

# Colorimetric Determination of Iron with Diacetone Alcohol - A New Analytical Reagent

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**Summary:** The potential of diacetone alcohol as a new analytical reagent has been investigated for numerous cations. These studies have provided basis of a new and simple method for the spectrophotometric determination of Fe(III). The reddish brown coloured complex of Fe(III) with this new reagent at the natural pH (1.33) obeys Beer - Lambert's law over useful range of iron concentration (25-150 ppm). The visual limit of identification is 5 parts of iron per million parts of solution. This reagent may also be used to differentiate between ferrous and ferric ions.

## Introduction

A number of spectroscopic methods have been reported for the determination of ferric and ferrous ions [1-27]. The present work describes a new and simple spectroscopic method for the determination of Fe(III) in solution. It uses diacetone alcohol as the analytical tool, which is a colourless reagent, a desirable property of colorimetric and spectrophotometric reagents. So far it has been only indirectly employed in the analytical work in the determination of vanadium alone [28].

A systematic study of the colour reactions of diacetone alcohol with inorganic compounds has been made. More than fifty salts were tested and it was observed that this alcohol forms directly a coloured complex with iron. The nature of the reaction and chemical behaviour of this complex has been studied both visually and spectrophotometrically. Most of the diverse ions did not interfere with this reagent. These and other related aspects of our investigations have been reported in this paper.

### Experimental

Diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) (BDH) was used for the entire analytical work. Analytically pure ferric ammonium sulphate was used as a source of Fe(III). All other inorganic salts and acids used correspond to analytical requirements. Distilled water has been used to make different solutions.

All spectrophotometric measurements were made on Spectronic 21 (Bausch and Lomb) spectrophotometer (320-1000 nm) using 10 mm glass transmission cells. All pH measurements were made with Hanna HI 417 digital pH meter. All measurements of the solution were made with graduated pipettes accurate to 0.005 mL. visual measurements were made in glass test tubes.

#### Standard iron solution

A standard iron solution was prepared from ferrous ammonium sulphate ( $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ ) of reagent quality. A sample of 7.022 gm of the salt was dissolved in about 100 mL of the distilled water. Concentrated sulphuric acid (5 mL) and bromine (1 mL) were added to the solution. The solution was boiled until all the iron oxidized and excess bromine expelled. This solution containing one gm of  $\text{Fe}^{+++}$  was made upto 1 litre by adding distilled water for use as a stock solution.

Similar amount of ferrous ammonium sulphate was dissolved in distilled water (1 litre) for ferrous iron solution. Fresh solutions were prepared, whenever required.

#### Diverse ion solution

Stock solutions of various salts for studying their possible colour reactions with diacetone alcohol were prepared so that each milliliter contained 1 mg of the desired cations. These solutions were also used to find the effect, if any, of various ions on the colour reaction of diacetone alcohol with iron (II and III).

#### Study of colour reaction of diacetone alcohol with selected cations

In order to have an idea of some colour reaction of diacetone alcohol with different inorganic salts various trial experiments were made. In this connection small amount of this

alcohol (0.5 mL) was added to 1-2 mL of the stock solution of the required salts. More than fifty salts of different cations were tested. Observations were also made after heating the reaction mixture in the test tube. No colour formation was observed even on heating with any of the following cations:

$\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Hg}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Sn}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{UO}_2^{++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Bi}^{+++}$ ,  $\text{Sn}^{++++}$ ,  $\text{Th}^{++++}$ ,  $\text{Zr}^{++++}$ , and  $\text{Ce}^{++++}$ .

Copper sulphate solution, which is of blue colour changed to greenish blue with addition of diacetone alcohol, when strongly heated. Only solutions of salts of both Fe(III) and Fe(II) produced distinct reddish-brown coloured complexes. The Fe(II) complex lost intensity of the colour on strong heating, while Fe(III) complex, remained stable under similar conditions. From these observations it has been inferred that Fe(III) was the only cation which produced a stable and distinct colour under all conditions. Therefore, further work was concentrated only on Fe(III) cations.

#### Tests carried out to study the formation of Fe(III) complex with diacetone alcohol

##### Spot test

To 1-2 mL of the test solution was added 0.2 mL of diacetone alcohol. The appearance of a beautiful reddish brown colour indicated the presence of Fe(III) in the test solution. Then, a drop of this test solution was dropped on a filter paper, followed by the addition of a drop of diacetone alcohol. Reddish-brown coloured spot was observed on the filter paper.

##### Determination of $\lambda_{\text{max}}$

Absorbances of the reddish-brown coloured complex formed in different test solutions were recorded at various wave-lengths, when the same fixed concentration of Fe(III) was used in the blank solutions as well. A plot of these values of absorbance against the wave lengths indicated  $\lambda_{\text{max}}$  of this Fe(III) complex at 480 nm.

##### Calibration curve and determination of concentration of Ferric ions in various samples

For the construction of preliminary standard curve, solution containing 25, 40, 50, 65, 75, 85, 100, 115, 125, 140, 150 and 175 ppm of Fe(III)

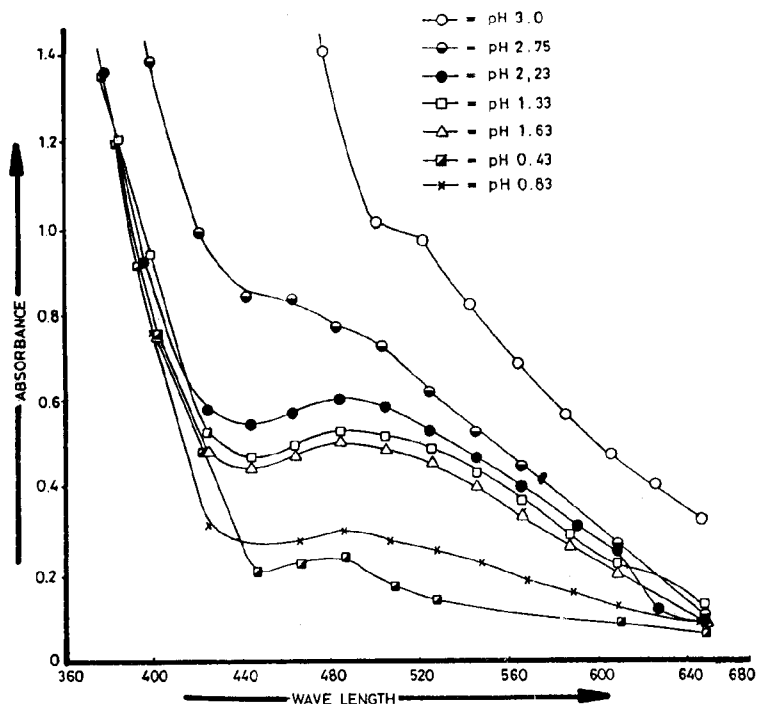


Fig. 1 Effect of pH on absorbance of iron complex formed with diacetone alcohol

were prepared. To every sample solution (2 mL) 2 ml of diacetone alcohol (diluted with water in the ratio 1:4) was added, and absorbance was measured spectrophotometrically in all the cases. A plot of these values of absorbances against concentration (ppm) of Fe(III) afforded a linear plot with origin at zero. The Beer-Lambert's law is well obeyed from 25 to 150 ppm concentration of ferric ions. The calibration curve gave satisfactory results regarding the concentration of ferric ions in different samples following within this range.

#### *Sensitivity of the reaction*

In order to determine sensitivity of this colour reaction, stock solution containing 1 gm of Fe(III) per litre (1000 mg per liter or 1000 ppm) was prepared. From this stock solution different solutions containing 1, 5 and 10 ppm were prepared. To 3 mL of each of these solutions diacetone alcohol (1 mL) was added. It was possible to determine respective order of Fe(III) concentrations. It was found that the limit of sensitivity of the complex was restricted to 5 part of Fe(III) in 1000, 000 parts of the solutions, when the observations were made visually.

#### *Effect of pH on the coloured complex*

Variation in hydrogen ion concentration affected the intensity and hue of the coloured complex produced by diacetone alcohol with Fe(III). The colour was the most stable at the natural pH (1.33) of the complex. The original colour of the complex disappeared at pH below 0.8 and assumed a yellowish tinge. Similarly, the reddish brown colour of the complex started to change at pH 2.5. It completely changed to brown at pH 2.75.

Spectrophotometric measurements were also made on a series of solutions containing Fe(III) complex, by varying the pH from 0.8 to 3.0. The absorbance measured were made at 20 nm intervals from 380 to 460 nm. The results of absorbance vs. wavelength curves are shown in (Fig. 1). It may be obvious from these points that variation in hydrogen-ion concentration affected both the intensity and hue of the coloured complex formed by diacetone alcohol with Fe(III).

#### *Effect of temperature*

A series of solutions varying in ferric concentration from 25 ppm to 1000 ppm were

prepared. To 4 mL of each solution, 0.2 mL of diacetone alcohol was added. Absorbance, were measured spectrophotometrically before and after heating the complex on water bath (at 100°C) and bunsen burner. It was found that the colour of the complex was stable to heating in the beginning, but intensity decreased with rise in temperature. However, if the heated solution of the complex was allowed to cool down to ambient temperature, all the samples of the complex attained original intensity.

Ferrous complex was also stable at room temperature. However, strong heating on a bunsen burner completely destroyed the colour, which failed to restore on cooling.

Table-1 shows spectrophotometric data obtained from temperature effect measurements

Table-1: Effect of temperature on absorbance of Fe(III) diacetone alcohol complex

No.	Concentration of Fe(III) in complex (ppm)	Before heating	After heating on water bath (at 100°C)	After heating vigorously on bunsen burner	After standing for 3 hours
01.	25	0.25	0.09	0.05	0.24
02.	50	0.34	0.10	0.06	0.34
03.	100	0.40	0.12	0.10	0.39
04.	250	0.42	0.37	0.35	0.40
05.	2000	0.44	0.43	0.40	0.42

#### Effect of time

It was noticed that colour intensity of Fe(III) with diacetone alcohol remains unchanged for 24 hrs. However, all the observations and tests in the experimental work were made within 30 minutes after the formation of the complex.

#### Effect of diverse ions

For measuring the effect of diverse ions the solutions of different metal ions [ $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ag}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Sr}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Hg}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Sn}^{++}$ ,  $\text{UO}_2^{++}$ ,  $\text{Bi}^{+++}$ ,  $\text{Ce}^{++++}$ ,  $\text{Th}^{++++}$ ,  $\text{Zr}^{++++}$  etc., with different combinations of anions) were prepared so that the concentration of corresponding ion solution was usually 1000 ppm. A standard solution of iron was also prepared containing 200 ppm Fe(III). Every ion solution (2 mL) was added to iron solution (2 mL) followed by the reagent (0.5 mL diacetone alcohol). Visual observations were made to match the complex formed with a standard of the corresponding concentration of Fe(III).

These studies indicated that there are relatively fewer ions which cause interference e.g.,  $\text{Ag}^+$ ,  $\text{Cu}^{++}$ ,  $\text{Mn}^{++}$  in the colour reaction and none which cannot be removed by ordinary procedure of analysis.

It is clear from the preceding results that diacetone alcohol may be successfully used as a new analytical reagent for the spectrophotometric determination of ferric ions. This reagent forms a colourless solution in water, which is very desirable property of colorimetric and spectrophotometric reagents. It affords a stable and distinct reddish-brown coloured complex with ferric ions at the natural pH of 1.33. At higher acidity the colour disappears at pH below 0.8 and assumes a yellowish tinge. It begins to change to brown at pH 2.5 and completely transforms to brown at pH 2.75. The reddish-brown coloured complex of this reagent obeys Beer-Lambert's law over useful range of iron concentration (25-150 ppm). The visual limits of identification is 5 parts of iron in one million parts of solution. The present method is fairly simple and straight forward. A large number of diverse ions don't interfere with the determination of ferric ions. However, the molar-ratio method did not provide any conclusive information regarding the stoichiometry of the complex formed with  $\text{Fe}^{+++}$ . But it should not be taken to imply that the complex is of indefinite composition. It is just possible that its composition is not indicated by its indirect method of determining it [29].

The ferrous ions also form reddish-brown coloured complex with this reagent, but the coloured species are less stable to heat. On strong heating the colour of the ferrous complex gets discharged and fails to restore on cooling, while the colour of the ferric ions attains original intensity on cooling to ambient temperature. Thus, this reagent may also be used to distinguish between ferrous and ferric ions.

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