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1,2-Dibenzoyl Cyclopentadiene Derivative as New Potential Chelating Agent in Geological Materials

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In this paper, 2,3-bis(*p*-methoxybenzoyl)cyclopentadiene (DPMBCP) has been studied as a chelating agent and pKa value was determined by means of spectrophotometric measurements. The sigmoid curve of optical density against pH was constructed and pKa value was obtained from log I against pH, having the value of 8.27 ± 0.02 at $\lambda = 421$ nm and temperature $(t) = 25 \pm 0.1$°C. Interaction of Fe^{3+}, Ce^{4+}, La^{3+} with DPMBCP in water/ethanol (1:1) (v/v) solution studied and for Fe^{3+} and Ce^{4+} leads to the formation of complex species in the recommended condition.

The optimum conditions for solvent, the pH and concentration of ligand were studied and interference effects, linear range detection limit, specific absorptivity, Sandell sensitivity and other analytical parameters were also evaluated. The method is sensitive, simple and an alternative for spectrophotometric determination of Fe^{3+} and Ce^{4+}, but not for La^{3+}. The reproducibility for Fe^{3+} is shown by a relative deviation of about 0.67%. This system obeys the Beer's law and is suitable for iron determination in the concentration range from 0.1 to 1 $\mu g/cm^3$, with a correlation coefficient (r^2) of 0.9992. Analytical application has been tested for geological materials (iron-rock), in which the results were compared with atomic absorption measurement.

Very good concordances were obtained between these two different techniques, suggesting the potential of present spectrophotometric method for iron analysis.

Key Words: Iron complex, Cerium complex, Dissociation constant, Spectrophotometry.

INTRODUCTION

DPMBCP belongs to 1,2-diacyl cyclopentadiene compounds characterized by a seven-member ring[1–5], which solely exists in the enol form. The proton chemical shifts for these compounds suggest the presence of a very strong intramolecular hydrogen bond[4, 6, 7]. These compounds are classified by Gilli and Bertolasi[8] as ζ-diketone enols and are potentially capable of forming complexes with metal ions.

Linn and Sharkey[9] prepared 2,3-dibenzoyl cyclopentadiene (DBCP) in neutral atmosphere. Any attempt on the preparation of a sandwich form of iron with DBCP has not been successful, which was attributed to the π-electron delocalization in the cyclopentadiene ring[10]. In spite of extensive studies on the complexation of the β-diketones[11, 12], to the best of our knowledge, no report has appeared on the formation of complexes by this class of compounds.

Iron is the fourth most abundant element in the earth's crust occurring in nearly all types of rocks and soil minerals as both Fe^{2+} and Fe^{3+}.[13] Concerning its biological activity, iron is a highly versatile element, serving as an active centre of proteins responsible for oxygen and electron transference in metalloenzymes such as oxidases and dehydratases[14].

Iron determination and speciation methods in enviromental and biological samples have been developed with high sensitivity. The determination of different oxidation states of iron in a variety of samples is generally achieved by complexation with specific chelating agents followed by a spectrophotometric measurement. Tiron (4,5-dihydroxy-1,3-benzenedisulfonic acid)[15], 1-(2-pyridylazo)-2-naphthol (PAN)[16], dithiocarbonate[17], cupferron [18], 8-hydroxy-quinoline[19], β-diketones[20] and many other chelating reagents have been used for Fe^{3+} determination, after oxidizing the Fe^{2+}. New chelating agents have been introduced both for determination of trace elements and preparing chelating resins. Spectrophotometric[21, 22] or chemiluminescence[23, 24] detection and many other analytical methods have been developed for determination of iron with high sensitivity. In this paper a newly synthesized ligand, DPMBCP, is introduced for determination of Fe^{3+}. Decrease in the absorbance of ligand during complexation was aimed to apply a simple, highly selective and sensitive determination method for iron(III) in geological samples.

EXPERIMENTAL

Materials: DPMBCP was prepared according to the Linn and Sharkey method[9] from lithium cyclopentadiene and *p*-methoxy-benzoylchloride in an argon atmosphere. The yellow crystals were recrystallized from glacial acetic acid to yield yellow needle-like crystals (65% yield), m.p. 157–158°C, ^1H NMR ($CDCl_3$): δ 3.91 (s, 6H), 6.49 (t, J = 3.6 Hz, 1H), 7.02 (d, J = 8.6 Hz, 4H), 7.28 (d, J = 3.6 Hz, 2H), 7.84 (d, J = 8.6, 4H), 18.62 (s, 1H). The prepared compound was investigated by elemental analysis, IR spectroscopy and ^1H NMR. A stock solution (10^{-3} M) of ligand was prepared by dissolving the requisite amounts in pure ethanol and diluted as required to obtain the working solutions. All chemicals (E. Merck) were of analytical reagent grade and were used without further purification. Ce^{4+}, Fe^{3+} in different concentrations were prepared from $Ce(SO_4)_2$, $Fe(NO_3)_3$ standard solutions. $HClO_4$ and NaOH were used for pH adjustment. Interference studies were made using different salt solutions, preferentially in the chloride form (for cations) and sodium (for anions). De-ionized water and pure ethanol were used for preparing solutions.

Apparatus: All spectrophotometric measurements were made with a Shimadzu 3100S spectrophotometer, coupled with a colour plotter model 200 91027 at 25.0°C. Stoppered quartz cells of 1.00 cm optical path length were always utilized. A Varian model AA-20 atomic absorption spectrometer was used for comparing the results. The pH measurements were made with Metrohm Herisau E-603 pH-meter, calibrated regularly before use with standard buffer solutions. All measurements were performed in the presence of 50% ethanol (v/v) at 25°C. Solutions were prepared with deionized water purified with an Advantech Millipore F2HN 6496SC system.

Spectrophotometric analysis: Ligand indifferent solvents was investigated and aqueous/ethanol (1 : 1) (v/v) was selected (Figs. 1 and 2). Spectrophotometric analysis of 2×10^{-5} M ligand solution was investigated in aqueous/ethanolic (1 : 1) (v/v) media and different pH, in the range of 250–500 nm spectral range at 25 ± 0.1°C. The pH values were adjusted by adding appropriate amounts of NaOH and $HClO_4$. Standardization of combined electrode in C_2H_5OH (50%) was

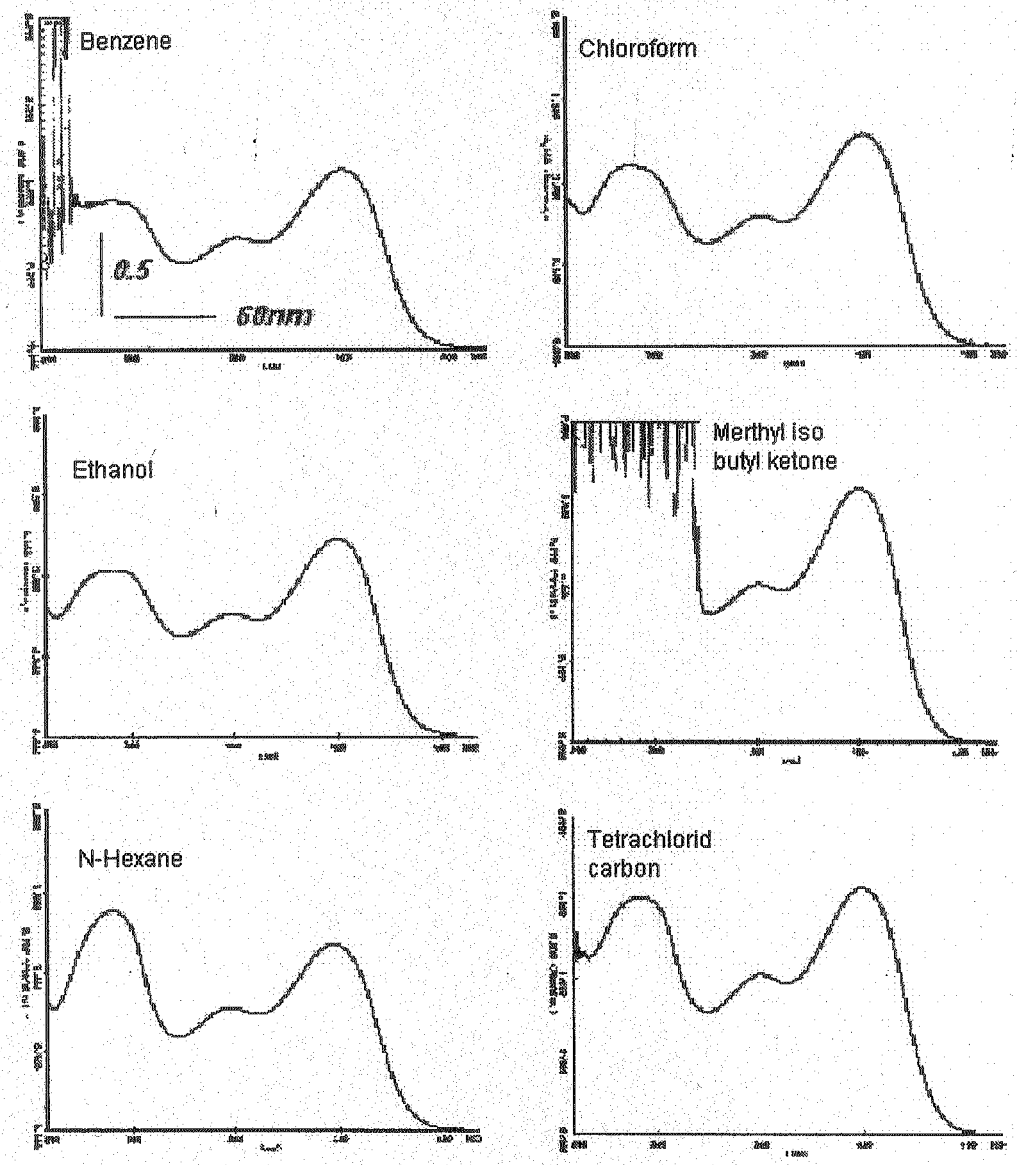

Fig. 1 Ligand in different solvents: DPMBCP = 5.9×10^{-5}

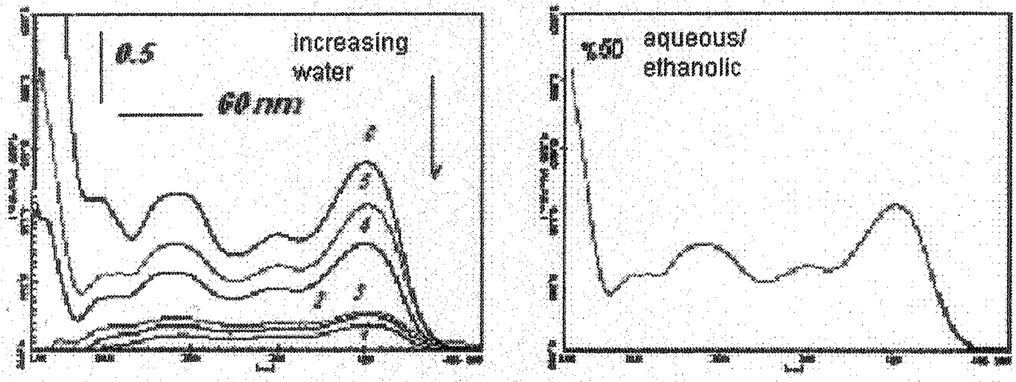

Fig. 2. Ligand in different aqueous/ethanol concentrations: (1) 1.5, (2) 1.38, (3) 1.27, (4) 1.08, (5) 1, (6) 0 (DPMBCP = 2.1×10^{-5})

performed in acidic and basic range as explained in literature[25, 26]. The reported pH values are referred to the suitable solvent scale. The changes in electronic spectra of PDMBCP with pH are shown in Fig. 3.

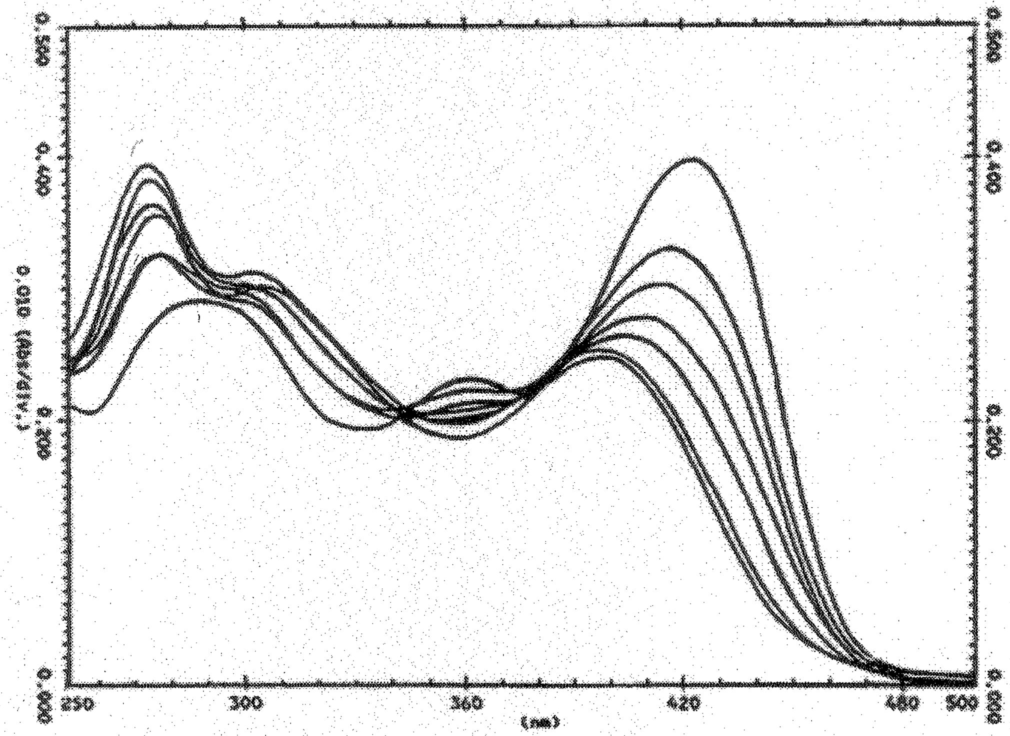

Fig. 3. Spectrophotometric titration of DPMBCP with NaOH in aqueous/ethanolic (1 : 1) (v/v) (DPMBCP = 2×10^{-5}M and pH = 5–10)

Determination of acidic constant: Spectrophotometry is an ideal method for determination of acidic constants when a substance is not soluble enough for potentiometric studies or when its pKa value is particularly very low or high (*e.g.*, less than 2 or more than 11)[27, 28]. The method depends on direct determination of the ratio of the molecular species that is the neutral molecules to the corresponding ionized species in a non-absorbing solution, in which its pH values are either known or measured. A series of solutions in highly acidic and basic media are prepared, their absorbances are measured and the corresponding absorptivities are calculated from the Beer's law $A = \varepsilon_{bc}$. If the concentrations of the species and anionic form of compound and acid dissociation constant of diketone to be [HA], $[A^-]$ and Ka respectively, the following equation could be used:

$$HA \longleftrightarrow H^+ + A^-$$

$$K_a = \frac{[A^-][H^+]}{[HA]} \frac{\gamma_{A^-} \gamma_{H^+}}{\gamma_{AH}} \tag{1}$$

$$pK_a = pH - \log \frac{a_{A^-}}{a_{HA^-}} = pH - \log \frac{(\varepsilon - \varepsilon_{A^-})}{(\varepsilon_{HA} - \varepsilon)}$$

$$= pH - \log I$$

where ε_{HA} and ε_{A^-} are the molar absorptivities of HA and A^- at $\lambda = 421$ nm, respectively, and ε is the total molar absorptivity of HA and A^- at any given pH value at the same wavelength. The following procedure was applied.

A stock solution of 10^{-4} M DPMBCP was prepared in aqueous/ethanolic (1 : 1) (v/v) solution. 2.5 mL of this solution was transferred into a 5 mL volumetric flask and diluted to mark with 0.1 M $HClO_4$ in 50% ethanol solution for preparation of acidic solution of the ligand. For basic solution, 2.5 mL of the stock solution was transferred into a 5 mL volumetric flask and diluted to mark with 0.1 M NaOH in 50% ethanol and the total concentration of compound in forms of HA and A^- was measured. Four series of each sample at different concentrations were prepared $[0.5 \times 10^{-5} - 2 \times 10^{-5}$ M] in acidic and basic solutions and the optical density of each solution was obtained. The UV absorption maxima (λ_{max}) and half protonation values are shown in Table-1.

TABLE-1
pK_a DATA FOR THE STUDIED COMPOUND

Spectral maximum (λ_{max}, nm, (ε))		Acidic measurement			
Anion form[a]	Acidic form[b]	λ^c (nm)	m[d]	pKa	Correlation
395.6 (1.27×10^4)	421.8 (2.087×10^4)	421	1.0149	8.27 ± 0.02	0.9971

a: measured in 1 M NaOH, b: measured in 0.1 M $HClO_4$, c: for pK_a measurement,
d: slope of log I *vs.* H graphs.

For determination of pK_a value, spectrophotometric titration with NaOH was performed and the change of absorbance with pH was utilized, which is depicted in Figs. 4 and 5.

Investigation of Fe^{3+}, Ce^{4+}, La^{3+}: For Fe^{3+} determination, 2.5 mL of the acidic Fe^{3+} solution containing 0.2 M $NaClO_4$ was taken in a 5 mL volumetric flask followed by addition of 2.5 mL (DPMBCP × 10^{-3}) solution and adjusting the pH at 2 and diluting to mark with 0.3 M $HClO_4$, ethanol and de-ionized water. After the complexation was complete, the absorbance of each solution was measured at 421 nm against a blank. The stoichiometry of the Fe-DPMBCP complex was investigated by mole ratio method. In this method the iron concentration was held constant while the concentration of DPMBCP was increased, the absorbance at 421nm was plotted *vs.* the mole ratio of DPMBCP/iron and the result was 2 : 1 (ligand/iron). For Ce^{4+} and La^{3+} determination, solutions containing 0.1 M $NaClO_4$ and 5.9×10^{-5} DPMBCP in different pH was prepared and the absorbances of the complex and the ligand were measured at 421 nm.

RESULTS AND DISCUSSION

Spectrophotometric studies: DPMBCP is not soluble in water but by adding ethanol concentration up to 50% (v/v) the solvation is complete (Fig. 1). This compound is considerably soluble in many organic solvents such as ethanol, benzene, chloroform, methyl isobutyl ketone, N-hexane, carbon tetrachloride as well as in alkaline aqueous solutions (Fig. 2).

In 50% aqueous/ethanolic solution, the electronic spectrum of DPMBCP displays mainly three absorption band maxima, at 421, 361 and 286.4 nm. The intensities of the first two bands decrease on increasing the pH and a new peak appears at about 272.8 nm (UV range). The spectra of DPMBCP in the pH range of 5–12 show the existence of an isosbestic point at 343 nm, indicating acid-base equilibrium in solution for this new reagent. The recorded spectra for this pH range are presented in Fig. 3.

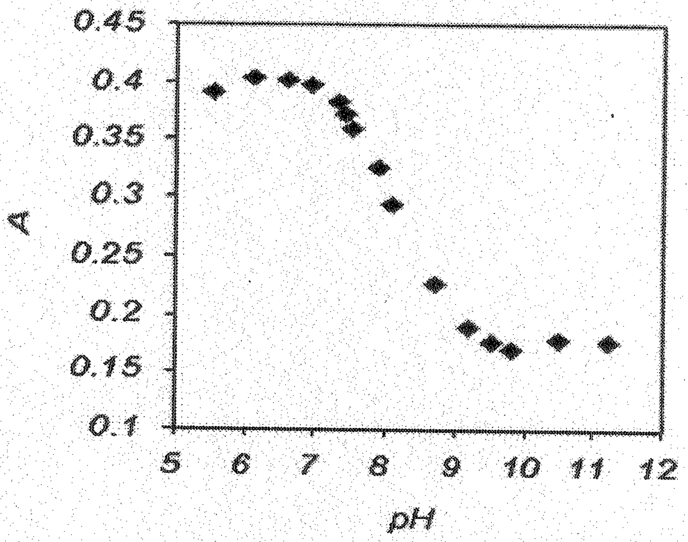

Fig. 4. Sigmoid curve of A-pH for the pK_a determination of DPMBCP (DPMBCP = 2×10^{-5}M and pH = 5–10 in 421 nm)

From the spectrophotometric titrations and the plot of absorbance *vs.* pH and calculating log I, the calculated pK_a in this medium was obtained to be 8.27 ± 0.02.

DPMBCP was quite stable in ethanol and ethanolic solution on standing for over one month. Spectra of these solutions during this period of time did not show any significant changes.

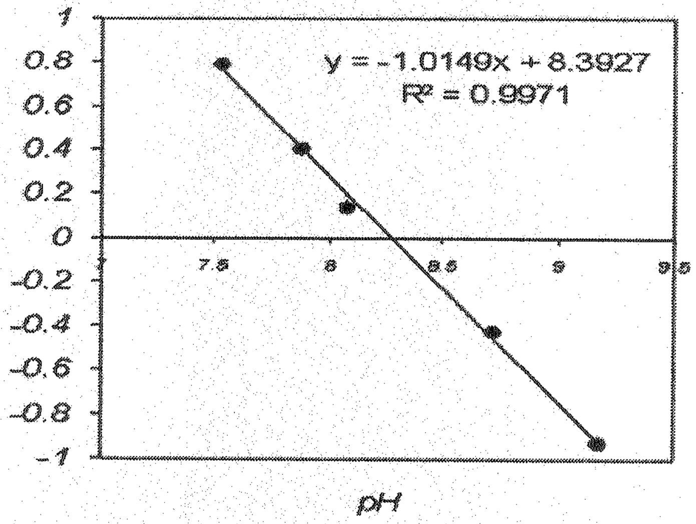

Fig. 5. Linear plot of log I-pH for the pKa determination

Iron, cerium and lanthanim complexation: Addition of cations to the ethanolic/aqueous (1:1) (v/v) solution of the ligand was studied at different hydrogen ion concentrations which for Ce^{4+} and Fe^{3+} leads to the lowering of intensity of the band maximum at 410 and 421 nm (hypsochromic effect) (Figs. 6 and 8). The conditions for effective complexation of Fe^{3+} were improved by studying the effects of various factors such as pH, reagent concentration and ionic strength, in order to develop a sensitive spectrophotometic method for the determination of Fe(III) with the newly synthesized ligand (DPMBCP).

Effect of pH: The influence of pH on the Fe^{3+}-DPMBCP complex was studied to find out the optimum pH range for Fe^{3+} determination. The complexation of Fe^{3+} with DPMBCP into ethanolic/aqueous media was investigated over a pH range of 1–7 (Fig. 7). $HClO_4$ and NaOH were used for adjusting the pH. The complexation of metal ion starts at a pH of 1.0 and reaches its maximum at about 2.0 where the

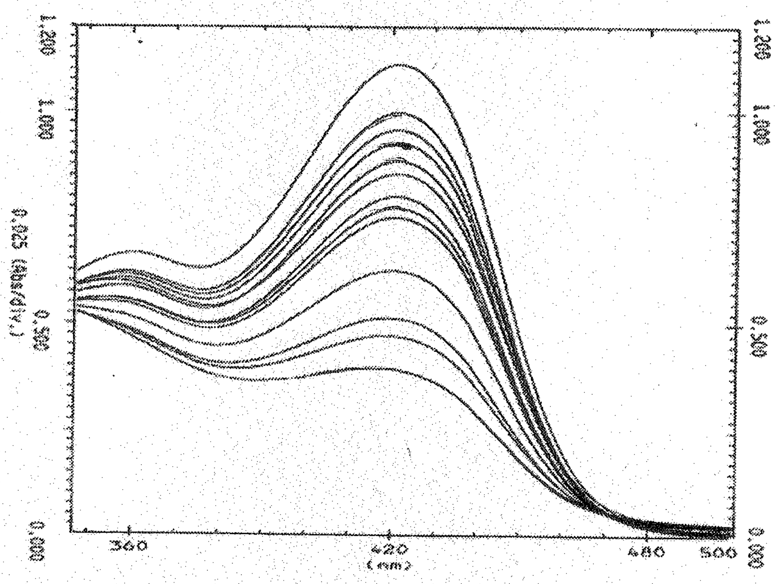

Fig. 6. Absorbance variation of ligand with complexation in different concentrations of iron at pH = 2 (DPMBCP = 5×10^{-5}M and Fe^{3+} = 0.1–1.5 μg/cm³)

difference of absorbance between ligand and complex is at its maximum value. For Ce^{4+}, the influence of pH was studied over the pH range of 1–12 and the complexation of Ce^{4+} reaches its maximum at about 8 after 5 h in 60°C (Fig. 8).

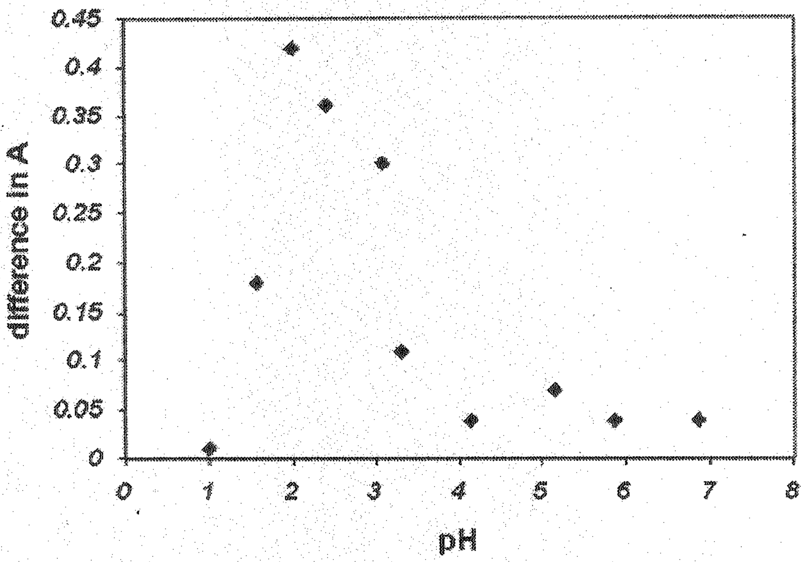

Fig. 7. Effect of pH on the absorbance of ferric-DPMBCP complex (Fe^{3+} = 0.8 g/cm^3, DPMBCP = 5×10^{-5}M

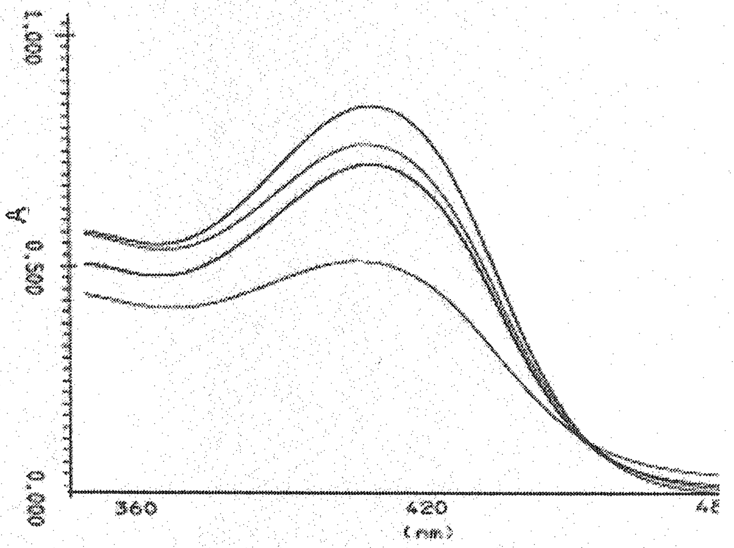

Fig. 8. Absorbance variation of ligand with complexation in different concentrations of Ce^{4+} at pH = 8 (DPMBCP = 5.9×10^{-5} M, Ce^{4+} = 0.422–1.13 μg/cm^3)

Effect of reagent concentration: A series of experiments was carried out at pH *ca.* 2.0 to investigate the type of interaction between Fe^{3+} and DPMBCP in solution. It was found that Fe^{3+} forms a 1 : 2 complex with DPMBCP. The effect of reagent concentration was studied by keeping 0.28 μg/mL Fe^{3+} solution in 0.1 M $NaClO_4$, to maintain the ionic strength constant. Different ligand/metal ratio concentrations were employed (1–10) and the maximum difference in absorbance between ligand and complex was observed to occur at more than 5-fold as shown in Fig. 9.

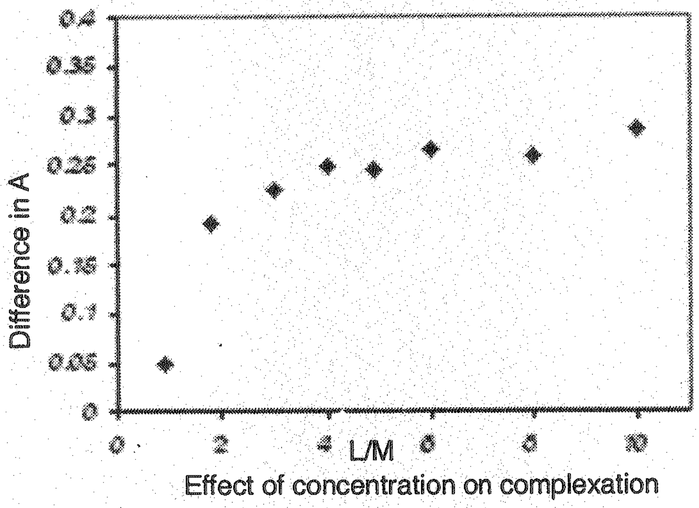

Fig. 9. Influence of DPMBCP concentration on the complexation of iron (DPMBCP = 5×10^{-6}–5×10^{-5} M/L, F^{e3+} = 0.28 μg/cm^3)

Effect of ionic strength and diverse ions: The complexation was performed in different concentrations of $NaClO_4$ (0.001–0.1 M) and no considerable variation was observed in the absorbance of the solutions. The effect of foreign anions and cations on the complexation of iron with DPMBCP has been studied in detail. The tolerance limit was taken as the concentration of foreign ions that caused an error of not more than 5% in the determination of the analyte (Table-2).

TABLE-2
INFLUENCE OF FOREIGN IONS ON THE SPECTRO-PHOTOMETRIC DETERMINATION OF Fe^{3+} (1 μg/cm^3) USING DPMBCP (5×10^{-5} M) AT pH = 2

Foreign ions	Mole ratio	Foreign ions	Mole ratio
Na(I), K(I)	> 1000	Cl^-, Br^-, NO_3^-	100
Ca(II), Mg(II), Ba(II)	100	CH_3COO^-, ClO_4^-	> 1000
Al(III)	50	SO_4^{2-}	10
Cr(III)	10		

Validity of linear equation and correlation coefficient for decreasing absorbance: A calibration curve was made under the optimum conditions. The present studies indicate that the Beer's law was obeyed for Fe^{3+} at the concentration range of 0.1–1 μg/ cm^3, with a correlation coefficient value of 0.9992 was obtained for Fe^{3+} DPMBCP complex. The values of slope and the intercept for the best fitted line were obtained to be 2.45×10^4 and 0.0558, respectively and the limit of detection was 0.06 μg/cm^3.

Precision, accuracy, specific absorptivity, Sandell sensitivity of the method for iron determination: To obtain the precision and accuracy of the method, determinations were carried out for a set of some measuringof 0.56 μg cm^{-3} of Fe^{3+}, under optimum conditions. Calculations revealed that the standard deviation of the method was 0.005 μg cm^{-3} and the relative standard deviationwas 0.67%. Also the specific absorptivity was 0.4191 mL/g cm and the Sandell sensitivity was 2.33×10^{-3} μg cm^{-2},[29] which suggests relatively high precision of the method.

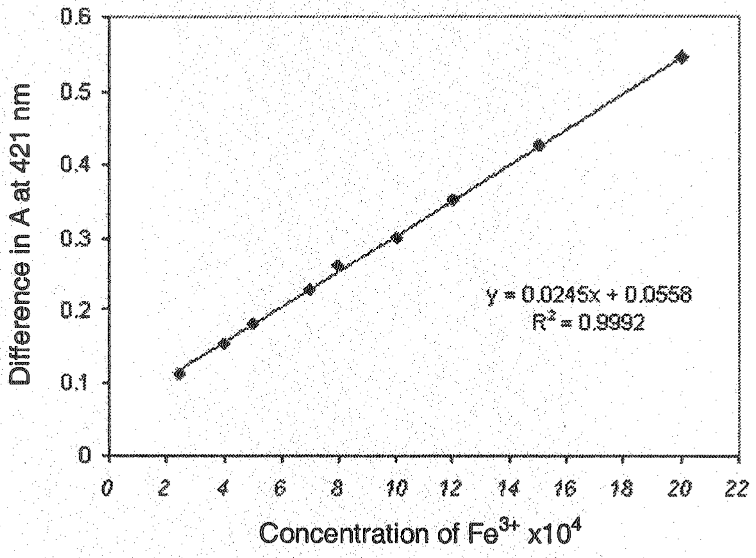

Fig. 10. Calibration curve for the present Fe^{3+}/DPMBCP system under ideal experimental conditions at 421nm (DPMBCP = 5×10^{-5} M, Fe^{3+} = 0.1–1 μg/cm^3)

Applications: Suitable amount of iron rock [standard reference material: bauxite (Dominican) and iron ore], 0.1 g was transferred to a beaker and treated with concentrated $HClO_4$ (30 mL) and HCl (50 mL) under heating and agitation, for complete dissolution. Vapours of HCl were eliminated by continued boiling and water was added to maintain the volume. The final solution free of chloride ion was transferred to a 500 mL volumetric flask and diluted to mark with dionized water. Analytical applications were obtained by applying standard addition recovery test. The results were confirmed by atomic absorption UV-Vis spectrophotometry. The process was repeated four times with each sample and the calculated average values are presented in Table-3. Excellent concordance was obtained between the two methods for the material tested, showing the potential of spectrophotometric method described here.

TABLE-3
EXPERIMENTAL RESULT ENCOUNTERED FOR IRON ROCK THROUGH SPECTROPHOTOMETRIC ANALYSIS AND ATOMIC ABSORPTION[a]

Sample	CFe (ppm), stock solution		
	Spectrophotometry	AAS	E_R (%)
Iron ore	73.84	73.14	0.95
Bauxite	33.07	32.68	1.18

[a]DPMBCP = 5×10^{-5} M, $C_{Ethanol}$ = 50% (v/v).
Blank = acid + mineral solution + ethanol.
Sample = blank + ligand

Conclusion

In this investigation a new reagent DPMBCP was studied in different solvents and the proper solvent mixture chosen for studying and its pK_a was determined.

Decreasing absorbance of the ligand at 421 nm during iron complexation indicates the potentiality of the ligand for a successful determination of Fe^{3+}.

Under the best experimental conditions different absorbances for the ferric complexes and ligand are obtained at 421 nm. The system obeys the linear equation with good precision. It is suitable for iron determination, over a concentration range of 0.1–1 μg/mL. Among diverse ion effects only I^- and HPO_4^{2-} interfered significantly ($E_R > 5\%$).

Analytical application was successfully tested for natural iron-rock and the results were compared with atomic absorption measurements. Very good correlation was obtained between these two techniques, showing the clear potential of spectrophotometric method described here. Excellent stability of complex (at least 3 days) (Fig. 11) and reproducibility were observed for analytical purposes.

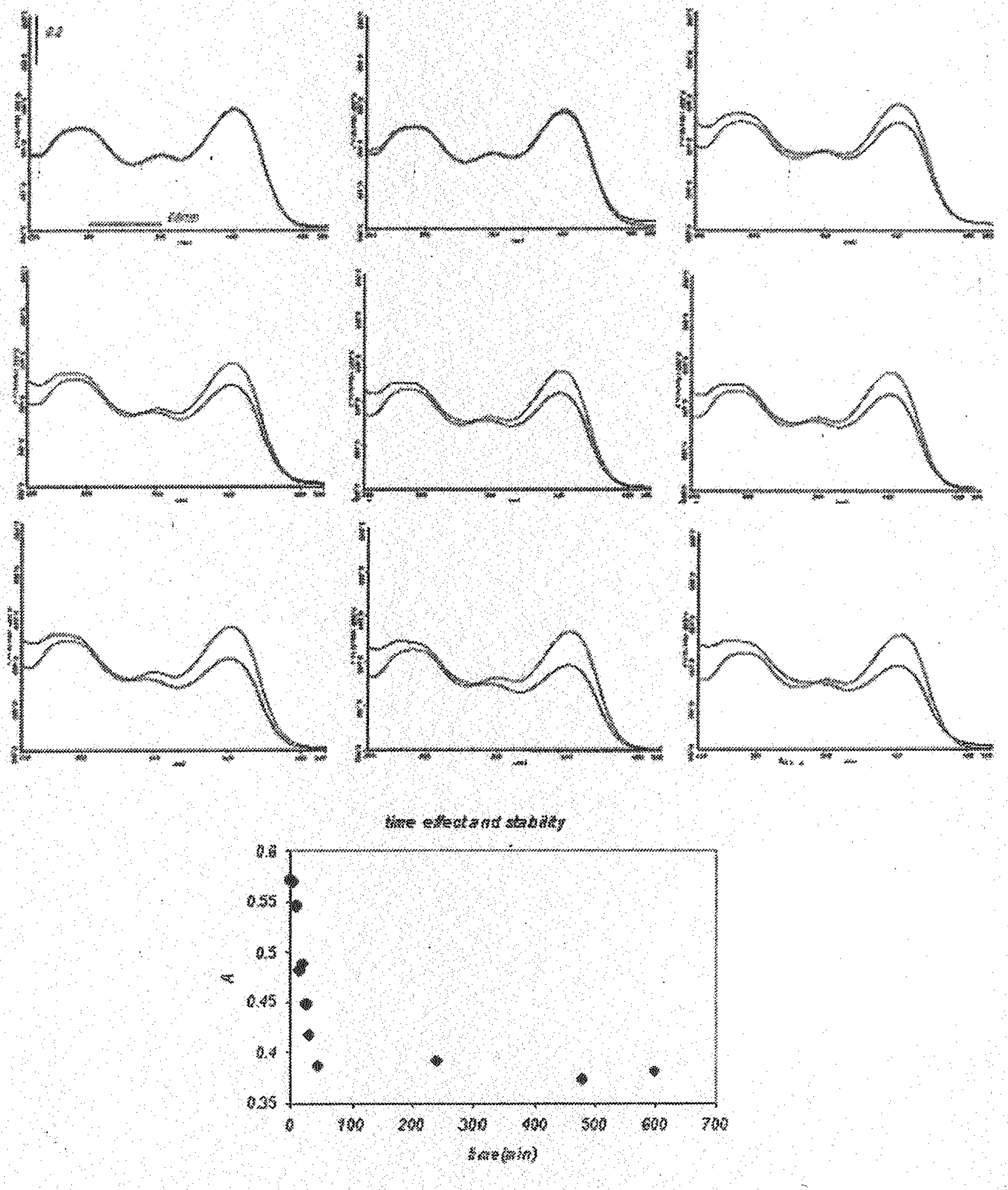

Fig. 11. Effect of time on complexation and stability complex for Fe^{3+}

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