Spectrophotometric Determination of Nitrate Ion in Presence of Chloride Matrix

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Abstract

^{89}Sr a radionuclide used for bone pain palliation — is produced in Fast Breeder Test Reactor (FBTR) via the ^{89}Y (n, p) ^{89}Sr reaction. The final ^{89}Sr source is obtained after processing the irradiated Y_2O_3 target using nitric acid. The final product ^{89}Sr is injected in HCl medium whose concentration must be 0.05–0.5M. The final product which was obtained after the chemical processing in the nitric acid is converted into its chloride form. The estimation of nitrate ion in the ^{89}Sr source is an indication of i) the efficiency of the conversion and ii) the ^{89}Sr source is free from the nitrate ion impurity. Hence it is necessary to determine the presence of nitrate in the product. So a method was developed in the laboratory to estimate the nitrate ion concentration in presence of bulk chloride ion concentration by spectrophotometric method.

Keywords: Spectrophotometry, Nitrate ion, Chloride matrix, Diazotization

1. Introduction

Various methods have been proposed for the determination of nitrate ion in chemical samples including water samples, but the results obtained by these methods are significantly influenced by the presence of chloride ion[1-4]. The most widely used method for the direct estimation of nitrate is Colorimetric method. But it has a serious limitation that the presence of high level of chloride leads to low or no reproducible nitrate value. Moreover, the azo dye formation is pH dependent[5,6].

Methods based on the reduction of nitrate to ammonia have been used. These methods give best results only for macro amount of nitrates. Ion selective method is also another efficient method to determine the concentration of nitrate ion[7]. The Ion Selective Electrode (ISE) is affected by numerous analytical interferences which may increase (or) decrease the apparent analytic concentration and causes damage to the electrode. Effect of most interference can be minimized (or) eliminated by adding appropriate chemical reagents to the sample. Obtaining the most accurate results therefore requires some knowledge of sample composition. The temperature changes also affect the electrode potential (reference electrode), therefore standards and samples must be equilibrated at the same temperature (±10°C)[8,9].

The most sensitive method for nitrate generally was based on reduction of nitrate to nitrite, then diazotization and coupling with a color forming reagent. Preliminary investigations revealed that various concentration of chloride had no effect on the diazotization and coupling reactions when nitrite concentration was to be determined spectrophotometrically[10-14]. However, the presence of chloride did have a significant effect on the reduction of nitrate to nitrite. Therefore, this study was directed towards seeking a method that would provide satisfactory

reduction of nitrate to nitrite in solutions that contained different concentrations of chloride.

2. Materials and Methods

2.1 Preparation of Reagent and Standards

2.1.1 Mixed Acid Solution

It was prepared by dissolving the chemicals (a) Ammonium chloride = 16.66 g, (b) Citric acid = 4 g (c) Dibasic sodium phosphate = 0.266 g (d) Sodium chloride = 10 g (e) Copper (II) Sulphate = 0.016 g (f) Acetic acid = 2 mL, for a final volume of 100 mL.

2.1.2 Colour Developing Agent

The color developing agent was prepared by grinding the following chemicals together in a mortar i.e. (a) Ammonium chloride = 5 g (b) Sodium citrate = 3.33 g (c) Manganese (II) sulphate = 1 g (d) Sulphanilic acid = 0.2 g (e) Alpha Naphthylamine = 0.3 g (f) Cadmium = 0.3 g. This mixture was ground well to make it homogeneous and then it was stored in a tightly capped plastic vial that was covered with Aluminum foil to keep light out.

2.1.3 Stock Nitrate and Chloride Solution

0.75 mg/mL of nitrate solution was prepared by adding 0.0514 g of sodium nitrate to a 50 mL volumetric flask and making up to the volume with Millipore water. 0.2 g of Stock chloride solution was prepared by dissolving 10 g of sodium chloride in 50 mL of volumetric flask by using Millipore water and diluted to 50 mL.

2.2 Preparation of Standard Nitrate Solution A and B

0.015 mg/mL of nitrate solution A was prepared by pipetting 1mL of stock nitrate solution into a 50mL volumetric flask and making up to the volume with Millipore water. Standard nitrate solution B contained the same concentration of nitrate as standard solution A and, in addition contained 0.2g of sodium chloride per mL.

2.3 Calibration

Five samples of different concentrations were taken for the determination of standard calibration curve (Table 1) i.e. since this experiment involves the verification of the only method reported on the determination of nitrate in chloride matrix. A calibration curve was plotted by using standard nitrate solution B. The volumes of 1.00 to 6.00 mL of standard solution were pipetted into 125 mL reagent bottles. 5 mL or less of stock chloride solution was added such that the standard solution plus chloride solution equal to 6 mL. Next 15 mL of mixed acid solution and 4 mL of Millipore water was added to each reagent bottle. 1 g of color developing agent was added to this. The absorbance of the solution was observed at 527.5 nm in a UV-visible spectrophotometer and it was recorded against the reagent blank of 10 mL of Millipore water throughout the procedure.

Table 1. Various concentrations of Samples for the determination of Standard Calibration

Sample No.	Mixed acid solution (mL)	standard B solution (mL)	stock chloride solution (mL)	Millipore water (mL)
1	15	1	5	4
2	15	2	4	4
3	15	3	3	4
4	15	4	2	4
5	15	5	1	4
BLANK	15	0	0	10

The procedure involves the mechanism of a) nitrate ion was reduced in to nitrite ion by using cadmium as a reducing agent b) mixed acid solution provided a satisfactory reduction of nitrate to nitrite by powdered cadmium in the presence of chloride c) nitrite ion undergoes a diazotization and coupling with a color developing agent cadmium in presence of chloride[15,16].

3. Results and Discussion

3.1 Determination of the Unknown Concentration of Nitrate in a Sample

Generally, the concentrations are directly proportional to absorbance[17,18]. In this experiment, all the samples showed regular absorbance values with respect to its concentrations (Table 2 and Figure 1). From this calibration curve we can find out unknown concentration of nitrate ion in the presence of chloride. However the method is to be standardized to get the calibration curve with fixed amount or negligible variation of the matrix of chloride content which is expected to be comparable with the sample of our interest.

## 3.2 Formation Kinetics of Azo Dye Complex

Absorption spectra of all the samples after half an hour from the time of addition of colour developing agent were recorded (Figure 2). This results shows that absorbance maximum is at 560 nm instead of 527.5 nm along with

Table 2. Various concentrations of Standard nitrate solution (B) and stock chloride solution
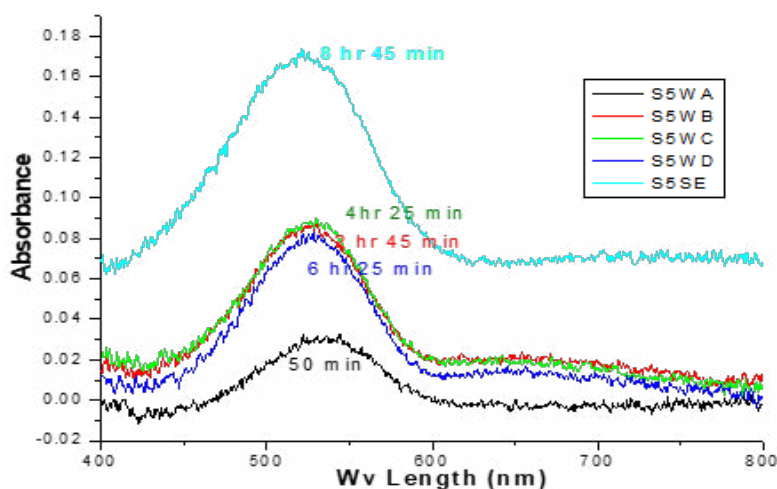
Sample	Standard nitrate solution B (mg/mL)	Stock chloride solution (mg/mL)
1	0.077	0.2
2	0.0616	0.4
3	0.0462	0.6
4	0.0308	0.8
5	0.0154	1
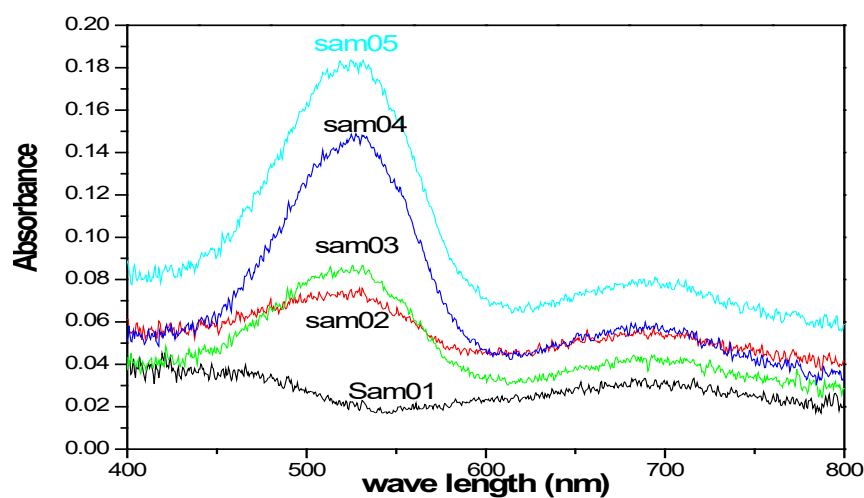
Figure 1. Absorption spectra with respect to its concentrations for the calibration.
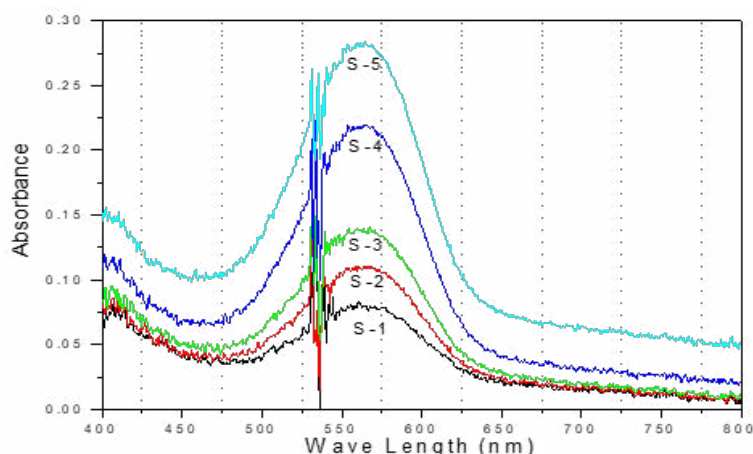
Figure 2. Absorption spectra of samples after half an hour from the time of addition of colour developing agent.

Figure 3. Absorption spectra of samples every 1 hour after adding the colour developing agent.

a noise at 530 nm which may be due to the incomplete formation of the complex. Hence half an hour time is not sufficient for the completion of complex formation.

The spectrum was taken every one hr from the time of addition of colour developing agent (Figure 3). The solution was also kept overnight and the spectrum was taken at the end of 24th hr. It was observed that the absorbance value for the first one hr is lower than the second hr which is equal to that of the third and fourth, while the absorbance value for fifth and six hr were more than second to fourth. The variation of absorbance with time is in the order of 1st hr (sam1) < 2nd hr (sam2) = 3rd hr (sam3) = 4th hr (sam4) < 5th hr (sam5) < 6th hr > 24th hr. From this experiment, it is inferred that the formation of the azo dye complex formation is incomplete for the first one hr and it is complete and stable from 2–6 hrs from the time of addition of colour developing agent. After 24th hr the absorbance value is low suggesting that the complex is unstable. However this observation was confirmed to be due to mechanical shaking by comparing the observation of no such effect without mechanical shaking.

## 3.3 Effect of Shaking on the Stability of Azo Dye Complex

After adding colour developing agent the solution was kept for shaking using mechanical shaker. Then spectrum was taken every one hr (A) from the time of shaking (Figure 4). In this spectrum, shaking gave a high absorbance values for the sample at first time. Spectrum was taken for the same sample after two hours (B), it shows higher absorbance value, but the spectrum taken for the same sample after three hours (C) the absorbance value decreased and also after 4 and 5 (D and E) hours the spectrum taken for the sample it showed low absorbance values.

The absorbance value was high for the first and second hrs and thereafter it showed irregular absorbance value. This experiment suggested that shaking is one of the important parameter which affects the stability of azo dye complex. In the previous experiments, the samples were not shaken and the azo dye complex was stable for a particular period. But shaking the sample highly affected
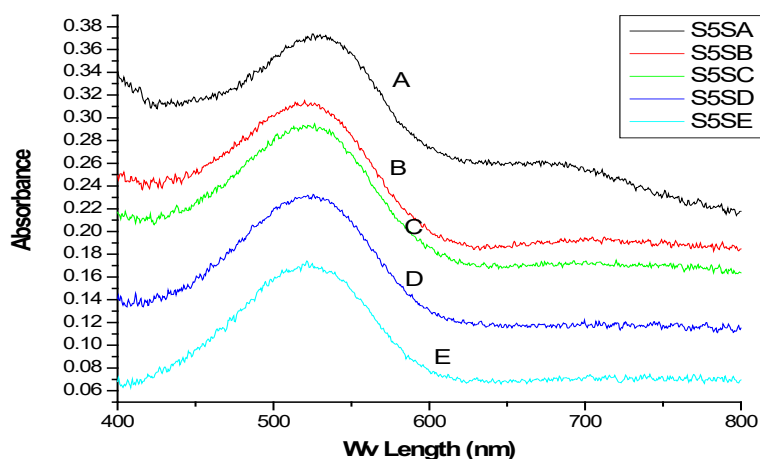
Figure 4. Absorption spectra of shaking samples at different time intervals Determination of Nitrate ion.
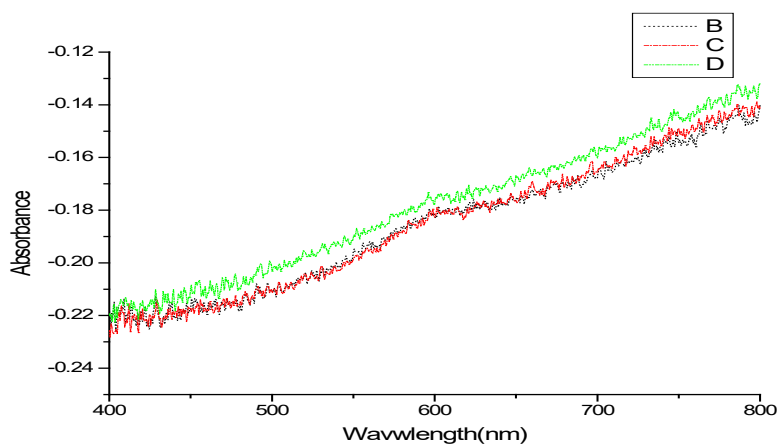
Figure 5. Absorption spectra of samples after 3 hrs from the addition of colour developing agent.
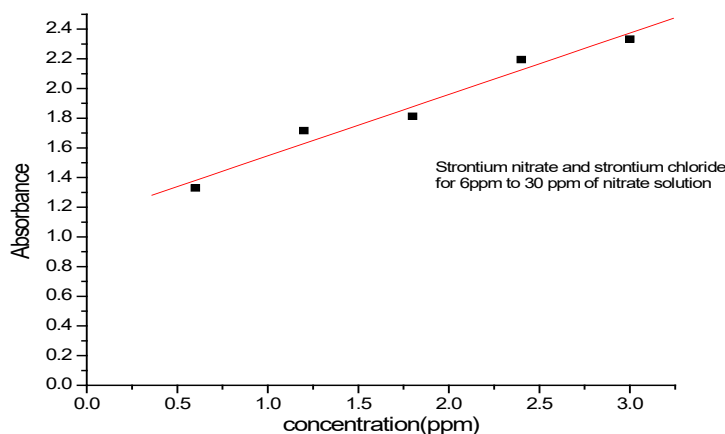
Figure 6. Calibration curve.

the stability of the azo dye complex. It was therefore concluded that the shaking disturbed the stability of the complex and is not necessary. However this observation was confirmed to be due to the shaking by comparing the observation of no such effect without shaking.

Three samples (B, C, D) containing same known concentration of nitrate with 5, 10 and 15 mL of con. HCl were taken and evaporated to dryness under IR lamp. 10 mL of water and 1g of color developing agent were added to the dried mass of 15 mL of mixed acid solution. It was mixed well and the sample was kept for 3 hours for the azo dye formation and the spectrum was taken for the sample (Figure 5). In this case, sample 3 gave a negative absorbance value which shows the absence of nitrate. From this it is inferred that in sample 3 all the nitrates were converted completely into chloride. But sample 1 and 2 showed low absorbance values indicating the incomplete conversion of nitrate to chloride ion. Thus by using sufficient amount of Conc. HCl for evaporation the complete conversion of nitrate to chloride can be ensured by calibration curve (Figure 6).

4. Conclusion

The final source obtained was in its nitrate form i.e., $Sr(NO_3)_2$. However the final product for the medical application was in chloride form. Hence, the strontium nitrate was converted to its chloride by heating with hydrochloric acid. As a part of the quality control, the absence of nitrate ion in the final source has to be confirmed by assaying the source for the nitrate. Hence a procedure is standardized for the nitrate determination in the chloride matrix. This method is very helpful to determine nitrate ion concentration in the presence of Chloride ion.

5. References

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