J. Flow Injection Anal., Vol. 24, No. 2 (2007) 109–113

Flow Injection Spectrophotmetric Determination of Iron Based on Its Catalytic Effect on the Oxidation of Variamine Blue by Hydrogen Peroxide

Elmorsy Khaled *; H.N.A.Hassan and Ahmed.M.H.Moghieb

Micro analytical Lab., Appl. Org. Chem. Dept., National Research Center, Dokki, Cairo, Egypt

Abstract

A simple, rapid and sensitive kinetic spectrophotometric method for the determination of trace amounts of iron (II) was developed based on its catalytic effect on the oxidation of variamine blue with hydrogen peroxide in the presence of triethanolamine as activator to form a deep violet blue colored species with an absorption maximum at 560 nm. The reaction was monitored using FIA and batch methods. The calibration graphs were linear in the concentration range 5.4-130 and 3.4-40 ng of iron for the FIA and batch, respectively. The FIA technique showed good average recoveries with lower detection limit compared with the batch technique. The method was highly selective to iron (the tolerance limit for 20 ions was listed) and successfully applied for iron determination in pharmaceutical preparation, polluted air and tap water with average recoveries agreed with the official method.

Key word: Kinetic; Iron (II); Variamine blue; Flow injection; Batch analysis; Polluted air; Pharmaceutical preparations; Tap water.

1. Introduction

Iron is widely distributed at various concentration levels throughout the environment and plays an important role in ecological systems. Several spectrophotometric methods for the determination of different oxidation states of iron (II) using chelating agents were reported [1, 2].

Because of the growing need for high sensitive analytical methods, the catalytic kinetic method has become an attractive procedure as the trace determination can be achieved without the use of expensive or special equipment with lower probability to receive interferences [3-7]. Many batch procedures for the catalytic determination of iron have recently been reported, based on its catalytic action on the oxidation of organic substrates with hydrogen peroxide [8-10], peroxydisulphate [11], bromate [12] or periodate [13]. Though the batch methods allowed the determination of iron at sub-ppb levels, they include time as a variable to be strictly controlled and require a stable reaction temperature with constant mixing of the reagents. However, catalytic flow-injection methods provide advantages of rapidity, easy assembly and efficient to control such serious experimental conditions [14-15]. Several FIA methods have been reported for the determination of iron in different samples employing the oxidation of organic dyes reactions [16-21]. For the development of a new indicator reaction for practical applications in catalytic and FIA measurements, attention should be paid to the reaction time to be short as possible, using one chromogenic reagent without additional components for an indicator reaction as well as using of the fixed time method for the ease of measurement and simplicity of the flow system.

The aim of the present work was to establish a kinetic spectrophotometric method for batch and FI determination of iron (II) offering the fast measurement with adequate sensitivity, based on its catalytic effect on the oxidation of variamine blue by hydrogen peroxide and the analysis of iron in different samples. The proposed procedures was carried out at a shorter time under more ambient conditions when compared with some published methods for the catalytic determination of iron which need boiling of the reaction medium for about 15 min followed by cooling the reaction mixture [22-26]. Formation of the colored species occurred in one step reaction rather than the oxidative coupling reaction [27-29] which simplify the FIA system and the analytical procedures. In addition, the reaction rate can be followed using the fixed time method which simplify the measuring and instrumentation rather than the initial rate method.

*Corresponding author.
E-mail: elmorsykhaled@yahoo.com

2. Experimental

2.1. Reagents

All reagents used were of analytical grade and double distilled water was used throughout the experiment. Stock Fe (II) and Fe (III) solutions were prepared by dissolving $Fe(NH_4)(SO_4)_2.12H_2O$ (VEB laboratory Apolda, Germany) and $FeSO_4.7H_2O$, respectively, in 0.1M H_2SO_4. The contents of iron in both stock solutions were estimated by atomic absorption measurements. Fresh working solutions were prepared daily by diluting the stock solutions with water. Variamine blue solution was prepared by dissolving the appropriate weight of the VB. HCl (BDH) in hot water and filtration followed by standardization potentiometrically via titration with tetraphenyl borate using simple coated wire electrode [30]. Suitable concentration of hydrogen peroxide solution was prepared using 30% H_2O_2 solution (Merck). Triethanolamine solution ($3.5x10^{-3}$M) was prepared by dissolving 100 µl TEA solution (VEB laboratory Apolda, Germany) in water and diluting to 250 ml. For FIA system, reagent R1 was a mixture of the VB dye ($2.2x10^{-3}$M, 65ml), acetate buffer pH5 (108ml) and TEA solution ($3.5x10^{-3}$M, 77ml), while the R2 was 0.05M of H_2O_2.

2.2. Real Samples

2.2.1 Pharmaceutical Preparations

The iron content in FER-IN-SOL drops (anti-anemic formulation, Bristol-Myers Squibb Egypt) was estimated by suitable diluting of the drops followed by addition of 2ml of 10^{-3}M ascorbic acid. In case of Ferro Sanol Doudenal capsule (Minipharma), two capsules were dissolved in 10 ml of 4.0M sulfuric acid, and heating in a water bath (70°C) to completely dissolve. The solution was then filtrated with a filter paper, and the filtrate was diluted with water into a 1000-ml volumetric

flask and 2ml of 10^{-3}M ascorbic acid was added to prevent oxidation of iron (II) to iron (III). Then 5 ml was diluted with water to 250ml with water, and the iron contents were measured by the proposed method.

2.2.2. Air sample

Ambient air samples were collected for 24-hrs with a flow rate of 2L/min. in the ambient atmosphere and indoor air in a residential area. Air samples were drew using calibrated vacuum pump through 47 mm diameter cellulose membrane filters in an open–faced holder [31]. The filter is about 100% efficiency for fine particles 0.1 µm. Digestion was carried out a mixture of sulfuric acid, nitric acid and perchloric acid (25 ml). The total iron was reduced to Fe (II) by adding 2 ml of ascorbic acid (10^{-3}M) and analyzed using the proposed method.

2.2.3. Tap water

Tap water was acidified to pH 1 with hydrochloric acid, heated to remove chlorine then 1 ml of 10^{-3}M ascorbic acid was added to reduce total iron to iron (II).

2.2. Apparatus

A V-570 double beam spectrophotometer (Jasco) was used with 10 mm light-path cells for absorbance measurements. Batch measurements were carried out in a double-jacket thermostated glass cell using Haake thermosetting circulating water bath with temperature stability of 60±1°C, while the FIA measurements were carried out at 80±1°C. The pH measurements were done using a 692-pH meter (Metrohm), with a combined pH glass electrode model 6.0202.100.

FIA manifold: A schematic diagram of the flow-injection manifold is shown in (Fig. 1) which was composed of a four channel peristaltic pump (Ismatec, Zurich, Switzerland, MCP) and a sample injection valve (ECOM, Ventil C, Czech Republic) with exchangeable sample loops (5-200µL). Solution transferring were Tygon tubes (Cole-Parmer, R-3603 with 2.8 & 1 mm i.d. for R1, R2 and the sample carrier stream, respectively). No air bubbles are formed in the FIA reaction coils, so that debubbling devices are not required.

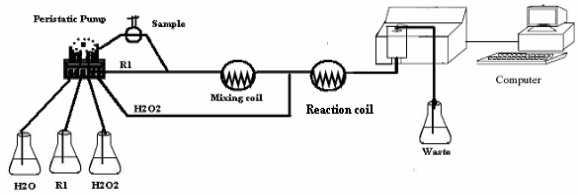

Figure 1: Schematic diagram of the FIA system manifold used for the determination of iron

2.4. General Procedures

2.4.1. FIA measurements

A 50µL of iron solutions with different concentrations was injected directly into the carrier stream (flow rate 6.25 ml min^{-1}) where they are mixed with the R1 in the mixing coil, then with the oxidant in the reaction coil at 80±1.0°C. The reaction product was then sent to a home made flow cell (2x4mm, with light path length of 10 mm) to detect the change in the absorbance of the effluents from the reaction coil at 560nm. The Peak height was proportional to the iron concentration and used for the construction of the calibration curve, five replicate injections per sample were made in all instances.

2.4.2. Batch measurement:

Test solutions containing different iron (II) contents were transferred to a 50ml reaction cell followed by 3 ml of VB solution of $2.2x10^{-3}$M, 3.5 ml of TEA ($3.0x10^{-3}$M) and 5 ml of 0.2 M acetate buffer pH5. The volume adjusted to 18ml with water, and the reaction solutions were thermostated at 60±1°C for 3 min. A suitable amount of hydrogen peroxide ($3.5x10^{-3}$M) was heated in a parallel double-jacket thermostated glass cell at 60±1°C and the reaction was initiated by the addition of 7 ml of $3.5x10^{-3}$M hydrogen peroxide. The absorption of deep violet blue color was measured after 145 sec from initiation of the reaction at 560 nm against water. The calibration graph was constructed by plotting the absorbance against the iron concentration.

3. Results and Discussion

3.1. Oxidation of variamine blue by hydrogen peroxide and the accelerating effect of iron on the color development.

Variamine blue (VB) is a well known redox indicator [32, 33] which is oxidized by different oxidizing agents such as bromate, iodate, periodate, persulphate and hydrogen peroxide to give a deep violet (quinoid) blue color. The oxidation of VB is instantaneous in the presence of persulphate and periodate while in the presence of bromate or iodate it is not as fast.

Oxidation V.B. with hydrogen peroxide undergoes at a very slow rate while in the presence of trace Fe (II), the oxidation process is quite fast owing to the catalytic effect of iron. This cause a rapid change from the pale blue color for the reduced form to an oxidized deep violet blue color with a maximum absorption at 560 nm and molar absorptivity 1000 time higher than the reduced form. Therefore, by measuring the increase in the absorbance of the oxidized VB at 560nm, the Fe (II) contents can be measured (Fig. 2).

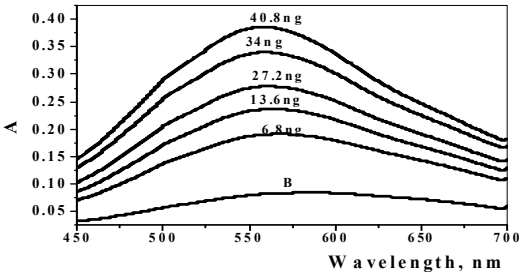

Figure 2: Absorption spectra of variamine blue at different iron concentrations, Conditions; 3 ml of $2.2x10^{-3}$M VB, 3.5 ml TEA $3x10^{-3}$M & 7ml H_2O_2 $3.5x10^{-3}$M at pH5 and 60°C.

It was observed that the reaction rate is relatively high in the presence of Fe (II) than that in the presence of Fe (III), so ascorbic acid was added to reduce ferric ion to ferrous and thus the total iron can be determined. Some trials were done in order to determine both ferric and ferrous ions separately by the addition of fluoride as masking agent for ferric ion but the results were unsatisfactory.

3.2. Optimization of reaction variables

3.2.1. Batch measurements

The chemical variables such as reactant concentrations, reaction temperature, pH and the effect of different activators were optimized (Table 1 & Fig. 3) in order to achieve the highest sensitivity for the determination of iron in both batch and FIA measurements.

The influence of VB concentration on the reaction rate was studied. The difference between the rates of both the catalyzed and uncatalyzed reactions increased by increasing variamine blue concentration and reaches its maximum value at 3 ml of $2.2x10^{-3}$M VB which was selected for the following studies.

The reaction rate of both catalyzed and uncatalyzed reactions increased by increasing the oxidant concentration and the net rate increases to reach its maximum value with 7ml H_2O_2 with concentration $3.5x10^{-3}$M.

Table 1: Selected conditions for the kinetic determination of iron

Variable	Batch		FIA	
	Range studied	Optimal	Range Studied	Optimal
pH	4-6	5.0	4-6	5.0
VB	1-9ml ($2.2x10^{-3}$ M)	3.0 ml	2×10^{-4}-2.5×10^{-3}M	5.7×10^{-4}M
H2O2	1-9ml ($3.5x10^{-3}$M)	7.0 ml	$3.5x10^{-3}$-0.2M	0.05M
TEA	0.5-5.5ml ($3.0x10^{-3}$ M)	3.5 ml	1.5×10^{-4}-2×10^{-3}M	1×10^{-3}M
Temperature	30-90°C	60 °C	30-90°C	80 °C
Sample volume (µl)			5-200	50
Reaction coil (cm)			35-85	35
Flow rate			4.2-21	12.5
Sample flow rate			2-12.5	6.25

At the optimum concentration of the dye and the oxidant, the effect of pH on the sensitivity was studied using acetate buffer (0.2M) at different pH values (Fig. 3). The highest reaction rate was obtained at pH 5 while higher pH values cause precipitation of the dye. The voltammetric studies on the redox potential of the dye in acetate buffer show that the redox potential decreased by increasing the pH to reach it minimum value at pH 5 (375mV) which make its oxidation process easier at this pH.

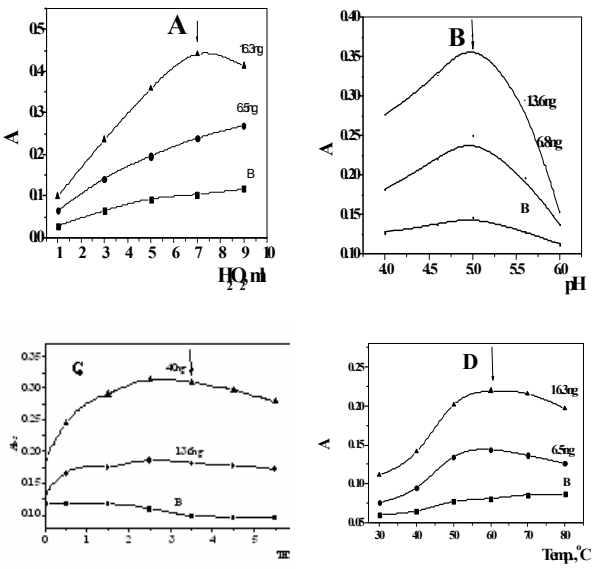

Figure 3: Effect of the reaction variables on the catalytic spectrophotometric determination of iron using the batch method, A; oxidant concentration, B; pH, C; TEA concentration and D; effect of temperature

Although catalytic reactions offer good sensitivity, addition of suitable complexing agents (activators) permits the improvement in their sensitivity and selectivity. Several attempts have been made to enhance the detection limit of iron (II) by using activator ligands such as 1,10-phenanthroline, 2,2'-bipyridyl, neocuprione, oxalate as well as triethanolamine (TEA). TEA showed the highest activation effect followed by oxalate and 1,10-phenathroline.

The rule of the activator in the catalytic reaction is the acceleration of the reaction through facilitation of the charge transfer from the catalyst (usually metal ion) to the dye, also the redox potential of some metal cations changed via formation of such complexes with activators which is reflected on the increasing of the reaction rate. The conditional redox potential of Fe(III)/Fe(II) systems increase in the presence of activators, because the difference in the stability constant of Fe(II) and Fe(III) with these ligands, (the formation constant, $\log\beta_3$, of the Fe(III) with 1,10-phenathroline is 14.1, 2,2'-bipyridyl is 17.6, oxalate is 18.46 & TEA is 41.2) [34]. The rate of the catalyzed reaction increased with increasing TEA concentration up to a definite concentration (3.5ml of $3x10^{-3}$M) and then decreased gradually at the higher concentration range. Such dependence is a characteristic feature for the types of activated reactions when the activator is concerned with the formation of ternary complexes of the activator-metal substrate [35]. The coordination sphere of the catalyst is fully occupied by the activator and any complexation with substrate does not occur at higher concentrations of activator.

The influence of the reaction temperature on the reaction rate was studied, in the range 30-90°C. The results showed that by increasing temperature up to 60°C, whereas higher temperature values cause decreasing the sensitivity due to increasing the rate of the uncatalyzed reaction, therefore, the reaction was thermostated at 60°C. The apparent activation energy of the reaction calculated by using Arrhenius equation was 199.43 kJ/mol.

3.2.2. Flow injection variables

The experimental conditions such as the reagent concentration, flow rate, sample volume, coil length, temperature and the sequence of reagent mixing were optimized in order to achieve the highest sensitivity. In order to simplify the flow injection system, a mixture of the VB, buffer and activator (each at the suitable concentration) was used and signed as R1. The concentration of both VB and TEA was changed in the R 1 within 250 ml flask and the optimum concentrations of VB & TEA were $5.7x10^{-4}$ and 10^{-3}M, respectively.

The slower flow rate and longer reaction coil increased the reaction time as well as the rate of the catalyzed and uncatalyzed reactions. For the sake of sensitivity and sampling frequency, a 15-cm mixing coil and 35-cm reaction coil were employed. The dependency of the peak heights and residence time (time to recover the base line) with flow rate was studied applying different flow rates (4.2-21ml min^{-1}), the flow rate of 12.5ml min^{-1} was selected as the slower flow rate gave a broad peak with long tail, while the faster one will depress the peak height (Fig. 4). At these conditions, the reaction time was 50 sec (from mixing of reagents till measuring in the flow cell) and the cycle run was 130 sec, so more than 25 injections per hour can be measured. The recorded peaks were sharp and the base line was stable. An increase in the injection volume from 5 to 200µl improved the peak height, though the sampling frequency decreased. The injection volume of 50µl was chosen as a compromise between the sensitivity and the analysis time. Different sequence of the reagent mixing were tested including mixing of the (H_2O_2+R1) + Fe, (R1+Fe) + H_2O_2 and (H_2O_2+Fe) + R1 and the mixing of iron & R1 then with the H_2O_2 was the most suitable.

For FIA, a relative higher temperature is needed to heat the flow stream and a reaction temperature of 80°C was selected for the procedure as it gave the highest peak height

while the higher temperature causes the formation of air bubbles without improvement of the reaction rate. The concentration of the oxidant was varied from 0 to 0.2M and the optimum concentration was found to be 0.05M.

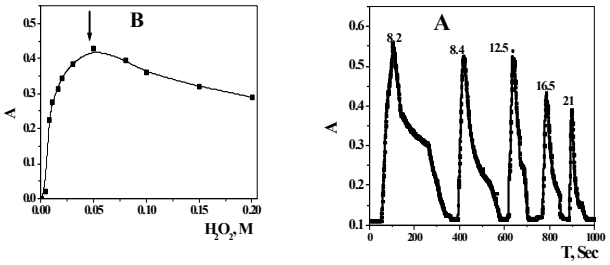

Figure 4: Effect of the flow injection variables on the catalytic spectrophotometric determination of iron, A; effect of flow rate and B; effect of oxidant.

3.3. Linear range

Following the analytical procedures mentioned above as well as the optimization conditions, the linear equation for the calibration graphs of Fe (II) in the batch & FIA techniques gave a linear regression equation Y=0.07043+0.0085 [Fe,ng], Y=0.10727+0.00487 [Fe, ng] with correlation coefficients 0.99925 & 0.99885, respectively (Fig. 5). In the batch method, the linear range was 3.4-40 ng/ml in final solution while in the FIA, the calibration graph was linear for 5.4-130 ng of the injected iron. For comparing the sensitivity of FIA and the batch method, the calibration graphs for the batch method was done at the same time of FIA (50 sec) and the FIA technique shows superiority in the sensitivity (sensitive 4 times more than the batch) as well as the high sampling output.

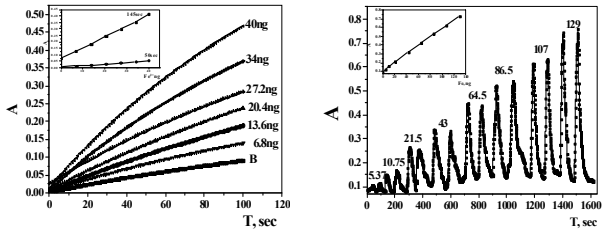

Figure 5: Calibration curves for iron (II) determination using FIA and Batch measurements

In the batch measurement, the limit of detection defined as three times of standard deviation of the blank (3σ) was 50 ng (2ng/ml). The corresponding value for FIA was 1.94ng (38.8ng/ml of the sample) which represents 3xSD of five replicates measurements.

3.4. Interference

In order to investigate the analytical applicability of the proposed method, the effect of several interfering ions was examined by carrying out the addition of 530 in the batch method or injection of 65 ng of iron in the FIA modes and in the presence of each ion where the maximum amount of substance causing an error of ±5% in iron determination was denoted as the tolerance limit (Table 2).

Interfering effects of Cu^{2+} and Au^{3+}, Cr^{3+} and Zr^{4+} were also noticed as they enhance the reaction by their catalytic action on the oxidation of VB with H_2O_2. The interference of copper can be suppressed using trien or triethylenetetramine as complexing agents without a noticeable effect on the iron determination. Oxidizing agents such as V (V), Cr(VI), IO_4^-, $S_2O_8^{2-}$and Sn^{4+} gave positive interference as they directly oxidized the dye and some coloration reactions occurred before the addition of hydrogen peroxide. Reducing agents such as ascorbic acid did not show interference up to 100 & 10000 fold excess of iron in both the batch and FIA mode, respectively.

Table 2: Maximum tolerance limits of diverse ions in the determination of 530 ng iron in the batch mode and injection of 65 ng of iron in the FIA methods.

Element	Concentration Fold		Element	Concentration fold	
	Batch	FIA		Batch	FIA
Cd^{2+}	500	1000	I^-	500	1000
Ag^+	500	1000	CO_3^{2-}	300	500
Pb^{2+}	800	2000	Br^-	20000	25000
Cu^{2+}	40	100	Cl^-	2000	3000
Sn^{4+}	50	50	F^-	500	1000
Hg^{2+}	1000	1000	S^{2-}	1	1
Cr^{3+}	50	150	PO_4^{2-}	100	100
Cr^{6+}	15	15	CN^-	70	100
Mn^{2+}	1000	2000	EDTA	1	1
Zr^{4+}	10	50	Ascorbic acid	200	20000
Au^{3+}	5	50			

In the case of metal ion catalysis, complexing agents forming highly stable metal complexes with such catalysts can be determined by their inhibitory effect on the catalyzed reaction [36-38]. The influence of some complexing anions (CN^-, EDTA and S^{2-}) consists of a decrease in the catalytic reaction rate by 30, 91.5 and 80.5 % respectively. Thus, the proposed method can be also applied for the determination of sulfide or EDTA by their inhibitory effect in the concentration range 4-24 and 1.8-7 ppm for sulfide and EDTA respectively.

It was found that application of the FIA will reduce the effect of the aforementioned interfering ions except that of EDTA or sulfide. The tolerance limits for these interfering ions are much higher than the levels normally present in real samples, so the proposed method is directly applicable to the determination of iron without the need of masking agent or separation procedures.

3.5. Application

To validate the application of the proposed procedures, it was applied for the determination of iron in different samples such as polluted air, tap water and pharmaceutical preparations. Calibration and standard addition methods were adapted for the iron determination and the analytical results are shown in Table 3. The average recovery of iron (II) was found to be quantitative and the repeatability of the method was satisfactory compared with the atomic absorption measurements.

4. Conclusion

This paper demonstrated that VB can be utilized as a useful substrate for the catalytic spectrophotometric determination of iron (II) by either the batch & FIA techniques using TEA as activator. The proposed FI method has many advantages of permitting the simple, accurate and precise determination of iron (II) down to nanogram levels; wider determinable range (5.4-130 ng) compared with the batch methods with the ability of analysis more than 25 per hr. The sample analysis time was very short when compared with some published method for the catalytic determination of iron and carried out at more ambient conditions [22-26] in one step reaction [27-29] with higher sensitivity (ε=6.89x10^5 $mol^{-1}cm^{-1}$). The method success in the determination of iron in different samples with average recoveries agreed with that of the atomic absorption. A comprehensive study will be done to improve the

Table 3: Catalytic spectrophotometric determination of iron in different samples using both the batch and FIA methods.

Sample	Batch				Flow injection			
	Taken [a]	Found	Recovery%[b]	SD	Injected [c]	Found	Recovery% [b]	SD
Authentic [d] sample	353.50	357.13	101.0	±2.5	21.51	22.56	104.9	±2.2
	530.50	544.20	102.6	±0.8	64.53	65.98	102.2	±1.9
	888.75	871.25	98.0	±1.3	129.04	129.52	100.4	±1.1
Fer-In-Sol	173.00	168.25	97.3	±2.5	44.00	42.42	96.4	±1.8
Ferro Sanol Duodenal	200	196.4	98.2	±2.2	75	71.55	95.4	±2.5
Polluted air[e]	95.25	89.00	93.5	±5.3	35.50	33.30	93.7	±1.5
Tape water	91.00	86.25	94.8	±6.5	8.26	8.05	97.4	±1.4

a- The taken values were estimated by the AAS.
b- Average of five replicates.
c- The amount of iron in 50µl sample
d- The average recovery values were obtained by calibration method.
e-The iron content in the polluted air sample was 0.033µg/m3.

selectivity and the sensitivity of the iron determination using other synthesized or commercial indicators as well as application of potentiometric or voltammetric technique for following the reaction rate.

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(Received July 5, 2007)
(Accepted October 3, 2007)