

New Method of Synthesis of Calix-4-arenes as Analytical Reagent for Spectrophotometric Determination of Iron (III)

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الخلاصة

حضر المركب Calix-4-arenes لاستخدامه في التقدير الطيفي لايون الحديد الثلاثي , اوضحت الطريقة الطيفية المقترحة حساسية وانتقائية وسرعة في التقدير, اعتمدت الطريقة على تكوين معقد ازرق مع الكاشف الجديد الذي يعطي امتصاصيه عاليه عند الطول الموجي 592 نانوميتر و دالة حامضية pH=7.0 و حدود الخطية كانت بين $1.18-8.0 \mu\text{g.ml}^{-1}$ مع حد كشف مقداره $0.75 \mu\text{g.ml}^{-1}$ كما اعطت استقرار امتصاصية المعقد لاكثر من 24 ساعة حسب حساسية الطريقة ونسب الاسترجاع ضبطها فكان (R.S.D.% = 0.92%) و (Re% = 99.45%) و (Erel = 0.55 %) . درست طبيعة المعقد الذائب من خلال حساب نسبة الفلز الى الكاشف (1:1) عند دالة حامضية pH=7 و ثابت استقرارية ($0.415 \times 10^{10} \text{ L}^1.\text{mole}^{-1}$) . تم تحديد الظروف المثلى لتكوين المعقد. كما طبقت الطريقة المقترحة بنجاح لتقدير الحديد الثلاثي في النماذج التحليلية .

Abstract:

A compound of Calix-4-arenes was prepared, as a sensitive and selective spectrophotometric method was proposed for the rapid determination of Iron (III) in analytical sample, the proposed method was based on the formation blue complex with Calix-4-arenes as a chromogenic reagent that has a highly absorption at λ_{max} 592 nm. The reaction was instantaneous at pH=7.0, the absorbance of complex was stable for about 24hr. Linearity was observed from $1.18-8.0 \mu\text{g.ml}^{-1}$ with detection limit of $0.75 \mu\text{g.ml}^{-1}$. Recovery and relative error values of precision and accuracy of method were found to be R.S.D.% = 0.92%, Re% = 99.45% and Erel = 0.55 % . The nature of complex showed that (Metal : Ligand) ratio was 1:1 at pH=7 and the stability constant of ($0.422 \times 10^{10} \text{ L}^1.\text{mole}^{-1}$). The influence of chemical and physical parameter and are evaluated . The proposed method was applied successfully to determine Fe (III) in analytical sample.

Introduction:

The calixarenes are a class of cyclooligomers synthesized via a phenol-formaldehyde condensation. The rigid conformation calixarenes enables to act host molecules as a result of their preformed cavities. By functionally modifying either the upper and/or lower rims (the upper rim means use the bulk and long chain substitution in *para* position while the lower rim the substituent's linkage at phenolic oxygen), it is possible to prepare various derivatives with differing selectivities for various guest ions and small molecules. Calixarenes lend themselves well to many applications because of the multiplicity of options for such structural elaboration. Calixarenes to be used in ionselective electrode (ISE) and bulk optode sensing devices, they must be immobilised into organic membranes^[1-3] (films/coatings) which are hydrophobic in nature. Furthermore, if aqueous analysis is desired, the calixarenes must be water insoluble otherwise immobilisation would be undermined by water dissolution of the ionophore from the device. It is essential that the calixarenes used in this way be lipophilic with very low water soluble materials.^[4-8]

The McKervey group began work on calixarene synthesis back in the 1980s. Their first major accomplishment in the field involved the modification of the lower rims of the tetra-, hexa- and octa- calixarenes by the introduction of a series of acetate esters. The calixarene ester derivatives were shown to have characteristics which make them attractive agents for use in potentiometric ion sensors. The resulting calixarenes demonstrated outstanding selectivity for various cations. Calixarenes displayed selectivity toward the sodium cation. It was reasoned that the presence of the *t*-butyl groups in the upper rim forced the calixarene into a permanent cone conformation which allowed the esters to form the necessary cavity for coordination^[8-10].

In this work, synthesis, characterization and analytical study of Calix-4-arenes were used as organic reagent for spectrophotometric determination of Fe(III), also a new spectrophotometric method is described for the determination of Fe(III) in analytical sample which that use in the work.

Materials and Methods:

Instruments

Infrared spectrum was recorded on FT-IR Test scan Shimadzu model 8400 Fourier transform infrared spectrophotometer covering the range 400-4000 cm^{-1} . The electronic spectrum was recorded in ethanol on Unico model 4802UV/Vis double beam spectrophotometer recording. $^1\text{H-NMR}$ spectrum in $\text{DMSO } d_6$ with TMS as internal standard were obtained from a JeolFX-90Q Fourier $^1\text{H-NMR}$ spectrometer at university of London, college of Queen Mary. Molar conductance of solid

complex in DMSO (dimethyl sulfoxide) was measured by using WTW-Terminal 740 digital conductivity meter. pH measurements were carried out using WTW pH meter model 720. Gallen kamp capillary melting point apparatus was used to measure the melting points of the ligand and its complexes.

Reagents:

All chemicals were used in the present investigation are of analytical grade from Fluka and Aldrich companies

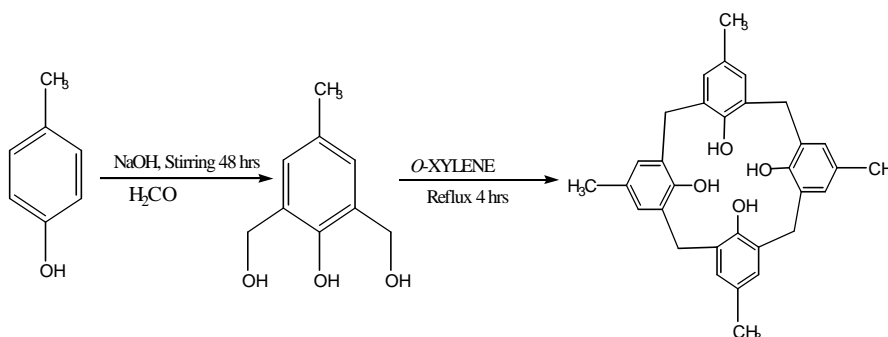
All solutions were prepared with distilled water.

Preparation of [2,6-dimethylol 4-methyl phenol]

To a solution of NaOH (50g, 125mmole) in H₂O (200mL) was added *p*-cresol (108g, 100mmole). The mixture was stirred until a clear brown solution was obtained, stirring was continued while a (37%) solution of (CH₂O) (formaldehyde) (215g, 200mmole) in H₂O was added with contentions stirring. The yellow solution was allowed to stand for 48hrs. , after which time a white solid had precipitated. This was filtered and washed with saturated NaCl solution (200mL). The white precipitate was dried under vacuum. The Na salt [Na(2,6-dimethylol-4-methyl phenolate)] was dissolved in 1.5 times the amount of water and neutralized with dilute acetic acid with stirring. The free alcohol crystallized out as white crystals, recrystallised from acetone- water (3:1) ratio, filtered and dried to give 130g, (90%) product, melting point (128°C).^[11]

Preparation of [Calix]-4- arenes

The condensation reaction of four equivalent of 2,6-dimethylol 4-methyl phenol (100 mmole, 67.2 g) in (200 mL) of *O*-xylene, the mixture was stirred half hour, then allowed to reflux to four hours, the orange precipitate was formed, the result precipitate washed in (5 mL) cold methanol, and (25 mL) 2% citric acid, the two layer solution were obtained, separated by equalized funnel, the organic layer take and dried by MgSO₄, filtered, the filtrate dried by vacuum, the deep yellow precipitate yielded, 65g, (33%). The preparation of ligand was showed in Scheme1.



Scheme-1: Synthesis route of Calix-4-arenes ligand

Preparation the solid complex of Fe(III)

(0.2 mmole) ligand mixed with 15mL of ethanol, then 0.2mmole of FeCl₃.6H₂O that dissolved with a minimum amount of ethanol (5 mL) in a 50ml beaker , that precipitate by reflex about 2hr. the complex filtrated and purification , than dried and stored in tightly closed container. Some physical properties of the prepared ligand and it's complex were tabulated in (Table-1).

Compound	Molecular weight(g/mole)	λ_{\max} nm	Color	Melting point	Conductivity S.mol ⁻¹ .cm ²
Reagent	480.590	306	Yellow-brown	108 C°	6.42
Fe (III)-complex	601.432	592	blue	230 C° Dec.	369.4

Table-1: Some physical properties of reagent and Fe (III)-complex

Results and Discussion

I-Characterization of ligand

Electronic spectra

The ultra violet spectrum of bis(hydroxy methyl) p-cresol and calyx-4-arens *Fig (1)* and *Fig (2)* respectively, appeared , peaks at 284nm ($\epsilon_{\max} = 1154 \text{ molar}^{-1} \text{ cm}^{-1}$) of starting material and (245,284 nm) ($\epsilon_{\max} = 1383,1135 \text{ molar}^{-1} \text{ cm}^{-1}$)due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ respectively

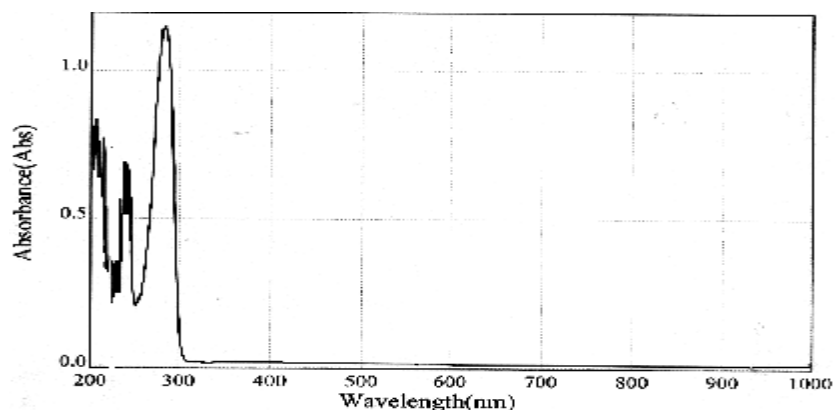


Fig-1: UV-Vis spectrum of 2,6-dimethylol 4-methyl phenol

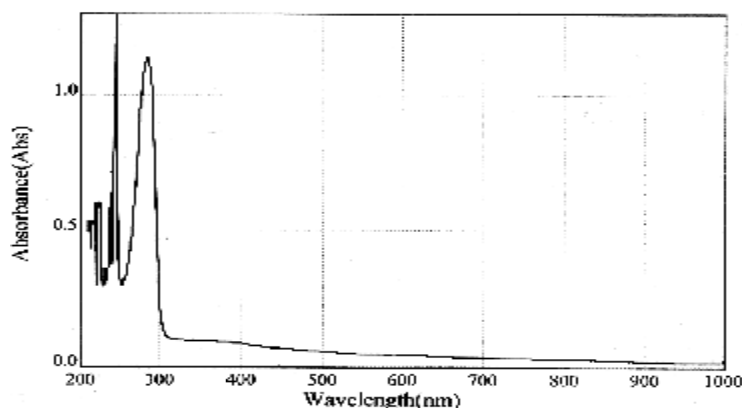


Fig-2: UV-Vis spectrum of [calix]-4-arenes

¹H NMR spectra

The ¹H NMR spectrum of [calix]-4-arenes Fig (3) shows signal at ($\delta=8.35$ ppm ,4H) assigned to Ar-OH groups , The signals at ($\delta=7.10$ ppm ,4H , $\delta=6.25$ ppm ,4H) attributed to aromatic protons of four benzene rings, due to the aromatic rings are exist in twested configuration the Ar-CH₂ groups appears twin signals at ($\delta=3.50,3.20$ ppm ,8H) and methy groups Ar-CH₃ shows twin signal at ($\delta=2.25,2.10$ ppm ,12 H),the signal at ($\delta=2.60$ ppm) assigned the solvent DMSO-d⁶.

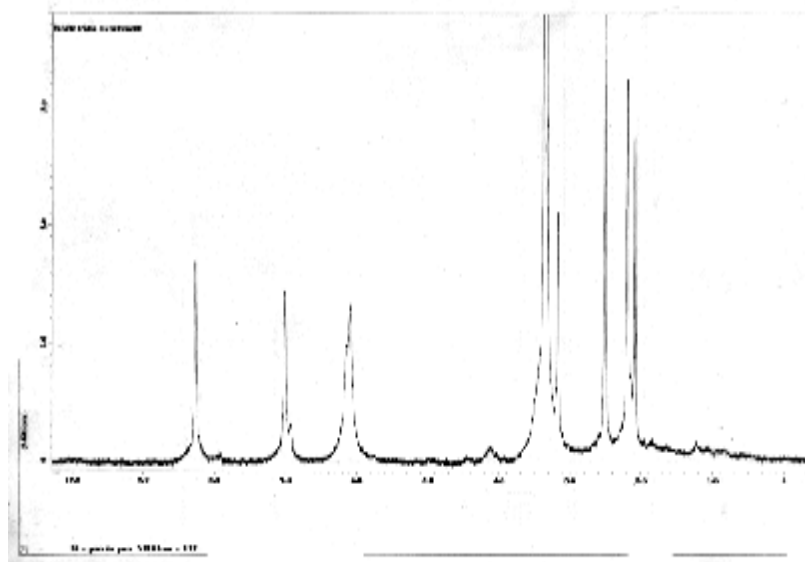


Fig-3: ¹H NMR spectrum of [calix]-4-arenes

FT-IR spectra

The IR spectrum of *bis* (hydroxyl methyl)-*p*-cresal (Fig-4) displayed two bands at 3400cm^{-1} and 3308 cm^{-1} can be aromatic and aliphatic hydroxyl groups respectively. The weak bands at 3050cm^{-1} and $(2893)\text{cm}^{-1}$ assigned to $\nu(\text{C-H})$ stretching of aromatic aliphatic (C-H) respectively ,the other bands at $(1568.1442$ and $1205)\text{cm}^{-1}$ due to the vibration frequencies of rings .While the IR spectra of (calyx)-4-arenes . (Fig-5) shows the disappearing of band at 3400 cm^{-1} due to aliphatic (OH) and the shifting of other bands indicating of the obtaining of calix-4-areanes.

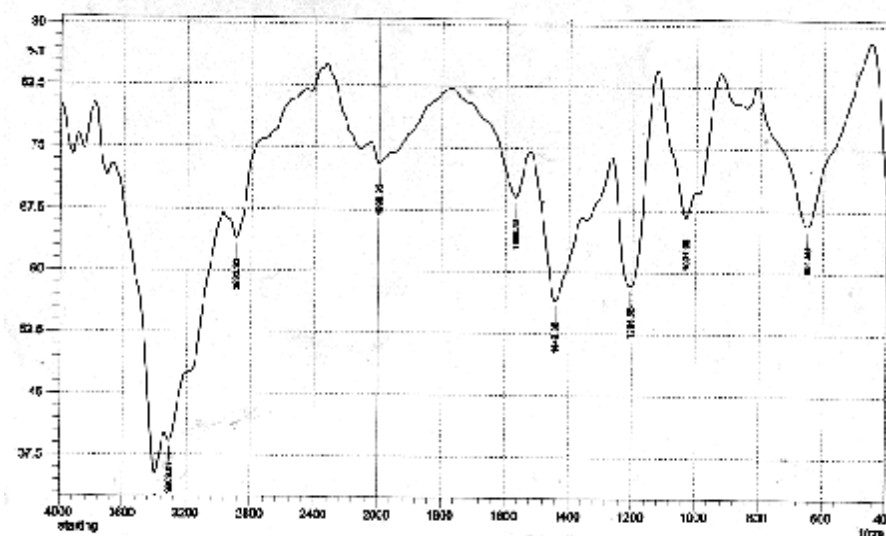


Fig-4: FT-IR spectrum of 2,6-dimethylol 4-methyl phenol

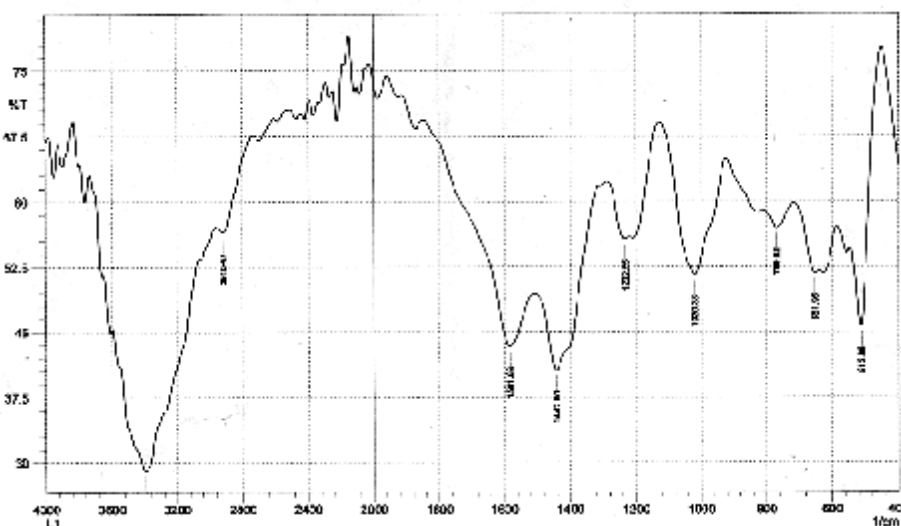


Fig-5: FT-IR spectrum of [calix]-4-arenes

II-Characterization of complex

Electronic spectra

The electronic spectral data of the ligand and its complexes were recorded in DMSO. The UV-Visible spectrum of the ligand, Fig (2) shows twin absorption peak at (245, 284 nm) ($\epsilon_{\max} = 1383, 1135 \text{ molar}^{-1} \text{ cm}^{-1}$) due to the $\pi \rightarrow \pi^*$ and due $n \rightarrow \pi^*$ transitions respectively^[12]. While the electronic spectrum of the Fe(III) complex Fig (6) exhibited the following data .

The Fe(III) complex shows peak at 252nm (39682 cm^{-1}) ($\epsilon_{\max} = 3700 \text{ molar}^{-1} \text{ cm}^{-1}$) and at 333 nm (30030 cm^{-1}) ($\epsilon_{\max} = 3920 \text{ molar}^{-1} \text{ cm}^{-1}$) assigned to intraligand charge transfer , the peak at (592)nm (16891 cm^{-1}) ($\epsilon_{\max} = 651 \text{ molar}^{-1} \text{ cm}^{-1}$) and shoulder peak at 960nm, (10416 cm^{-1}) ($\epsilon_{\max} = 230 \text{ molar}^{-1} \text{ cm}^{-1}$) that attributed to d-d transition, which are suggesting the existence of ${}^4T_{1g} \rightarrow {}^4T_{2g}$ and ${}^4T_{1g} \rightarrow {}^4A_{1g}$ transitions which that corresponding with an octahedral geometry of Fe(III) ion^[13]

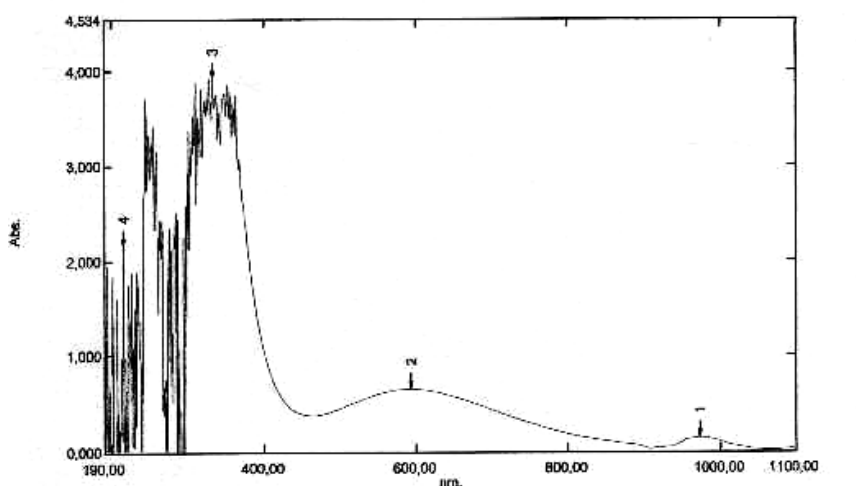


Fig-6: UV-Vis spectrum of Fe(III)-complex

IR spectra

The infrared band of the ligand and complex of Fe(III) assignments that the broad band at 3400 cm^{-1} in the free ligand spectrum Fig(5) which assigned to $\nu(-\text{OH})$ stretching.^[14] the lower frequency for $\nu(-\text{OH})$ due to hydrogen bonding^[15], this band in IR spectrum of complex was shifted and reduced intensity due to complex formation(2) There is also a shifting noticed in the $\nu(\text{C-O})$ of phenol group from 1232 cm^{-1} toward 1390 cm^{-1} producing another evidence about involvement of phenol group in coordination with metal ions *via* oxygen atom^[16]

New bands in the region 451 cm^{-1} were assigned in the spectra of metal complexes. These bands were not present in the spectrum of ligand, and they due to

$\nu(\text{M-O})$ vibration ^[17]. The appearance of these bonds support the involvement of hydroxyl groups and oxygen atoms in complexation.

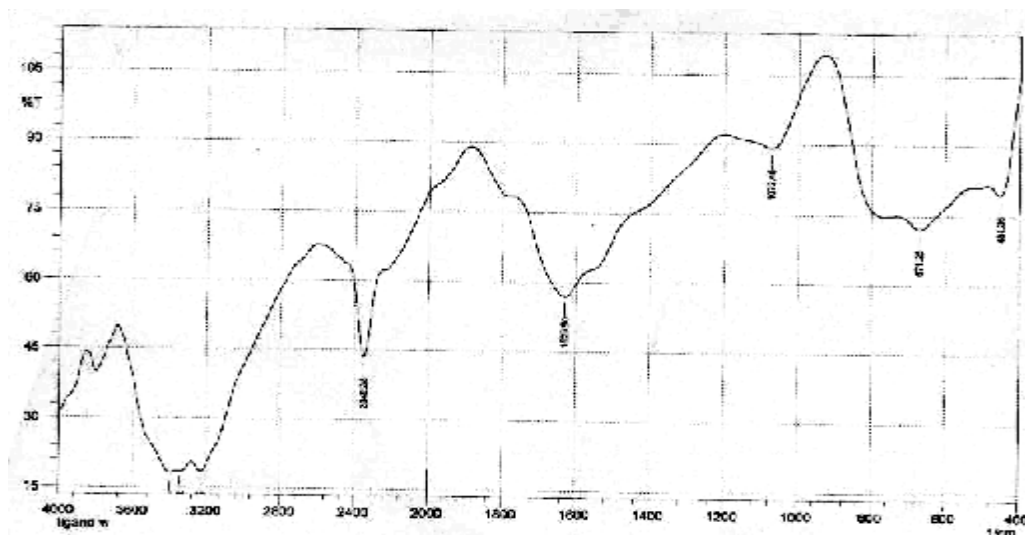


Fig-7: FT-IR spectrum of Fe(III)-complex

Optimization study of the Fe (III)-complex

Fe (III) ion react with Calix-4-arenes in neutral medium to form a violet complex that has a maximum absorption at λ_{max} 592 nm Fig (6) . The absorbance of the blue complex is directly related to the concentration of Fe (III) and that can be used for its spectrophotometric determination. The development of the color intensity and stability of complex depends on the reaction condition and were optimize as follows:

Influence of pH

The pH was studied between (3-9) adjusted by means of dilute HCl and NaOH solution, where the maximum absorbance obtained in the range of (pH =7). At pH > 7 a decreases in absorbance because the precipitation of Fe(III) complex or form unstable ionic complexes ^[18].

Influence of time:

The color intensity reached a maximum after Fe(III) solution had been reacted immediately with reagent and become stable after 10 min , therefore 10 min. development time was selected as optimum in the general procedure. The blue complex was stable for 24 hr.

Order addition effect

The effect of order addition in absorbance of formation complex, depended a two sequence that tabulated in *Table 2*

No.of test	Sequence of addition	Abs. of Fe(III)-complex
1	M+L+pH	0.092
2	L+M+PH	0.117

**Table-2: Effect of order addition, $[Fe^{3+}] = 10 \mu g.ml^{-1}$, $[L] = 200 \mu g.ml^{-1}$
M= Fe^{3+} , L=reagent**

Influence of metal concentration

When various concentration of metal solution in the range of (1–60 $\mu g.ml^{-1}$) were added to fixed amount of reagent [Calix]-4- arenes 200 $\mu g.ml^{-1}$. Concentrations of metal 40 $\mu g.ml^{-1}$ give the highest absorbance Fig (8) and were for further experiments.

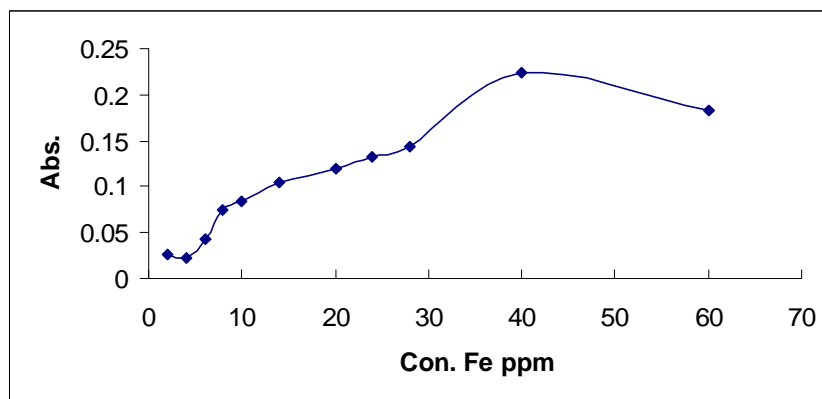


Fig-8: Concentration of metal effect, $[L] = 200 \mu g.ml^{-1}$, pH=7

Influence of reagent concentration

When various concentration of [Calix]-4- arenes solution in the range of (5 – 250 $\mu g.ml^{-1}$) were added to fixed amount of Fe(III) 40 $\mu g.ml^{-1}$. Concentrations of reagent 200 $\mu g.ml^{-1}$ give the highest absorbance Fig (9) and were for further experiments.

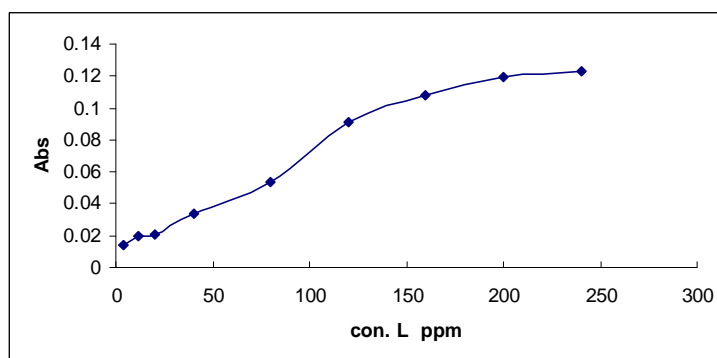


Fig-9: Concentration of ligand effect, $[Fe^{3+}] = 40 \mu g.ml^{-1}$, pH=7

Stoichiometry of complex

The stoichiometry of the complex was investigated using mole – ratio and job method under the optimizes conditions. The result obtained Fig (10) and Fig (11), show a 1:1 metal to reagent complex was formed. The formation of the complex may probable be occur as follows

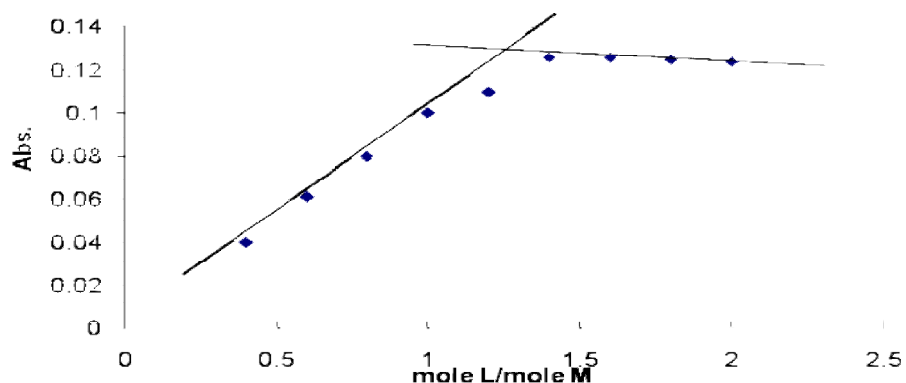


Fig-10: Mole ratio of Fe (III)-complex

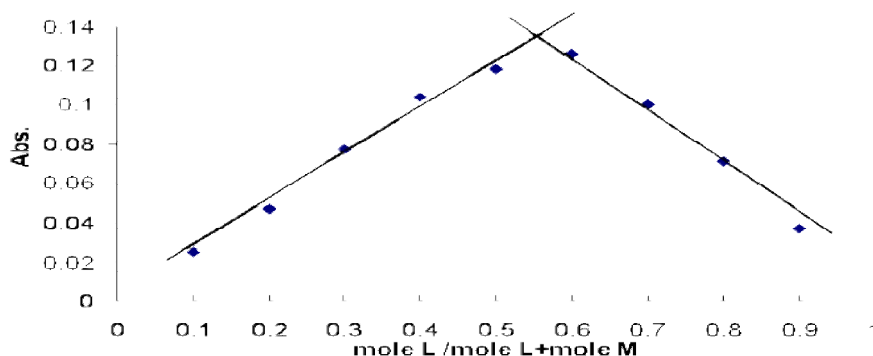


Fig-11: Job's method of Fe (III)-complex

As applied to the molar ratio method, stability constants are obtained spectrophotometrically by measuring the absorbance of solutions of ligand and metal mixture at fixed wavelength λ_{max} and pH values. The degree of formation of the complexes is obtained according to the relationship^[19], $K = (1 - \alpha) / \alpha^2 c$, and $\alpha = (A_m - A_s) / A_m$, where A_s and A_m are the absorbance's of the partially and fully formed complex respectively at optimum concentration. The complex have stability constant $0.415 \times 10^{10} \text{ L.mole}^{-1}$ that appear the complex highly stability which can used a reagent to spectrometric determination of Fe(III) .

Calibration curve

Under the optimum condition linear calibration graph Fig (12), was obtained over the concentration range of (1.18 -8.00 $\mu\text{g.ml}^{-1}$).The limited of detection (signal/ noise = 3) was $-0.75 \mu\text{g.ml}^{-1}$ and the correlation coefficient was 0.974.

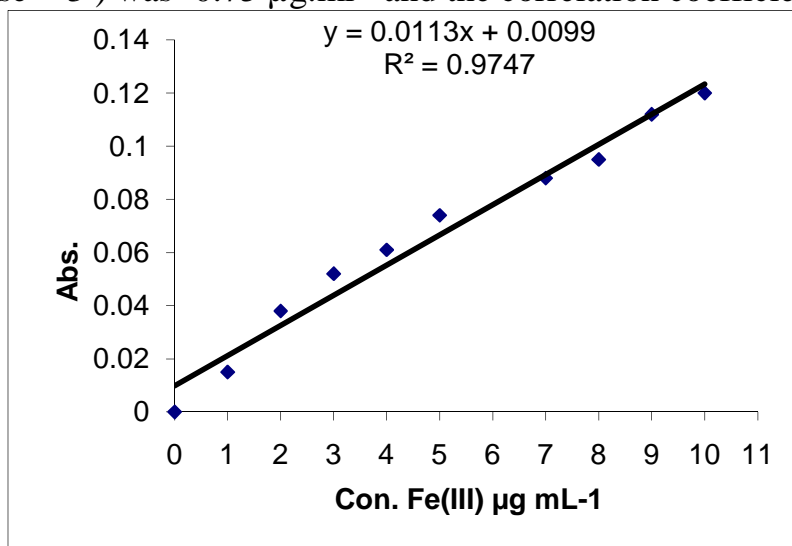


Fig-12: Calibration curve of Fe (III)-complex

Precision and Accuracy

The relation standard deviation evaluated from five independent determination of $10 \mu\text{g.ml}^{-1}$ of Fe(III) was 0.92%, this result show that the method is highly precise while the accuracy of the method was determined by calculating the Erel% and Re% for and $10 \mu\text{g.ml}^{-1}$ of Fe (III) which was found to be 0.55% and 99.45% respectively.

Influence of foreign ions

The selectivity of the proposed methods was investigated by the determination ($10 \mu\text{g.ml}^{-1}$) of Fe (III) in the presence of a series of $10 \mu\text{g.ml}^{-1}$ of cations and $100 \mu\text{g.ml}^{-1}$ anions at pH =7 (Table 3 and Table 4 respectively) . The results show the tolerance limit was taken as the amount that caused an error of 0.112 in the absorbance.

Species	Absorbance of Fe(III) complex	Error %
Complex without addition	0.112	---
Ni²⁺	0.072	35.71
Zr⁴⁺	0.103	8.04
Al³⁺	0.115	-2.68
Mn²⁺	0.089	20.53
Hg²⁺	0.096	14.29
Cd²⁺	0.103	8.036
Mg²⁺	0.108	3.57

Table-3: Determination tolerance limits of some foreign cations

Species	Absorbance of Fe(III) complex	Error %
Complex without addition	0.112	---
NO₃⁻	0.096	14.29
F⁻	0.001	99.11
C₂O₄⁼	0.077	31.25
Ac⁻	0.034	69.64
SO₄⁼	0.085	24.11
CrO₄⁼	0.098	12.50
SCN⁻	0.063	43.75

Table-4: Determination tolerance limits of some foreign anions

Which they are also reacting with Calix-4-arenes reagent at the same choosing conditions and they were masked by using suitable masking agent . The results obtained are summarized in Table 5.

Masking agent 0.5 ml (0.01M)	Absorbance of Fe(III)-Complex
Complex without addition	0.112
EDTA	0.010
Thiourea	0.017
Ascorbic acid	0.012
Potassium cyanite	0.012

Table-5: Effect of masking agents

Analytical application

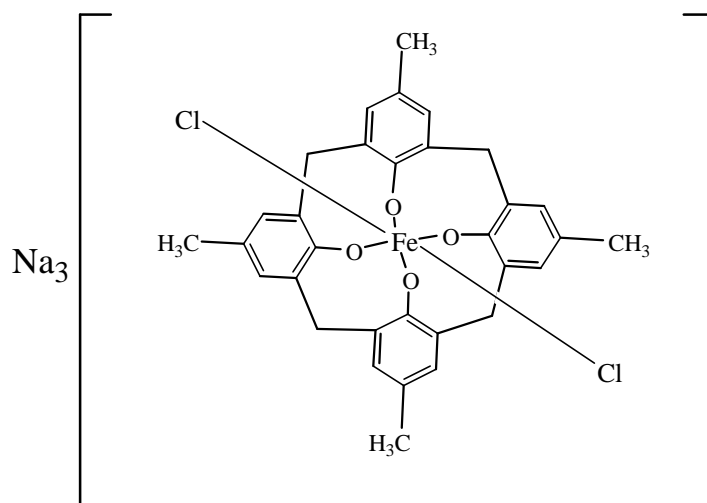
A validity of the method was checked successfully by determine the Fe(III) in 0.5 gm of clay sample dissolve in 1L than prepared solution $10 \mu\text{gml}^{-1}$ of Fe(III) than determined at the optimum conditions of the method this method show a low difference of iron (III) concentration by using the calibration curve ,the data of application tabulated in (Table-6) .

Sample	Concentration of Fe(III) prepared μgml^{-1}	Absorbance measured	Concentration of Fe(III) measured μgml^{-1}	wt/wt% measured of Fe(III)	Error %
Prepared Fe(III)	10	0.134	9.945	99.45%	0.55%
Clay sample (Pantonat)	-----	0.180	13.34	2.7%	-----

Table-6: Application data of determination of Fe (III) in clay sample

Suggestion of structural formula of Fe(III) complex

According to these results from FT-IR spectrum, absorption spectra study and conductivity measurement while the composition of the complex was studied by Job's method and mole ratio method. Both methods indicated that the ratio of metal ion to ligand molecules was 1:1(M:L). The octahedral geometry around Fe(III) ion can be suggested, as follow



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