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Potentiometric Determination of Some Strong Oxidants Using Fluoride Ion-Selective Electrode

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A new, simple, inexpensive and sensitive method for the micro-determination of strong oxidants of hydrogen peroxide (H_2O_2), peroxyacetic acid (PAA), permanganate (MnO_4^-), dichromate ($Cr_2O_7^{2-}$), chromate (CrO_4^{2-}) and cerium(IV) has been investigated and developed. In this work, the oxidation reaction of Fe(II) to Fe(III) in the presence of oxidants is based on the method. The change potential of complexation of flouride ion with Fe(III) was monitored by a fluoride ion-selective electrode. A series of experiments were conducted to establish the optimum analytical parameters to achieve maximum sensitivity in the determination of above oxidants. The experimental parameters such as ionic fluoride and iron(II) concentrations, temperature and pH of solutions were optimized. The results showed that determination of H_2O_2, peroxyacetic acid, MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-} and Ce(IV) could be performed in their concentration ranges of 1.0-1.0, 0.1-10.0, 0.1-10.0, 0.1-20.0 and 0.5-20.0 µg mL^{-1}, respectively. The proposed method was successfully applied to the determination of strong oxidants in synthetic water samples.

Key Words: Strong oxidants, Potentiometric determination, Fluoride ion-selective electrode.

INTRODUCTION

Hydrogen peroxide (H_2O_2), peroxyacetic acid (PAA), permanganate (MnO_4^-), dichromate ($Cr_2O_7^{2-}$), chromate (CrO_4^{2-}) and cerium(IV) are strong oxidants in chemistry. H_2O_2 is used widely as a disinfectant and a bleaching agent in various industrial and household products[1]. Peroxyacetic acid is widely used in the food industry for disinfecting buildings and equipment and for sterilizing plastic bottles particularly it used for packaging fruit juices and sweetened drinks. It is also used for medical purposes, mainly for sterilizing the surfaces of the instruments[2]. Permanganate is used as an oxidizing agent in diverse chemical reactions in the laboratory and industry for the synthesis of many different kinds of chemical compounds[3]. It is also used as disinfectant, deoderizer, aquaculture, wastewater treatment, neutralize hydrogen sulfide biomedical and miscellaneous[4,5]. Dichromate is a common inorganic chemical

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reagent, most commonly used as an oxidizing agent in various laboratory and industrial applications[3]. It also used to oxidize alcohols, determination of ethanol, cleaning laboratory glassware of organic contaminants[3,4]. Cerium(IV) is industrially important and is used in nuclear reactors, alloys with nickel and chromium, microwave devices, lasers, agriculture and miscellaneous[4-6]. In analytical chemistry, standardized aqueous solutions of MnO_4^-, $Cr_2O_7^{2-}$ and Ce(IV) are some times used as oxidizing titrants for redox titrations. Therefore, determination of these oxidants is very important. Several methods have been reported for the determination of them such as titrimetry[7,8], electroanalytical techniques[9-11], spectrophotometry[12-16], chemiluminescence[17] and chromatography[18-20].

To the best of our knowledge, no one has reported any potentiometric method for the determination of oxidants by ion-selective electrodes. In this paper, is shown that potentiometric method using fluoride ion selective electrode (FISE) can be employed for the determination of strong oxidants such as H_2O_2, PAA, MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-} and Ce(IV). In this work, the oxidation reaction of Fe(II) to Fe(III) in the presence of oxidants is based of the method and the change potential of complexation of flouride ion with Fe(III) was monitored by a fluoride ion-selective electrode (FISE). Application of potentiometric technique using FISE for the determination of oxidants is high selectivity, sensitivity and freedom from optical interferences. Therefore, this method is applicable to determination coloured and turbid solutions.

EXPERIMENTAL

All reagents were analytical reagent grade. Triply distilled water was used throughout the study. Stock solutions (1000 μg mL^{-1}) of H_2O_2, PAA, MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-} and Ce(IV) were prepared in 100 mL flasks by dissolving 0.25 mL of hydrogen peroxide (Merck), 0.22 mL of peracetic acid (Merck), 0.1329 g of potassium permanganate (Merck), 0.1369 g of potassium dichromate (Merck), 0.1674 g of sodium chromate (Merck) and 0.2885 g of $Ce(SO_4)_2\cdot 4H_2O$ (Merck) in water and diluting with water to the mark. H_2O_2 and PAA are unstable and prepared repeatly after 1 h. Solutions of H_2O_2 and PAA are stored in dark bottles in low temperature. A stock solution of 0.05 M iron(II) was prepared by dissolving 1.463 g of $FeSO_4\cdot 7H_2O$ (Merck) in water and diluting with water to the mark. A 0.1 mol L^{-1} fluoride solution stock was prepared by dissolving 0.4199 g of sodium flouride (Merck) in water and diluting to 100 mL and was stocked in a polyvinyl chloride (PVC) flask. Acetate buffer solution (0.05 M, pH 3.0) was prepared using acetic acid and NaOH solutions and adjusting its pH with a pH meter.

A solid-state fluoride-selective electrode (Metrohm Model 6.0502.150) was used in conjunction with a double junction Ag/AgCl reference electrode (Metrohm Model 6.0726.100), whose outer compartment was filled with a 10 % (w/v) KNO_3 solution. The Metrohm Model 780 potentiometer, attached to a Pentium(IV) computer, was used for recording the potentiometric data. All measurements were carried out in a thermostated (25.0 ± 0.2 °C), double-walled reaction cell with continuous magnetic stirring. The electrode was stored in 1 × 10^{-3} M potassium chloride solution when not in use. For pH measurements, a Metrohm Model 780 pH meter with combination glass electrode was used.

Procedure: 25.0 mL of double distilled water, 2.0 mL of buffer solution, 1.0 mL of stock fluoride solution and 1.0 mL stock solution of iron(II) were added to the thermostated (25.0 ± 0.2 °C) reaction cell. 10.0 mL of the standard or sample solution of H_2O_2, PAA, MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-} or Ce(IV) was injected into the cell quickly and after the stabilization of the potential all data were recorded. The potential changes *versus* time were recorded at the time intervals of 1.0 s. After each run the cell was emptied and washed twice with double distilled water.

Using the standard analyte solutions, a calibration graph of ($10^{\Delta E/S}$-1) *versus* concentration (fixed-time method)[21] is constructed, where ΔE is the potential variation in a selected time interval Δt (usually 100 s) and S is the slope of the fluoride electrode response, which is determined periodically by successive additions of micro-amounts of 100 µL of 1.0 × 10^{-2}-3.0 M NaF standard solutions in 25.0 mL of water mixed with 2.0 mL of buffer solution. The potentiometric slope of the electrode response (s) was checked periodically by successive addition of NaF standard solutions.

RESULTS AND DISCUSSION

A series of experiments were conducted to establish the optimum analytical to achieve maximum sensitivity in the determination of H_2O_2, PAA, MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-} or Ce(IV). The experimental parameters, such as iron(II) and fluoride concentrations, temperature and pH of solutions were optimized.

Study of electrode characteristics: The very fast response of FISE and its Nernstian behaviour toward fluoride ions in acidic solutions indicates that this electrode might be employed effectively in the studies of reactions involving changes in the fluoride ion concentration. The characteristics of the fluoride-selective electrode in the acetate buffer were studied. In order to evaluate the operating characteristics of the FISE at pH < 4, calibration graphs were constructed for sodium fluoride in the concentration range of 1.0 × 10^{-2}–1.0 × 10^{-6} M at pHs 4.0, 3.0, 2.5 and 2.0. The slope was found to be 56.8 mV/decade and remained almost constant to 0.2 mV over 7 months of usage in this system at pH 3.0.

Effect of iron(II) concentration: Fig. 1 shows the effect of iron(II) concentration on the potential changes (ΔE) in the concentration range of 5.0 × 10^{-2}-5.0 × 10^{-4} M. The results showed that at 5.0 × 10^{-3} M Fe(II), the ΔE for all species was highly. As it is seen, at high concentrations of iron(II), the ΔE due to Fe(III)-fluoride complex formation decreases. This might be due to the fact that high concentrations of Fe(II) would result in a positive interference from Fe(II) that could have arisen from incomplete conversion of Fe(II) to Fe(III)-fluoride complex *via* mixed ligand complex formation. Thus, a concentration of 5.0 × 10^{-3} M Fe(II) was chosen as the optimum iron(II) concentration.

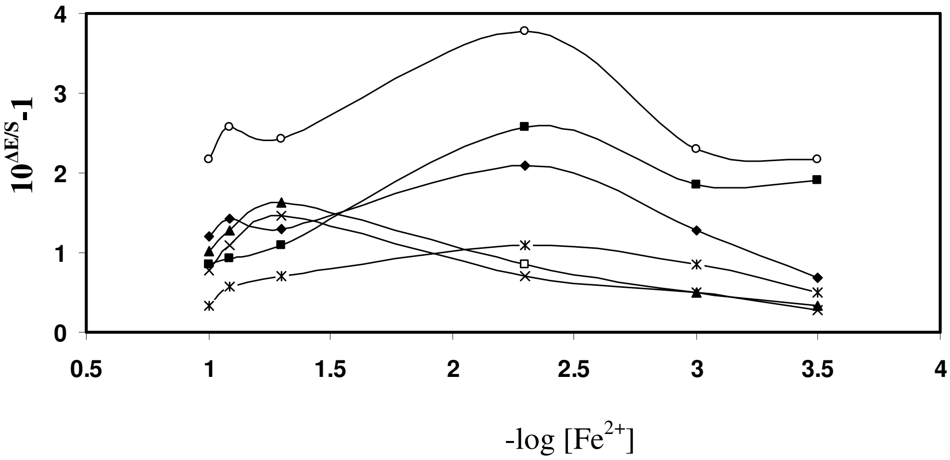

Fig. 1. Effect of Fe^{2+} concentration on the reaction of 10.0 µg mL^{-1} of PAA (◆), Ce^{4+} (*), H_2O_2 (○), MnO_4^- (■), $Cr_2O_7^{2-}$ (▲) and CrO_4^{2-} (×). Conditions: 1.0×10^{-3} M F^-, pH 3.0, 25 ºC

Effect of fluoride concentration: The effect of F^- concentration over the ranges of 1.0×10^{-5}-1.0×10^{-1} M fluoride ion on the potential changes (ΔE) and linear range of calibration graph of oxidants was investigated. When the concentration of F^- is low, a gentle slope in the calibration graph is realized while a high concentration of F^- produces is high a steep slope in the calibration graph. The results show that only when the concentration of F^- is higher than 10 times actual detection limit of the electrode a linear calibration graph may be obtained. The results also indicate that the concentration of F^- has a great effect on the linear range and the change potential value. The linear range of the calibration graph is about 0.3-4.0 times the concentration of F^-. Moreover, if the reaction be employed as a pseudo-first-order reaction, concentration of fluoride in this work would be of great importance. So the fluoride concentration must be in excess, but by increasing the fluoride concentration, the potential change is decreased and the sensitivity is lower. If the fluoride concentration is too low, the potential may not be steady. Since, maximum values of potential change with all oxidants were observed in concentration of 1.0×10^{-3} M. Therefore, a concentration of 1.0×10^{-3} M fluoride ion was selected as the optimum concentration for further studies.

Effect of pH: Acidity of the solution influences potential response of FISE and the complexation rate of Fe^{3+} with fluoride. The effect of pH on the potential change of Fe^{3+} with F^- over the pH range of 1.0 to 5.0 was examined. As shown in Fig. 2, Fe^{3+} had larger values of potential change (ΔE) in the pH of 3.0. Above pH 3.0, the potential change decreased evidently due to the occurrence of the hydrolysis reaction competing with the complexation between fluoride and metal ions and under pH 3.0, the potential change decreased too, probably owing to the formation of hydrogen fluoride, to which the fluoride electrode is insensitive. Thus, pH of 3.0 was selected as the optimum pH for further studies.

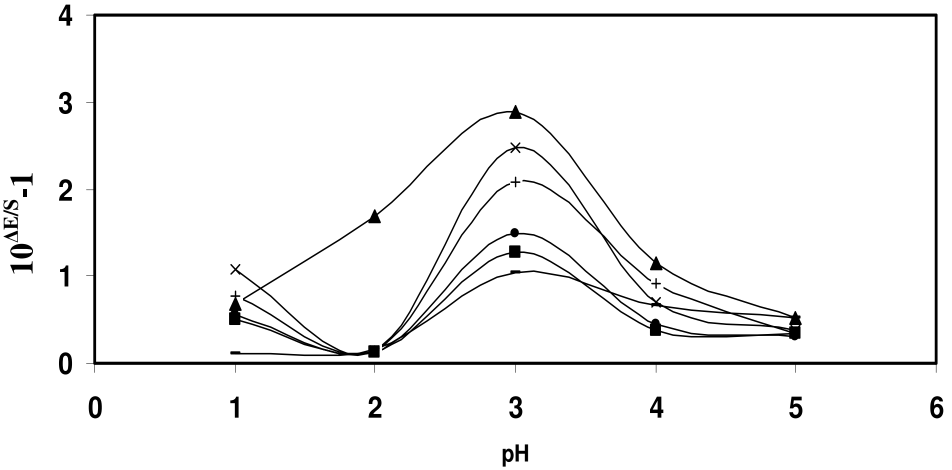

Fig. 2. Effect of pH on the on the reaction of 10.0 µg mL^{-1} of PAA (+), Ce^{4+} (–), H_2O_2 (▲), MnO_4^- (×), $Cr_2O_7^{2-}$ (◆) and CrO_4^{2-} (■) reactions. Conditions: 1.0 × 10^{-3} M F^-, 1.0 × 10^{-3} M Fe^{2+}, 25 °C

Effect of temperature: The temperature of solution evidently affects the reaction rate of the kinetic reaction. But higher temperatures do not have a positive effect on the complexing reaction of Fe^{3+} with fluoride. Therefore, the temperature of solution was kept at 25.0 ± 0.2 °C by thermostatic water bath in all of the measurements.

Analytical parameters: A linear correlation was found between ($10^{\Delta E/S}$-1) and concentration for each oxidants and concentration in the range given in the Table-1. Intercepts, slopes and corrrlation coefficients for the calibration data of the H_2O_2, PAA, MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-} and Ce(IV) are also presented in the Table-1.

TABLE-1
CHARACTERISTIC OF CALIBRATION GRAPHS FOR THE DETERMINATION OF H_2O_2, PAA, MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-} AND Ce(IV)

Species	Linear range (µg mL^{-1})	Slope (mL $µg^{-1}$)	Intercept	Correlation coefficient (n = 7)	Detection limit* (µg mL^{-1})
H_2O_2	0.1-20.0	0.9194	9.3704	0.9992	0.05
PAA	0.1-10.0	0.0940	0.2987	0.9991	0.06
MnO_4^-	0.1-10.0	0.2220	1.3039	0.9999	0.08
$Cr_2O_7^{2-}$	0.1-20.0	0.0633	1.2162	0.9990	0.05
CrO_4^{2-}	0.5-20.0	0.0508	0.2298	0.9991	0.20
Ce^{4+}	1.0-30.0	0.0365	0.1651	0.9980	0.50

*Concentration corresponding to a net analytical signal equals to three limes the standard deviation of the blank.

Interference study: The study of interference ions was performed by a standard mixture solution containing 10 µg mL^{-1} of each both oxidants and a certain amount of foreign ions. The following excesses of ions do not interfere (*i.e.*, caused a relative error of less than 5 %): more than a 1000-fold (largest amount tested) amount of

Na^+, K^+, Zn^{2+}, Cu^{2+}, Cd^{2+}, Mg^{2+}, Be^{2+}, Bi^{3+}, As^{3+}, IO_3^{3-}, I^-, Br^-, Cl^-, NO_3^-, BO_3^{3-}, $C_2O_4^{2-}$, CH_3COO^-; a 100-fold amount of Mn^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Cr^{3+}, Ca^{2+}; a 10-fold amount of SO_4^{2-}, PO_4^{3-}, Hg^{2+} and a 1-fold amount of Zr^{4+}, Ti^{4+}, Al^{3+}.

Application: To evaluate the analytical applicability of proposed method, known amounts of H_2O_2, PAA, MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-} and Ce(IV) were spiked into some water samples. The results (Table-2) demonstrate that the proposed method can be employed satisfactorily for the determination of oxidants in water samples.

TABLE-2
DETERMINATION OF H_2O_2, PAA, MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-} AND Ce(IV) IN DIFFERENT WATER SAMPLES (n = 4)

Sample	Spiked (μg mL^{-1})					
	Ce(IV)	$Cr_2O_7^{2-}$	MnO_4^-	CrO_4^{2-}	H_2O_2	PAA
Mineral water	2.0	2.0	2.0	2.0	2.0	2.0
	5.0	5.0	5.0	5.0	5.0	5.0
	8.0	8.0	8.0	8.0	8.0	8.0
Tap water	2.0	2.0	2.0	2.0	2.0	2.0
	5.0	5.0	5.0	5.0	5.0	5.0
	8.0	8.0	8.0	8.0	8.0	8.0
Well water	2.0	2.0	2.0	2.0	2.0	2.0
	5.0	5.0	5.0	5.0	5.0	5.0
	8.0	8.0	8.0	8.0	8.0	8.0
Sample	Found (μg mL^{-1})					
	Ce(IV)	$Cr_2O_7^{2-}$	MnO_4^-	CrO_4^{2-}	H_2O_2	PAA
Mineral water	2.12(±0.12)	1.97(±0.09)	1.96(±0.17)	2.13(±0.14)	2.08(±0.10)	2.04(±0.11)
	5.21(±0.23)	4.88(±0.20)	4.93(±0.28)	4.81(±0.27)	5.07(±0.22)	4.97(±0.25)
	8.30(±0.34)	8.25(±0.35)	7.52(±0.26)	7.32(±0.21)	8.13(±0.24)	8.10(±0.22)
Tap water	2.15(±0.10)	1.91(±0.13)	1.91(±0.15)	2.17(±0.16)	2.10(±0.10)	2.05(±0.12)
	5.25(±0.16)	4.88(±0.20)	5.20(±0.23)	5.23(±0.18)	4.92(±0.20)	5.03(±0.22)
	7.73(±0.32)	7.82(±0.30)	7.77(±0.42)	8.27(±0.24)	8.19(±0.32)	8.07(±0.25)
Well water	2.20(±0.15)	2.15(±0.14)	2.13(±0.17)	2.15(±0.14)	1.93(±0.08)	1.95(±0.13)
	5.37(±0.13)	4.73(±0.16)	5.32(±0.33)	5.35(±0.27)	5.34(±0.12)	5.22(±0.20)
	0.68(±0.23)	7.75(±0.26)	7.73(±0.36)	8.41(±0.24)	7.83(±0.25)	8.13(±0.25)

Conclusion

In this work, it is shown that potentiometric method using fluoride ion-selective electrode can be well adopted for determination of oxidants. The proposed method as new, inexpensive and sensitive method offer good accuracy and precision that can be applied for a wide range of H_2O_2, PAA, MnO_4^-, $Cr_2O_7^{2-}$, CrO_4^{2-} and Ce(IV) concentrations. In this method, it is not required to use complex pretreatment or toxic organic solvents. In other words, this method belongs to green chemistry.

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