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Rapid Simultaneous Quantitative Determination of Ferric and Ferrous Ions in Geological Solution Sample with New Synthesized β-Diketone α-(2-Methoxy benzenthio) acetylacetone

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A rapid and precise method for simultaneous measurement of ferrous and ferric ion concentrations in solution with new synthesized β-diketone (2-methoxy benzenthiol) acetyl acetone (hereafter 2MBTAA) is reported. The determination of both ferric and total iron concentration is carried out in the same solution at the same light wavelengths, which significantly reduces the error of the analytical procedure. The method is based on the colorimetric measurement of red coloured ferric β-diketone complex formed at low pH. After the addition of hydrogen peroxide, which leads to the oxidation of ferrous ion, the 2MBTAA forms a complex with all the iron ions in solution. The maximum wavelength of the complex was 464 nm. The relationship between iron concentration and the absorbance obeys Beer's law under the optimum conditions that were studied. The optimal ratio and volumes of the reagent used were also determined. The effect of the interference ions was studied, It was found that the colour complex was stable for a long time (at least 10 h).

Key Words: 3-(2-Methoxybenzenthiol) pentane-2,4-dione, Spectrophotometry, Fe(II) oxidation.

INTRODUCTION

Iron is the fourth most abundant element, by weight, making up the crust of the earth[1]. Concerning its biological activity, iron is a highly versatile element, serving as the active centre of proteins responsible for oxygen and electrons transference in metalloenzymes such as oxidizes and dehydrases[2]. Iron is an essential element for living organisms, being considered as the transaion metal is more important for the biological system, about 70% of active iron in mammals is encountered as prophyrnic complexes in hemoglobins, myoglobins and cytochromes. The colorimetric determination of iron ions is regarded as the most precise and simple method.

The most popular colorimetric reagents such as 1,10-phenanthroline[3], bathophenanthroline(4,7-diphenyl-1,10-phenanthroline)[4], ferrozine(3-(2-pyridyl)-5,6-

bis(4-phenylsulfonic acid)-1,2,4-triazine)[5] and 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ)[6] are the common chelating agents for Fe(II). Triton(4,5-dihydroxy-1,3-benzene disulfonic acid[7] and 1-(2-pyridylazo)-2-naphthol(pan)[8] are the chelating reagents for Fe(III).

Atomic absorption spectrophotometry is useful for the determination of iron, but it measures only total iron; the method requires also an expensive spectrophotometer. The main problem in the above method is that only one of the oxidation states of iron (either Fe(II), Fe(III) or total Fe) can be measured at a time. This requires an additional reduction or oxidation step in order to find the concentration of the second oxidation state of the iron ions. Therefore, quantitative determination of both oxidation states of iron is relatively complicated and sometimes inaccurate. The new synthesized diketone forms a red coloured complex with Fe(III) in acidic media. The β-diketone forms chelates with various metallic ions and has enol-keto forms in a solution by a tautomerism. After dissociation of one proton from enol-form, the anionic group more strongly coordinates with a metal ion to form a complex. The acetylacetone is the simplest β-diketone that is known to form various complexes with about 60 metallic elements[9].

3-(2-Methoxybenzenethio) pentane-2,4-dion (Fig. 1), known as α-(2-methoxybenzene-thio) acetylacetone (2MBTAA) was used as a chelating agent in this work.

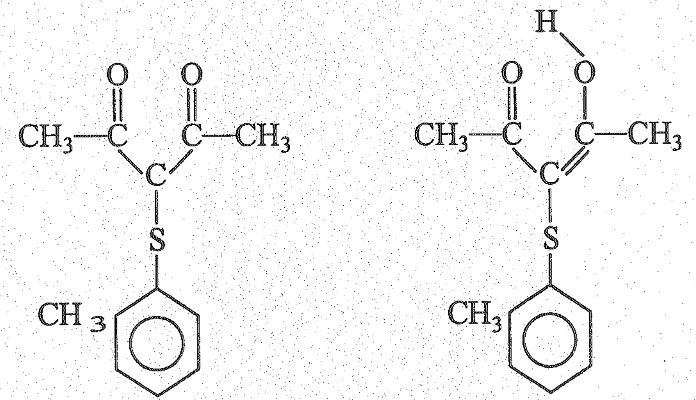

Fig. 1. (2MBTAA) used this study

The aim of this work is to propose a simple and rapid colorimetric method for the simultaneous quantitative determination of both ferrous and ferric ions in solutions, using the new synthesized ligand as indicator. The effect of various parameters of this analytical method were studied including the wavelengths of maximum absorption, the volumes and ratio of the reagents, the effect of various ions, mole ratio of complex, as well as the stability of the colour complexes with time.

EXPERIMENTAL

All spectrophotometric measurements were made with a Shimadzu 3100S spectrophotometer, coupled with a colour plotter model 20091027 at 25.0°C. Stoppered quartz cells of 1.00 cm optical path length were always utilized. A Varian model AA-20 atomic absorption spectrophotometer was used for comparison of results. pH measurements were made with Metrohm Herisau E-603 pH-meter, solutions were prepared with deionized water purified with an advanced Millipore F2 HN 6496SC system. The studied β-diketone (2MBTAA) was synthesized and was checked with H NMR and IR.

All chemicals (Merck, Darmestadt, Germany) were of analytical reagent grade and were used without further purification. Ligand solution (10^{-2} M) was prepared in ethanol. Fe(III) in different concentrations was prepared from $Fe(NO_3)_3$ standard solution and Fe(II) solution was prepared from $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$. $HClO_4$ and NH_3 were used for pH adjustment. Interference studies were made using different salt solutions, preferentially nitrate form (for cations) and sodium form (for anions).

Volumetric flasks of 5, 10 and 25 mL were used to prepare all samples analyzed by spectrophotometer. Aqueous solutions of ferric nitrate and ferrous nitrate were prepared containing between 0.5 and 25 ppm.

RESULTS AND DISCUSSION

Effect of pH on Complexation: The pH of Fe(III)-(2MBTAA) mixtures were varied between 1–10 by the use of $HClO_4$ or NH_3 solutions, since maximum absorbance was obtained at about pH 2.0. This value was selected as the working pH.

Effect of the light wavelength: The coloured complexes of Fe(III) with (2MBTAA) were formed immediately after mixing the solutions and the colour formed was stable for at least 10 h. For this reason absorbance was measured 10 min after preparing the complex. 2MBTAA forms a red coloured complex with Fe(III) in ethanol/water (50% v/v). Our first goal was to find the wavelength of the maximal optical absorbance of this complex using a solution containing 2.5 mL aqueous solution of Fe^{3+} (11 mg/L) as the nitrate to form 2.5 mL β-diketone (6×10^{-3} M) with a final concentration of 5.5 mg/L ferric ions. This solution was red-coloured due to the ferric-β-diketone complex. Blank was used containing 2.5 mL Fe^{3+} (11 mg/L) mixed with 2.5 mL ethanol. The effect of the wavelength on the light absorbance by these solutions is shown in Fig. 2.

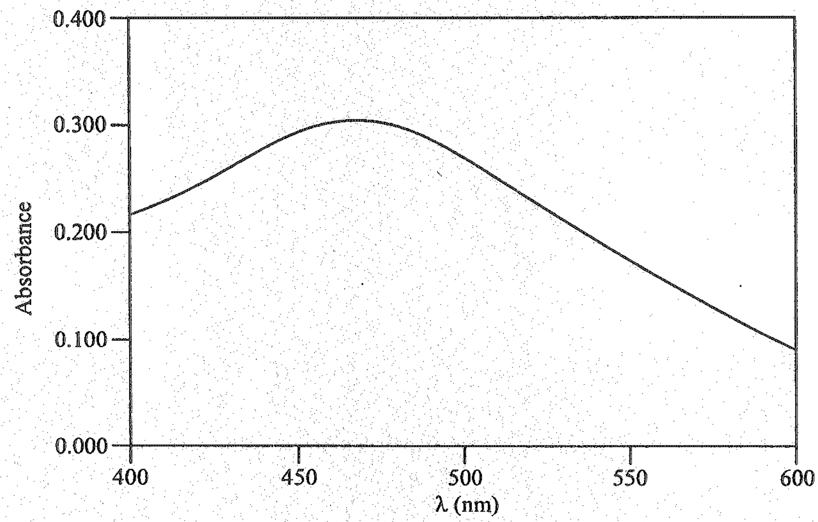

Fig. 2. Absorbance *vs.* wavelength for the ferric-(2MBTAA) complex (without H_2O_2)

It can be seen that the maximal absorbance was observed at a wavelength of 464 nm in solution. A darkened red complex with all the iron ions is formed when H_2O_2 is added to the solution of iron-(2MBTAA) complex. We studied the effect of the light wavelength on the optical absorbance of solution containing this complex. The complex was prepared by adding 50 μL of 30% aqueous solution of H_2O_2 to the solution of the red-coloured complex obtained in the previous experiment.

The colour immediately turned into darkened red colour. The maximal absorbance in solutions was observed at a wavelength of 464 mn (Fig. 3).

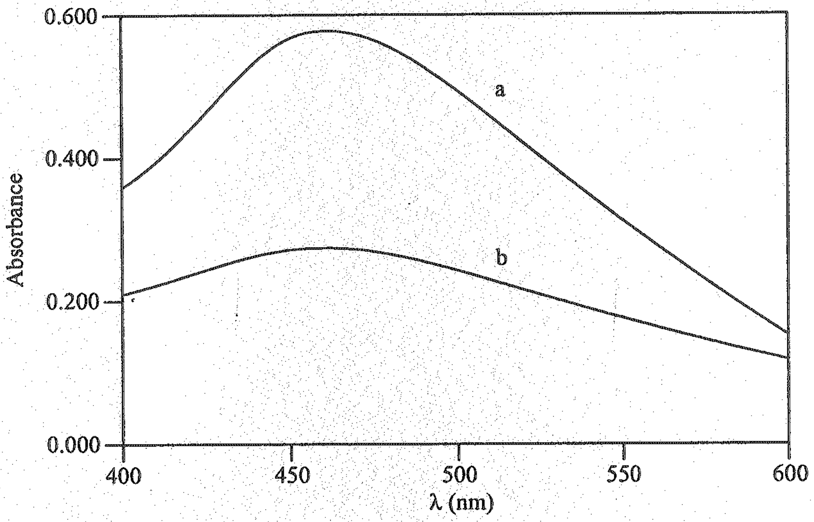

Fig. 3. Absorbance *vs.* wavelength for the complex of total iron with MPTAA: (a) with H_2O_2, (b) without H_2O_2

Effect of the reagent concentration: The effect of volumes of H_2O_2 (30%) (v/v) and (2MBTAA) concentration, used in the analysis, was studied next. The volumes and concentrations of these solutions were varied between 0.01 and 1 mL H_2O_2, 1 and 10 mole ratio (2MBTAA)Fe^{3+}. Our results showed that the optimal volume 50 μL H_2O_2 and 5-fold molar excess of reagent to that of metal ion leads to the maximum absorbance.

The following procedure was adopted in the next experiment:

1. For the measurement of ferric ion: 2.5 mL of aqueous ferric nitrate solution (pH = 2) with 2.5 mL of β-diketone. The light absorbance was measured at 464 nm.
2. For the measurement of total iron: 50 μL of 30% H_2O_2 solution was added to the above solution. The spectrometric measurement was performed at 464 nm.

The effect of ferric and total iron concentrations on light absorbance: The dependence between the ferric iron concentration and the light absorbance was studied next. The Fe^{3+} concentration in the solution was varied between 05–22 ppm after addition of β-diketone. The relationship was linear in the entire range of concentrations studied (Fig. 4) and obeys the Beer's law with the linear regression equation

$$A = 0.024 \times 10^5 C_{Fe^{3+}} + 0.044$$

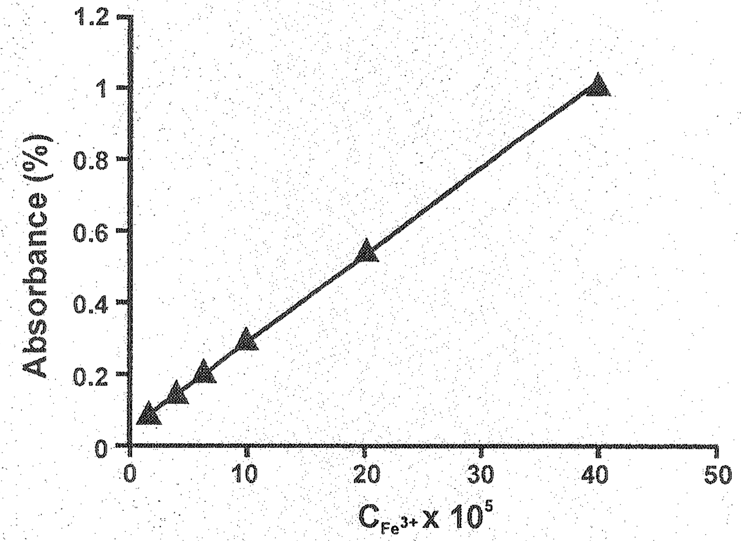

Fig. 4. Absorbance *vs.* concentration for the ferric-MPTAA complex (without H_2O_2) [iron concentration in graph = $C_{Fe}{}^{3+} \times 10^5$

where A is the absorbance and $C_{Fe}{}^{3+}$ is the iron concentration in M × 10^5. The correlation coefficient was equal to 0.999 for absorbance of up to 1, corresponding to Fe^{3+} concentration of 22 ppm in the analyzed solution. The relation between total iron concentration in the initial solution (containing constant ferrous concentration and different ferric concentration) ($C_{Fe\,(total)}$) and absorbance (Fig. 5) is linear and also obeys Beer's law. The following linear regression equation was obtained again:

For 'a' curve: $A = 0.024 \times 10^5 \ (C_{Fe\,(total)}) + 0.2861.$

For 'b' curve: $A = 0.024 \times 10^5 \ (C_{Fe\,(total)}) + 0.5296.$

The correlation coefficient was 0.999. This relationship is valid for $A < 1.0$.

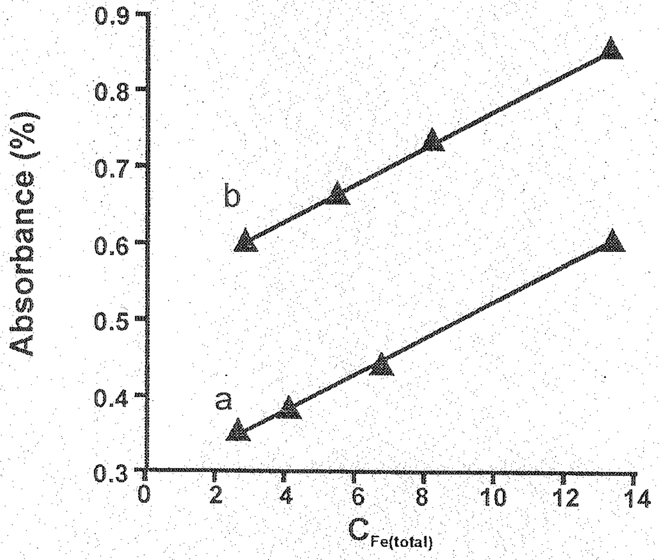

Fig. 5. Absorbance *vs.* concentration for the ferric-MPTAA complex (with H_2O_2: (a) in presence of 5.6 ppm Fe(III), (b) in presence of 11 ppm Fe(III)

The ratio between ferrous and ferric ion concentrations

The effect of ferrous ion concentration on determination of Fe^{3+} was studied next. The concentration of Fe^{3+} was measured in solutions containing ferrous and ferric ions in ratios between 0 and 20. The effect of ferrous iron on the measurement of Fe^{3+} is shown in Fig. 6. It can be seen that ferrous iron has practically no effect on the ferric iron determination; only when Fe^{2+} increased, the intensity of the red colour increased, which is probably due to the oxidation of ferrous iron by atmospheric oxygen. The ferrous ion concentration was calculated from difference between the total iron and ferric ion.

Stability of colour complex in time and stoichiometry of the complex

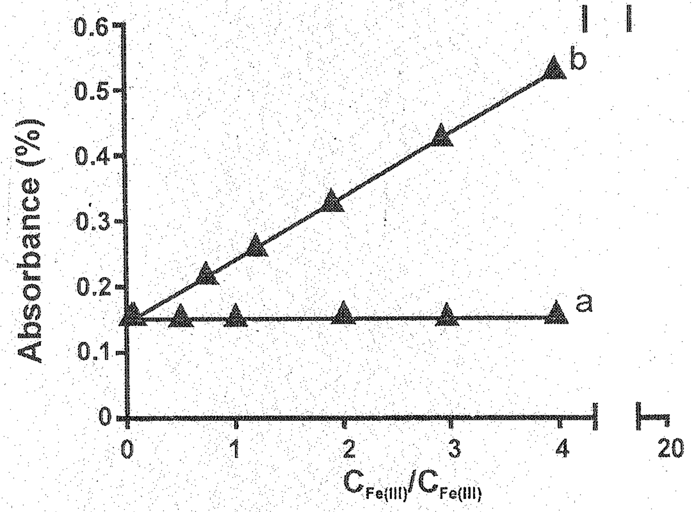

Fig. 6. The effect of ferrous ion on ferric and total iron determination: (a) without H_2O_2, and (b) with H_2O_2; $C_{Fe(III)} = 2.2$ ppm

The stability of colour complex in time was also studied. Solution containing ferric iron was used and coloured solution was kept at a temperature of 25°C. Our results showed that the absorbance of red complex did not change significantly during 10 h after their preparation; the maximum change observed was below 1.3% of the initial value. Stoichiometry of the complex was found 3/1 ligand/metal by continuous method.

Interference effects in iron determination

The effect of cations and anions, usually found along with iron in solutions, on the precision of the present analytical method, was studied. The following cations (as nitrate) were used: Mg^{2+}, K^+, Na^+, Ca^{2+}, Al^{3+}, Si^{2+} did not affect the ferric iron determination with ratios of at least 50, 50, 50, 40, 10, 10 g/g Fe, respectively. The following anions (as Na) were used: NO_3^-, ClO_4^-, Cl^-, SO_4^{2-} did not affect the ferric iron determination with ratio upper 50 g/g Fe.

The effect of the above-mentioned ions on the total iron determination was also studied; the presence of H_2O_2 did not affect the above result for total iron. Bauxite (Dominican B 103) was used as reference material[10]. That containing 61.34 ppm Fe^{3+} was spiked with 33.52 ppm of Fe^{2+} and determined with the proposed method. It is presented in Table-1. Very good concordance was obtained between theoretical and experimental methods for the material tested.

TABLE-1
EXPERIMENTAL RESULT FOR IRON REFERENCE MATERIAL[a]

Sample	C_{Fe} (ppm), stock solution		E_R (%)
	Theoretical	Spectrophotometry	
Bauxite	61.45	62.34	1.45
Bauxite + Fe^{2+}	33.52	34.03	1.53

a: β-diketone = 3×10^{-3}M; Blank = acid + minerals solution + ethanol; Sample = blank + ligand

Conclusion

A rapid and precise spectrophotometric method for quantitative measurement of both ferric and ferrous in solution is reported. Both forms of iron are measured in the same single sample, which significantly reduces the error in measuring the ratio between both oxidation states of iron ions. The most appropriate conditions for the analytical procedure were determined. The concentration of total iron in the analyzed solution should be below 22 ppm. It has been shown that the colour complexes are stable in time, no significant change in absorption was detected at least 10 h after their preparation. The stoichiometry of the complex is 3/1 (ligand/metal). The effect of the cations and anions usually present in solution was studied.

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