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Analysis of Water for Nitrate and Nitrite Nitrogen–by Potentiometry and UV Visible Spectroscopy- A Comparison

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Abstract:
In the present study analysis of different water samples was done for the estimation of nitrite and nitrate concentrations by electroanalytical and spectral techniques. The electroanalytical methods used were colorimetry and potentiometry. In the UV visible spectral analysis nitrite is determined through the formation of a reddish purple azo dye produced at a pH of 2- 2.5 by coupling deoxidized sulphanilamide with N-(1- naphthyl)ethylene diamine dihydrochloride (NED). The applicable range of the method for spectrophotometric measurement is 10 – 1000 µ gm/L nitrite- nitrogen. Nitrate is reacted with phenoldisulphonic acid to give a yellow colour with an absorption maxima at 410nm. The factors effecting the reproducibility and accuracy by both the methods were determined and compared and the analysis of the data is given.

Keywords: Colorimetry, Potentiometry, UV visible spectroscopy.

1. INTRODUCTION:

Nitrogen, an important component of protein is essential for all living things. Nitrogen exists in the environment in many forms and, changes forms as it moves through the nitrogen cycle. However, excessive concentrations of nitrate-nitrogen or nitrite-nitrogen in drinking water can be hazardous to health, especially for infants and pregnant women(1,). Nitrate is a common contaminant found in groundwater that can have serious health effects if consumed at high levels. Nitrate is colorless, odorless and tasteless. Low levels of naturally occurring nitrate can be normal, but excess amounts can pollute ground water(2). The primary health hazard from drinking water with nitrate-nitrogen occurs when nitrate is transformed to nitrite in the digestive system. The nitrite oxidizes the iron in the hemoglobin of the red blood cells to form methemoglobin, which lacks the oxygen-carrying ability of hemoglobin. This creates the condition known as methemoglobinemia (sometimes referred to as "blue baby syndrome"), in which blood lacks the ability to carry sufficient oxygen to the individual body cells causing the veins and skin to appear blue. as "blue baby syndrome"), in which blood lacks the ability to carry sufficient oxygen to the individual body cells causing the veins and skin to appear blue (3). Nitrate in water is undetectable without testing because it is colorless, odorless, and tasteless. A water test for nitrate is highly recommended for households with infants, pregnant women, nursing mothers, or elderly people. These groups are the most susceptible to nitrate or nitrite contamination (4). A potential cancer risk from nitrate (and nitrite) in water and food has been reported. A possibility exists that nitrate can react with amines or amides in the body to form nitrosamine which is known to cause cancer. Nitrate must be converted to nitrite before nitrosamine can be formed (5). Nitrite is present in groundwater to a much lesser extent because it is rapidly converted to nitrate, nitrite (NO2) is a contaminant with similar physical properties to nitrate (6, 7).

2. METHODOLOGY

Analysis is described for the determination of nitrate in water by colorimetry and potentiometry.

Colorimetry

In colorimetry, the light absorptive capacity of a system (coloured solution) is measured and this measurement is related to the concentration of the coloured substance in the solution. When monochromatic light passes through a transparent medium (coloured solution) the rate of decrease in intensity with the concentration and thickness of the medium is directly proportional to the intensity of the light. The colorimetric method is based on the reaction of water sample with certain reagents and on the measurement of the optical density of the coloured compound which absorbs maximally at 520m. Hence all measurements were made at 520 nm. Absorbance of the chromophore is directly proportional to the amount of nitrate N present. Sodium salicylate is the reagent used. Chemicals: sodium salicylate (0.5% water solutions, prepared freshly), sulphuric acid (conc. 96%), sodium hydroxide (c= 10 mol/L: 400 g NaOH is dissolved in distilled water in 1000 mL volumetric flask), potassium nitrate (NO_3^-) = 100mg/L – stock solution: 0.1631 g KNO_3 is dried in temperature 105°C and dissolved in 1000 mL distilled water in volumetric flask).10 mL water samples (solutions in concentration range) with 1 mL sodium salicylate are evaporated in an evaporating dish, and cooled. 1 mL of concentrated H_2SO_4 was added so that way the entire residue dehumidified and allowed to stand for 10 minutes and transferred to a 50 ml volumetric flask. 7 mL NaOH was added and after cooling to room temperature, the volume was made to 50 mL with distilled water. After 10 minutes, the stain remains and the absorbance is measured at 520 nm against a blank prepared in the same way . For colorimetric determination of nitrate by sodium salicylate , a calibration curve relating 15

absorbance to concentration of nitrate nitrogen and a calibration curve of absorbance to nitrate concentrations were plotted (Fig. 2) where A is absorbance and c is concentration (mg/L).

Potentiometry:

Determination of nitrate in waters, with sequential detection by potentiometric sensors, is done. The equipment used consisted of a potentiometer (a potential measuring device), a reference electrode and an indicator electrode (a nitrate ion selective electrode).The half cell potential of the reference electrode is a known constant and this electrode is completely insensitive to the composition of the solution under study. A series of standards containing 10 – 100 micro grams per litre of nitrate are prepared. A nitrate ion-selective electrode Orion 93-07 was used to check the analytical signal. The electrode potential was measured by an Orion pH/mVmeter 407 A to 1 mV. For calibration standard solutions of 10 -1 to 10-4M sodium nitrate were used. As a known addition reagent 10- 2 M sodium nitrate solution was used. For direct potentiometry a standard graph was used. The one-step known addition was performed .Six known addition (0.10, 0.15, 0.20, 0.25 and 0.30 ml of 10 .2 M sodium nitrate) were added to 10 ml of the sample and after each addition the electrode potential was checked and recorded. It is worth mentioning that the analysis was performed with constant stirring.

UV visible spectral analysis:

Nitrate is reacted with phenoldisulphonic acid to give a yellow colour with absorption maxima at 410nm. Chloride interference is removed by precipitating the chloride. Nitrate levels in excess of 0.2 mg/L cause positive interference but such concentration rarely occurs in surface waters. The sample should not exhibit appreciable colour to prevent any change in the nitrogen balance through biological activity. Natural water is analysed properly after sampling stored 40 mg of $HgCl_2$ per litre as extended six folds by measuring at 480 nm and also two fold by diluting prepared sample to 100ml of 50 ml. Water samples exceeding 50mg/L of nitrate showed development of hypertrophy in humans (9).Nitrate is endogenously reduced to nitrite and subsequently to N- nitroso compounds. Consumption of water contaminated with nitrates may increase cancer risk (8). Nitrite is an intermediate oxidation state of nitrogen, both in the oxidation of ammonia to nitrate and in the reduction of nitrate. Such an oxidation and reduction may occur in waste water treatment plants, water distribution systems and natural waters. Nitrite can enter a water supply system as a corrosion inhibitor in industrial processed water. Nitrite is the actual etiologic agent of, methaemoglobinemia (blue baby syndrome). Nitrous acid, which is formed from nitrite in acidic medium, can react with secondary amine to form nitroso- amine (RR'N-NO), many of which are carcinogens. Nitrite is determined through the formation of a reddish purple azo dye produced at a pH of 2- 2.5 by coupling deoxidized sulphanilamide with N-(1-naphthyl) ethylene diamine dihydrochloride (NED). The applicable range of the method for spectrophotometric measurement is 10 – 1000 µ gm/L nitrite- nitrogen.

INTERFERNCES

Free chlorine and nitrogen trichloride interfere in the estimation of nitrite nitrogen. The ions, Sb^{3+} ,$Au^{3+,}$ Bi^{3+}. Fe^{3+}.Hg^{2+},Pb^{2+},Ag^{+}, chloroplatinate and meta vandate interfere because of precipitation under test conditions and should be absent. The turbid samples were filtered and 20 ml samples were taken in 25 ml volumetric flask and made upto the mark with distilled water. 1 ml of sulphanilic acid was added to the volumetric mixed thoroughly and was allowed to stand for 3 to 6 min. 1 ml of NED solution was added and diluted upto 50 ml, mixed thoroughly and allowed to stand for 10 min. Within 2 hours the absorbance was measured at 543 nm using 1 cm cuvette.

3. RESULTS AND DISCUSSION:

Colorimetric analysis involves an electrophillic aromatic substitution (nitration) between nitronium and salicylate (11). The nitrate electrode contains an internal reference solution in contact with a porous plastic organophilic membrane which acts as selective nitrate exchanger (12). When the membrane is exposed to nitrates present in water , a potential, E is developed across the membrane which is measured against a constant reference electrode potential , E0 .The magnitude of E depends on the concentration of nitrates present(9). The results obtained with nitrate ion selective electrode were compared with those obtained from colorimetric analysis.

Spectral analysis.

Free chlorine and nitrogen trichloride interfere in the estimation of nitrite nitrogen. The ions, Sb^{3+} ,$Au^{3+,}$ Bi^{3+}. Fe^{3+}.Hg^{2+},Pb^{2+},Ag^{+}, chloroplatinate and meta van date interfere because of precipitation under test conditions and should be absent.
The correlation between absorbance and concentration is linear and for the concentrations lower than 200µg NO_2-N/L, the computation was conducted as shown.

NO_2-N and NO_3-N (µ g/L) = C_{std} * Vol_{std} *(A_{sample} - A_{blank}) /$Vol_{sample*}$ (A_{std}-A_{blank})
Where C= concentration
Std.= standard
Vol=volume
A = absorbance
A graph was plotted between absorbance and concentration as shown in figure-1 and the results tabulated as shown in tables 1 and 2.

TABLE.1.

S. No.	Concentration of sample(µ gm/L)	Sulphanilic acid	NED	Abs.
1	0.1	1	1	0.234
2	0.2	1	1	0.435
3	0.3	1	1	0.657
4	0.4	1	1	0.982

TABLE.2.

S. No	Vol of nitrite (ml)	Phenoldisulphonic acid	Distilled water	Conc. NH_3	Conc. Mg/N	Abs.
1	10	2	20	7	0.10	0.256
2	20	2	20	7	0.15	0.457
3	30	2	20	7	0.20	0.752
4	40	2	20	7	0.25	0.954
5	50	2	20	7	0.30	1.09
6	60	2	20	7	0.35	1.99

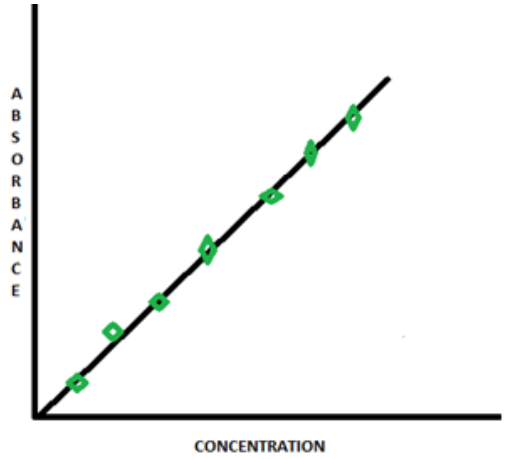

Figure.1.

4. CONCLUSION:

Methods for nitrate analysis require expensive equipment and complicated procedures. In the present study an attempt was made to develop a simple and accurate procedure for nitrate analysis. Analysis of nitrate nitrogen in water was successfully performed colorimetrically and an attempt was made to study the concentrations of nitrate in water sample by using the reagent sodium salicylate .The results were found to be accurate and reproducible(10) . This new method utilizes a non- hazardous reagent and was found to be much simpler ,less expensive & less time consuming with proper filter chosen . Results obtained by colorimetric methods were compared with those obtained by potentiometry and both the methods give good reproducibility. The nitrate and nitrite nitrogen levels in various samples of water were analysed spectrophotometrically. Nitrate is reacted with phenoldisulphonic acid to give a yellow colour with absorption maxima at 410nm. Nitrite is determined through the formation of a reddish purple azo dye produced at a a pH of 2- 2.5 by coupling deoxidized sulphanilamide with N-(1- naphthyl) ethylene diamine dihydrochloride (NED). The method followed was by spectrophotometric analysis, was accurate and the results were reproducible (11) and also less time consuming.

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