DETERMINATION OF IRON IN WATER SAMPLES

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CONTENTS

ABSTRACT

In this method the catalytic effect of iron (III) has been achieved by the reaction of 9,10-diaminoanthracene and *p*-phenylenediamine with N-monomethylaniline instead of N,N-dimethylaniline. In the presence of hydrogen peroxide and acetic acid as an activator, the produced colour is measured at 765 and 730 nm within 20 min. The concentration ranges are 2.236 to 22.360, 8.96 to 89.6 μg per liter (for Fe II, III respectively) and molar absorptivities are 9.41×10^6, 4.73×10^5 L mol^{-1} cm^{-1} for 9,10-diaminoanthracene and *p*-phenylenediamine respectively. At the same time, 8-hydroxyquinoline has been used for spectrophotometric determination of ferric ions at 760 nm in acetate buffer pH 4.7. Beer's law is obeyed in the concentration range 0.0450 to 0.447 mg ferric ions per liter. Indirect coulometric technique has been adopted as a new method to determine iron. It is well known that ferric ions form a stable complex with 8-hydroxyquinoline in acetate buffer pH 4.7. The excess oxine can be determined coulometrically at 40 milliamp. constant coulometric current. Bromination is achieved by the generation of bromine from N-bromosuccinimide at a platinum anode.

These methods are compared with each other statistically and applied for the determination of iron in water samples of the Kingdom of Saudi Arabia, in addition to a sample of organic fungicide, e.g., Ferbam, and some inorganic samples of magnetite, hematite, siderite and pyrite.

1. INTRODUCTION

Iron is an abundant element in the earth's crust, but exists generally in minor concentration in natural water systems. The form and solubility of iron in natural waters are strongly dependent on the pH and the oxidation-reduction potential of the water.

Several methods have been developed for determination of iron ions including spectrophotometric /1-4/, titrimetric /5-7/, amperometric /8,9/, potentiometric /10/, atomic absorptiometric /11/, densitometric /12/, gas chromatographic /13/, coulometric /14/, polarographic /15/ and high performance liquid chromatographic /16/ techniques.

2. INSTRUMENTS, MATERIALS AND METHODS

A Pye Unicam SP 1800 spectrophotometer is used, while the apparatus for coulometric technique is reported in ref. /17/, with two small platinum plates connected to the apparatus for amperometric detection of the end-point. An Orion research microprocessor pH/millivoltmeter 811, equipped with the Orion model 91-20 glass combination pH electrode for pH adjustment, is also used.

All solutions are prepared with analytical reagent grade BDH, using bidistilled water.

a) 1×10^{-4} M solution of ferric ions is prepared by dissolving 0.049 g of $Fe_2(SO_4)_3 . 5H_2O$ in 1 L distilled water in the presence of 1:1 H_2SO_4 acid; 1 ml of this solution contains 11.18 μg/ml Fe^{3+}. This is diluted in order to get concentration down to 1×10^{-9} M solution.
b) 1×10^{-2} M solution of 8-hydroxyquinoline (oxine) in 2M acetic acid solution.
c) 0.01% 9,10-diaminoanthracene in ethanol.
d) 0.01% *p*-phenylenediamine in ethanol.
e) 0.01% N-methylaniline in 0.1 M hydrochloric acid.

f) 30% v/v hydrogen peroxide.
g) 1:1 v/v acetic acid solution.
h) 10% potassium cyanide solution.
i) 0.5 solution of N-bromosuccinimide.
j) 10% thiourea.
k) Buffer solution pH 4.7 acetate is prepared by dissolving 56.0 g of sodium acetate trihydrate in distilled water; 25.0 ml of glacial acetic acid are added and diluted to 1 L.
l) Buffer solution pH 10.0 is prepared by adding 50.0 ml of 0.05 M sodium bicarbonate to 10.7 ml of 0.1 M sodium hydroxide and completing to 100 ml.
m) Buffer solution pH 7.0 is prepared by adding 50.0 ml of 0.1 M potassium dihydrogen phosphate to 29.1 ml of 0.1 sodium hydroxide and diluting to 100 ml.
n) Ammonia buffer solution pH 10.0 is prepared by dissolving 54.0 g of ammonium chloride in 200 ml of water; 350 ml of 25% ammonium hydroxide are then added and completed to 1 L.

Oxidative Coupling Reaction, Procedure (1)

Into 25 ml volumetric flasks transfer an aliquot portion of the sample solution containing up to 25 μg ferric ions, 1 ml acetic acid, 4 ml of diaminoanthracene or phenylenediamine followed by 4 ml of N-methylaniline and 0.2 ml of hydrochloric acid. The mixture is kept in a boiling water bath for 10 ml.

Then the catalytic reaction is started by mixing 0.2 ml of 30% hydrogen peroxide and the mixed solution is kept in the boiling water bath for 10 min. The coloured solution after completion to volume with 1:1 v/v acetic acid is measured at 765 and 730 nm with 9,10-diaminoanthracene and *p*-phenylenediamine against a reagent blank prepared in exactly the same manner omitting the ferric ions solution. The concentration of unknown samples is obtained from calibration curves previously prepared using ferric ions in concentration ranges of 0.056 to 0.559, 0.224 to 2.224 μg in 25 ml with 9,10-diaminoanthracene and *p*-phenylenediamine respectively.

8-Hydroxyquinoline as Chromogenic Agent, Procedure (2)

Into a 25 ml volumetric flask introduce an aliquot volume of the sample

solution containing up to 10.1 μg ferric ions. Add 1 ml of 1:1 nitric acid and boil for 5 min; after cooling 0.5 ml of potassium cyanide and 3 ml of 0.01 M 5-hydroxyquinoline are added. The solution is made up to volume using acetate buffer pH 4.7 and left to stand for 20 min. The produced colour is measured at 760 nm against a reagent blank prepared in exactly the same manner omitting addition of ferric ions solution.

The iron concentration of water samples is obtained from calibration curves previously prepared using ferric ions solution in concentration range of 1.12 to 11.18 μg in 25 ml.

Coulometric Titration, Procedure (3)

Place 40 ml of the supporting electrolyte N-bromosuccinimide into the coulometric cell, followed by 10 ml acetate buffer pH 4.7, 10 ml of the accurately measured volume of standard ferric ions solution, 0.5 ml of potassium cyanide, and 20 ml of the standard oxine solution. Charge the cathode compartment with the same volume of N-bromosuccinimide and 10 ml acetate buffer pH 4.7. Pass a current of 40 milliamp. while stirring the solution magnetically. Adjust the sensitivity of the indicating apparatus to a suitable value. Near the end-point transient deflections occur and serve to give warning of its approach. The end-point is indicated by the first permanent deflection and then the reading of the counter is taken. The experiment is repeated again without addition of ferric sample and the concentration of iron can be calculated.

3. RESULTS AND DISCUSSION

In order to get the optimum conditions for the determination of ferric ions in water samples, the effects of various factors were studied.

(a) Effect of pH

Buffer solutions with different pH's including phosphate (pH 7 and 9), acetate (pH 4.7) and ammonia (pH 10.0) were used to study their effects on the colour formation at a constant reaction time of 20 min at room temperature 25°C. The highest stability and sensitivity of the produced colour was obtained in the presence of acetate buffer pH (4.7), showing its maximum absorbance at 760 nm (Fig. 1). The oxidative coupling reaction was effected

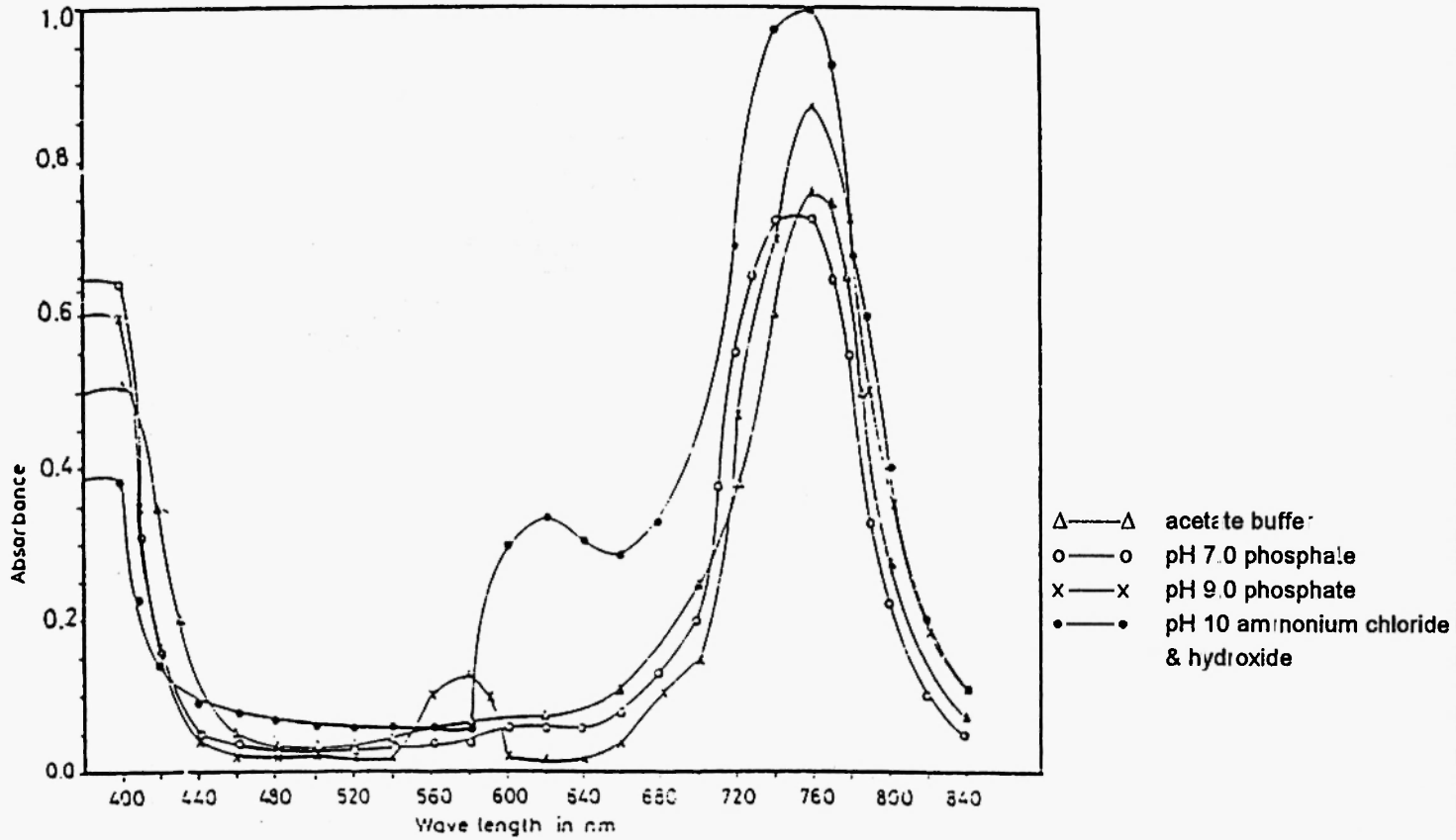


Fig. 1: Absorption curve of iron solution with 8-hydroxyquinoline

using a boiling water bath. It was found that iron catalyzed the reaction in the presence of hydrogen peroxide as an activator and 1:1 acetic acid, with absorbance maxima at 730, 765 nm and *p*-phenylenediamine and 9,10-diaminoanthracene respectively as illustrated in Fig. 2.

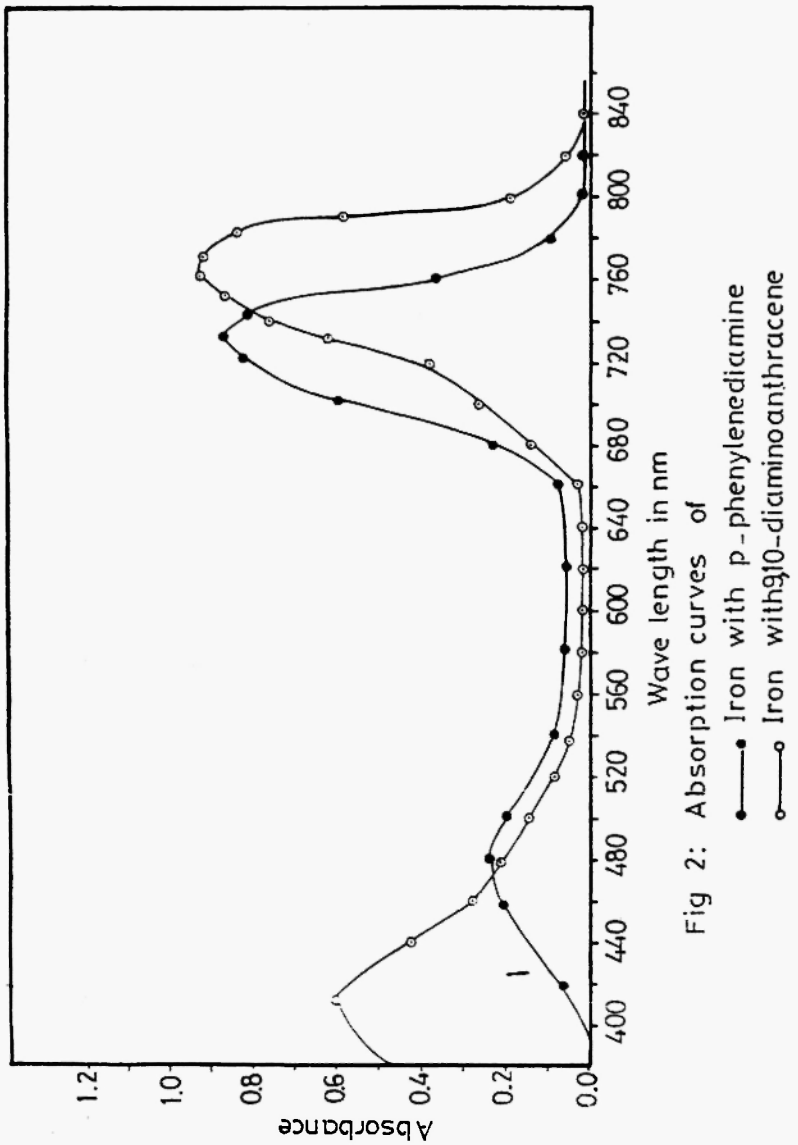


Fig 2: Absorption curves of
—● Iron with p-phenylenediamine
—○ Iron with9,10-diaminoanthracene

(b) Effect of time

The colour formation in these reactions was studied at varying time. It was found that the oxidative coupling reaction proceeded faster at elevated temperature when using the water bath. The absorbance increases, reaching its maximum at a fixed time of 20 min at 765, 730 nm with 9,10-diamino-anthracene and *p*-phenylenediamine respectively, and fades after an hour. On using 8-hydroxyquinoline as a colour reagent, the colour reaches its maximum at 760 nm within 20-60 min at room temperature as shown in Fig. 3.

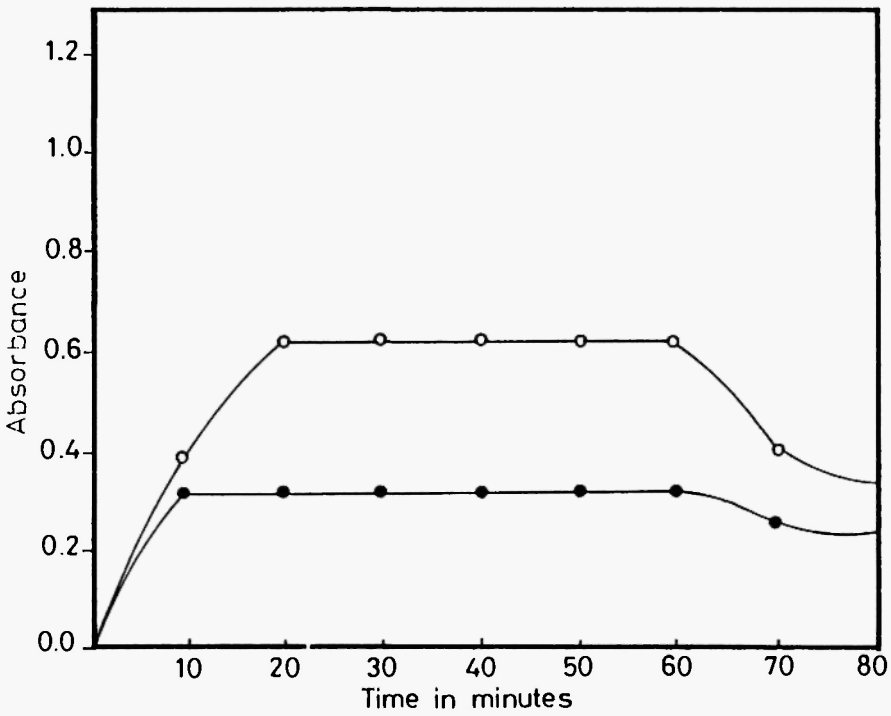


Fig. 3 : Effect of time on the reaction of Iron solution with 9.10-diaminoanthracene o—o and ●—● 8-hydroxyquinoline.

(c) Effect of concentration of *p*-phenylenediamine, 9,10-diamino-anthracene, N-methylaniline and 8-hydroxyquinoline

The concentrations of these reagents are chosen from the curve in Fig. 4 in order to obtain a constant and maximum absorbance under the specified conditions.

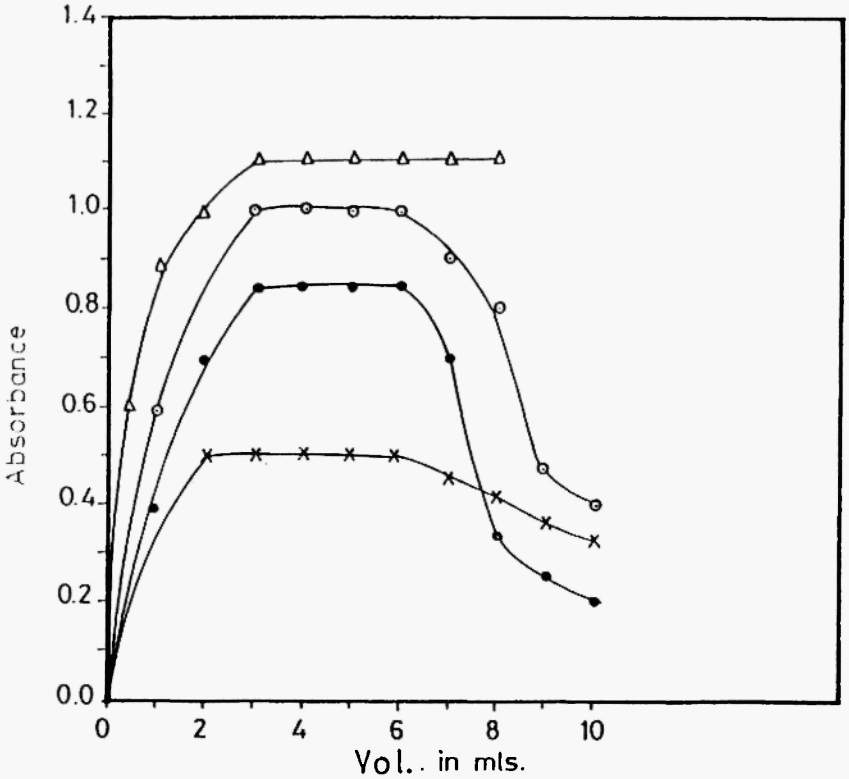


Fig. 4: Effect of the volumes of o—o, 9,10-diaminoanthracene, •—•, *p*-phenylenediamine, x—x, N-methylaniline and Δ—Δ, 8-hydroxy-quinoline.

(d) Effect of hydrogen peroxide concentration

It is found from Fig. 5 that, within the range of 0.1 to 0.3 ml of 30% volume of hydrogen peroxide, the suitable volume can be chosen for the initiation of the reaction.

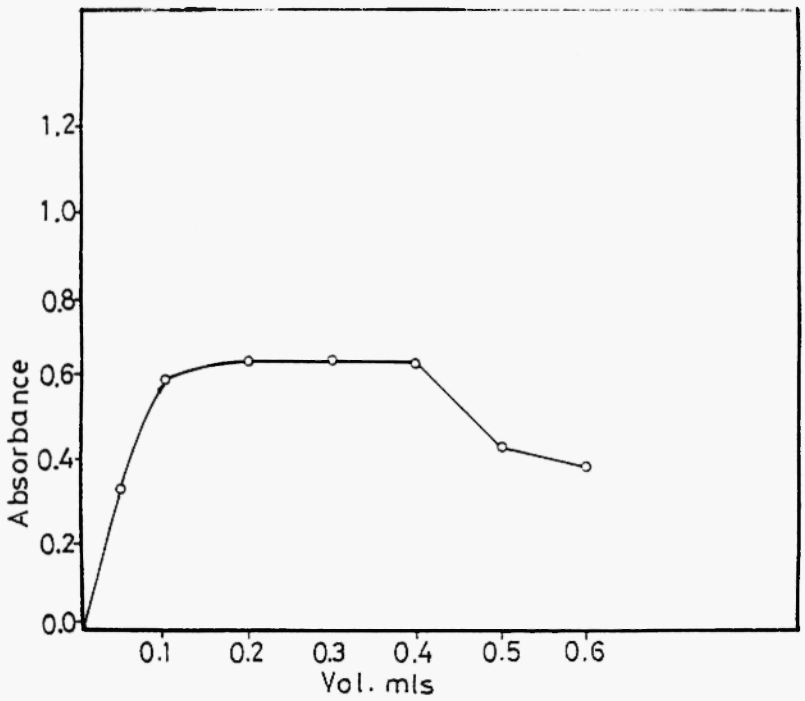


Fig 5: Effect of the volumes of 30% hydrogen peroxide

CONCLUSION

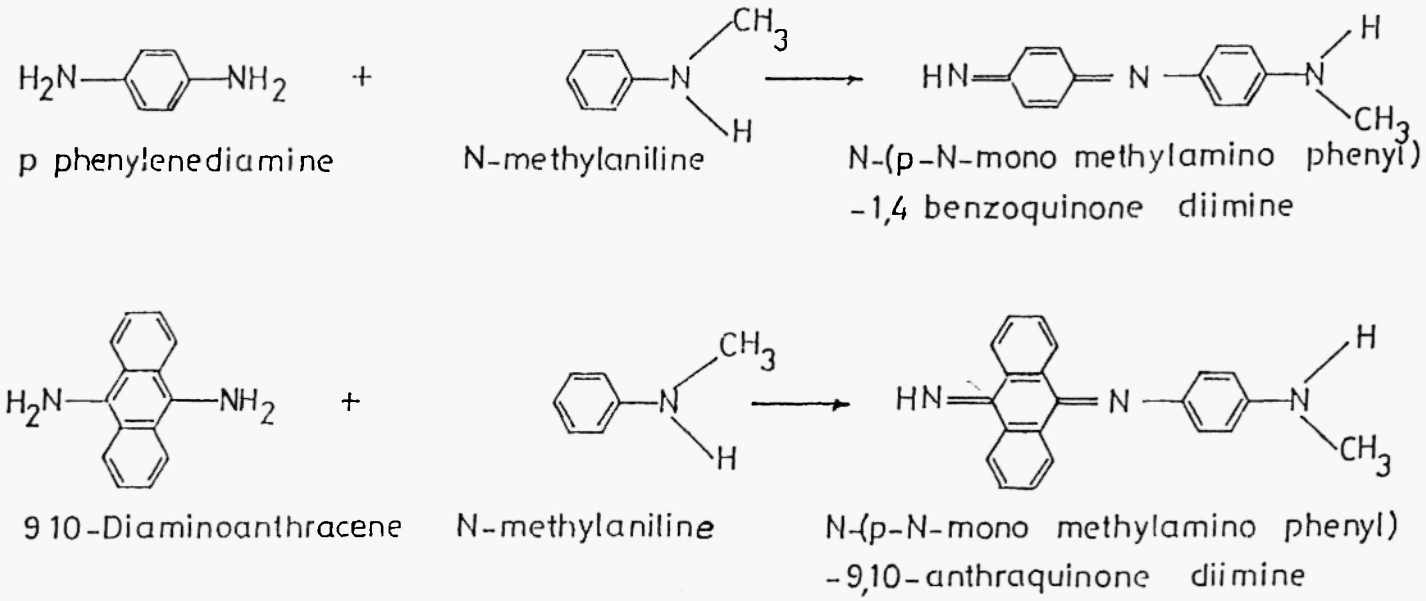
Iron in low concentration can be determined spectrophotometrically at 760 nm using 8-hydroxyquinoline in acetate buffer pH 4.7 within a range of 0.045 to 0.447 mg Fe^{3+} ions per liter with molar absorptivity of 1.79×10^4 L mol^{-1} cm-1.

The interference of many cations can be overcome by proper control of the pH of the solution and using complexing reagents. Potassium cyanide in the presence of acetate buffer at the required pH (4.7), in an amount of 0.5 ml of 10%, is sufficient to mask cadmium, zinc, mercury (II), copper, cobalt and nickel ions. These cations may also be removed from the reaction medium by the use of anion exchange.

The coulometric technique has been adopted as a new technique for determination of iron in the presence of 8-hydroxyquinoline as its coordination number is six. By proper control of the pH of the solution by the use of a complexing agent such as potassium cyanide, and using pH 4.7, numerous interfering cations may be eliminated. The excess 8-hydroxyquinoline can be directly determined without separation of the produced iron oxinate. It is well known that bromine may be electrogenerated with 100% current efficiency by the oxidation of N-bromosuccinimide acting as a supporting electrolyte at a platinum electrode. Bromination of free oxine proceeds and thus four Faraday are required per mole of oxine. The bromine liberated is consumed immediately for bromination of oxine with the formation of 7,5-dibromo-8-hydroxyquinoline. The end-point is detected amperometrically. Near the end-point, transient deflections occur and serve to give warning of its approach. The end-point is at the first permanent deflection and the reading of the counter is taken. The experiment is carried out in addition to a blank carried out in exactly the same manner without the addition of the iron sample solution. This technique is much more time-saving, accurate and precise than the indirect iodometric titration. In this technique, complications due to adsorption of iodine can be avoided and brown additive compounds of iodine with the dibromo compound may be eliminated, which otherwise introduce an uncertainty in the end point. There is no loss on storage or change in titre, so the obtained result is considered accurate. The method can be applied for determination of iron in water samples containing very low concentrations down to 1×10^{-9} M, i.e. 4.97 μg per liter, and is more sensitive than the spectrophotometic method that can be used down to 0.045 mg liter.

Shigenori Nakano *et al.* /18/ stated a method for the determination of ferric ions which depends upon its catalytic effect in the presence of hydrogen peroxide and acetic acid as an activator to form a colour with N-phenyl-*p*-phenylenediamine. In this study it is found that Fe (III) ion catalyzes colour formation in a different system from that of Shigenori Nakano *et al.* It is based on the reaction of 9,10-diaminoanthracene and *p*-phenylenediamine with N-monomethylaniline in the presence of hydrogen peroxide and acetic acid as an activator for the catalytic effect of Fe (III) instead of using N,N-dimethylaniline in the presence of hydrogen peroxide and acetic acid as an activator, scheme 6.

The absorbance shows its maximum at 765 nm which is due to the formation of N-(*p*-N-monomethylphenyl) 9,10-anthraceneoquinonediimine



Scheme 6: Oxidative Coupling Reaction of
a- P-phenylenediamine with N-monomethylaniline
b- 9,10-Diaminoanthracene with N-monomethylaniline

with 9,10-diaminoanthracene. At 730 nm the absorbance is due to N-(*p*-N-monomethylphenyl) 1,4-benzoquinonediimine with *p*-phenylenediamine. The modified adopted method is more sensitive, can be used within the range of 0.056 to 0.559, 0.224 to 2.224 μg Fe^{3+} ion per 25 ml, i.e. 2.24 to 22.40, 8.96 to 89.60 μg per liter for the reagents 9,10-diaminoanthracene and *p*-phenylenediamine respectively, with molar absorptivities respectively 9.41×10^6 and 4.73×10^5 L mol^{-1} cm^{-1}. From this data it is clear that 9,10-diaminoanthracene is the best coupling oxidative reagent in this method and can be chosen for the application. The coloration produced is also catalyzed by Fe (II) ion, being oxidized to Fe (III) ion by hydrogen peroxide. As little as 2.236 μg per liter of Fe (II, III) can be determined easily by their catalytic effect at a fixed time after the initiation of the reaction, especially with 9,10-diaminoanthracene. In this experiment it was found that a concentration of copper ions above 100 μg greatly affects the catalytic reaction in the presence of 0.1 to 10 μg of Fe^{3+} ions. This interference can be masked by addition of 1 ml of 10% thiourea.

The oxidative coupling method using 9,10-diaminoanthracene and coulometric techniques are compared with each other statistically, using Student's t test. No significant difference is revealed between the methods at 95% confidence limit.

These two methods have been applied for the estimation of iron in the following inorganic compounds: magnetite, hematite, siderite and pyrite, in

Table I: Determination of Iron in Some Organic and Inorganic Compounds.

Samples of Iron	% recovery, ± st. dev.	
	9, 10-diaminoanthracene	Coulometric titration *
Magnetite	98.92 ± 0.31	98.95 ± 0.61
Hematite	98.63 ± 0.51	98.67 ± 0.43
Siderite	97.89 ± 0.13	98.01 ± 0.26
Pyrite	97.83 ± 0.09	97.84 ± 0.41
Frebam	99.11 ± 0.23	99.09 ± 0.12

* Each result is the mean of three experiments ± standard deviation.

addition to the organic fungicide compound Ferbam. These compounds are dissolved in aqua regia and the produced ferric ion analyzed by the two methods: oxidative coupling and coulometric, and the results are shown in Table 1.

Table 2 represents the concentration of iron in water samples of the Kingdom of Saudi Arabia. In order to locate the pollution by iron ions,

Table II : Determination of Iron in Water samples of Kingdom of Saudi Arabia.

Water Samples	Concentrations in ppm	
	9, 10-diaminoanthracene	Coulometric titration
		*
1- Eastern province tap water of Dammam city.	0.45 ± 0.06	0.44 ± 0.02
2- Northern province tap water.	0.24 ± 0.03	0.23 ± 0.02
3- Western province tap water and Zamzam well.	0.28 ± 0.04 0.32 ± 0.02	0.28 ± 0.03 0.32 ± 0.02
4- Ground surface water Wadi Khulays and Wadi Layla.	0.29 ± 0.06 0.27 ± 0.03	0.29 ± 0.05 0.27 ± 0.04
5- Surface Water Arabian Gulf.	0.25 ± 0.07	0.26 ± 0.07
6- Industrial waste water of oil refinery Aramco.	2.22 ± 0.10	2.23 ± 0.20
7- Laboratory waste water.	0.95 ± 0.03	0.96 ± 0.01

* Each result is the mean of three experiments ± standard deviation.

different sources of water samples are used, e.g. tap water of Damman city, ground water supplied by Wadi Khulays and Wadi Layla, surface waters (Arabian Gulf), individual private wells, e.g. the Zamzam well located in the Holy Site of Mekkah and others in the western province and northern province of Saudi Arabia, industrial waste of the oil refinery of Aramco and laboratory waste water. The concentration of iron ions was found to be in the range of 0.24 ± 0.03 to 2.22 ± 0.01, 0.23 ± 0.02 to 2.23 ± 0.20 for the 9,10-diaminoanthracene and coulometric techniques respectively. This is different from the permissible concentration limit stated by the World Health Organization /19/ to be 0.3 ppm.

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