

SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM SULFOBENZOL AZOPYRROCATECHOL AND DIFFERENT LIGAND COMPLEXES WITH SURFACTANTS

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Abstract. The multi-ligand complex for the formation of zirconium with sulfobenzene azopyrocatechin and surfactants was studied spectrophotometric method. The maximum absorption of the complex occurs at 530 nm. The complex is formed in a relatively acidic environment, and at pH = 3, the maximum amount of zirconium ions passes into the complex. The linear range is 0.24–6.5 $\mu\text{g mL}^{-1}$, the limit of detection is 3 $\mu\text{g mL}^{-1}$, and the limit of quantification is 9.2 $\mu\text{g mL}^{-1}$. Analytical parameters affecting the determination of zirconium were calculated statistically. The volume of the extraction solution, the pH and the amount of ligand were found to be important factors influencing the formation of the complex.

Keywords: zirconium, sulfobenzol azopyrocatechol, 3D modeling.

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Received: 15 September 2021; **Accepted:** 28 November 2021; **Published:** 7 December 2021.

1. Introduction

Zirconium is one of the most difficult elements to analytically determine. In natural minerals, it is often found in combination with hafnium. Due to the similar chemical properties, it is hard to differentiate hafnium and zirconium during analysis. It is very resistant to base environments. It is colourless and hydrated in a strongly acidic environment. In its pure form, zirconium has a weak neutron absorption capacity, but it is possible to double the minimum neutron absorption capacity for use in nuclear technology (Hedrick, 2000). Thus, it becomes resistant to corrosion at high temperatures. Used in vacuum technology, in the manufacture of refractory parts. Zirconium compounds are used in adhesives, antiperspirants, aqueous polymers, ceramic paints, to increase the brightness of optical glasses, in paints as a drying and rust preventing agent, paper and photographic gelatin hardeners, preparation of soaps and toothpastes (Agrawal & Sudhakar, 2002). Due to a number of superior chemical properties, the zirconium mineral began to take the place of toxic and expensive chemical compounds in industry.

Determination methods using first-order derivative spectrophotometry for zirconium determination (Abbaspour & Baramakeh 2002; El-Sayed *et al.*, 2010; Varghese & George 2012), solid phase extraction (Faghihian & Kabiri-Tadi 2010; Pourreza *et al.*, 2011) cloud point extraction (Ghasemi *et al.*, 2012; Shariati & Yamini 2006), inductively coupled plasma mass spectrometry (Yang and Pin 2002; Firdaus *et al.*, 2007; Sun & Li 2015; Firdaus, 2018) and inductively coupled plasma atomic emission spectrometry (Lee, 2003; Schenk & Almirall 2012; Mortada *et al.*, 2013), PVC

membrane-based electrodes and sensors (Arida, 2008; Gupta *et al.*, 2009), as well as methods of concentration and separation of zirconium with hafnium (Oszwałdowski & Jakubowska, 2003; Oszwałdowski *et al.*, 1998; Rezaee *et al.*, 2012; Wang *et al.*, 2000; Yang *et al.*, 2002; Wang *et al.*, 2015) and other methods (Bassan *et al.*, 2010; Ghasemi Zolfonoun, 2010; Loh *et al.*, 2005; Pourreza *et al.*, 2010; El-Sayed *et al.*, 2017; Sharma *et al.*, 2001) have been developed for determination of zirconium. Recently, microextraction methods have been used to determine zirconium (Afzali *et al.*, 2014; Bagda & Tuzen, 2015).

Literature survey showed that various solvent extraction methods for the separation and pre-concentration of zirconium are available. Different reagents such as, Cyanex 923 (Gupta *et al.*, 2005), 2-hydroxy-5-nonylacetophenone-oxime (LIX 84-IC) (Reddy *et al.*, 2004), 2-ethylhexyl phosphoric acid mono-2-ethyl-hexyl ester (PC-88A) (Reddy *et al.*, 2004) and eriochrome cyanine R (Hanan & Salim, 2009) have been reported for extraction of zirconium.

Microextraction methods allow for less use of organic solvents, simplification of the sample preparation process, easy and inexpensive analysis, as well as analysis with many analytical devices (Alver *et al.*, 2012). In the present study, the dispersive liquid-liquid microextraction (method was used for the determination of zirconium. The analytical reagent sulfobenzol azopyrocatechin (1-(3,4-dioxyphenylazo)-4-sulfobenzol) was used, and as a surfactant, cetylpyridinium chloride was used. The addition of a surfactant accelerates the extraction of the metal complex into the organic phase. Analytical properties of the obtained different ligand complex were studied by spectrophotometric method.

2. Experimental part

2.1. Reagents and devices

The optical density of color solutions was measured on the JENWAY 6300 spectrophotometer using a quartz microcuvette. The Denley BS400 centrifuge (Denley Instruments Ltd., Billingshurst, UK) was used to accelerate phase separation. A Hamilton syringe was used for rapid injection (Hamilton Company, NA, USA). The pH of all solutions was measured using the Cond./TDS/Temp universal pH meter.

Sulfobenzol azopyrocatechol was dissolved in ethanol to form a solution with a concentration of 5×10^{-3} mol L⁻¹, the structural formula of sulfobenzol azopyrocatechol is shown in Fig. 1. SBAP was synthesized according to the method (Firz-David and Blanzhe, 1957), purified by crystallization from the solution in ethanol and the amount of the main product found in it by titanometric titration (Eshworth, 1968) was 98.8%. A standard zirconium solution with a concentration of 135 µg mL⁻¹ was prepared by dissolving “highly pure” metallic zirconium in a mixture of HF+ HClO₄. Then hydrogen fluoride is evaporated and separated, mixed with 4 M HClO₄ and 5 M H₂SO₄ (Korostelev, 1964). 45 µg mL⁻¹ working solution was obtained by diluting the parent solution of zirconium with distilled water. 0,1% OP-10 solution was used as a surfactant.

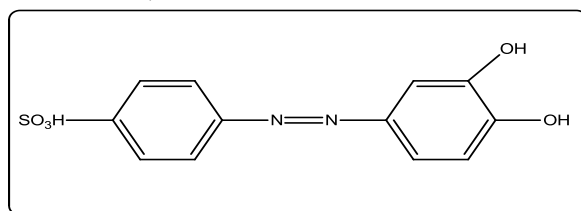


Figure 1. Structure of sulfobenzol azopyrocatechol

2.2. Method

The test tube contains a 200 μL sample of Zr solution with a concentration of 45 $\mu\text{g mL}^{-1}$ and 400 μL from sulfobenzol azopyrocatechol with a concentration of 5×10^{-3} mol L^{-1} . A mixture of 500 μL of acetone (dispersant) and 300 μL of chloroform (extractor) is rapidly injected over it with a 2.0 mL syringe. The metal complex is extracted into small balls formed in the system. The mixture is centrifuged at 4000 rpm for 5 minutes. This time, the small balls combine to form a large droplet and settle to the bottom of the test tube. The aqueous phase remaining on top is pipetted. The organic phase remaining at the bottom is then diluted with acetone to 2.0 mL and the optical density is measured on a spectrophotometer at a wavelength of 530 nm.

2.3. The effect of pH

Measurements were made at pH values of 1-6 to study the effect of acidity on the extraction process. Absorption was observed to be optimal at pH=2-4 (Fig. 2). Maximum absorption occurs at pH=3. Therefore, pH=3 was selected for subsequent experiments.

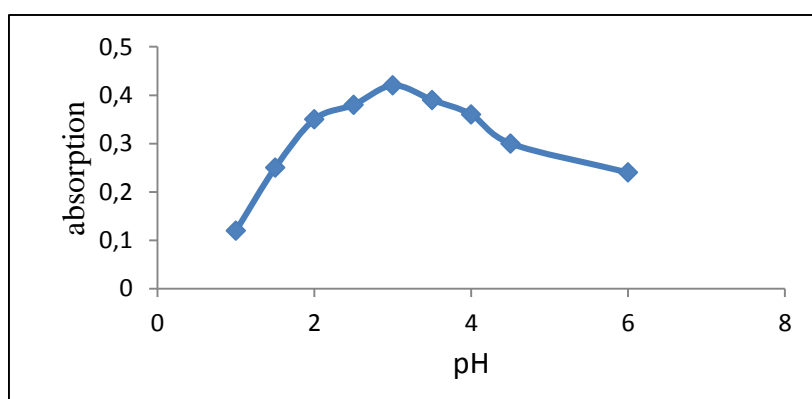


Figure 2. The effect of pH on absorption

2.4. The effect of type and volume of extracting and dispersing solutions

A number of properties of the solutions were taken into account when selecting an extracting solution and a dispersing solution. The extracting solution must be soluble in water, have a specific weight greater than the specific weight of the water, and have the capability of extracting the metal complex. The dispersing solution must be easily soluble in water and in the extracting solution. Therefore, chloroform and dichloromethane were used as the extracting solution, and acetone, acetonitrile and ethanol as the dispersing solution. Their dipole moments were taken into account when selecting solvents. The dipole moment of chloroform (1.15) is smaller than the dipole moment of water (1.87), so it is insoluble in water, and the dipole moment of acetone (2.69) is large, so it dissolves well in water. To determine the volume and type of the extracting solution, experiments were performed on volumes of chloroform and dichloromethane in the range of 50-500 μL , with a volume of 600 μL of the dispersing solution. As can be seen from the figure, dichloromethane is the smallest for the absorption of the Zr (IV) complex as the extracting solution. Maximum absorption was achieved when chloroform was used. Absorption of the complex at 300 μL of chloroform was maximal (Fig. 3a). In subsequent experiments, 300 μL of chloroform was used as the extraction solution.

To determine the volume and type of the dispersing solution, experiments were carried out by selecting the volume of the extracting solution at 300 μL at the volumes of

acetone, acetonitrile and ethanol in the range of 100-800 μL . Maximum absorption was observed at 500 μL of acetone (Fig. 3b). Therefore, 500 μL of acetone was used as the dispersing solution in subsequent experiments.

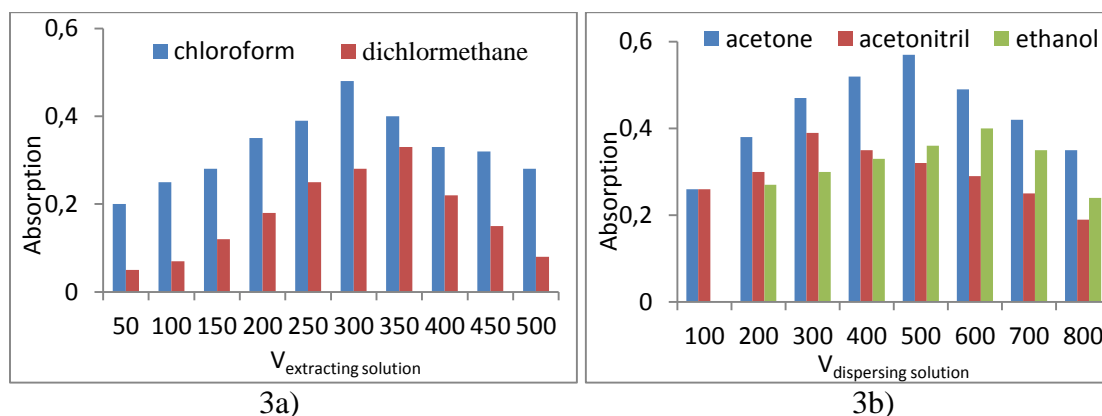


Figure 3. The effect of extracting solutions (3a) and dispersing solutions (3b) on absorption

2.5. The effect of the amount of ligand and surfactant

The amount of ligand is another variable that affects the extraction yield. For this purpose, the volume of SBAP with a concentration of $5 \times 10^{-3} \text{ mol L}^{-1}$ was changed in the range of 100-800 μL and colored complex compounds with Zr (IV) ions were obtained. The effect of the amount of ligand on the analytical signal is shown in Fig. 4.

As can be seen from Figure 4, an increase in the transfer of Zr (IV) ions into the complex is observed with a change in the amount of ligand in the range of 100-800 μL . Absorption is low when the volume of SBAP is less than 300 μL . When the volume of the ligand is 400 μL , the highest absorption is observed. Therefore, the volume of SBAP was selected as 400 μL for subsequent studies.

Volumes of 100, 150, 200, 250 and 300 μL of 0.1% OP-10 solution were used to study the effect of OP-10 on the yield. Better results were obtained when the volume of OP-10 was 200 μL , and therefore 200 μL was selected for further works.

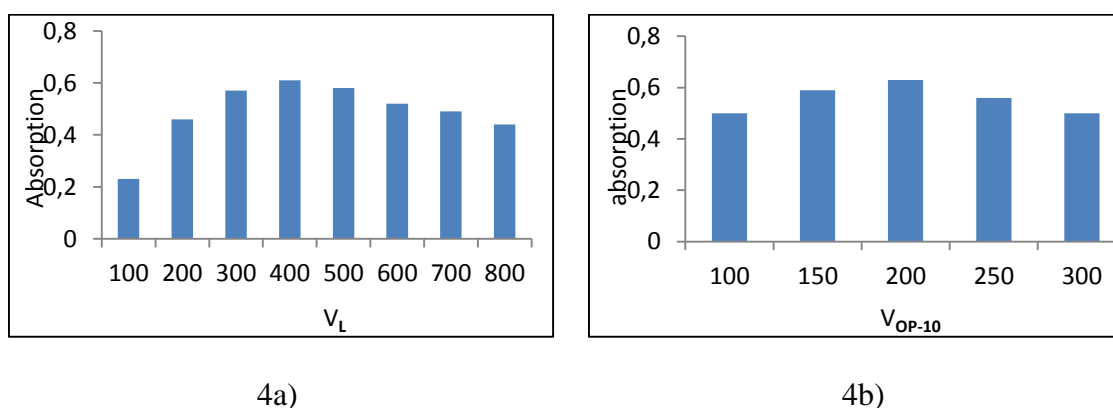


Figure 4. The effect of the volume of ligand (4a) and the volume of surfactant (4b) on absorption

2.6. Salt effect

It has been studied in the literature that ionic strength in extraction methods increases the extraction yield (Mohammadi *et al.*, 2009; Johrami *et al.*, 2007). For this purpose, more NaCl is used. The addition of salt to the solution increases the ionic strength and makes the more polar components less soluble in water. To study the effect of the electrolyte solution on the extraction, various amounts of NaCl salt were added while keeping the other parameters constant. For this purpose, 0 mL, 0.1 mL, 0.2 mL, 0.3 mL, 0.4 mL, 0.5 mL, 0.6 mL, 0.7 mL, 0.8 mL, 0.9 mL, 1.0 mL 2.0 mL of 20% NaCl salt solution was added into 12 test tubes. It was observed that the analytical signals did not change much despite the increase in ionic strength when up to 0.7 mL of salt solution was added. The analytical signal changes when 0.8 mL or more is added.

2.7. The effect of foreign ions

At this stage, the effect of foreign ions was studied in order to determine the selectivity of the method. 100 mg L⁻¹ stock solutions were prepared from each foreign cation (K⁺, Ag⁺, Ca²⁺, Ba²⁺, Zn²⁺, Mg²⁺, Hg²⁺, Fe³⁺, Co²⁺, Cd²⁺, Ni²⁺, Cu²⁺) and from the foreign anion (NO³⁻, SO₄²⁻, CO₃²⁻), and 0.5 mL was used. The ratio of the amount of foreign ions that do not interfere with the determination to the amount of Zr (VI) ion in the solution is given in Table 1.

Table 1. The effect of foreign ions on the determination

Foreign ions	Added	Molar ratio	Foreign ions	Added	Molar ratio
K ⁺	KCl	850	Co ²⁺	Co(NO ₃) ₂	400
Ag ⁺	AgNO ₃	850	Cd ²⁺	Cd(NO ₃) ₂ 6H ₂ O	400
Ca ²⁺	Ca(NO ₃) ₂	700	Cr ³⁺	Cr(NO ₃) ₃ 9H ₂ O	350
Ba ²⁺	BaCl ₂	550	Cu ²⁺	Cu(NO ₃) ₂ 3H ₂ O	200
Zn ²⁺	Zn(NO ₃) ₂ 6H ₂ O	550	SO ₄ ²⁻	Na ₂ SO ₄	400
Mg ²⁺	MgCl ₂	500	CO ₃ ²⁻	Na ₂ CO ₃	300
Hg ²⁺	HgCl ₂	450	NO ³⁻	Ca(NO ₃) ₂	300
Fe ³⁺	Fe(NO ₃) ₃	450	CH ₃ COO ⁻	CH ₃ COONa	200

2.8. The effect of other experimental conditions on the determination

In the temperature range of 20-35°C and the volume of the water phase in the range of 10-50 mL, the extraction yield is high, and in parallel, the color intensity of the complex does not decrease.

The mixed solution is centrifuged to separate the organic phase from the water phase. The centrifuge speed was changed in the range of 1000-5000 rpm, and it was observed that the organic phase was better separated when the speed was 4000 rpm. The effect of centrifugation time on absorption was also studied and the results of experiments conducted in the interval of 2-10 minutes were compared, the best results were obtained during 5 minutes of centrifugation.

The effect of extraction time on absorption means the period from the moment of addition of buffer solution, ligand, extracting and dispersing solution to Zr (VI) ion to the start of centrifugation. Extraction time was studied in the range of 2-15 minutes while keeping optimal conditions constant. The obtained results showed that the extraction time did not have a significant effect on the analytical signal.

2.9. Analysis of zirconium in various water samples

The amount of zirconium was determined in various water samples to investigate the validity of the method. The samples of zirconium of known concentration were added to 1000 mL of water and analyzed by the proposed method. In each water sample, the limit of detection of zirconium (LOD) and the limit of quantification (LOQ), as well as the relative error were determined. The results are shown in Table 2.

Table 2. Analysis of zirconium in various water samples. Zirconium of known concentration was added to 1000 mL of water

Sample	Added ($\mu\text{g L}^{-1}$)	Detected ($\mu\text{g L}^{-1}$)	LOD ($\mu\text{g L}^{-1}$)	LOQ ($\mu\text{g L}^{-1}$)	Relative error (%)
Tap water	-	Not detected	3	9.3	98
	5.0	4.98			
	10.0	10.01			
River water	-	Not detected	2.8	8.9	97
	5.0	5.02			
	10.0	9.97			
Industrial wastewater	-	Not detected	3.1	9.1	93
	5.0	4.96			
	10.0	9.96			
Natural mineral water	-	Not detected	3.2	9.2	92
	5.0	4.99			
	10.0	10.01			

Compared to different methods of analysis of zirconium this method can be considered a sensitive and selective method (Table 3). The simplicity of the method allows you to perform analysis in the laboratory with less time and simple devices.

Table 3. Comparison of this method with other analytical methods

Reagent	Object being analyzed	Linear range	λ_{max} , nm	LOD	pH	Literature
DBC-arsenazo	Water sample	0-1.20 $\mu\text{g mL}^{-1}$	560	0.22 $\mu\text{g mL}^{-1}$	HNO ₃ , 8 M	Zhang <i>et al.</i> , 2013
Aluminium hydroxide	-	0-10 mg L ⁻¹	-	0.17 mg L ⁻¹	8	Shokrollah and Gohari 2017
Platanus orientalis tree leaves	Water	0.4-8 $\mu\text{g mL}^{-1}$	422	0.086 $\mu\text{g mL}^{-1}$	HCl, 6 M	Monji <i>et al.</i> , 2008
Cyanex272	Soil	-	670	3.2 $\mu\text{g L}^{-1}$	HNO ₃ , 0.01M	Karve and Gholave 2014
Sulfobenzol azopyrocatechol	Water sample	0.24-6.5 $\mu\text{g mL}^{-1}$	530	3 $\mu\text{g mL}^{-1}$	3	This method

The extraction recovery of the complex is an indicator of the selectivity of the analytical method. The extraction recovery of the complex formed by zirconium with the tri-n-octyl amine reagent is 94% (Jaykishon *et al.*, 2018), with Alamine 336 was 98% (Banda *et al.*, 2013), with Cyanex 272 was 71% (Taghizadeh *et al.*, 2008) with this method with SBAP was 99.5%. This shows that the method has a high selectivity.

2.10. Statistical calculations, optimization of results

Box Behnken statistical analysis method was used to optimize the complex formation and extraction process (Minitab 19). First, a normality test was performed for graphs of factors affecting absorption. The volume of the extracting solvent, the volume of the dispersing solvent, the pH, the volume of the ligand, the volume of the surfactant, the centrifugation time, the centrifugation speed, and the salt effect were selected to determine the highest “effective” variable. Factors and their low and high values are given in Table 4. Plackett Burman statistics were used to determine which of the 8 variables that could affect the results of the analysis were “effective” or “ineffective”. For this purpose, a design matrix consisting of 12 experiments with 8 factors was prepared.

Table 4. Values of independent variables calculated by Plackett Burman design

Independent variables	Symbol	Low value	High value
Volume of extraction solvent, μL	VES	50	500
Volume of dispersion solvent, μL	VDS	100	800
pH	pH	1	6
Volume of ligand, $\text{C} \times 10^{-5} \text{ mol L}^{-1}$	VL	100	800
Volume of surfactant, μL	VS	100	300
Centrifugation time, minutes	CT	2	10
Centrifugation speed, rpm	CS	1000	5000
Effect salt	ES	0.1	0.8

An initial statistical study of the results with the Plackett Burman design found that the variables that affect the extraction process more and were statistically significant were the volume of ligand, pH, and the volume of extracting solution (Fig. 5).

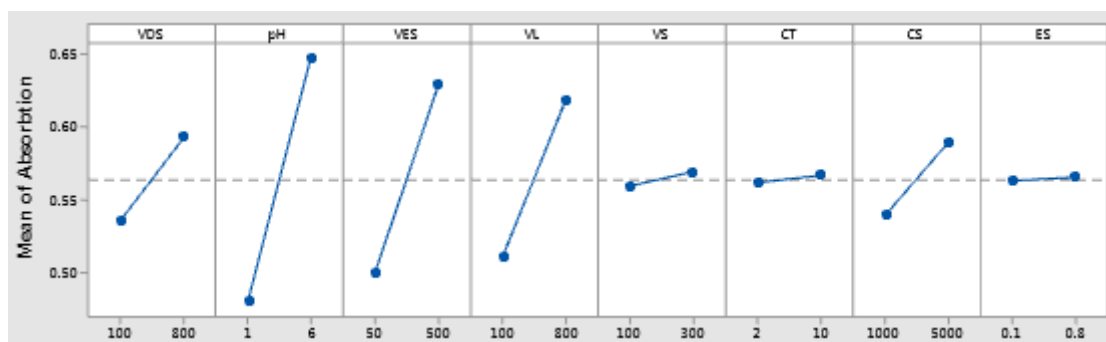


Figure 5. Factorial graph for extraction

A three-level, three-factor Box Behnken design was used to optimize the effect of these three parameters on the extraction process. The p value for pH, VES, and VL were 0.016, 0.035, and 0.008, respectively. The $P > 0.05$ value indicates that these parameters are more effective (Trinh and Kang 2010). For the accuracy of the model, the calculated value of R^2 must be at least 0.80 (Yang *et al.*, 2013). In this study, $R^2 = 0.989$

To evaluate the effects of the factors in more detail, their 3D graphs are shown (Fig. 6).

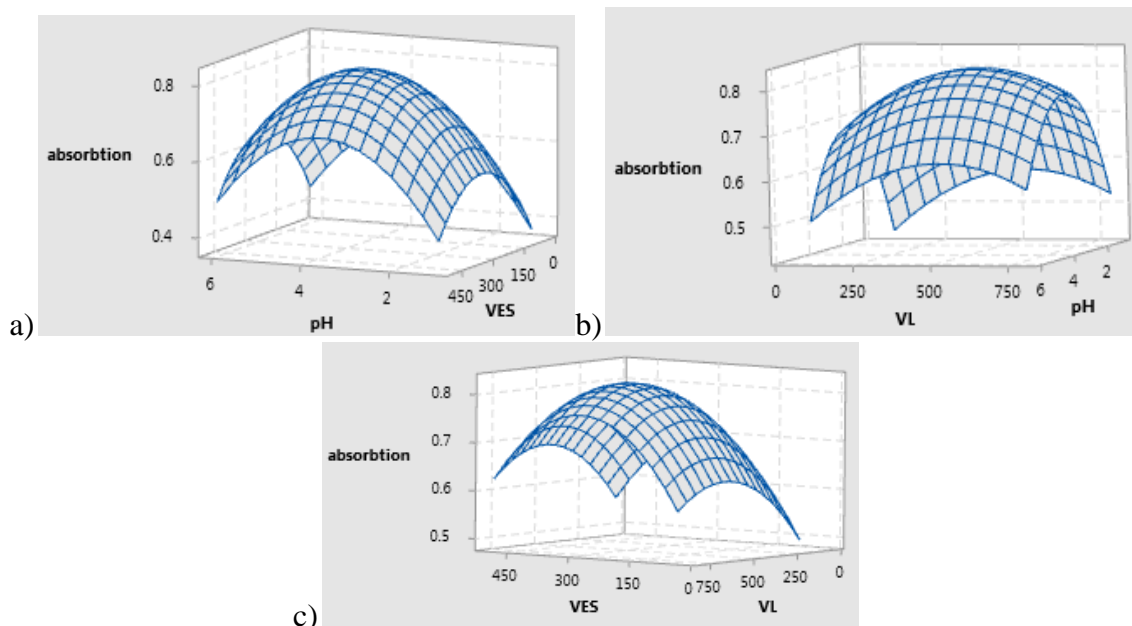


Figure 6. The effect of a) VES and pH, b) pH and VL, c) VES and VL on absorption during extraction

As can be seen from the graphs, when looking at the effect of pH and VES on absorption at the mean value of the volume of ligand ($VL=450 \mu\text{L}$), it is observed that pH has a greater effect (Fig. 6a). In particular, at a pH of 3.5, absorption reaches the maximum value. When $VES=275 \mu\text{L}$ remains constant, absorption is still maximal at pH 3.5 (Fig. 6b). When looking at the effect of VES and VL on absorption at $pH=3.5$, it appears that VL has a greater effect on absorption (Fig. 6c). According to the results of statistical analysis, the optimal values of independent variables to achieve maximum absorption are $pH=3.5$, $VL=450 \mu\text{L}$ and $VES=275 \mu\text{L}$.

3. Conclusion

1. As a result of determination of zirconium by DMMME method, optimal $pH=3$ compliance with Beer's law was determined $0.24-6.5 \mu\text{g mL}^{-1}$. Analytical detection limit of zirconium is $3 \mu\text{g mL}^{-1}$, the analytical limit of quantification is $9.2 \mu\text{g mL}^{-1}$, $\lambda_{\text{max}}=530 \text{ nm}$. When comparing these parameters with other methods of determination of zirconium, it can be said that this method is a selective and effective method. The stoichiometric composition of the components in the complex is $\text{Zr: SBAP:SPX} = 1:2:2$.
2. Using the Plackett Burman design, the factors that most affected the extraction were found to be the ligand concentration, the volume of the extracting solution, and the pH. Using the Box Behnken design, it was determined that the ligand concentration was the factor that most affected the absorption among these three factors.
3. This method was used to determine zirconium in various water samples under optimal conditions.

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