SPECTROPHOTOMETRIC DETERMINATION OF SULPHATE WITH BARIUM – HEMATOXYLIN COMPLEX

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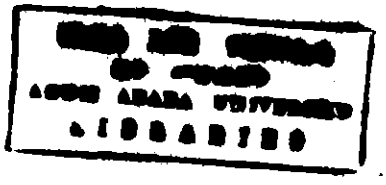

By

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Abstract

Spectrophotometric Determination of Sulphate with Barium-Hematoxylin Complex

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The determination of sulphate by using Barium - hematoxylin complex has been done for the quantitative determination of sulphate in soil and ground water samples. The formation of complex between Barium and hematoxylin has been studied and the absorbance was measured spectrophotometrically at λmax 556nm. The ratio of the ligand to metal was dormant by mole ratio method and was found to be 1:1. The reaction of a sample solution containing sulphate with the Barium-hematoxylin complex decreases the absorbance of the complex and this decrease in absorbance is directly proportion at to the amount of sulphate present and this was the basis of our method. The effect of experimental variables has been studied to establish the optimum conditions of the complex formation. It has been found that consistent and reproducible results are obtained by carrying out the reaction at room temperature for 30 minutes. The colour system has been found to obey Beer's law in the concentration range 0.5 - 2.2 μg ml^{-1} of sulphate. The detection limit and precision of the method were found to be 0.014 μg/ml and 0.71% respectively. On the basis of these studies, a simple

and precise method has been developed for the determination of sulphate. The method has been developed to the analysis of soil samples and ground water. The results obtained have been compared with other methods. The proposed method has been found to give results which are in good agreement with those of routinely used methods.

1. INTRODUCTION

The use of organic reagents for analytical application has been getting increasing importance in Spectrophotometric, Gravimetric, Volumetric techniques, Extraction in Column Chromatography and TLC for elution as well as detection. They are also often used in combination with many instrumental techniques, such as Spectrophotometry, Fluorometry, Electrometry, Atomic Absorption, Ion exchange etc.

The analytical requirements imposed by the complex composition of the substance has led to rapid advances in analytical chemistry mainly in the field of new instrumental techniques. However, the chemical reaction of a suitable reagent with the substance to be determined still remains the true basis of numerous methods of detection, separation and determination. In this respect organic reagents play a predominant role and find wide application in spectrophotometric methods, titrimetric, spotests and last but not least in separation methods (precipitation, masking, solvent extraction and ion exchanger) and preconcentration procedures.

The tests for and determinations of substances with organic reagents can often be preformed with higher sensitivity and selectively . The separations is also more effective if organic reagents are employed. Organic reagents are attractive for the simple reason that a large number of them are known and there fore the scope and number of their application in analytical practice continue to increase. Photometric determination of inorganic substances with

organic reagents is most frequently based on reactions which yield products absorbing (emitting) radiation with in the frequency range of electronic spectra. The absorption of UV and visible radiation is thus measured with spectrophotometer.

Determination of Inorganic Anions

Photometric methods of determining non-metals are less studied field of photometric analysis compared with determination of metal. Many non-metals do not form coloured compounds and their determination is therefore based on reactions in which coloured compounds are destroyed. Reactions in which heteroligand (tertiary, mixed) complexes are formed have come into broad use during the past years. They have significantly contributed towards the development of new photometric methods for the determination of non-metals. For example, the only method available for direct determination of fluoride ion is based on the reaction in which a hetero ligand complex of cerium with alizarin and fluoride ion is formed [1-4]. Some extraction photometric methods of determining other non - metals are also based on the formation of such complexes.

The determination of anions using other methods such as electro analytical methods , volumetric, and gravimetric methods are available, however employing organic reagents and determining photometrically is still little known.

Despite the fact that, organic reagents form complexes

with metals, they can also be applied to the determination of inorganic anions using displacement reactions.

Theory and characteristics of Spectrophotometric methods

Spectrophotometric methods are commonly used for the determination of inorganic substances with organic reagents. The reliability of the method depends on the nature of the organic reagent used. Organic reagents used in spectrophotometric methods should be sufficiently stable and resistant to aerial oxidation or to photometric decomposition. The same should hold for the reaction products. Moreover, in the absorption spectrum of a product there must be a characteristic intense absorption band, at sufficient distance from that of the reagent or of a substance being determined.
(Product) λmax - (reagent) $\lambda max \geq 100$ nm. The reagent for which λ (product) = λmax reagent are less suited for spectrophotometric and are applicable only when the absorption coefficient differ by a factor of at least 2.

1.2 Spectrophotometric Determination of Metal Ions

Spectrophotometric determination of metal ion is based on the formation of metal complexes. The formation of a stable metal complex required the presence of acidic or basic analytical functional groups in the molecule of the reagent (Ligand), preferably in those positions which allow the

formation of a five or six membered chelate ring. Coloured metal complexes are formed only when the organic reagent has a Π-electron chromophoric groups in the molecule, the ring group should also form a part of the Π- electron system and no insulating groups is permitted between the acid group and the conjugated system of the molecule.

Completeness of Complexation Reactions

Both the accuracy and precision of a photometric determination depend on the completeness of a given reaction. As the reaction solution usually contains components competing in the reaction, it is necessary to consider the conditional stability constant for the general complexation equilibrium [9].

$$M+nL = ML_n \qquad (1)$$

In which the determination is based on

$$\beta'ML_n = [ML_n]/C_M(C_L')_n \qquad (2)$$

where $\beta'ML_n$ is the conditional stability constant and C'M and C'L are the total concentration of the metal and the ligand unconsumed in the formation of the complex ML_n'. If the reaction is considered as complete when 99% of the metal being determined is transformed into the particular complex ML_n, it follows that

$$[MLn]/C'_M = \beta'ML_n(C_L')^n > 10^2 \qquad (3)$$

the ligand is usually an anionic species of a weak acid H_jL and so its concentrations pH dependent.The expression in

equation 3 can be used for the calculation of the necessary minimum excess of the reactant, or for an estimation of the pH range over which ML_n attains the required value.

1.3 Photometric Sensitivity and Limit of determination

The sensitivity of a quantitative photometric method is now usually defined as the slope = dA/dc of the calibration curve C=f(A) at the origin [5], where C is the concentration of the substance to be determined and A is the absorbance of the solution.The initial linear portion of the calibration curve can be expressed as

$$C = (A - A_{\circ}) (dA/dc)^{-1} \qquad (4)$$

Where $A_{\circ}$ is the absorbance of the blank. The steeper the slope of the calibration line, the higher is the sensitivity of the determination, it is thus proportional to the absorption coefficient of the species which is measured and to the path length through the cuvette. The sensitivity of a photometric determination can thus be increased if the wavelength is chosen in the region of a high absorption maximum and if a long enough cuvette is taken for the measurement.

The lowest concentration (or amount) of a given substance which can be determined by employing a specified procedure is called the limit of determination (C_{min}). This is usually expressed as the lowest weight amount (e.g μg) or as

the lowest molar concentration, M, or in any other convenient way, e.g as μg ml^{-1}, percentage, PPM, which show a statistically significant difference from zero or the average value of the blank. Kaiser defines the limit of determination by the following equation [6],

$$C_{min} = (A_{min} - A_o)\ (dA/dC)^{-1} = 3S_o(dA/dC)^{-1} = 3S_o/\epsilon l \qquad (5)$$

where s_o is the standard deviation of the blank determination.

Sandell defines [7] the limit of determination (called sensitivity) as the weight in μg per 1 ml of solution, which corresponds to an absorbance A= 0.001 measured in a cuvette of cross section area 1 cm^2 and l = 1 cm (its dimension are μg cm^{-2}). This definition of limit of determination, C_s is given by:

$$C_s = M/\epsilon \quad (\mu g/ml) \qquad (6)$$

where M is the molar mass of the substance to be determined. The disadvantage of this mode of expressing the limit of determination is that the spread of the blank determinations is not taken into account.

1.4 Precision of Photometric Determination

In 1930 Ringbom's [8] introduced a method of plotting spectrophotometric data in which percent transmittance, T (or percent absorbance , A) is plotted against the logarithm of concentration, . When these functions are plotted a sigmoid or S-shaped curve is obtained. Ringbom has shown that the accuracy is greatest when the value of

$$\Delta C/C = 2.303/(\Delta T \Delta \log C) \qquad (7)$$

reaches a minimum, i.e, at the point of the steepest slope ($\Delta C/C/\Delta T$) is the relative analysis error and $\Delta T/\Delta \log C$ is the slope of the curve.

A useful application of the Ringbom's plot is for the determination of concentration limit within which the analysis error is minimum. The concentration range can be evaluated by construction a tangent to the steepest portion of the curve. The slope is then translated to points of tangency to the curve one on the lower and one on the upper limits of the curve. These points define concentration limits with in which the relative analysis error is minimum.

1.5 Spectrophotometric methods for determination of composition of complex

There are several methods [9,10,11,] for determining the composition of metal complexes of these, the most commonly used methods for investigating complexes in solutions are the continuous variation , the mole ratio, and the

absorptiometric methods [12].

Mole Ratio Method.

Convenient and reliable method for determining the composition of the complexes in solution is the mole ratio method.The principle of this method is that a series of solutions is prepared in which the concentration of one component usually C_M is kept constant and that of the other varied.The absorbance of the solution is measured at a suitable wavelength and plotted against the ratio of the variable and constant concentration.

ABSORPTIOMETRIC METHODS

The complex formation equilibrium between metal M and ligand L can be represented by,

$$M + nL = ML_n \quad (8)$$

The formation constant is given by.

$$K = [ML_n]/[M][L]^n \quad (9)$$

$$\log[ML_n]/[M] = \log K + n\log[L] \quad (10)$$

Since $[M] = C_M - [ML_n]$

equation (11) can be written as ,

$$\log[ML_n]/C_M - [ML_n] = \log K + n\log[L] \quad (12)$$

Where C_M is the total concentration of metal ion. If one stable complex is formed ,which has selective light absorption, then from Beer's law $[ML_n] = A'/\epsilon$ and $C_M = A_{max}/\epsilon$,(for l= 1 cm) where A = equilibrium absorbance, A_{max} = maximum absorbance with an excess of the ligand.Equation (11)

can thus be written as

$$\log A/A_{max}-A = \log K + n\log L \qquad (13)$$

Thus,the slope of the curve obtained by plotting $\log A/A_{max}-A$ against lög [L] gives the number of ligands,in the complex (n).

2. LITERATURE SURVEY

2.1.Analytical chemistry of sulphate

Sulphate is found in soils and ground water as $CaSo_4.2H_2o$,Na_2So_4 and $MgSo_4$ [13].Ground water containing sulphate can attack concretes,and other materials containing cement,placed in the ground or on the surface . Reaction takes place between the sulphates and the aluminate compounds in cement,causing crystallization of complex compounds.The expansion which accompanies crystallisation induces internal stresses in the concrete which results mechanical disintegration [14].

Measurements of the sulphate content of ground water enables the ground condition to be classified according to potential sulphate attack.Hence a preinvestigation is necessary in that appropriate precautionary measures,such as the use of sulphate resisting cement or of a richer denser concrete mix,can be taken during construction.

Sulphate in soils can also cause disintegration of precast members,such as slabs and concrete pipes, and can lead to corrosion of metal pipes placed in contact with soils.The soluble sulphates (sodium and magnesium) are much more aggressive to concrete than calcium sulphates,which is relatively insoluble in water.The presence of sulphate in soil as $CaSo_4$ also has disadvantage for plant growth in that it decreases permeability of soil by increasing the amount of exchangeable sodium which has progressive destruction of the

particle aggregates,and with particle dispersion [15].This is brought about by anaerobic oxidation which removes calcium from slightly soluble calcium sulphate to insoluble calcium carbonate there by increasing sodium percentage.

2.1.1. The importance of determination of sulphate

The presence of sulphate in soils and ground water is a very serious problem specially for heavy constructions such as dams.Concretes buried underground that is steel bars covered by these concretes will be corroded and this will bring about a collaption and failurity of the construction.Accordingly, the need of determination of sulphate is important so that safety measures could be taken after the amount of sulphate is known.To resist sulphate attack concrete has to be dense or sulphate resisting cement must be recommended if the amount of sulphate is too high.According to the Ethiopian standard [16], the sulphate content in soil, and ground water, and recommendations are shown in table (1).

High in take of sulphate (1g-2g/litre) in human have a catharic effect,resulting in purgation of alimentary canal [17],but concentrations below these are apparently physiologically harmless.Sensitive people are responsive to magnesium sulphate level as low as 400 mg/litre and new users or those taking occasionally may be affected by concentrations in excess of 700 mg.

In soil 2:1 extract g/L	in ground water mg/l	Type of cement recommended and mixing proportion
<0.2	<300	ordinary portland cement (280kg/m^3
0.2-.5	300-1200	ordinary portland cement (380kg/m^3
1.9-3.1	1200-2500	sulphate resisting portland cement (330kg/m^3
0.3.1-5.6	2500-5000	sulphate resisting cement (370kg/m^3

Table (1) Sulphates in ground water and soils ; classification and recommendation.

2.2 EXISTING METHODS OF SULPHATE DETERMINATION

Several methods are available for the determination of sulphate,but each method has its own problem,hence the need of searching a new method is still imperative. Several Gravimetric, Titrimetric, Spectrophotometric, and Electroanalytical methods are reported in the literature, and each method is summarized below.

2.2.1 Early methods of sulphate determination

A. Gravimetric method of determination of sulphate

This method is still working in many laboratories but is time consuming and suffers from many interferences. The method is based on, addition of Barium Chloride to a sample solution containing sulphate and Barium will form precipitate with sulphate.

B. Titrimetric methods for determination of sulphate [19-23]

Titrimetric methods are directly or indirectly based on the methods of addition an excess Barium to the sample solution containing sulphate, and by using a suitable organic reagent as a titrant and as an indicator. For most cases EDTA is used as a titrant. Menis and co workers [19] have also determined sulphate by Automatic Spectrophotometric titration at 520 nm with 0.00125 M Barium perchlorate solution using thoron (2,2(hydroxy-3,6-disalpho-1-naphtylazo)-benzene Arsenic acid) as indicator. Frey [23] titrated sulphate to maximum turbidity with 0.02 N barium chloride solution with the help of a photometer. Microgram amount of sulphate have

been determined by turbidometric titration with standard barium chloride solution.Titration were performed using a filter photometer, and the end point was located from a plot of relative optical density against volume of titrant added.[43].

c. **Turbidimerically determination of sulphate** [24-26]

Sulphate may be determined by the turbid appearance of suspended barium sulphate. The turbidity of the sample is compared with that of a series of standards precipitated under similar conditions.

D. **Nephelometrically determination of sulphate** [27,28]

The amount of sulphate present in a solution is estimated nephelometrically as barium sulphate. Rough comparisons can be obtained in test tubes or graduated cylinders. The amount of sulphate per 25 ml must be between 0.02 and 0.2 mg for a satisfactory barium sulphate dispersion to be obtained. The method is based on addition of $BaCl_2$ to a sample, mixing and letting it to stand for 15 min. and comparing in a nephelometer.

E. Colorimetric Determination of Sulphate

The variation of the colour of a system with change in concentration of some component forms the basis of colorimetric analysis. The colour is usually due to the formation of a coloured compound by the addition of appropriate reagent. The intensity of the colour may then be compared with that obtained by reacting a known amount of the substance in the same manner [29].

It must however be pointed out that colorimetry analysis is only a special case of the more general photometric chemical analysis. The later may be defined as the analysis which is based upon the quantity of light absorbed by a coloured solution (spectrophotometry ,colorimetry), or by a suspension (turbidimetry) [30], or by the amount of light scattered by a suspension (nephelometry) [31], or the amount of light scattered by a solution with ultraviolet light as the exciting radiation (Fluorometry) [32].

Sulphate can be determined colorimetrically [33-39] based on the general principle, so that by the formation a slightly soluble metal organic- reagent coloured compound,the addition of sulphate to the solution will bring a decolorization (decrease in colour intensity) and liberation of free ligand.The absorbance is measured at a fixed wave length.

The reaction of slightly soluble barium-chloroanilate with sulphate in acidic solution to form barium sulphate,and the liberated chloroanilic acid is used for the determination of sulphate,and the absorbance is measured at 530 nm.

f.Spectrophotometric determination of sulphate

Sulphate ion does not form coloured compound with most reagents.All photometric methods for determining sulphate are therefore based on the reaction in which coloured compounds are destroyed.Best method, for determining sulphate are based on decomposition of coloured complexes of barium with

nitrochromazo and Orthoanilic B [44-45].Nitrochromazo was first used as indicator for barium ion in volumetric determination of sulphate in presence of phosphates and arsenates [47] and phosphorous and arsenic containing organic compounds [48].This method was used in determining sulphate in biological materials [49].

Widely used are photometric methods based on destruction of suspensions of chloroanilate and chromate of barium with sulphate.Barium chloroanilate is decomposed to chloroanilic acid which passes into the solution, and the intensity of its colour is proportional to the sulphate content [50-52]. This method was used for determining sulphate in water [53],soil samples [54],in petroleum [55] and coal ash [56].The reaction between barium chromate and sulphate ion is used in determining sulphur as sulphate.The method is based on determining the colour intensity of chromate, or dichromate,that is liberated in the reaction.The method is applicable for analysing many materials including analysis of sulphate in soils [57].

Precipitation of sulphate with benzidine is also used for photometric determination of sulphate ion [58].Benzidine sulphate is precipitated, separated and dissolved in hydrochloric acid.Benzidine is diazothized and coupled with N-(1-Naphthyl)_Ethylene diaminehydrochloride.The reaction product is purple, and its colour intensity is proportional to the sulphate content .

There are also methods for determining sulphate based on decomposing lacquers of thorium [59],zirconium and

cerium[60,61],ferricthiocyanate [62],barium-rhodizonate [63],complex of thorium with xylenol orange(64).Nephelometric or turbidimetric methods of various modifications are also recommended for determining sulphates [65].Small amounts of sulphates are reduced to hydrogen sulphide with stannous chloride [66],a mixture of iodine and hypophosphite [57,68] or by some other reductants,with subsequent determining sulphides as methylene blue.

Determination of sulphate with Nitrochromazo

The method is based on the decomposition of barium with nitrochromazo (2,7-bis(4-nitro-2-sulphophenyl-azo)-1,8 dihydroxy-naphthalene-3,6-disulphonic acid) in a weak acidic media with sulphate ion. AS the complex is decomposed,its colour changes from blue to violate.The reaction takes time and all barium sulphate is precipitated in six hours.90 % Of the salt precipitates in the first 90 min.of the reaction.In order to decrease solubility,determination is carried out in 50-70 % water acetone or water alcohol solution.The ratio of barium -nitrochromazo ion should be 1;1.

Determination of sulphate with barium chloroanilate

Barium chloroanilate suspension(barium salt of 2,5-dichloro 3,6-dihydroxy.B.benzoquinone) reacts with sulphate ion to liberate an equivalent quantity of chloroanilic acid,the concentration of which is determined from the

absorbance at 330 or 530 nm.In order to increase sensitivity of the method,the reaction is carried out in 80 % solution of isopropyl alcohol.The concentration of chloroanilic acid corresponds to the sulphate content.

Determination of sulphate by zirconium alizarinate

Sulphate ion reacts with zirconium alizarinate to form sulphate complex of zirconium and alizarine.Alizarine content is determined by the decrease of the absorbance of zirconium-alizarine lacquer,or the liberated alizarine is extracted and its content is determined by the intensity of the yellow colour of its solution in Carbon tetrachloride. Moreover, alizarine can be back extracted with alkali, and its concentration determined by the intensity of the free alizarine colour in alkaline medium.In the later case the liberated alizarine is extracted with ether, and back titrated in alkaline medium.Zirconium-alizarinate reacts slowly with sulphate ion.For this reason,zirconium solution is added first and then alizarin.

2.2.2 MODERN METHODS OF DETERMINATION OF SULPHATE

I.Spectrophotometric methods [69-77]

Trace sulphates in air and water were determined specrophotometrically by using 2-Aminopermidine hydrobromide (RHBr) at pH 3.5-4 [69]. RHBr reacts with sulphate to form white precipitate of $RHSo_4$, which reacts with nitric acid to

form red purple 2-Amino-4,6,9-trinitroperimidine,the absorbance of which is measured at 540 nm.

A spectrophotometric method for determination of sulphate based on the reaction of sulphate with Ba-Methylthimol was reported.it was based on the formation of a blue complex in sodium hydroxide medium.The absorbance was measured at 460 nm [70].Indirectly, sulphate was determined by precipitating with excess 2-aminopermidium bromide solution followed by determining the unreacted reagent by extracting and spectrophotometrically with bromo - phenol blue at 425 nm [71].It is also determined indirectly by adding an excess of barium and formation of barium sulphate.The excess or the unreacted barium is again complexed with thorin and the absorption of the complex is measured spectrophotometrically at 520 nm [72].The same principle was also applied for an indirect determination of sulphate by adding lead to sample solution containing sulphate.The unreacted lead is again complexed with EDTA and the absorbance is measured spectrophotometrically at 242 nm [73].

Direct method for the determination of sulphate was also developed by Toshitaka and Masahito [74],it is based on the formation of complex between Mo(V) and Sulphate in HCl medium. The absorbance was measured at 720 nm.But the method suffers from a lot of interfering ions which form a blue complex.

Inspite of extensive studies on the determination of sulphate ion,few suitable colorimetric methods have been developed.Nearly all the spectrophotometric methods available

for the determination of sulphate ion are based on indirect methods .In some instances,sulphate ion was first reacted with sparingly soluble reagent such as thorium borate-Amaranth [77],barium chloroanilate [78],zirconium or thorium alizarinate [79] ,barium chromate [80] ,barium iodate [81], and the liberated components from the respecting reagents were measured spectrophotometrically by taking into account the stoichiometric replacement with sulphate ion.These methods have been subsequently modified to improve their accuracy,sensitivity,and have found a variety of applications [85,86]. However,these indirect methods require laborious procedures to insure that the heterogeneous reactions are quantitative.

II. Electroanalytical method

Among electroanalytical methods for the determination of sulphate,several works are reported on potentiometric titration. Direct titration using indicator electrode and barium chloride as a reagent has been reported [87].The extreme sensitivity of the electrode to chloride and probably other anions almost totally obscures the end point break,and makes the titration almost useless except in some special circumstances.Kolthoff and Pan [88] studied the titration of sulphate with lead nitrate,using amperometric determination of end point,and found the titration to be accurate and relatively free of interference from most common ions. Rose and Martin.S.Front [89] developed lead selective electrode

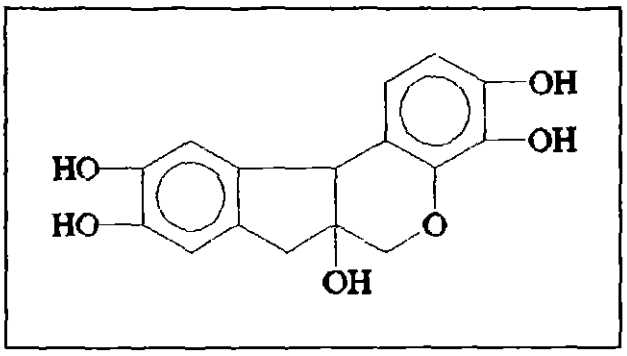
which allows the potentiometric determination of the end point in the direct titration of sulphate with standard lead solution. All the methods proposed above have their own disadvantage in that they suffer from interference of many cations and anions. Most methods are time consuming,and lack sensitivity. Hence, a simple, accurate, and selective method for the determination of sulphate is still necessary.

2,3 Hematoxylin as analytical reagent

2.3.1 General characteristics

Hematoxylin is a white crystalline solid with melting point 148-150° C (monohydrate) soluble in ethanol,diethylether, and slightly soluble in water

Structure



MW = 302.29, Systematic name: 7,11,b-Dihydro(B) indeno(1,2,d) pyran-3,4,6a,9,10(6H) pentol.

A solution of this substance is prepared by dissolving the material in a minimum of alcohol and dilute it to the required volume with water [90]. Literature suggests that a

solution of hematoxylin can stay stable for about a week only, and this is due to slow oxidation to give haematein which involves the lose of two atoms of hydrogen.It was thought that the reaction mechanism involves a primary ionization step.Hematoxylin is more stable in acidic solution, thus acid or acid buffered hematoxylin keeps quite stable for up to six weeks.

2.3.2 Application of hematoxylin as analytical reagent

Hematoxylin is a well known analytical reagent for spectrometric and complexometric determination of several metals,such as Fe(111) [91] Ti(1V)[92],Mo(1V) [93],Al(111) [94],Ga(111) [95],rare earth elements of the cerium subgroups, [96].An indirect determination of fluoride using aluminium hematoxylin complex has been discussed by Hunter, Macunlity and Tery who have used aluminium -Hematoxylin complex for the determination of fluoride [90] in alkaline solution at pH 8-9. Aluminium reacts with hemtoxylin to give purple colour complex.The reaction also takes place at a pH 4.8, but it becomes very slow when the medium becomes increasingly acidic.This complex also becomes unstable below pH 4.2. The complex in acidic solution is attacked by fluoride ion which competes for aluminium and consequently the intensity of the colour decreases which is proportional to the amount of fluoride present.

Tarek and Zaki [95] have used hematoxylin for the determination of ultra micro amount of aluminium.A simple and

sensitive method for the determination of aluminium with hematoxylin and its oxidized form in the presence of cetryltrimethyl ammonium bromide (CTAB) are described. The complexes obeyed beer's law in the range 15-175 and 25-250 µg/ml using hematoxylin and oxidized hematoxylin respectively.The best result for chelate formation were obtained at pH 7.6 and 7 with molar absorption of 1.7×10^7 and 1.1×10^6 L mol^{-1} cm^{-1} respectively.In another paper Tarek and Zaki [96] have studied Hematoxylin as organic reagent for the spectrometric determination of gallium and indium. Hematoxylin forms complex with various metals and from the literature cited the absorbance of hematoxylin complexes at different pH is summarized below .

M-Hematoxylin	λ_{max}(nm)	pH	Reference
Fe(111)	530	5-5.6	[91]
Ti(1V)	655	3-4	[92]
Mo(1V)	415	---	[93]
Al(111)	620	7.4-8.5	[94]
Ga(111)	520	3	[96]
In(111)	520	5	[96]
Ti(iV)	440	5	[96]

3. OBJECTIVE OF THE PRESENT WORK

The literature review in the previous section reveals that quite a large number of methods such as volumetric, gravimetric, spectrophotometric and electroanalytical exist for quantitative determination of sulphate. Volumetric methods are non-specific and are susceptible to various interferences, and entail the use of strongly acidic media. Gravimetric method which is used for routine analysis of sulphate using $BaCl_2$ as a precipitating agent and weighing the precipitate is very time consuming.In addition, the method is not used for trace analysis. Spectrophotometric methods which are reported previously use acidic media, where there is a need of preseparation of the interfering ions by filtration and analysing the filtrate, which is again time consuming. Among the spectrophotometric method, the barium-chloroanilic method which deals with the reaction of barium with chloroanilic acid and addition of sulphate to this sparingly soluble salt brings about the libration of free chloroanilate ion which again the amount of chloroanilate ion librated is determined photometrically, according to the following reactions:

$$\underset{\text{Solid}}{BaL} + SO_4^{2-} + H^+ = \underset{\text{solid}}{\underline{BaSO_4}} + HL^-$$

so a transformation of one solid to another takes place .It is, therefore, obvious that a simple, accurate, and precise method for the determination of sulphate in soils and/or ground water is still required. The object in this work is thus to develop, a simple and precise method for the determination of sulphate using a complex of barium with hematoxylin.

4. EXPERIMENTAL

4.1 Equipment: A Beckman UV-Vis spectroPhotometer DU-16 Equipped with 1-cm cuvette and Beckman recorder which is used for absorbance measurement.

4:2 Reagents and Chemicals

4:2:1 Standard Hematoxylin Solution (10^{-2}M)

A standard solution of Hematoxylin was prepared by taking 3.3023 g of analytical pure grade reagent and dissolving it in 2.5 ml of ethyl alcohol and making the final volume 1 litre with distilled water.

4:2:2 Standard Barium Solution (10^{-2} M)

A standard solution of Barium was prepared by dissolving 2.4427 g of $BaCl_2 2H_2O$(reagent grade) in 1 litre of distilled water.

4:2:3 Standard Sulphate Solution (10^{-2})

A standard solution of sulphate was prepared by dissolving 1.4342 g of (High Pure analytical grade) Na_2So_4 in 1 litre of distilled water.

4:2:4 Universal Buffer

A mixture of Phosphoric, acetic and boric acids (0.04M) respectively was prepared and the required amount of 0.2 N NaOH was added in 100 ml of the mixture to obtain the required pH.

4:2:5 Solutions of Foreign Ions

Solution of foreign ions were prepared by dissolving of known quantities of reagent grade salts in distilled water to give 10^{-3} M solution.

4.3 Preparation of soil sample

100 g of air-dried soil sample that has passed 0.5 mm standard sieve was taken and put in 500 ml conical flask.To this solution, 200 ml of distilled water was added and the solution was stirred for 15 mint,and finally filtered in Wattman no 44 paper.A suitable aliquot (50 ml) of the 1:2 extract was taken and diluted to 500 ml.From this, a suitable amount of sample was taken for analysis .50 ml for titrimetric,150 ml for gravimetric ,and 1 ml was taken for spectrophotometric analysis.

4:4 Preparation of Underground Water

Underground water was sampled from the site of Nazareth at a depth of 10 mts from four places using underground drilling machine which has a sampler attached to it according to [14]. A suitable amount of sample was taken and analyzed by titrimetric methods, on the method of precipitation, i.e gravimetrically, and spectrophotometrically.

4:5 Procedure for the determination of the composition of complex by Mole Ratio Method:

To determine the ratio of Barium to Hematoxylin, a series of solutions was prepared in which the concentration of barium (1×10^{-4} M) and pH 9 were kept constant, and the concentration of Hematoxylin was varied. The absorbance was measured at 556 nm against distilled water as a blank and was plotted against the mole ratio of ligand to metal . Two straight lines were drawn from the two parts of the curve which intersected each other at a mole ratio of (1:1) Barium to Hematoxylin.

4.6 Procedure for the determination of the stability of the complex

To study the stability of the complex, to a 50 ml volumetric flask 5 ml of 10^{-4} M Ba-Hematoxylin complex was added , the pH adjusted to 9. The absorbance was measured at 556 nm at different time intervals.

4.7 Procedure to study the absorbance of Complex at different pH

To a 50 ml volumetric flask equal amount of (1:1) Ba-Hematoxylin complex was added (10 ml of 10^{-3}M). To this solution different amount of 0.025 N NaoH (1-5 ml) were added and the pH for each solution and absorbance at 556 nm were measured.

4.8 Procedure for the Construction of Calibration Curve

To construct a calibration curve, 5 ml of 4 x 10^{-4} M complex was added into each of seven 50 ml volumetric flasks each containing 1.2, 1.6, 2.0, 2.4, 2.8 and 3.0 ml of Standard sulphate solution respectively(4 x 10 -4 M) sulphate, was used throughout the procedure.

4.9 General Procedure for the Determination of sulphate

An aliquot of the solution containing 1-5 µg/ ml of sulphate was transferred to 50 ml volumetric flask and the pH was adjusted to 9 by addition of 5 ml of Buffer.(filtration of the precipitate was done where ever necessary) .To this 5 ml of complex ($4x10^{-4}$) was added and finally the volume was adjusted to the mark and the absorbance was measured after 5 mints at 556 nm.

4.10 Procedure for Studying the Effect of Foreign ions

The effect of Foreign ions was studied by adding a known quantity of the interfering ions to a solution containing 0.192 µg/ml of sulphate, and the absorbance was measured at 556 nm.

Satisfactory for upto six weeks [19].

5. RESULTS AND DISCUSSION

5.1 Complex Formation and Absorption Spectra

The reaction between hematoxylin and Barium to form complex was studied at different pH, but complex formation was facilitated in neutral and alkaline media (pH 7.2 - 9). Maximum absorption was obtained at pH 9. Above pH 9 the complex is stable and the absorption maximum shifts to 400 nm which is the absorption of hematoxylin at pH 5-7. At a lower pH (4.2), the complex is not stable and the absorption peak is too small and wide . The absorption of the ligand and the complex lie at the same λ max 556 nm (Fig1). However, the peak of the complex is much intense than the ligand at the same environment.When a known amount of sulphate is added, the peak intensity of the complex will decreases and finally it coincides with the peak of the ligand . The reason why there is no shift to the wavelength when complex formation occurs is due to the absence of electron transfer and delocalization of electrons in the ligand orbital.The intensity of the complex is higher than the ligand, and this can be explained due to the interaction of non bonding electrons in the ligand and the orbital of the metal.

5.2 EFFECT OF EXPERIMENTAL VARIABLES

5:2:1 Stability of the complex.

To study the stability of the complex the measurement of absorbance Vs time (in min.) was made, and the results are shown in table (2) and a plot of absorbance Vs time is given in Fig(2).From this it was found that the complex reaches equilibrium after 30 min. and is stable for 3 hrs. Beyond this the complex decomposes and the peak decreases.Hence, 3 hrs of stability time is enough for quantitative determination.During the analysis of the sulphate and for other experimental variables, the complex was allowed to stand for 30 min.

Time (min)	Absorbance at 556 nm
0	0.485
20	0.592
40	0.629
60	0.629
80	0.640
100	0.640
120	0.646
140	0.648
160	0.648
180	0.650
200	0.652
220	0.642
240	0.600
260	0,580
280	0.524

Table (2) effect of time on stability of complex $[Ba]^{-2} = 4x10^{-4}$

5:2:2 EFFECT OF pH ON ABSORPTION OF THE HEMATOXYLIN AND COMPLEX.

The reaction of barium with hematoxylin has been studied at different pH but the formation of complex was facilitated from pH 7.2- 12.In this range the stability decreases as the pH increases.At a pH 4.2- 5.8 the colour of the reaction product is yellow and above pH 5.8 the colour changes to

pink.When the pH increases the absorbance also increases but the stability decreases .The optimum pH where the reagent is stable for a quantitative measurement was found to be at pH 9,and this condition was used throughout the experiment for the determination of sulphate and for the measurements of other experimental variables.The absorbance of hematoxylin was also studied at different pH.It was found that it has three maximum peaks at different pH . The absorption peaks are shown in fig (2) and the pH range and the absorption maximum is shown in table (3).

pH range	λ max (nm)
2-4.8	380
5-7	440
7.2-14	556

Table (3)effect of pH on the absorbance of hematoxylin.

5.2.3. ORDER OF ADDITION OF REAGENTS

For the determination of sulphate,addition of sulphate to the reagent and vice versa was done but there was no marked change in absorbance between the two procedures .However, addition of reagent to a sample solution containing sulphate was used through out the procedure.

5.2.4 COMPOSITION OF THE COMPLEX

The composition of the complex was measured by the mole ratio method. The two straight lines (table 4 & figure 3) drawn from the two parts of the curve intersected at a mole ratio of 1:1 indicating complex formation between barium and hematoxylin . From the graph, the stability constant of the complex was calculated and found to be $\beta_1 = 5.3 \times 10^5$.

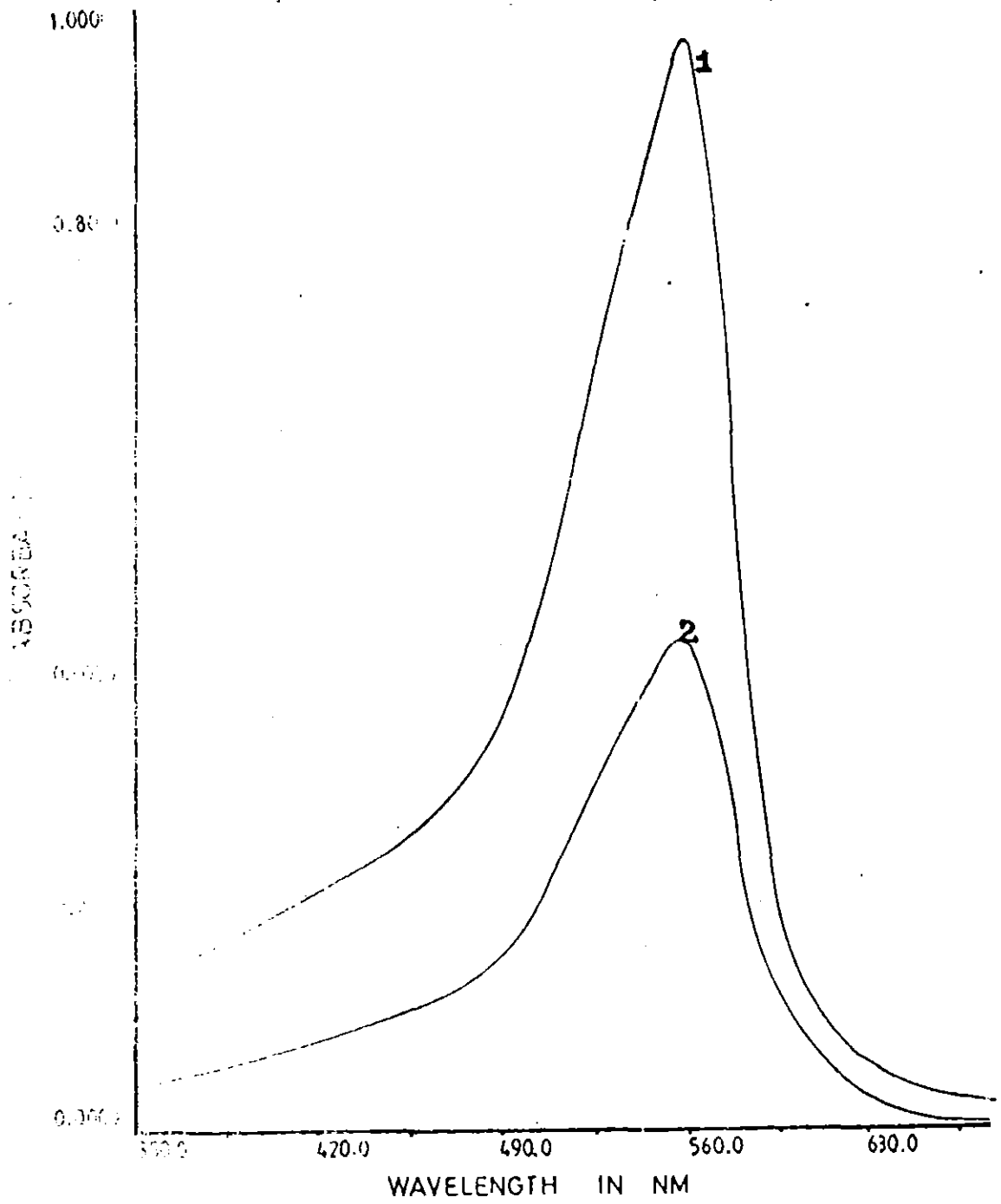


FIG (1) ABSORPTION OF Ba-HEMATOXYLINE SYSTEM ($5x10^{-4}$ M (1) AND HEMATOXYLINE $5x10^{-4}$ M (2)

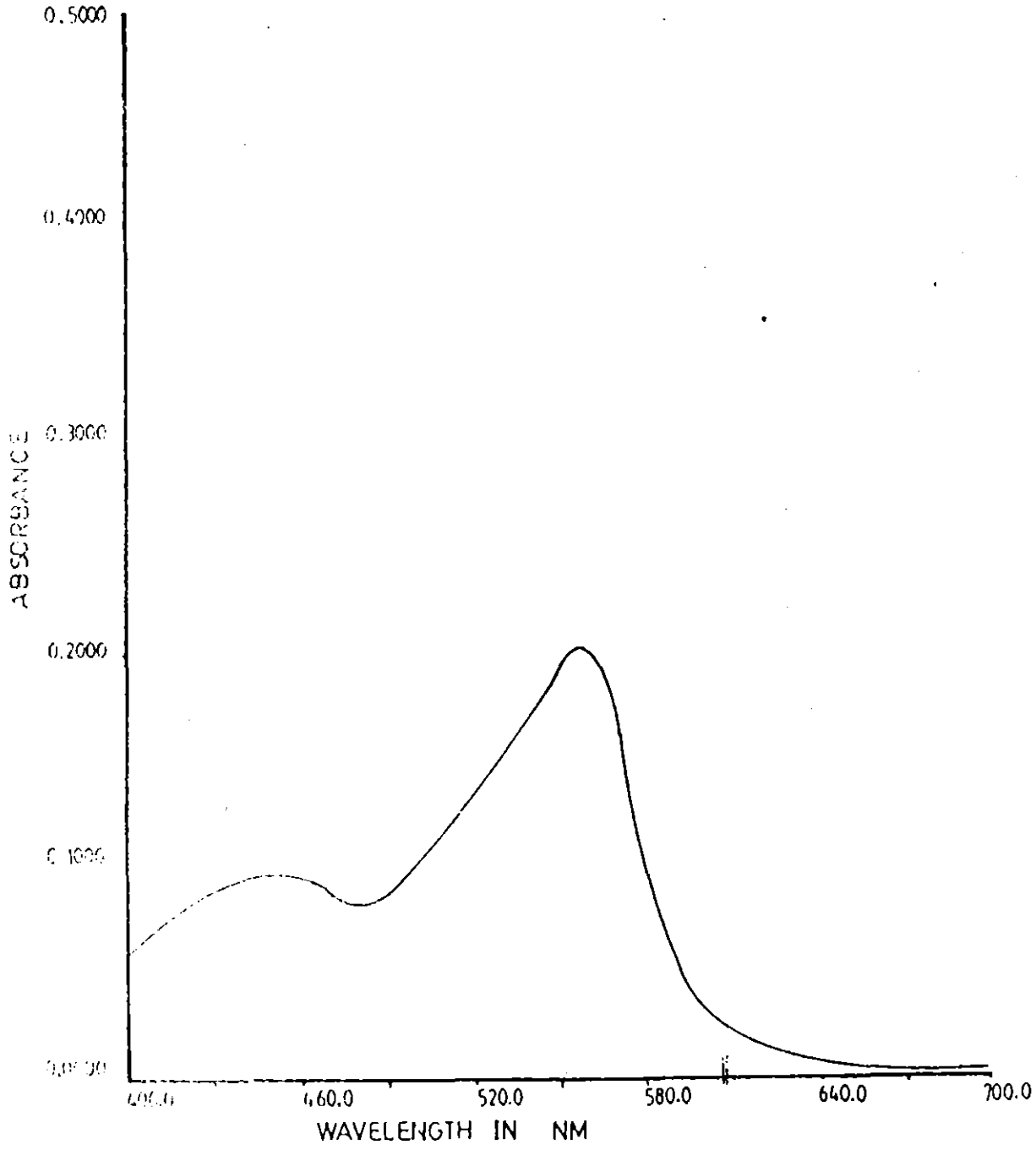


FIG (2) ABSORPTION SPECTRA OF HEMATOXYLIN AT DEFFERENT PH

Mole ratio of ligand to metal	Absorbance at 556 nm
0	0.00
0.2	0.258
0.4	0.688
0.6	1.062
0.8	1.440
1.00	1.625
1.2	1.813
1.4	1.875
1.6	1.937
1.8	1.938
2	2.000
2.4	2.010
2.8	2.030

Table (4) Results of mole ratio method for determination of the composition for Ba-Hematoxylin system [Ba]= 1x 10^{-4} M.

5.3 PHOTOMETRIC CHARACTERISTICS

The molar absorptivities, photometric sensitivities (7) and limits of determination (8),the concentration range obeyed by Beer's law and the optimum concentration range for the photometric determination evaluated from the Ringbom's plot [8] are summarized in table (5). The calibration curve data are given in table (6) and curves are shown in Fig.(5) and (6). The calibration curve is plotted by taking data from table (6) which is statistically treated.From the calibration curve, the slope was calculated from the steepest portion and this slope is directly proportional to the molar absorption coefficient. The concentration [illegible]

evaluated by drawing tangent to the flat portion of the curve. These results show that the Ba-hematoxylin system is sensitive and can be applied for the determination of trace quantity of sulphate .

The precision of the method was evaluated by performing five measurement of Na_2So_4 ($8x10^{-6}$) 38.4 µg/50 ml and measuring the absorbance at 556 nm. The results of five triplicate analysis and from this the relative standard deviation was calculated and are summarized in table (6). From the table we could observe that a relative standard deviation of 0.71% indicate that the method is precise and reproducible.

Coloured system	Ba-Hematoxylin complex
λmax nm	556
ϵ (L Mol^{-1} cm^{-1})	$3.31x10^{-4}$
Sandal sensitivity	0.0029
Limit of Determination, µg/ml	0.014
Con.Range from Beer's law(µg/ml)	0.5-2.2
Optimum concentration from Ringbom's plot(µg/ml)	0.3-2.0

Table (5) Photometric characteristics of the complex.

concentration of sulphate in µg/ml	Absorbance	Change in absorbance
0.0	0.702	0.0
0.92	0.575	0.127 ± 0.0005
1.23	0.538	0.164 ± 0.0041
1.54	0.488	0.214 ± 0.0019
1.84	0.446	0.256 ± 0.0024
2.15	0.397	0.305 ± 0.0062
2.30	0.248	0.454 ± 0.0010

Table (6) Calibration data for sulphate determination by barium-hematoxylin system.

Total No. of Samples	* Mean absorbance	Sd.deviation	Rel.sd.dev.
5	0.279	0.002	0.71

Table (7) evaluation of the precision of the method
*Average triplet analysis

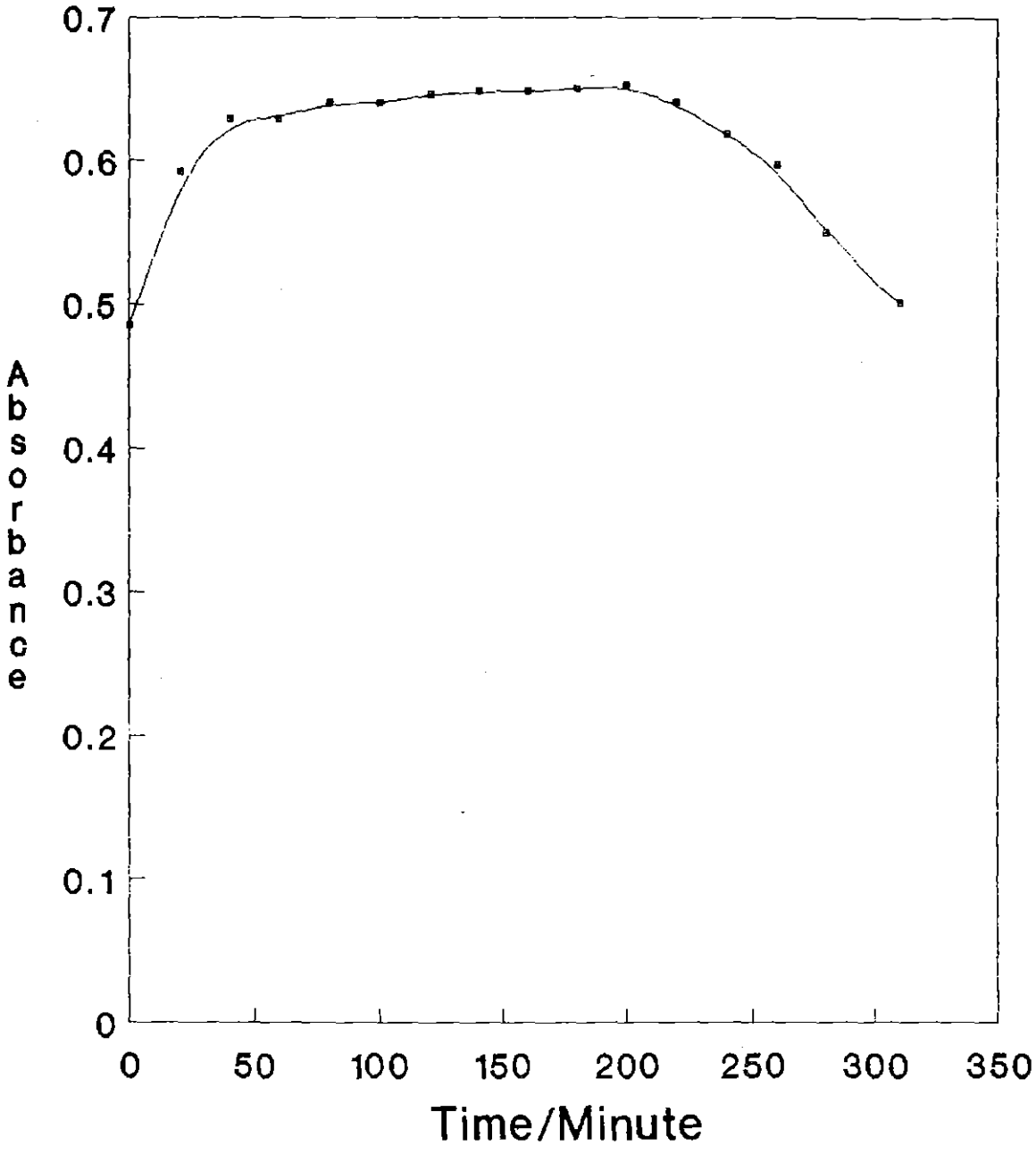


Fig. 3 Curve for the determination of the stability of the complex

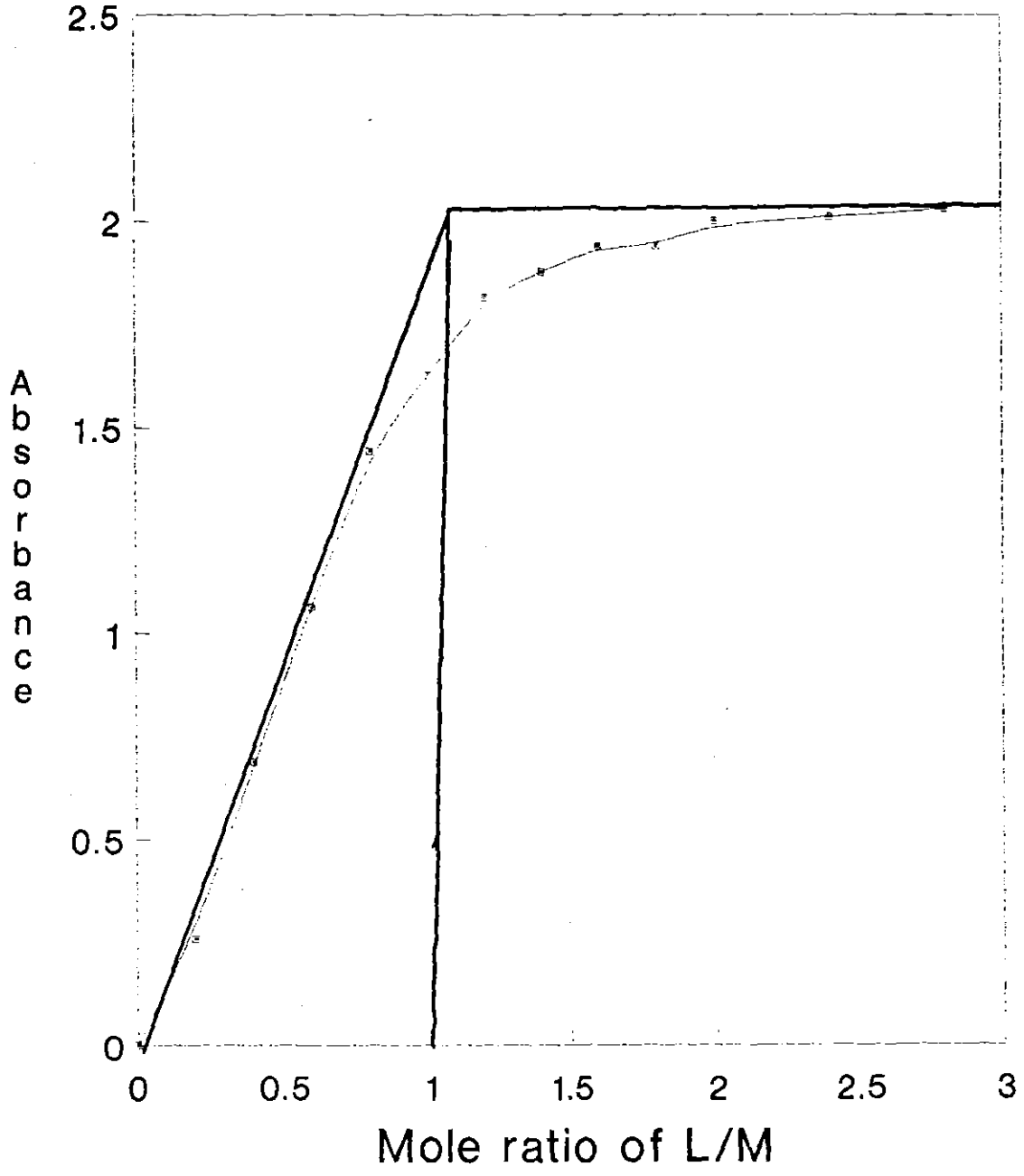


Fig. 4 Curve for the determination of the ratio of barium to hematoxylin by the mole-ratio method.

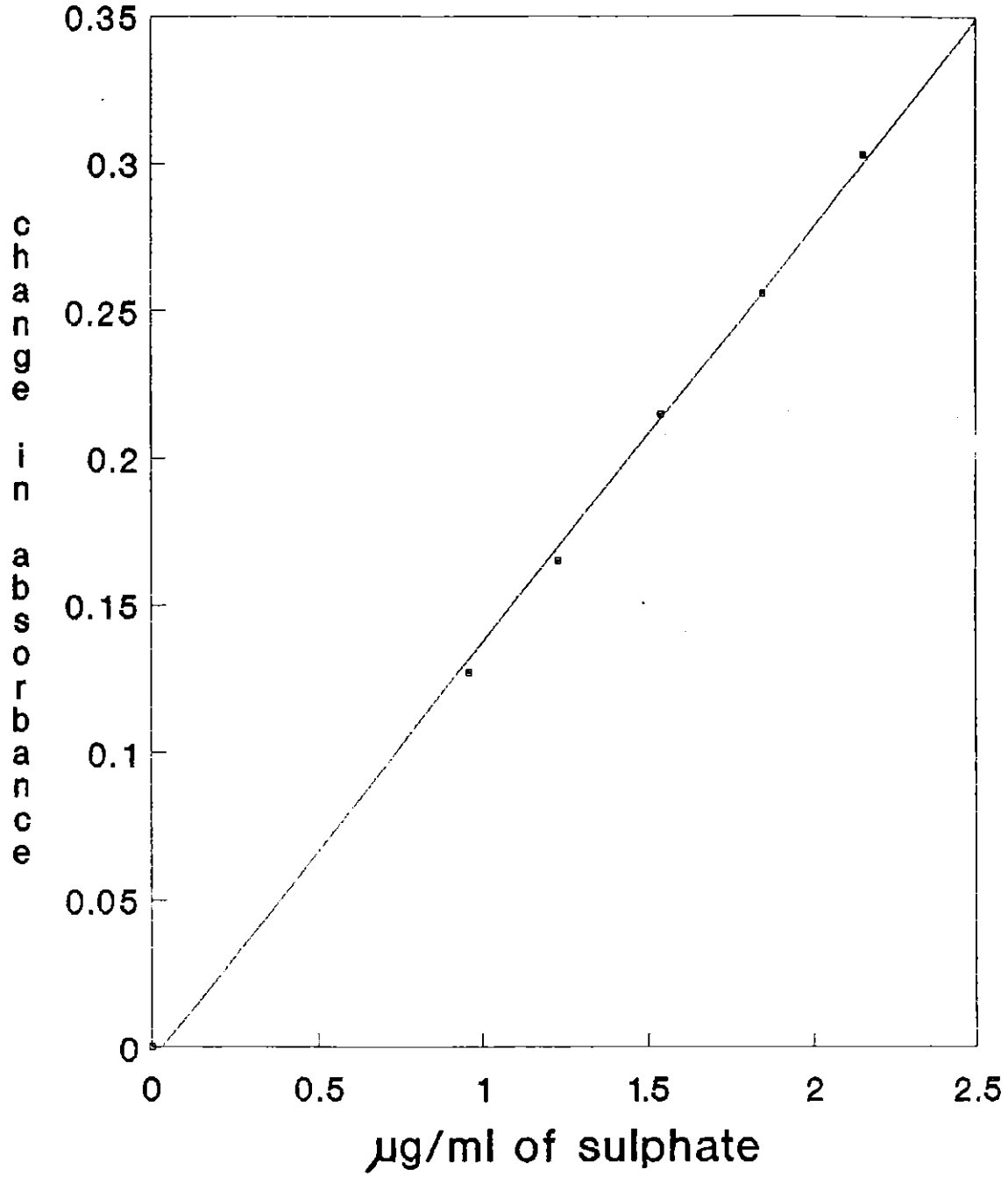


Fig. 6 Calibration curve for the determination of sulphate

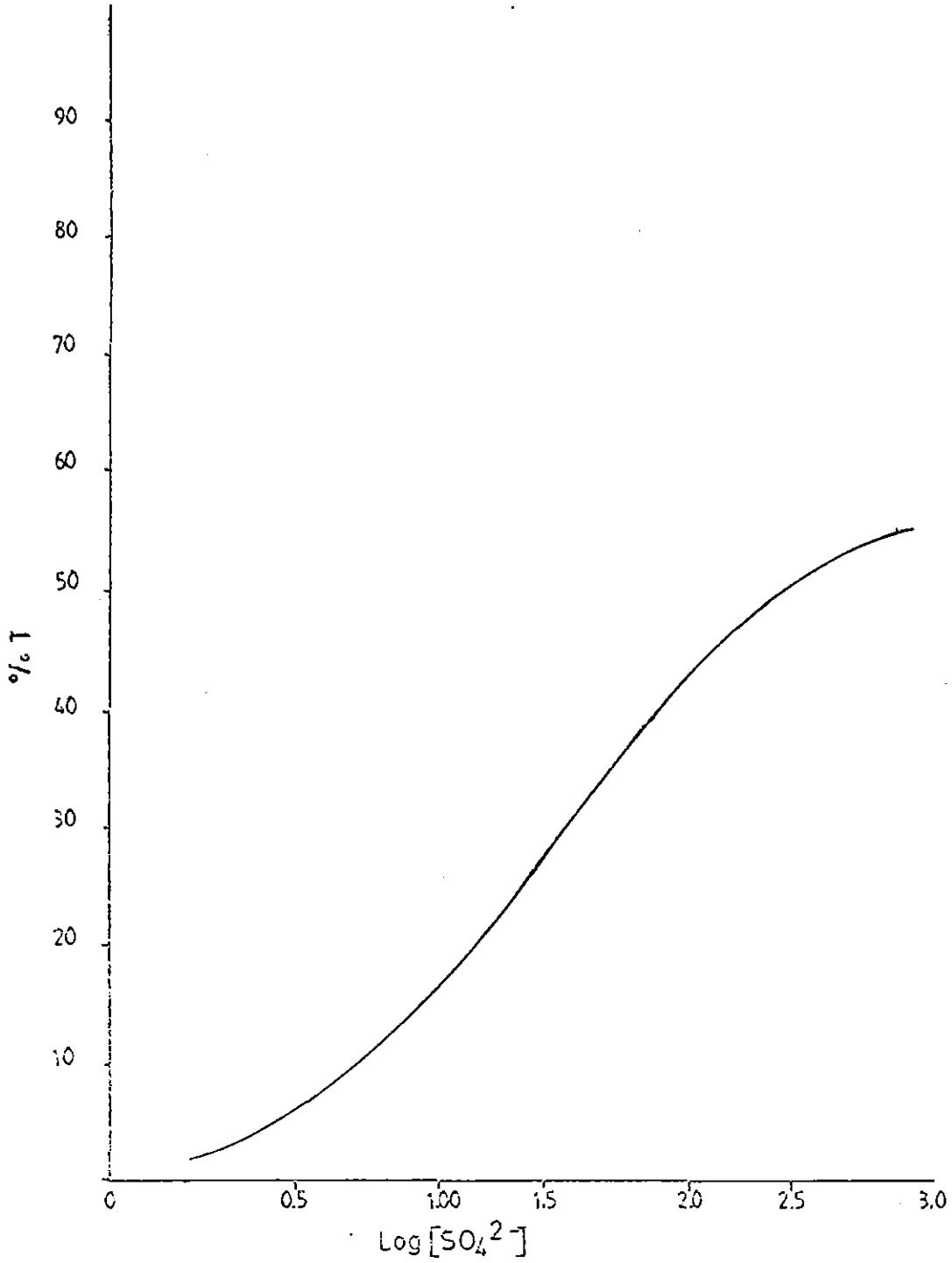


FIG (8) RINGBOM'S PLOT FOR THE DETERMINATION OF OPTIMUM CONCENTRATION RANGE FOR THE DETERMINATION OF SO_4^{2-}; Ba - HEMATOXYLIN SYSTEMS

5.4 Effect of foreign ions

To evaluate the selectivity of the newly developed method, the effect of foreign ions on the determination of sulphate has been studied. Since an alkaline medium was used, most of the cations of transition metals and other metals were precipitated at this pH. From alkaline earth metals, Ca and Mg interfere. Al(11i) forms complex with hematoxylin and hence, distracts the complex.It can be removed by addition of Fluoride to the system.

The most seriously interfering anions during the determination of sulphate were studied, and their concentration range where optimum condition for the measurement were summarized in table(8).From the table one can observe that the most seriously interfering ions are- Ca,Mg,Al,Pb, and Sn for small concentration of sulphate that is 2 $x10^{-6}$ M. Other interfering ions however, can only interfere when their concentration is high above $4x10^{-4}$ M.

Ion	Ksp.	Tolerance limit (M)
Nitrate	[a]4.5×10^{-3}	2×10^{-5}
Acetate		8×10^{-5}
Phosphate	[a]6.03×10^{-39}	2×10^{-5}
Fluoride	[a]1.1×10^{-6}	1×10^{-5}
Oxalate	[a]1.1×10^{-7}	8×10^{-5}
Carbonate	[a]5.1×10^{-9}	8×10^{-5}
Calcium	[b]9.1×10^{-6}	8×10^{-6}
magnesium	[b]3×10^{-3}	8×10^{-6}
Aluminium		8×10^{-6}
Lanthanum	[b]3×10^{-5}	4×10^{-4}
EDTA		8×10^{-4}
Zirconium		1×10^{-5}
Lead	[b]1.6×10^{-8}	1×10^{-6}
Manganese		4×10^{-5}
Nickel		1×10^{-4}
Tin		8×10^{-6}

* Maximum concentration tested.

Table (8) Tolerance limit of foreign ions in determination of sulphate.

a = Ksp of barium-anion salt. b=Ksp of metal-sulphate salt.

Ksp of $BaSO_4$ $=1.1\times10^{-10}$.$[Ba]=3\times10^{-4}$ M,pH=9,$[SO_4]=2\times10^{-6}$ M

APPLICATION

In order to asses the analytical potentiality of the newly developed method, the Ba-hematoxylin system was applied to the analysis of underground water and soil samples for sulphate content. The method was also compared with gravimetry and titrimetry.

Soil and Underground water Samples:-

Underground water and soil samples were taken from Nazareth . Soil samples were taken from a depth of 3 mts and underground water was taken from a depth of 10 mts, and both samples were prepared for analysis according the method described earlier. The sulphate content of soil and underground water samples were also determined gravimetrically and volumetrically. The experimental results are given in table (9) and (10).For the determination of sulphate using the present method, 1 ml of aliquot was taken and diluted to 250 ml because of the amount of sulphate present was too much. From the table one can observe that the amount of sulphate found by the present method was divided by 250 and was found to be 1.744 µg/ml and this indicate that the present method is most sensitive than those of gravimetric and titrimetric methods.In addition, comparing the relative standard deviation from the table our method is more precise than the above methods either in soil or ground water analysis.

Method	Amount,ml	* Sulphate found, µg/ml	Relative Standard deviation
Ba-Hematoxylin	1	436.00	0.290
Gravimetric	50	411.26	7.130
Volumetric	50	441.46	0.314

Table (9) Determination of sulphate in soil sample
*Average of triplicate analysis

Method	amount taken in ml	sulphate found µg/ml	Rel.sd.deviation
Ba-Hematoxylin	1	55.67	0.87
Gravimetric	100	-	3.47
Titrimetrically	50	54.7	i.096

Table (10) Determination of sulphate in ground water.
[Ba] = 4x10-4 M.

The result of water analysis of gravimetry is not shown because of the result obtained is not reproducible and this can be seen from the relative standard deviation.

6.1 Comparison with other Spectrophotometric methods

A comparison of the proposed method for the determination of sulphate with recently reported spectrophotometric methods with regard to sensitivity, and

concentration range for determination of sulphate is given in table (11) .The comparison reveals that from spectrophotometric methods proposed, the chloroanilic method [28] is more sensitive but it lacks specificity, and suffers from interferences of many species.From the table one can observe that the concentration range of the present work is much lower than the previously reported methods except the Ba-rhodizonate which is not selective and fast.Thus, the proposed method for the determination of sulphate is more sensitive and selective than many of the reported methods.Hence, the newly proposed method could be preferred in determining sulphate.

Reagent	λ_{max}, nm	Concentration range, µg/ml	ϵ L-mol^{-} $^{1cm-1}$	Reference
Thorium-Amaranth	520	0-400	-	64
Barium-Rhodizonate	530	0.5-0.8	-	63
Barium-Chromate	545	0.3-100	-	57
Barium-Chloroanilate	530	-	2,3 x10^4	28
Barium Nitrochromazo	644	1.025-20	-	46
2-Amino-permidine	540	3-55	-	69
Barium methylthimol blue	460	0-10	-	70
Barium-Thorin	520	30-300		72
Barium-hematoxylin	556	0.5-2.2	3.31 x10^4	Present work.

Table (11) Data for the comparison of this method with other methods.

7.Conclusion

New method has been proposed for the determination of sulphate with Barium hematoxylin complex at a pH 9 by spectrophotometry.This method is preferred to other methods in that it is free of interference specially from most of transition metals ,because most hydroxides of transition metals are precipitated in the pH range 8-9.In addition, there is no need of special filtration of the precipitate of barium sulphate. The method can be applied directly for determination of sulphate.In the proposed method, the reaction between the complex (liquid) and sulphate (liquid) to produce barium sulphate (solid) is more favoured than the reaction between chloroanilate (solid) and sulphate (liquid) to produce barium sulphate (solid) The proposed method is applicable to diverse samples of soil and water.

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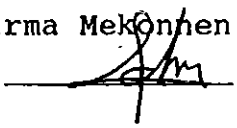
DECLARATION

I, the undersigned, declare that this thesis is my work,has not been presented for a degree in any university and all sources of material used for the thesis have been duly acknowledged.

Name; Girma Mekonnen
Signature; 

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