

Simultaneous Determination of Iron (III) and Aluminum (III) in the Presence of Titanium (IV) in Portland Cement using Derivative Spectrophotometry

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Abstract: A spectrophotometric method relies on the use of derivative ratio-zero crossing technique has been developed for simultaneous determination of Fe (III) and Al (III) in the presence of Ti (IV). The method depends on the formation of colored complexes of metal ions with 1,2,4-trihydroxyanthraquinone (purpurin, PURP) in 50% v/v ethanol-water medium at pH 2.5. The method was successfully applied for the determination of (1.6 – 5.58 mgL⁻¹) iron, and (0.269 – 2.15 mgL⁻¹) aluminum. The correlation coefficients for the obtained calibration graphs were 0.990 for iron (III), and 0.996 for aluminum (III). The sandell sensitivities of iron and aluminum were 0.24ng cm⁻² and 0.20ng cm⁻² respectively. The developed method was applied to the simultaneous determination of Fe₂O₃ and Al₂O₃ in Portland cement and was found to give satisfactory results.

Keywords: Iron (III), aluminum (III), cement analysis, purpurin, derivative spectrophotometry

1 Introduction

In cement industry, on-line control of cement composition is necessary to maintain the composition of the cement within strict requirements [1]. The improvement of the quality is tantamount to the improvement of the chemical composition. Several spectrophotometric methods were developed for the determination of iron and aluminum in some environmental [2]–[8], and alloy [9]–[11] samples. These methods include x-ray fluorescence XRF, atomic absorption spectroscopy AAS, inductively coupled plasma ICP, and capillary electrophoresis. The derivatization of spectra allows to remove spectral interferences and as a consequence derivative spectrophotometry has a unique feature that it opens the possibility not only for increasing selectivity [12]–[14] but also for increasing sensitivity [15], [16]. The zero crossing method developed by O' Haver has been applied successfully for the determination of metal

al.[17] developed a spectrophotometric method for resolving ternary mixtures; the method is based on the simultaneous use of the first derivative of the ratio spectra and measurements at zero-crossing wavelengths. Purpurin is known as a good analytical reagent, it was used for the determination of some metals in various samples [18]–[22]. In this work, fundamental studies of the complexation reactions of Fe (III), Al(III) and Ti(IV) with PURP were described, a rapid and sensitive first derivative ratio spectra zero-crossing method was used for simultaneous determination of Al(III) and Fe(III) in the presence of Ti(IV). The validity of the method was checked by analyzing Portland cement samples and the obtained results showed a good agreement with XRF results.

2 Experimental

2.1 Instruments

ions in their binary mixtures through the formation of complexes with the same organic ligand [14]. Salinas et

Ordinary absorption spectra and all derivative calculations were made on a T80+ (England) double beam UV/VIS

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Spectrophotometer using 10-mm matched quartz cells and slit width 2 nm. The pH of solutions was measured using AD1030 pH/mV pH meter equipped with a Radiometer combined glass electrode. Normal or derivative spectra of metal-PURP systems were measured against a reagent blank, similarly prepared but containing no metal ions. The solution spectra were recorded at room temperature in water-ethanol containing 50% v/v ethanol, while keeping the ionic strength at a constant value of $I = 0.1 \text{ mol L}^{-1}$ (NaClO_4).

2.2 Chemicals and Solutions

All chemicals were of analytical-reagent grade and doubly distilled water or absolute ethanol was used for the preparation of solutions.

2.2.1 Purpurin (sigma reagent)

Stock solution $2 \times 10^{-3} \text{ mol L}^{-1}$ was prepared by dissolving an accurately weighed amount of the purified reagent in absolute ethanol.

2.2.2 Standard iron (III) Solution

A $10^{-3} \text{ mol L}^{-1}$ stock standard solution was prepared using FeCl_3 AnalaR grade product in 0.1 mol L^{-1} HCl and standardized with EDTA.

2.2.3 Standard Aluminum (III) solution

A $10^{-3} \text{ mol L}^{-1}$ stock standard solution was prepared using AnalaR grade product $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The aluminum content of the solution was determined by conventional method [23].

2.2.4 Titanium (IV) Stock Standard Solution.

A stock standard solution (1 ml = 0.4 mg of TiO_2) was prepared by dissolving 0.2 g of high-purity TiO_2 in 10 ml sulfuric acid ($d = 1.84$) together with 5 g of ammonium sulfate, with heating. The solution was cooled and poured into 100 ml of water while stirring, then filtered into a 500 ml calibrated flask and diluted to the mark with H_2SO_4 (1 + 19). More dilute solutions were obtained as required by accurate dilution [24]. The titanium concentration was determined spectrophotometrically using Tiron reagent.

Perchloric acid, sodium perchlorate and standard sodium hydroxide solution were all prepared from analytical grade reagents.

Solutions of diverse ions used for interference studies were prepared from AnalaR products of nitrates, acetates or chlorides of the metal ions and potassium or sodium salts of the anions to be tested.

2.2.5 Dissolution of Cement Samples

A 0.3 g of the sample (dried at 110°C) was weighted and dissolved in the minimum volume of hydrochloric acid. Heated to dryness, then 10 ml of HCl (6 mol L^{-1}) was added to the residue, digested and the insoluble residue was filtered into a 100 ml calibrated flask and then diluted to volume with doubly distilled water [25].

2.3 Procedure

2.3.1 Simultaneous Determination of Fe (III) and Al(III)

An aliquot of a sample solution, containing iron (III) (36-150 μg) and aluminum (III) (6 -55 μg), was transferred into a 25-ml calibrated flask. Then, 5 mL of $2 \times 10^{-3} \text{ mol L}^{-1}$ purpurin solution was added, the pH was adjusted to 2.5 and diluted to volume, while keeping a final 50 % (v/v) ethanol content. The normal and the derivative spectra were recorded from 700 to 400 nm against a reagent blank. The absolute value of the first derivative was measured at 540 nm (zero-crossing point of Al (III) - PURP) and 580 nm (zero-crossing point of Fe (III)-PURP) for the determination of iron and aluminum respectively.

2.3.2 Simultaneous Determination of Fe (III) and Al(III) in the Presence of Ti(IV)

The obtained spectra of Fe-PURP complex, Al-PURP complex, and their ternary mixture with Ti-PURP complex were divided by a standard one of Al (III)-PURP and Fe(III)-PURP complex. The first derivative of ratio spectra were recorded. In the ternary mixture, the iron (III) concentration was proportional to the first derivative divided signal DD^1 at 638 nm and 650 nm (zero-crossing points of Ti (IV)/Al(III)). Aluminum (III) concentration could be determined by measuring the DD^1 signal at 458 nm (zero-crossing point of Ti(IV)/ Fe(III)), or by measuring the DD^1 signal at 480 nm (zero-crossing point of Fe(III)/Ti(IV)), best results were obtained by measuring the DD^1 signal at 458 nm.

2.3.3 Simultaneous Determination of Fe (III) and Al(III) in Portland Cement

Transfer a 0.2–0.5 mL aliquot of the prepared cement solution into a 25mL calibrated flask and add 5mL of PURP ($2 \times 10^{-3} \text{ M}$). Adjust the pH to 2.5 by the addition of 0.01 M sodium hydroxide. Dilute to volume while keeping final ethanol content of 50 % (v/v). Record the absorbance of the solution from 700 to 400 nm against a reagent blank. Divide the obtained normal spectrum by a standard one of Ti-complex, Al-complex or Fe-complex. Record the first derivative of the ratio spectrum and measure the amplitudes DD^1 at zero-crossing wavelengths as mentioned above. Iron (III) and aluminum (III) contents in Portland cement were calculated directly using proper regression equations.

3 Results and Discussion

3.1 Acid-base Properties of Purpurin

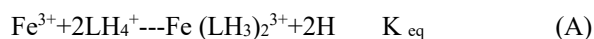
The acid-base equilibria of PURP were studied in our laboratory in 50% v/v ethanol–water medium and in the pH range 2.5–10.5, it was found that PURP exists in four different acid–base forms (LH_4^+ , LH_3 , LH_2^- , and LH^{2-}). The values of pK_{a1} ($\text{LH}_4^+/\text{LH}_3$), pK_{a2} ($\text{LH}_3/\text{LH}_2^-$), pK_{a3} ($\text{LH}_2^-/\text{LH}^{2-}$) are 5.18 ± 0.02 , 7.65 ± 0.01 and 10.27 ± 0.03 , respectively [26].

3.2 Complexation Equilibria of Metal Ions with Purpurin

The complexation equilibria were studied in solution containing an excess of metal ion, equimolar concentration and an excess of the reagent over the pH range 1.5–4. The absorbance versus pH graphs for all systems were interpreted logarithmically using the relationships given elsewhere [27],[28]. The number of protons released during complexation and the equilibrium constants K_{eq} were proved graphically.

3.2.1 Complexation Equilibria Fe(III) with Purpurins

The absorption spectra of Fe(III)-PURP complex showed the formation of a complex with a maximum absorbance at 580 nm, the formation of the complex started at pH 1.0 and increased up to pH 2.7. The logarithmic analysis of absorbance–pH curves indicated the formation of $\text{Fe}(\text{LH}_3)_2^{3+}$ with the liberation of two protons according to the equilibrium (A).



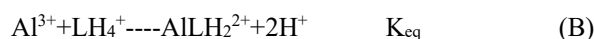
3.2.2 Complexation Equilibria Al (III) with Purpurin

The absorption spectra of Al(III)-PURP complex reflected the formation of a complex with a double headed band at 510 nm and 540 nm.

The color of the complex begins to appear at pH 2.0 and

reached its maximum intensity at pH 3.6 above which the absorbance decreased due to the hydrolysis of the complex.

The logarithmic analysis indicated liberation of two protons during the complexation according to the equilibrium (B).



3.2.3 Complexation Equilibria Ti (IV) with Purpurin

The absorption spectra of Ti(IV)-PURP complex showed the formation of complex with a band at 554 nm, the complexation begins at pH 1.5 up to pH 3.2. The logarithmic analysis of absorbance–pH curves indicated the formation of TiLH_2^{3+} with the liberation of two protons according to the equilibrium (C).



3.3 Equilibrium and Stability Constants

The equilibrium constants K_{eq} were determined by considering the equilibrium (A),(B),and (C), the stability constant of Fe(III)-PURP complex was related to equilibrium constant by the expression (I), while the stability constants of Al(III)-PURP and Ti(IV)-PURP complexes were obtained by considering expression (II)

$$\log \beta = \log K_{eq} + 2\text{pK}_{a1} \quad (\text{I})$$

$$\log \beta = \log K_{eq} + \text{pK}_{a1} + \text{pK}_{a2}. \quad (\text{II})$$

The calculated values of K_{eq} and β are shown in **Table 1**.

3.4 Stoichiometry of the Complexes

The composition of Fe-PURP complex at pH 2.5 is 1:2 (M:L) as verified by the molar ratio and the continuous variation methods, while that of Ti (IV) and Al (III) complex is 1:1 (M:L) at the same pH.

3.5 Analytical Characteristic of Ordinary Spectra

Under the optimum conditions, a linear calibration graphs for Fe-PURP and Al-PURP were obtained up to 7.8 ml L^{-1} and 2.69 mg L^{-1} respectively with a molar absorptivity $6.1967 \times 10^3 \text{ L mol}^{-1} \text{cm}^{-1}$ for iron at 580 nm, and $9.0331 \times 10^3 \text{ L mol}^{-1} \text{cm}^{-1}$ for aluminum at 540 nm. The reproducibility of the method was checked by analyzing a series of seven solutions containing 3.5 mg L^{-1} of iron and 1.35 mg L^{-1} of aluminum. The relative standard deviations (%RSD) were found to be 0.9% for iron and aluminum.

3.6 Simultaneous Determination of Fe(III) and Al(III) in Their Binary Mixtures

3.6.1 Absorption Spectra

Table 1: Mean values of equilibrium K_{eq} and conditional stability constants β .

	Fe (III) -PURP	Al (III) -PURP	Ti (IV) –PURP
Equilibrium constant (Log K_{eq})	(0.759) ^a (0.7805) ^b	(-1.4769) ^a (-1.266) ^b	(-0.2423) ^a (-0.2252) ^b
Conditional stability constant (log β)	11.13	11.45	12.60

^(a)From the absorbance vs. pH graphs for solutions with excess ligand.

^(b)From the absorbance vs. pH graphs for solutions with excess metal.

The absorption spectra of Fe-PURP, Al-PURP complexes and their binary mixture are shown in **Figure 1**. Since the absorption spectra of the two metal complexes overlap, the determination of iron and aluminum in their mixtures by ordinary spectrophotometry is frequently difficult. This problem has been overcome using zero-crossing method.

3.6.2 Zero-Crossing Method

Appropriate parameters were selected to record the first-derivative spectra using the zero-crossing method to select suitable wavelengths for obtaining linear analytical calibration graphs. The reproducibility of zero-crossing wavelengths of derivative spectra was checked by recording the first-derivative spectra of Fe–PURP and Al–PURP systems (pH 2.5) at different concentrations of the analytes **Figure 2**. The zero-crossing wavelengths of iron and aluminum in the first-derivative spectra are obtained at 580 and 540 nm respectively.

Figures 3 shows the first-derivative spectra of two series containing increment amounts of iron or aluminum ions. Iron and aluminum can be determined using the absolute value of the total derivative spectrum at a wavelength corresponding to the zero-crossing point of the other component. The first derivative values obtained at 540 nm (zero crossing point of Al(III)-PURP) and those obtained at 580 nm (zero crossing point of Fe(III)-PURP) are proportional to iron and aluminum concentrations respectively. The obtained regression equations are given in **Table 2**.

3.6.3 Effect of Diverse Ions

To assess the usefulness of the proposed method, the effects of diverse ions that are often associated with Al (III) and Fe (III) were studied. The tolerance of the method to foreign

ions was investigated with solutions containing 1.0 mgL⁻¹ of Al (III), 2.5 mg L⁻¹ Fe (III) and various amounts of

foreign ions. The tolerance criterion for a given ion was taken to be the deviation of the absorbance values by more than $\pm 2\%$ from the expected value. The determination of iron (III) and aluminum (III) was possible in the presence of K⁺, Na⁺, Mg²⁺, Ca²⁺, Cr³⁺, Sr²⁺, Mn²⁺, Zn²⁺, NO₃⁻, SO₄²⁻, SO₃²⁻, Cl⁻, I⁻, and Br⁻. Only Ti⁴⁺ interferes seriously and this interference was overcome by the use of derivative ratio zero crossing technique.

3.7 Simultaneous Determination of Fe(III) and Al(III) in the Presence of Ti(IV)

In order to resolve the ternary mixture, we needed carefully to select the zero-crossing wavelengths that permit an accurate determination of iron and aluminum in the presence of titanium. The zero-crossing wavelengths for Ti/Al were obtained at 638 and 650 nm, while those for Ti/Fe were obtained at 458 and 480 nm respectively.

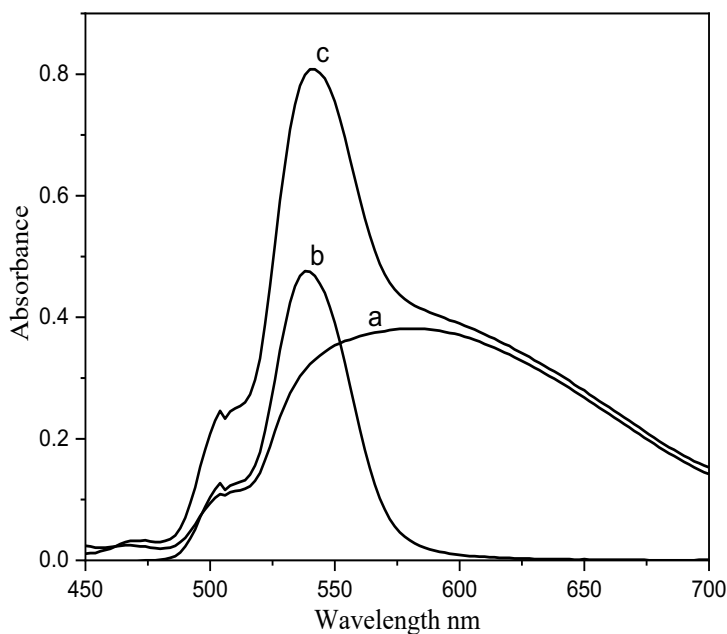
Figure 4 illustrates the ratio spectra and the first derivative of ratio spectra of a series of ternary mixtures containing increasing concentrations of iron, using Al(III)-PURP as a divisor, while **Figure 5** shows the ratio spectra and the first derivative of ratio spectra of ternary mixtures containing increment amounts of aluminum using Fe(III)-PURP as a divisor. In order to determine the concentration of Fe(III) the absolute first derivative divided value DD¹ was taken at 638 or 650 nm (zero crossing points of Ti/Al) which are proportional to the iron concentration. For Al(III) determination the DD¹ signal at 458 (zero crossing points of Ti/Fe) was measured.

3.7.1 Effect of Divisor

A standard spectrum of Al(III) 1.35 mg L⁻¹ was used as a divisor for the determination of iron(III) while a standard spectrum of Fe(III) 3.35 mg L⁻¹ was used as a divisor for the determination of aluminum(III). The use of these divisors gave the best correlation between the first derivative divided values (DD¹ signals) and the concentrations of the metal ions.

Table 2: Statistical data for calibration graphs.

Metal to be determined	Regression equations	R ²	S _m	S _b
<u>Binary mixtures</u>				
Fe (III)	${}^1D_{540} = 0.11581 C_{Fe} + 0.0023$	0.997	0.0024	0.0123
Al (III)	${}^1D_{580} = -0.0119 C_{Al} - 0.00121$	0.999	3.37×10^{-4}	5.21×10^{-4}
<u>Ternary mixtures</u>				
<u>Standard divisor 1.35 mg L⁻¹ Al (III)</u>				
Fe (III)	$DD^1_{638} = 13.251 C_{Fe} + 15.75$	0.98	0.088	0.042
	$DD^1_{650} = 5.89 C_{Fe} - 0.86$	0.99	0.036	0.049
<u>Standard divisor 3.35 mg L⁻¹ Fe (III)</u>				
Al (III)	$DD^1_{458} = 0.5657 C_{Al} - 0.3971$	0.996	0.0229	0.041

¹DD: The first derivative divided signalC_{Fe}: Fe(III) concentration (mg L⁻¹).C_{Al}: Al(III) concentration (mg L⁻¹)R²: Regression coefficientS_m: Standard deviation of slope.S_b: Standard deviation of intercept**Fig. 1:** Absorption spectra of (a) Fe(III)-PURP, (b) Al(III)-PURP complexes and (c) mixture of Fe(III)-and Al(III)-PURP complexes.[Fe(III)] = 3.35 mg L⁻¹, [Al(III)] = 1.35 mg L⁻¹, [PURP] = 4 × 10⁻⁴ M, 50% ethanol, I = 0.1 M (NaClO₄), and pH = 2.5

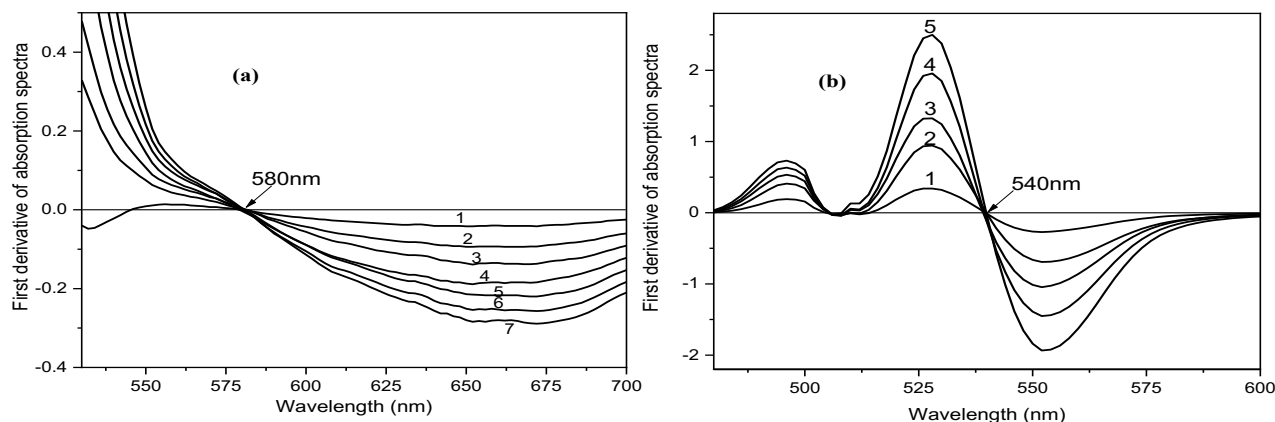


Fig. 2: First-derivative spectra of Fe(III)-PURP(a) and Al(III)-PURP (b) complexes

[Fe(III)] = 1) 1.11 ; 2) 2.23; 3) 3.35 ; 4) 4.46; 5) 5.58 ; 6) 6.70; 7) 7.81 mg L⁻¹

[Al(III)] = 1) 0.27 ; 2) 0.81; 3) 1.35 ; 4) 2.15; 5) 2.7 mg L⁻¹

[PURP] = 4×10^{-4} M, 50% ethanol, I = 0.1 M (NaClO₄), and pH = 2.5.

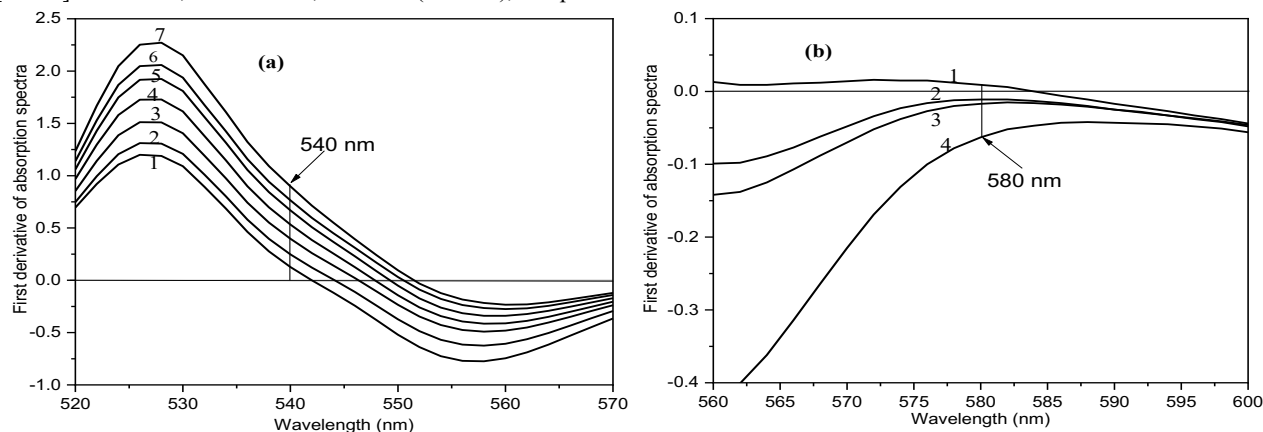


Fig. 3: First-derivative spectra of a mixture of Al(III)-PURP complex and an increasing concentrations of Fe(III)-PURP complex(a) and a mixture of Fe(III)-PURP complex and an increasing concentrations of Al(III)-PURP complex(b).

a) [Al(III)] = 1.35 mg L⁻¹, [Fe(III)] = 1) 1.11; 2) 2.23 ; 3) 3.35 ; 4) 4.46; 5) 5.58 ; 6) 6.70 ; 7) 7.81 mg L⁻¹

b) [Fe(III)] = 3.35 mg L⁻¹, [Al(III)] = 1) 0.26; 2) 0.81 ; 3) 1.35; 4) 2.69 mg L⁻¹

[PURP] = 4×10^{-4} M, 50% ethanol, I = 0.1 M (NaClO₄), and pH = 2.5

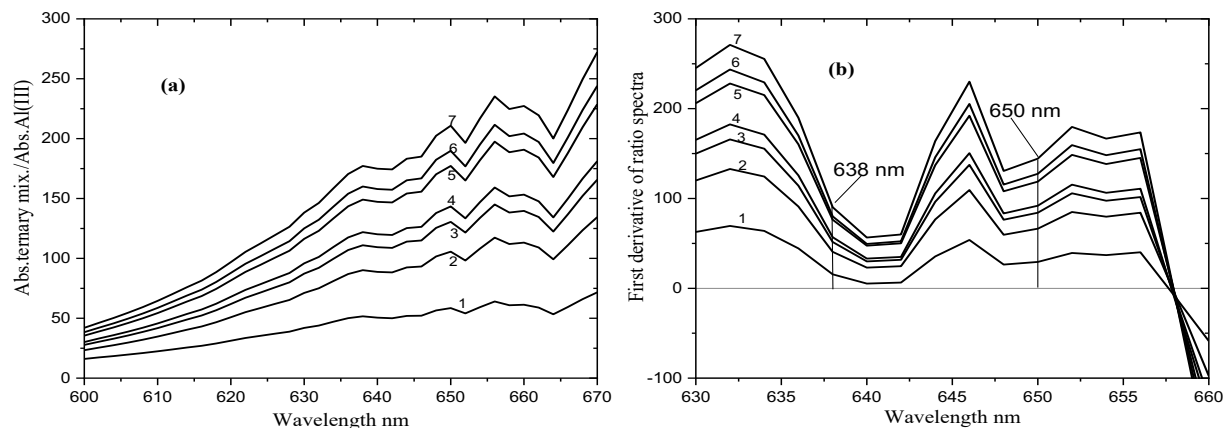


Fig. 4: Ratio spectra (a) and first-derivative of ratio spectra (b) of ternary mixtures of Fe(III)-, Al(III)-, and Ti(IV)-PURP complexes containing increment amounts of iron.

[Fe(III)] = 1) 0.55 2) 1.67 3) 2.79 ; 4) 3.9; 5) 5.02 ; 6) 5.58 ; 7) 6.14 mg L⁻¹, [Al(III)] = 1.35 mg L⁻¹, and [Ti(IV)] = 0.9 mg L⁻¹, [Al(III)] = 1.35 mg L⁻¹ as divisor, [PURP] = 4×10^{-4} M, 50% ethanol, I = 0.1 M (NaClO₄), and pH = 2.5

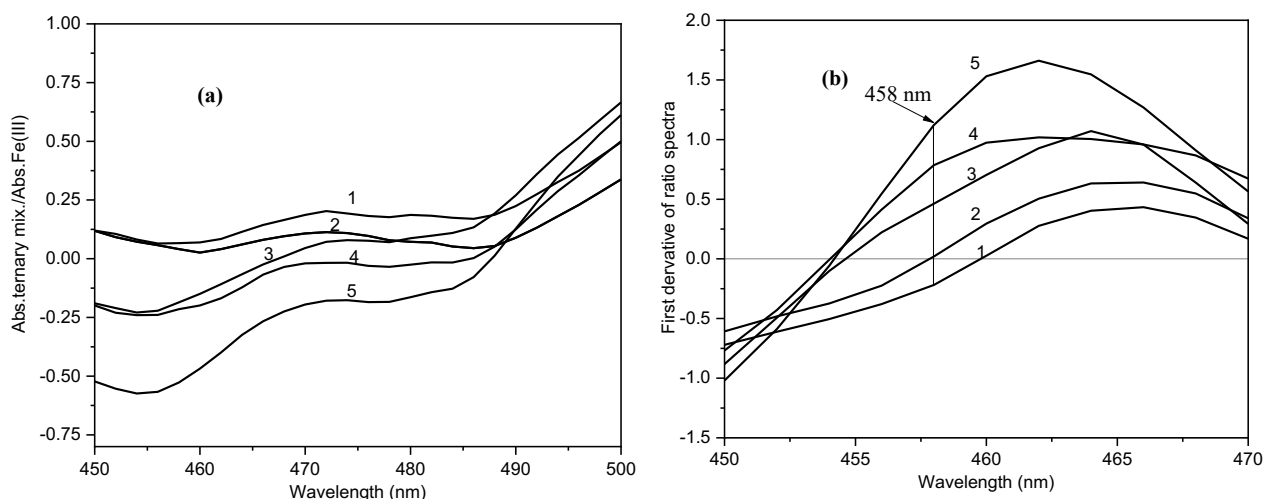


Fig. 5: Ratio spectra (a) and first-derivative of ratio spectra (b) of ternary mixtures of Al(III)-, Fe(III)-, and Ti(IV)-PURP complexes containing increment amounts of aluminum.

[Al(III)]= 1)0.26; 2) 0.81; 3) 1.35; 4) 2.15; 5)2.69 mg L⁻¹, [Fe(III)]= 3.35 mg L⁻¹, and [Ti(IV)]= 0.9 mg L⁻¹, [Fe(III)]=3.35 mg L⁻¹ as a divisor, [PURP]= 4×10⁻⁴ M, 50% ethanol, I= 0.1 M (NaClO₄), and pH=2.5

3.7.2 Calibration Graph and Statistical Results

The calibration graphs prepared by plotting the first derivative divided signal (DD¹) versus aluminum or iron concentrations gave a straight line over a range of 0.269-2.15 mg L⁻¹ of aluminum, and 1.67-5.58 mg L⁻¹ of iron. The regression equations are given in **Table 2**.

4 Applications

The proposed method was applied for the determination of

iron (III) and aluminum (III) in ordinary Portland cement (OPC). Fe₂O₃ and Al₂O₃ concentrations were determined by measuring DD¹ signals at appropriate wavelengths and using the regression equations indicated in **Table 2**. Fe₂O₃ concentration was determined by measuring DD¹ signals at 638 nm and at 650 nm (zero-crossing points of Ti(IV)/Al(III) complex), while the concentration of Al₂O₃ was determined by using Fe(III)-PURP complex as a divisor, and measuring DD¹ signal at 458 nm (zero-crossing point of Ti(IV)/Fe(III) complex). The obtained results were certified using x-ray fluorescence technique **Table 3**.

Table 3: Simultaneous spectrophotometric determination of Fe₂O₃ and Al₂O₃ in Portland cement material.

Material	Proposed method		XRF method	
Cement (OPC)	% Fe ₂ O ₃ 4.95 at 638 nm 4.97 at 650 nm	%Al ₂ O ₃ 4.49	% Fe ₂ O ₃ 5.03	%Al ₂ O ₃ 4.54

5 Conclusions

The proposed method allows the simultaneous determination of Fe(III) (1.6-5.58 mg L⁻¹) and Al(III) (0.27-2.15 mg L⁻¹) in their solutions containing Ti(IV), using derivative ratio-zero crossing technique. This work illustrates the potential of derivative spectrophotometry as a simple, rapid and accurate tool for simultaneous determination of Fe₂O₃ and Al₂O₃ in Portland cement relative to zero order spectrophotometric technique [24],[29].

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