

## A Simple and Rapid Spectrophotometric method for the determination of Iodate in table salt samples using Pyrogallol red dye

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### Abstract:

A simple and rapid spectrophotometric method for the determination of iodate in table salt samples has been standardized using the oxidation reaction of iodate with pyrogallol red dye in sulphuric acid medium. The determination of iodate was done by measuring the decrease in absorbance of pyrogallol red dye at 470 nm. A standard calibration curve was prepared, for iodate concentrations in the range of  $0.05 \mu\text{g mL}^{-1}$  to  $5 \mu\text{g mL}^{-1}$ . The effect of NaCl and  $\text{I}^-$  interference on iodate determination has been studied. The kinetics of the reaction between pyrogallol red and iodate has also been studied. The oxidation reaction was found to be first order with respect to iodate concentration. The method has been used for the determination of iodate in 10 different brands of locally available common salt samples.

**Key Words:** Iodate, Table salt, Pyrogallol

### Introduction:

Iodine is an important constituent of the thyroid hormones. These hormones regulate the rate of metabolism and affect the growth and functioning of many systems in the human body<sup>1</sup>. Low amounts of thyroid hormones in the blood due to iodine deficiency, stimulates the abnormal growth of the thyroid gland causing goiter<sup>2</sup>. Iodine deficiency can be controlled through the addition of iodized salt in cooked food. Iodization of salt is done by adding 20-80 of iodine per kilogram of salt in the form of sodium or potassium salt of iodide or iodate. In hot climatic conditions like India, iodide is easily oxidized to  $\text{I}_2$  and then lost by evaporation, while iodate is more stable, also the chemical stability of iodate is more in alkaline conditions than iodide<sup>3</sup>. Hence, potassium iodate is most commonly used for the fortification of salt in

India. In order to know the daily dietary intake of iodine it is essential to know the iodate concentration in various brands of commonly available salt samples.

Survey of the literature reveals that many analytical techniques have been used for the determination of iodate in salt samples. The most commonly used technique is spectrophotometry where iodate reacts with several chromogenic reagents to form colored species<sup>4-7</sup>. Iodate has also been oxidized to iodine in acidic medium which reacts with dyes to give spectrophotometric signals<sup>8</sup>. A spectrofluorometric method for determination of iodate with rhodamine 6G has been developed by studying the fluorescence quenching of rhodamine 6G at 540 nm<sup>9</sup>. Trace levels of iodate have been determined by gas chromatography mass spectrometry (GC-MS) by its reduction to iodide using ascorbic acid followed by its oxidation to iodine and its derivatization to 4-iodo-2,6-dimethylphenol<sup>10,11</sup>. Iodate has also been estimated in salt using ion chromatography with conductivity detection<sup>12</sup>. This method requires a pretreatment for the removal of large excess of chloride. Flow injection amperometry has also been used for the determination of iodate in iodized table salt<sup>13</sup>. The electrocatalysis of iodate reduction at tungsten oxide films has been used for the determination of iodate content in table salt samples<sup>14</sup>. A rapid chemiluminescence method has been developed for the determination of iodate based on its reaction with iodide in acidic condition<sup>15</sup>. Trace amounts of iodate and iodide in table salt samples have been estimated by Epithermal Neutron Activation Analysis using Cadmium shielding and boron carbide<sup>16</sup>. A flow injection spectrophotometric method has been standardized for the determination of iodate and per-iodate by their reaction with pyrogallol red in acidic media<sup>17</sup>. A simultaneous kinetic spectrophotometric determination of per-iodate and iodate has been done based on their reaction with pyrogallol red in acidic media by chemometrics method<sup>18</sup>. In the present work the pyrogallol red dye oxidation reaction has been standardized for the determination of iodate in table salt samples. The determination of iodate was done by measuring the decrease in absorbance of pyrogallol red at 470 nm. The effect of NaCl and I<sup>-</sup> on iodate determination has been studied. The kinetics of the reaction between pyrogallol red and iodate has also been studied and the reaction was found to follow first order kinetics. The method has been used for the determination of iodate in ten different brands of locally available iodized table salt samples. The iodate concentrations in these salt samples were found to be in the range of 10-50 mg kg<sup>-1</sup>. The novelty of this work is, in determination of Iodate with pyrogallol no pre-treatment is required and method is fairly sensitive.

**Experimental:**

**Reagents and Apparatus**

Analytical reagent grade chemicals (KI, NaCl, KIO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>) were obtained from Merck. Pyrogallol red dye (C<sub>19</sub>H<sub>14</sub>O<sub>9</sub>S) was obtained from Loba chemie, Deionized water (18 MΩ/cm) purified by model Quantum<sup>TM</sup> from Millipore was used throughout the present studies. A stock solution of iodate (2 mg mL<sup>-1</sup>) was prepared by dissolving 0.61 g of KIO<sub>3</sub> in water in 250 mL volumetric flask. Pyrogallol red dye solution was prepared by dissolving 9 mg of the dye in a mixture of 1:1 MeOH/H<sub>2</sub>O in a 100 mL volumetric flask. UV-Vis spectra of the samples and standard solutions were recorded using a UV-Vis Spectrophotometer UV-1650 PV from Shimadzu. The scanning rate was 200 nm min<sup>-1</sup> and the path length of the quartz cells was 1cm.

**Method:**

**Preparation of calibration curve**

For the preparation of a standard linear calibration curve iodate solutions were prepared in the concentration range of 10-1000 µg mL<sup>-1</sup> by necessary dilutions from the stock solution. For the concentration range of 0.2-20 µg of iodate, a 20 µL volume of iodate solution 10-1000 µg mL<sup>-1</sup> was added to a mixture of 1mL dye solution and 1mL of 0.05 M H<sub>2</sub>SO<sub>4</sub>. The total volume of this solution was made to 4 mL with de-ionized water. All the solutions were kept for a period of 5 min at 25°C after addition of IO<sub>3</sub><sup>-</sup> solution to it and the decrease in absorbance of pyrogallol red dye at 470 nm was measured. A blank sample was used in the calibration set where all the reagents except iodate solution were added.

**Optimization of Experimental parameters**

The concentration of sulphuric acid required for the oxidation of pyrogallol red by iodate was optimized by adding 1 mL of H<sub>2</sub>SO<sub>4</sub> of concentration varying between 0.01 M to 0.07 M to 1mL of dye solution. The total volume of all the solutions was made to 4 mL with deionized water. A 20 µL volume of iodate solution (400 µg mL<sup>-1</sup>) was added to all the solutions. All the solutions were kept for a period of 5 min and the absorbance spectra were recorded. For the optimization of the concentration of pyrogallol red dye 1mL of 0.05 M H<sub>2</sub>SO<sub>4</sub> was added to 1mL solutions of pyrogallol red having concentration in the range of 0.01 mg mL<sup>-1</sup> to 0.12 mg mL<sup>-1</sup> respectively. After addition the same procedure as described above was followed and the absorbance spectra were recorded

### **Kinetics of the Reaction**

The kinetics of the oxidation reaction of pyrogallol red due to presence of iodate was studied by taking 1mL of dye solution, 1mL of 0.05 M H<sub>2</sub>SO<sub>4</sub> and 2mL of distilled water in a quartz cuvette. 20 μL of iodate solution (120 μg mL<sup>-1</sup>) was added to this cuvette and the decrease in absorbance of pyrogallol red at 470 nm was recorded as a function of time at an interval of every one min for a period of 15 min. The same procedure was repeated for each of the iodate solutions over a concentration range of 200 – 800 μg mL<sup>-1</sup> of iodate solution. The decrease in absorbance value at 470 nm was plotted as a function of time in each case and the values of the rate constants were calculated. The order of the reaction with respect to iodate was also determined.

### **Effect of NaCl and I<sup>-</sup> on oxidation of pyrogallol red by iodate**

The effect of NaCl on the oxidation of pyrogallol red dye was studied by varying the amount of Analytical reagent grade NaCl (0-200 mg) in the solution containing a mixture of 1mL of acid solution and 1 mL of dye solution. The final volume of the solution was made 4 mL in all the cases by the addition of deionized water. 20 μL of iodate solution (200 μg mL<sup>-1</sup>) was added to all the solutions. All the solutions were kept for a period of 5 min and the decrease in absorbance of pyrogallol red dye at 470 nm was measured.

To study the interference due to I<sup>-</sup> on the oxidation of pyrogallol red dye varying amounts of iodide (0- 10 μg) were added to the solution containing a mixture of 1mL acid and 1 mL dye solution. After addition of the iodide solution the same procedure as described above for NaCl was followed and the absorbance spectra were recorded

### **Estimation of iodate contents in commercially available iodized salt samples**

About 10 g of locally available salt samples containing iodate were removed from packets and homogenized using mortar and pestel. These homogenized samples were used for the determination of iodate in the salt samples by pyrogallol red dye method. 1g of the homogenized salt sample was dissolved in 50 mL of deionized water. 1 mL of dye solution and 1mL of 0.05 M H<sub>2</sub>SO<sub>4</sub> were taken in a quartz cuvette. To this solution 2.20 μL of above salt sample solution was added and the decrease in absorbance at 470 nm was recorded after a time period of 5 min. The concentration of iodate in the salt samples was calculated by using the standard calibration curve.

### **Results and Discussion**

A method for the kinetic determination of iodate and periodate based on their reaction with pyrogallol red in acidic media has been standardized by Ghasemi et al and applied for the

determination of iodate in water samples<sup>18</sup>. In the present work the same reaction of pyrogallol red oxidation by iodate in acidic media has been used for the determination of iodate in locally available table salt samples.

### Standard Calibration Curve

Pyrogallol red (Pyrogallolsulfonephthalein), C<sub>19</sub>H<sub>12</sub>O<sub>8</sub>S is a complexing indicator (Fig 1). The solution of pyrogallol red prepared in alcohol-water mixture shows absorbance maxima at 470 nm. Pyrogallol red gets oxidized by iodate in acidic media to form a colourless product. The oxidation reaction of pyrogallol red with iodate can be monitored by the decrease in absorbance of pyrogallol red at 470 nm. A linear calibration curve was obtained for iodate concentrations in the range of 0.05 µg mL<sup>-1</sup> to 5 µg mL<sup>-1</sup>. The change in absorbance value at 470 nm with respect to the blank absorbance value at the same wavelength has been plotted as a function of amount of Iodate in the reaction mixture and is shown in the (Fig 2). It can be seen from the figure that the plot is a straight-line having equation  $[y = 0.0735 x + 0.0003 R^2 = 0.9885]$  indicating a linear decrease in the absorbance value of pyrogallol red with increase in concentration of iodate. The detection limit calculated from the 3σ value of blank is 0.04 µg IO<sub>3</sub><sup>-</sup>.

### Effect of different parameters on the oxidation of pyrogallol red

The oxidation of pyrogallol red by iodate is found to be greatly affected by the acidity of the reaction mixture. The effect of acid concentration on the oxidation of pyrogallol red was studied by varying the concentration of H<sub>2</sub>SO<sub>4</sub> from 0.01 M to 0.07 M and measuring the change in absorbance of pyrogallol red at 470 nm. It was found that the change in absorbance value increases rapidly for acid concentration from 0.01 to 0.04 M. The change in absorbance value remains almost constant beyond acid concentration of 0.05 M. The acid concentration was therefore kept 0.05 M for further experiments. The results were found to be in agreement with those observed by Ghasemi et al<sup>18</sup>.

The effect of the concentration of pyrogallol red on the oxidation rate was studied by varying the concentration of the dye between 0.01 mg mL<sup>-1</sup> to 0.12 mg mL<sup>-1</sup>. It was found that the change in absorbance increases upto a dye concentration of 0.09 mg mL<sup>-1</sup> beyond which it remains fairly constant. The concentration of the dye was kept 0.09 mg mL<sup>-1</sup> for further experiments.

### Kinetics of the oxidation reaction of pyrogallol red with iodate

The kinetics of the oxidation reaction of pyrogallol red with iodate was studied by measuring the decrease in absorbance at 470 nm due to addition of varying amounts of iodate to it as a

function of time. The concentration of pyrogallol red was kept fixed ( $0.09 \text{ mg mL}^{-1}$ ) and the concentration of iodate was varied between  $2.4 \text{ }\mu\text{g}$  to  $16 \text{ }\mu\text{g}$ . The absorbance spectra of the pyrogallol solution were monitored after an interval of every 1 min after the addition of iodate solution to it. The absorbance value of pyrogallol red was found to decrease rapidly during the first five minutes of the reaction. It was observed that the absorbance of pyrogallol red reached an optimum value after a period of 6-7 min after which there is no further change in the absorbance value (Fig 3). The absorbance value of pyrogallol red at any interval of time is directly proportional to the concentration of unreacted iodate at that time instant. Using these absorbance values the rate constant for the reaction with respect to iodate was calculated for each concentration of iodate. The rate constant values calculated from the first order equation showed constant values indicating the order of the reaction to be 1. The average value of the first order rate constant calculated from the equation in the present studies is  $3.69 \times 10^{-2} \text{ min}^{-1}$ . A plot of absorbance value of pyrogallol red proportional to the residual concentration of dye after addition of  $2.4 \text{ }\mu\text{g}$  of iodate as a function of time is given in (Fig 4). It can be seen from the figure that the plot gives best linear points suggesting the order of the reaction to be one. The equation for the plot is  $[y = -0.0152x - 0.0903 \text{ R}2 = 0.9771]$ . The slope of this plot is  $-0.0152$ . The rate constant value from the slope of the plot is  $3.50 \times 10^{-2} \text{ min}^{-1}$ . Fig 5 shows oxidation of pyrogallol red with Iodate.

#### **Estimation of iodate in commercially available iodized salt samples**

Since the method in the present work has been applied to iodate determination in table salt samples the effect of NaCl on the oxidation of pyrogallol red dye by iodate was studied. It was observed that there was no significant change in the absorbance of pyrogallol red dye at  $470 \text{ nm}$  due to presence of NaCl upto  $200 \text{ mg}$  (Fig 6). This suggests that the method can be used without any interference for iodate determination in iodized salt samples. In some countries iodide is added as an alternative to iodate for the iodization of common salt. However, in India iodate is preferentially added over iodide for iodization of salt. The presence of iodate in some locally available table salt samples has been determined and reported in our previous work<sup>19</sup>. The effect of I<sup>-</sup> on the oxidation of pyrogallol red by iodate was studied and the studies indicated that the presence of iodide upto  $1 \text{ }\mu\text{g}$  did not interfere in the iodate determination. Above  $1 \text{ }\mu\text{g}$  iodide showed interfere in the iodate determination. The iodate contents in ten different commonly consumed brands of iodized salt samples were determined in the present work. The results obtained are summarized in table I. It can be seen that the iodate contents obtained are in the range of 10-50 ppm. The iodine contents in all the

brands were more than that quoted by the manufacturer except for Brand-9. The results suggest that the consumption of these brands can provide adequate amount of iodine and prevent deficiency.

### Conclusions

The present work demonstrates a simple and rapid spectrophotometric method for the determination of iodate in table salt samples using pyrogallol red dye method. The method does not require sophisticated equipment and can be easily used for the quick screening of a large number of salt samples for iodate in any laboratory.

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### Figures:

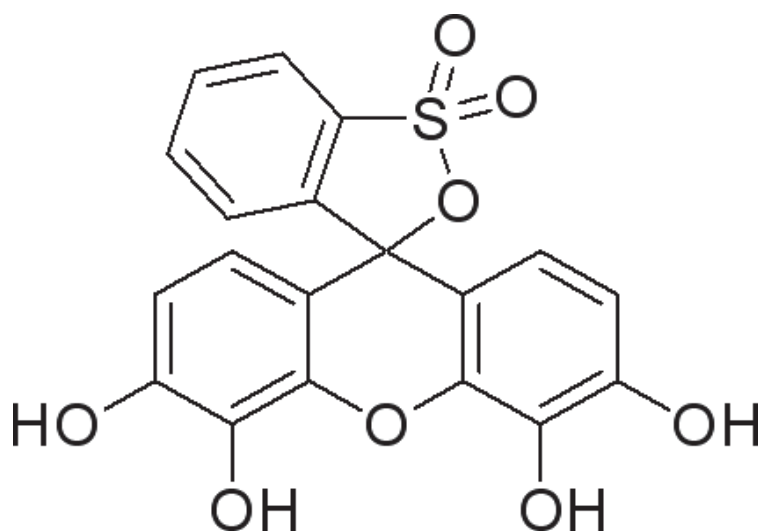
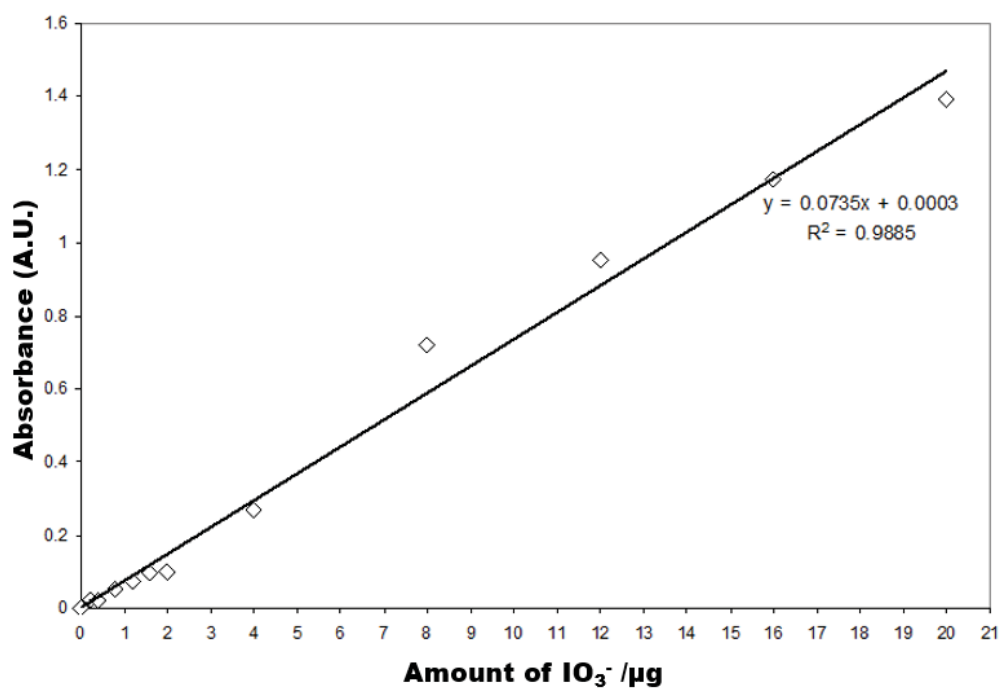
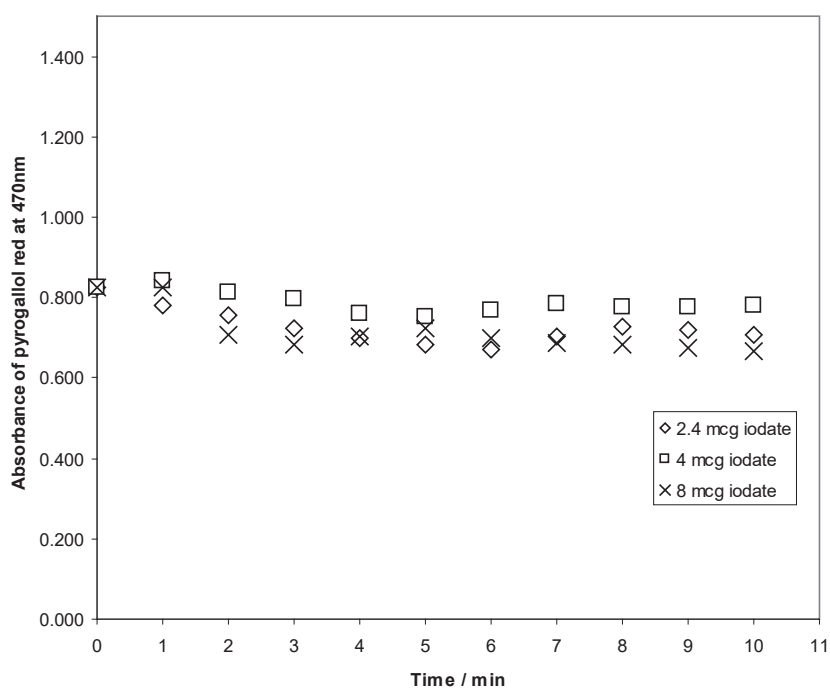


Fig 1: Structure of Pyrogallol red dye.

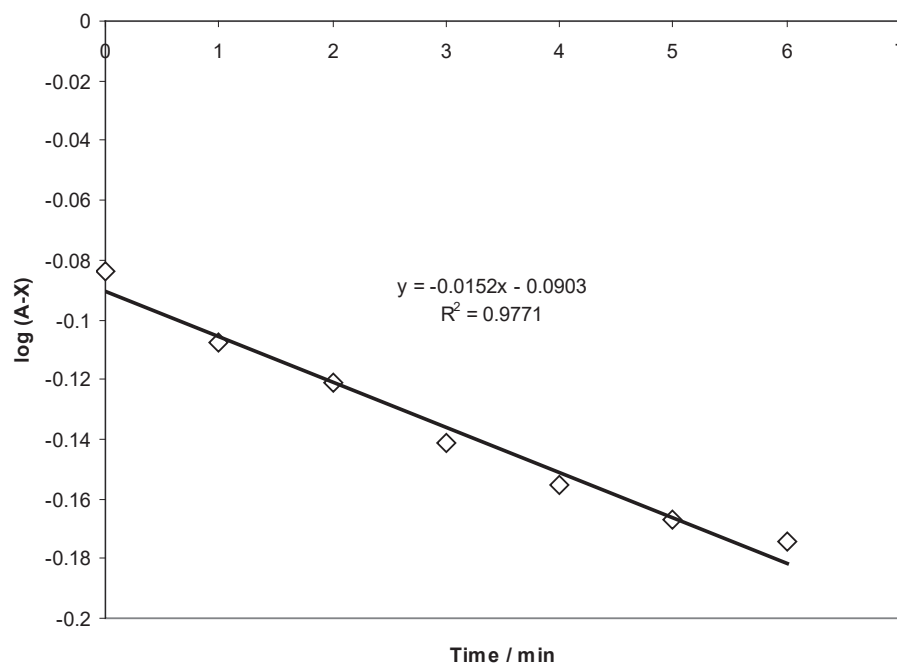


**Fig 2:** Variation of change in absorbance of pyrogallol red at 470 nm as a function of amount of Iodate

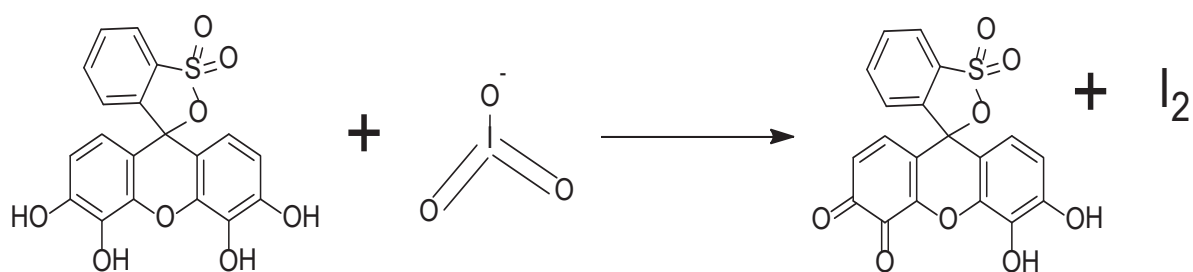


**Fig 3:** Kinetics of the oxidation of pyrogallol by Iodate

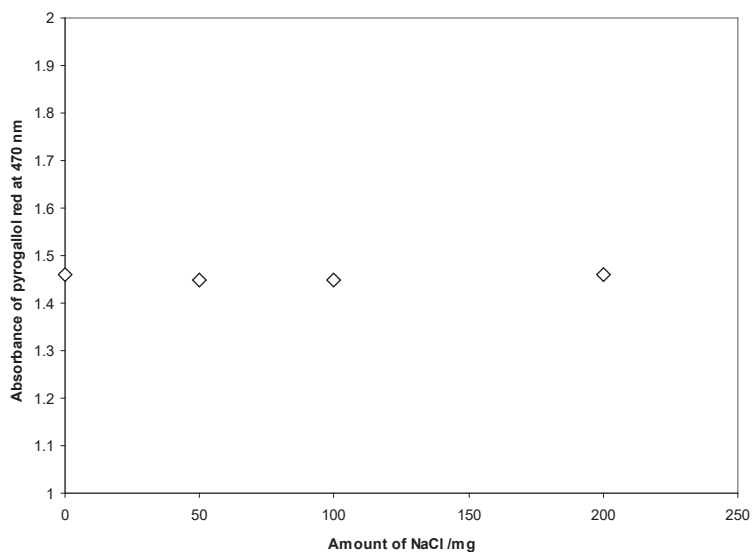




**Fig 4:** Plot of Absorbance of unreacted pyrogallol red as a function of time.



**Fig 5:** Oxidation of pyrogallol red by Iodate



**Fig 6:** Effect of NaCl on oxidation reaction of pyrogallol red with Iodate

**Tables:**

**Table 1:** Determination of iodate content in different iodized salt brands by pyrogallol red method.

| <b>Iodized salt Brand</b> | <b>Iodate content /<br/>mg kg<sup>-1</sup></b> | <b>Minimum Iodate<br/>content Quoted on<br/>packet / mg kg<sup>-1</sup></b> |
|---------------------------|--|---|
| Brand-1                   | 28.9 ± 0.1                                     | 15  |
| Brand-2                   | 48.49 ± 0.2                                    | 30  |
| Brand-3                   | 17.45 ± 0.1                                    | 15  |
| Brand-4                   | 17.58 ± 0.1                                    | 15  |
| Brand-5                   | 24.34 ± 0.1                                    | 15  |
| Brand-6                   | 26.45 ± 0.2                                    | 15  |
| Brand-7                   | 32.56 ± 0.2                                    | 30  |
| Brand-8                   | 15.43 ± 0.1                                    | 15  |
| Brand-9                   | 11.32 ± 0.1                                    | 15  |
| Brand-10                  | 25.63 ± 0.2                                    | 15  |

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