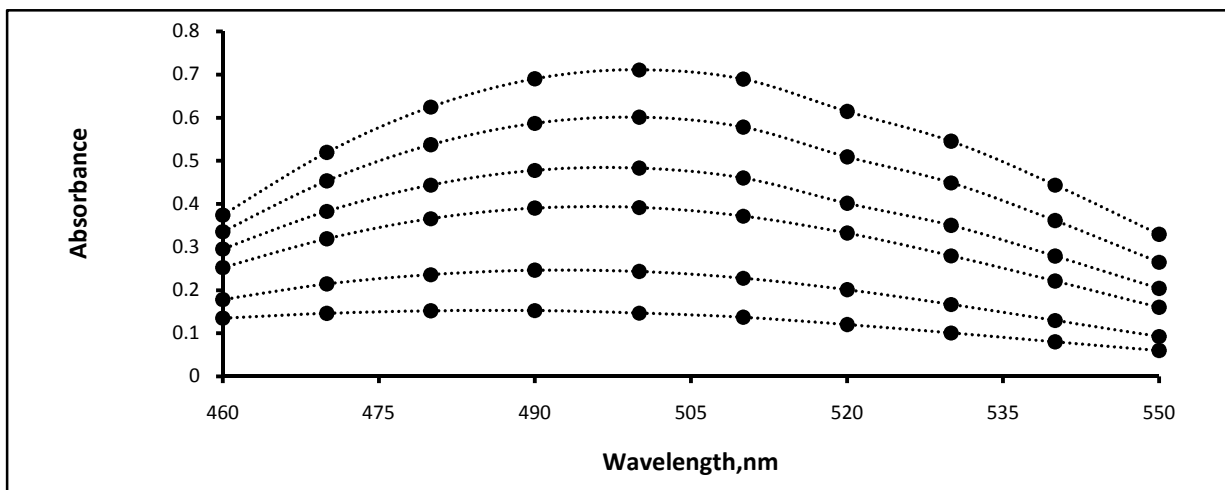


Figure-5
The absorption spectra for the standard solutions of the V(V) with different concentration

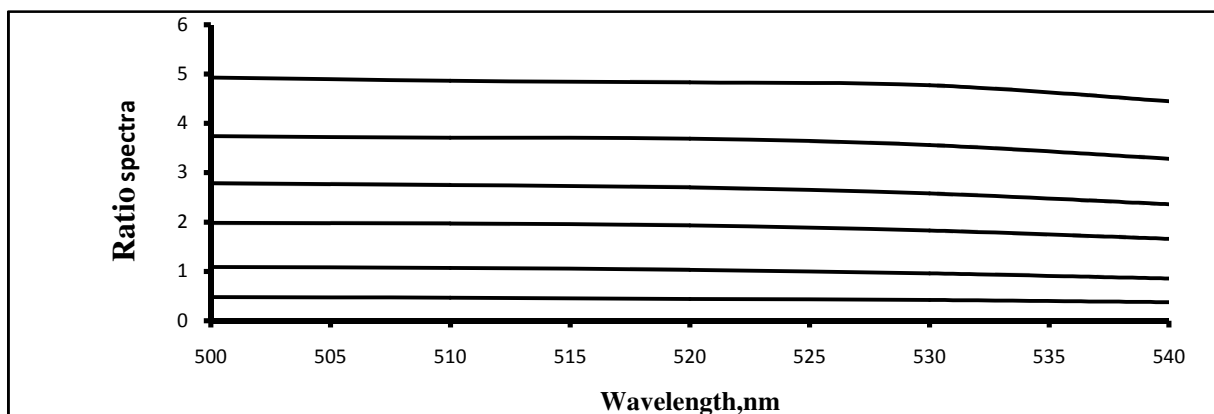


Figure-6
The ratio spectra obtained by dividing the normalized spectra of the Pb (II)

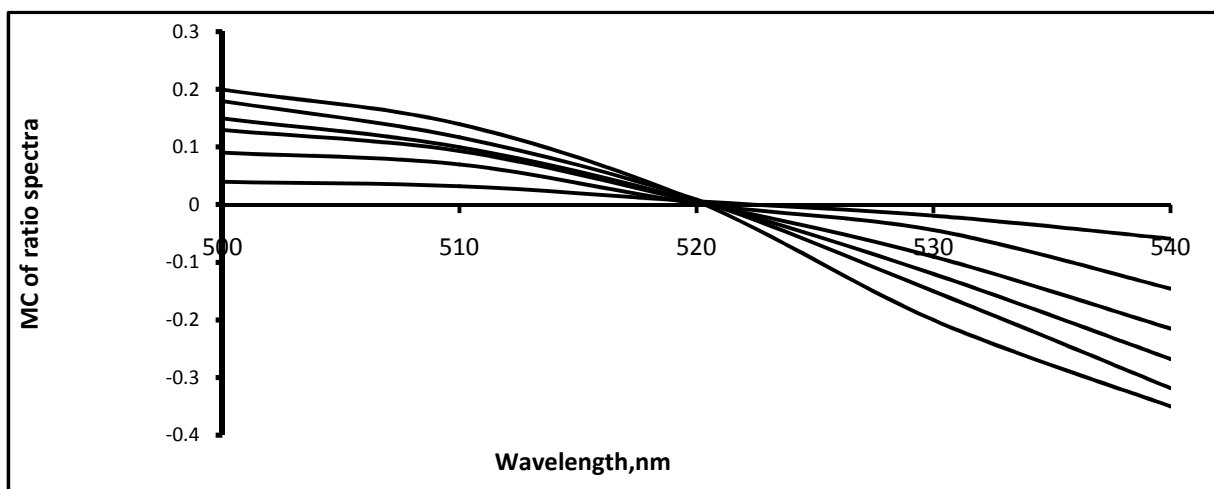


Figure-7
The mean centering of Ratio spectra for V(V) obtained with equation (3)

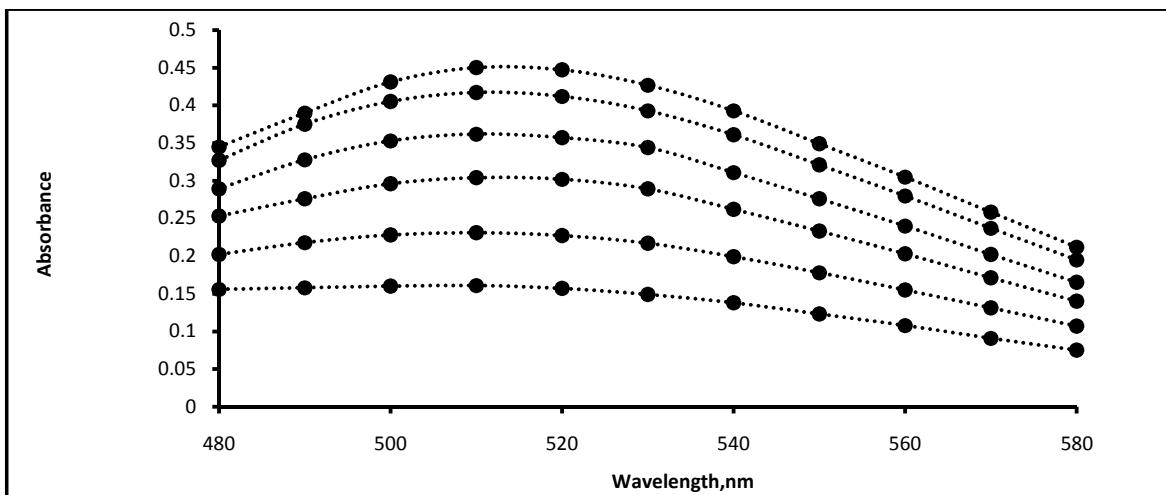


Figure-8

The absorption spectra for the standard solutions of the Pb(II) with different concentration

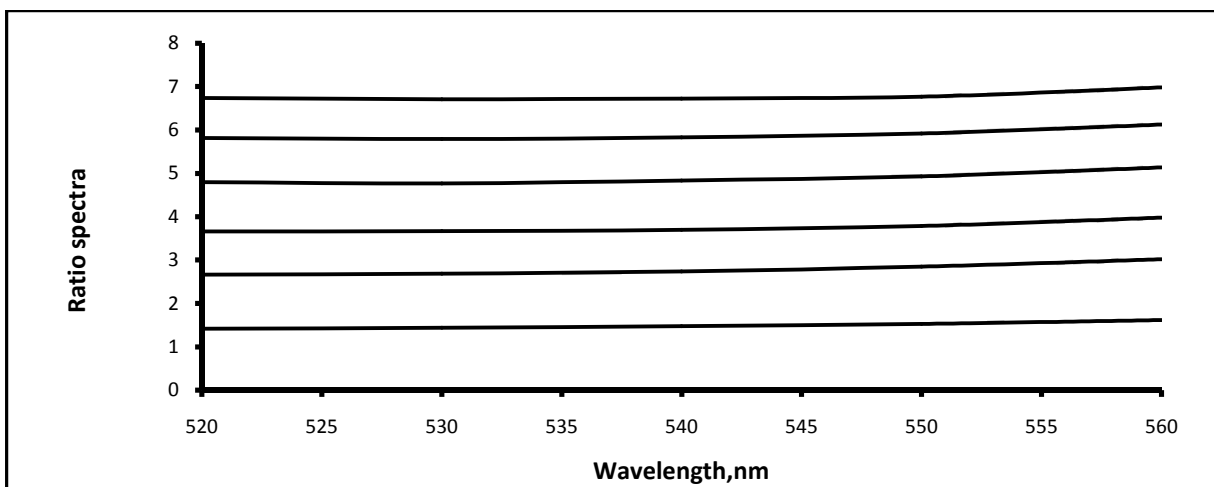


Figure-9

The ratio spectra obtained by dividing the normalized spectra of the V(V)

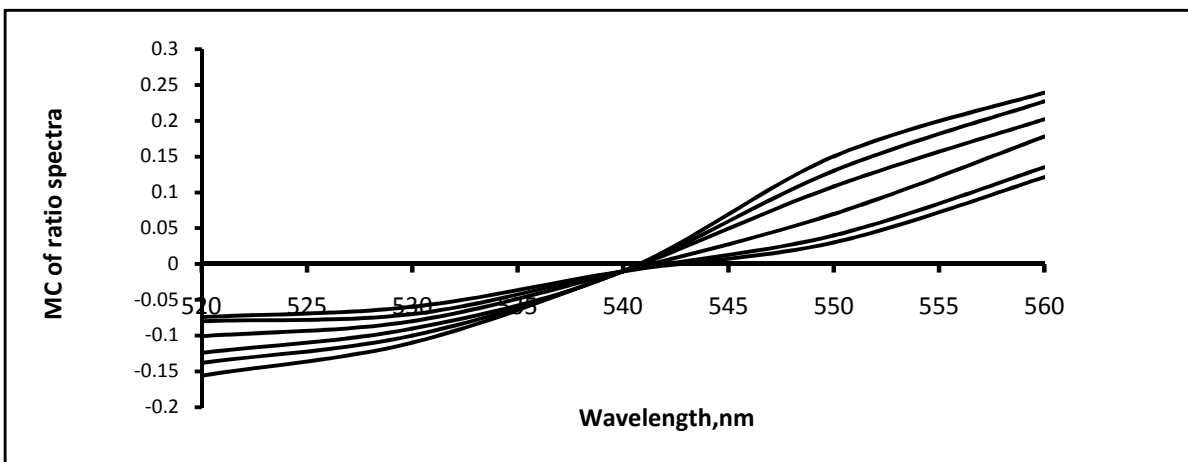


Figure-10

The mean centering of Ratio spectra for Pb(II) obtained with equation (3)

Conclusion

The proposed method offers significant advantages over conventional methods because of its speed and ease of operation. This method works without the need of preconcentration or extraction steps. Thus, the inherent errors involved in these time-consuming steps using toxic and carcinogenic organic solvents are avoided, and determination in aqueous phase using micellar system makes the procedure eco-friendly. The proposed spectrophotometric method has a low detection limit which enhances its sensitivity. Moreover, low cost of the instrument, easy handling and almost no maintenance have made spectrophotometry still a popular technique.

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