Catalytic-Spectrophotometric Determination of Trace Amounts of Iodide Based on Nuclear Fast Red-Iodate Reaction

N. Pourreza*, S. Rastegarzadeh and B. Moustafavi
Department of Chemistry, College of Science, Shahid Chamran University, Ahvaz, Iran
Fax: (98)(611)3337009; E-mail: pourrezan@yahoo.co.in

A sensitive catalytic-spectrophotometric method has been developed for the determination of trace amounts of iodide based on its effect on the reaction of nuclear fast red (NFR) with iodate in acidic media. The reaction is followed spectrophotometrically by measuring the change in absorbance of NFR (ΔA) at 516 nm using a fixed time method (3.5 min). The effect of different variables on the reaction was investigated and optimum conditions were established. The calibration graph was linear in the range of 7-70 ng mL^{-1} (r = 0.9994). The $3S_b$ detection limit was 5.7 ng mL^{-1} and the relative standard deviation (RSD) for ten replicate measurements of 30 and 50 ng mL^{-1} of iodide was 4.8 and 2.8 %, respectively. The method was successfully applied to the determination of iodide in table salt sample.

Key Words: Catalytic-spectrophotometric, Iodide, Nuclear fast red, Iodate.

INTRODUCTION

Iodide plays an important role in the performance of thyroid gland. Iodine is absorbed into the blood from gastrointestinal tract as iodide. Iodide circulating into blood enters thyroid and is concentrated to a level 25 times than in the blood. The over activity of thyroid can be controlled by treatment with anti-thyroid or iodide[1]. The deficiency of iodide can result in brain damage and mental retardation. Therefore, its determination is important for iodine supplementation.

Several techniques such as electrochemical[2], ion chromatographic[3] ICP-MS[4,5], X-ray fluorescence[6], neutron activation analysis[7] and spectrophotometric[8] have been employed for the determination of trace amounts of iodide. Apart from these techniques, kinetic spectrophotometric methods offer some features that have made them able to compete with other methods. Kinetic spectrophotometic method determinations can be made with high sensitivities, in a relatively short time and it is simple and inexpensive. Different kinetic methods have been described for determination of iodide[9-12]. However, more sensitive, selective and simple methods are still needed.

This paper describes a sensitive and rapid kinetic-spectrophotometric method for the determination of iodide based on its catalytic effect on the oxidation reaction of nuclear fast red by iodate in acidic media.

EXPERIMENTAL

A Jasco UV-Vis spectrophotometer model 7850 was used for recording the spectra and a Milton Roy Spectronic 20D spectrophotometer was used for absorbance measurements. A Colora C-1668 thermostat in which temperature could be fixed within ± 0.10 °C was used for maintaining the temperature.

All chemicals were of analytical reagent grade and purchased from Merck. Distilled, deionized water was used for the preparation of the solutions. A stock standard iodide solution (1000 µg mL^{-1}) was prepared by dissolving 0.2616 g of KI in water and diluting to 200 mL in a volumetric flask. This solution was standardized using iodometric method[13]. Diluted working standard solutions were prepared daily from this stock solution. Iodate solution 0.1 mol L^{-1} was prepared by dissolving 2.140 g of KIO$_3$ in water and diluting to 100 mL. Nuclear fast red solution (7.0 × 10^{-4} mol L^{-1}) was prepared by dissolving 0.0625 g of the reagent in water and diluting to 250 mL. A 1.3 mol L^{-1} solution of HCl was prepared by appropriate dilution of conc. hydrochloric acid (Merck, d = 1.18 and 37 %) used.

Recommended procedure: In a 10 mL volumetric flask were added 1.5 mL nuclear fast red (7 × 10^{-4} mol L^{-1}), 0.3 mL of HCl (1.3 mol L^{-1}) and 0.3 mL of potassium iodate (0.1 mol L^{-1}). After 30 s the appropriate amount of iodide solution was added and made up to mark with water. The absorbance was measured at 516 nm after 3 min. A blank solution was also prepared in the same way using distilled water instead of iodide solution and change in absorbance (ΔA) was calculated.

RESULTS AND DISCUSSION

It was found that iodate ion oxidizes nuclear fast red (NFR) very slowly in acidic media. The iodide ion could catalyze the reaction at trace amounts, so that it proceeded much faster. As can be seen from Fig. 1, the reaction rate increased in the presence of iodide and the absorbance decreased. As the maximum absorption occurs at 516 nm, the catalytic effect of iodide on the reaction was monitored spectrophotometrically by measuring the change in absorbance (ΔA) of nuclear fast red at this wavelength with time. A fixed time of 3 min was applied because highest ΔA was obtained.

Effect of variables: To obtain the maximum sensitivity in the determination of iodide, the effect of several variables on the rate of reactions was investigated as follows:
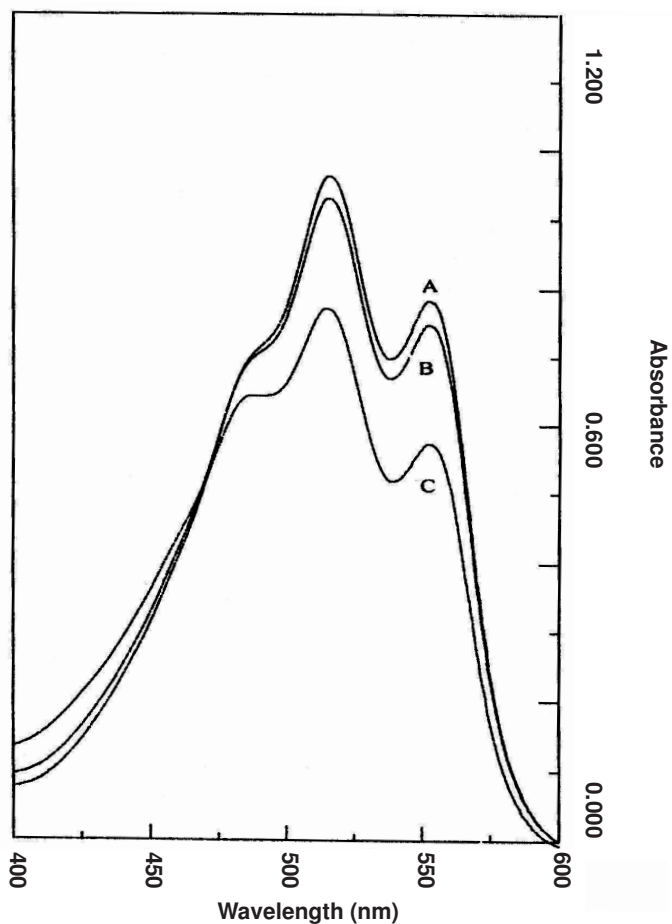
Fig. 1.   Absorbance changes of NFR in the presence (A) HCl, (B) HCl and iodate, (C) HCl, iodate and iodide

   The influence of nuclear fast red concentration on the change in absorbance (ΔA) was studied. The results in Fig. 2 shows that the highest change in absorbance occurred when, nuclear fast red concentration was 1.05×10^{-4} mol L^{-1} in the solution. Thus, this concentration was selected as the optimum.

   Since the preliminary experiments showed that the reaction proceeds in acidic media, the effect of HCl concentration on the ΔA was also investigated. The highest change in absorbance (ΔA) was obtained when acid concentration was 0.052 mol L^{-1} in the final solution.

   The effect of iodate concentration in the range of 1×10^{-3}–5×10^{-3} mol L^{-1} in final solution was studied. As obvious from Fig. 3, the maximum ΔA occurred at 3×10^{-3} mol L^{-1}. So, this concentration was used for further work.
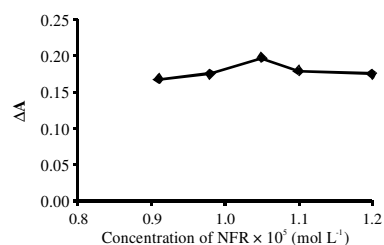
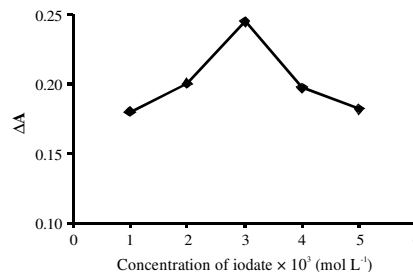Fig. 2.   Effect of NFR concentration on the change in absorbance

Fig. 3.   Effect of iodate concentration on the change in absorbance

It was found that the change in absorbance was increased with increasing temperature. A temperature of 25 °C was used as the working temperature, as it is the ambient temperature in which it is easier to work. However, for better sensitivity higher temperatures can be employed.

The effect of ionic strength on the change of absorbance (ΔA) was investigated using sodium nitrate. The obtained results show that the ΔA was independent of ionic strength up to 0.2 mol L^{-1} of sodium nitrate.

Calibration graph, detection limit and precision: The method was applied to a series of standard solutions of iodide applying recommended procedure under optimum conditions. The results indicated that the calibration curve was linear in the range of 7-70 ng mL^{-1} with an equation of $\Delta A = 0.00178C + 0.141$ and regression coefficient (r) of 0.9994, where C is the concentration of iodide in ng mL^{-1}. The $3S_b$ detection limit was 5.7 ng mL^{-1} and the relative standard deviation for ten replicate measurements of 30 and 50 ng mL^{-1} of iodide was 4.8 and 2.8 %, respectively.

Interference studies: To study the selectivity of proposed method the effect of various cations and anions on the change of absorbance of 60 ng mL^{-1} iodide was tested. The tolerance limit was defined as the amount of the diverse ion causing an error of $\pm$ 5 % in concentration of iodide. The results are shown in Table-1.

TABLE-1
TOLERANCE RATIO FOR THE DETERMINATION OF 60 ng mL^{-1} OF IODIDE IN THE PRESENCE OF FOREIGN IONS

Foreign ions	Tolerance limit (ng mL^{-1})
Na$^+$, K$^+$, Pb^{2+}, Cd^{2+}, Al^{3+}, HCO$_3^-$, NO$_3^-$, C$_2$O$_4^{2-}$, PO$_4^{3-}$, F$^-$, H$_2$PO$_4^-$	1000
Cl$^-$, Ba^{2+}, Mg^{2+}	700
Co^{2+}, Ni^{2+}	200
Cu^{2+}, Hg^{2+}, CO$_3^{2-}$	100
*MoO$_4^{2-}$	50
Fe^{3+}, Cr^{3+}	15
Fe^{2+}, Cr$_2$O$_7^{2-}$	5
NO$_2^-$, Br$^-$, SCN$^-$	1

*Masked by C$_2$O$_4^{2-}$

Application: In order to evaluate the applicability of the method to real sample, it was applied to the determination of iodide in a standard table salt containing 40 mg g^{-1} iodide. For this purpose 2 g of salt sample was dissolved in water and diluted to 100 mL. 0.5 mL of this solution was treated under recommended procedure. The method was also checked by addition of known amount of iodide to the sample. The results shown in Table-2 indicate that the method is suitable for the determination of iodide in salt samples.

TABLE-2
DETERMINATION OF IODIDE IN A STANDARD TABLE SALT
CONTAINING IODIDE (40 µg g^{-1})

Added iodide (ng mL^{-1})	Found total iodide in solution* (ng mL^{-1})	Found iodide in sample (ng mL^{-1})
–	–	41.1
5	46.0 ± 1.4	41.0
10	51.1 ± 1.4	41.1
15	55.6 ± 1.5	40.6

*x ± ts/√n at 95 % confidence.

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