RESEARCH ARTICLE Agricultural Science Digest, Volume 44 Issue 2: 244-249 (April 2024)

Simultaneous Assessment of the Nitrates and Nitrites in the Ground Water Samples using Optical Spectrophotometry and Validating the Appropriate Wavelength of Measurement

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10.18805/ag.D-5871

ABSTRACT

Background: Nitrate is a renowned pollutant in water and soil. Nitrate is used mostly as a nitrogen fertilizer. When nitrate seeps into the ground it can get into drinking water. Traces of nitrite and nitrate in drinking water may lead to methemoglobinemia in infants and with long term exposure is a possible cancer risk. Concentration of nitrate above 45 mg/L as nitrate and 10 mg/L as nitrate-nitrogen is unsuitable for domestic use according to BIS (Bureau of Indian Standards).

Methods: Nitrates are mainly determined by the spectrometric, colorimetric and ion chromatography methods. Majority of these methods are slow measurement, laborious and require the use of toxic and expensive reagents. In this study, ultraviolet spectrophotometric method is utilized for detection of nitrate optically with no chemical reagents. This method is simple and cost-effective. Nitrate and nitrite concentrations were analysed at various wavelengths (220 to 370 nm) and 240 nm was found to be efficient for detecting both nitrate and nitrite.

Result: Various groundwater samples in and around Karunya Campus and nearby residential places, Coimbatore, Tamil Nadu were analysed and compared with one borewell water sample from West Bengal State which was prone to contaminated ground water. The results show that all the ground water samples have nitrate and nitrite concentration within the permissible limit but the sample from West Bengal has higher concentration compared to Coimbatore samples.

Key words: Groundwater, Nitrates, Nitrites, Spectrophotometer.

INTRODUCTION

Nitrate and nitrite are found more commonly in groundwater than in surface water and are two of the more commonly detected well water contaminants. Principal sources of nitrate or nitrite contamination are fertilizers, septic tank waste, livestock manure and erosion of natural deposits. (Shukla and Saxena, 2018).

Beneath agricultural lands, nitrate is the primary form of nitrogen. It is soluble in water and can easily pass through soil to the ground-water table. Nitrate can persist in ground water for decades and accumulate to high levels as more nitrogen is applied to the land surface every year.

Nitrite is of health concern in the human body because it causes the haemoglobin in the blood to change to Methaemoglobin. Methaemoglobin reduces the amount of oxygen that can be carried in the blood. This results in cells throughout the body being deprived of sufficient oxygen to function properly. This condition is called methemoglobinemia.

Infants have relatively low acidity in their stomachs compared to adults. This allows for the growth of certain bacteria that readily convert nitrate to nitrite, which in turn causes methemoglobinemia. In infants, this is commonly called Blue Baby Syndrome, because the lack of oxygen causes the baby's skin to turn a bluish colour, particularly around the eyes and mouth. If untreated, infants can die from this condition.

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How to cite this article: Devakumari, M.S. and Shahbazi, K. (2024). Simultaneous Assessment of the Nitrates and Nitrites in the Ground Water Samples using Optical Spectrophotometry and Validating the Appropriate Wavelength of Measurement. Agricultural Science Digest. 44(2): 244-249. doi: 10.18805/ag.D-5871.

Submitted: 25-08-2023 **Accepted:** 12-12-2023 **Online:** 02-01-2024

In view of this, the World Health Organisation (WHO) has defined the maximum nitrate level of a contaminant in drinking water as 50 mg/L. As per the Indian situation, 45 mg/L is recommended by the Bureau of Indian Standards (BIS) as the permissible level of NO_3^- in drinking water.

In this study ground water samples were collected from the borewells present inside the Karunya Institute campus and analysed for NO_3^- and NO_2^- nitrogen and compared with few groundwater samples from the nearby areas and a sample from borewell of West Bengal state.

MATERIALS AND METHODS

Ultraviolet spectroscopy is a popular method used for determining concentrations of nitrate with the significant advantages of simplicity, rapidity, high accuracy and lack of reagent (Singh *et al*., 2019).

Preparation of the standards

Stock standards

Stock standard solution of 100 ppm nitrate was prepared by dissolving 0.685 g sodium nitrate in 500 ml distilled water. Stock standard solution of 100 ppm nitrite was prepared by dissolving 0.750 g sodium nitrite in 500 ml distilled water.

Working standards

Working standards for nitrates were prepared in the range 10, 20, 30, 40, 50 ppm and for the nitrites in the range of 1, 2, 3, 4, 5 ppm.

Selection of wavelength

The working standards for nitrate and nitrite were read at 220 nm, 240 nm, 300 nm, 350 nm, 370 nm wavelengths in UV/VIS Spectrophotometer (LABMAN Model).

The above wavelengths were selected based on the earlier research done in this field. Bastian *et al*. (1957) and Armstrong (1963) reported that nitrate ion showed the maximum absorption at the wavelengths of 203 and 300 nm. Wang and Wang (2021) proposed a method for direct, reagent-free, ultraviolet spectroscopic method for the simultaneous determination of nitrate (NO_3^-), nitrite (NO_2^-) based on measuring the absorption spectra of samples at 200-300 nm.

According to Jiao *et al*. (2013) the absorption spectrum of composite sample of nitrates and nitrites with the same concentration indicates that the absorbance of sodium nitrite at the 340-400 nm is almost unaffected by sodium nitrate.

Holm *et al*. (2000). proposed an ultraviolet (UV) technique that measures the absorbance of NO_3^- at 220 nm and found that the method was suitable for screening uncontaminated water (low in organic matter).

Standard graphs were plotted automatically in the instrument and the R^2 values were noted. As in scientific studies, the R-square may need to be above 0.9 for a regression model to be considered reliable. Values of R close to 0 imply that there is little to no linear relationship between the data. Values of R close to 1 imply that there is a positive linear relationship between the data.

The wavelength which had R^2 value close to 1 was identified and the samples were analysed in that specific wavelength.

Before reading the ground water samples, spiked water samples with known concentrations of nitrate and nitrite were quantified and crosschecked to confirm the accuracy of wavelength selection and reagents preparation.

The pH and TDS (Total dissolved salts) of the water samples were also measured using hand-held pH and TDS sensors.

Sample details

All samples are from borewells located in the Karunya Campus and from nearby villages and towns at Coimbatore District.

S1- Saibaba Colony (N 11°1′25.1544″, E 76° 56′38.5008″).
S2- Vadavalli (N 11°1′29.9964″, E 76°54′13.6836″).
S3- Ganapathy (N 11°2′21.6024″, E 76°58′43.3488″).
S4- Thondamuthur (N 11°00′21.00″E 76°49′24.59″).
F1- Karunya Campus South Farm Entrance (10°56′24″,76° 44′24″E).
F2- Karunya Campus South Farm Centre well.
F3- Karunya Campus South Farm Agroforest.
F4- Karunya Campus North Farm Open borewell.
F5- Karunya Campus North Farm Periya Thoppu.

RESULTS AND DISCUSSION

The absorbance of the working standard was measured at different wavelengths and the standard graph was obtained as follows (Fig 1 to Fig 5).

At 240 nm R^2 value for both nitrite and nitrate were 0.8954 and 0.9861, higher and reliable than other wavelengths and hence considered as the best wavelength for measuring both nitrite and nitrate of the ground water samples (Fig 2).

The ground water samples were analyzed for nitrate, nitrite, pH and EC (Table 1, 2 and 3). The nitrate and nitrite concentrations were recorded at 240 nm.

All the samples tested have nitrate concentration within the permissible limit of 45 mg/L (BIS standard).

The sample from West Bengal recorded the highest of 10.09 ppm, followed by F1 4.294 ppm. The S1 (Sample from Saibaba Colony groundwater) recorded the lowest of 1.478 ppm. Background nitrate concentration up to 10 mg/l in groundwater could be natural (ECETOC, 1988). So, we can conclude that all the analysed samples were not contaminated by external factors.

Table 1: NO_3^- (240 nm).

Sample	Absorbance	Concentration (ppm)
S1	0.022	1.478
S2	0.043	2.968
S3	0.008	2.540
S4	0.060	4.128
F1	0.063	4.294
F2	0.048	3.319
F3	0.037	2.538
F4	0.051	3.500
F5	0.048	3.319
WB	0.147	10.09

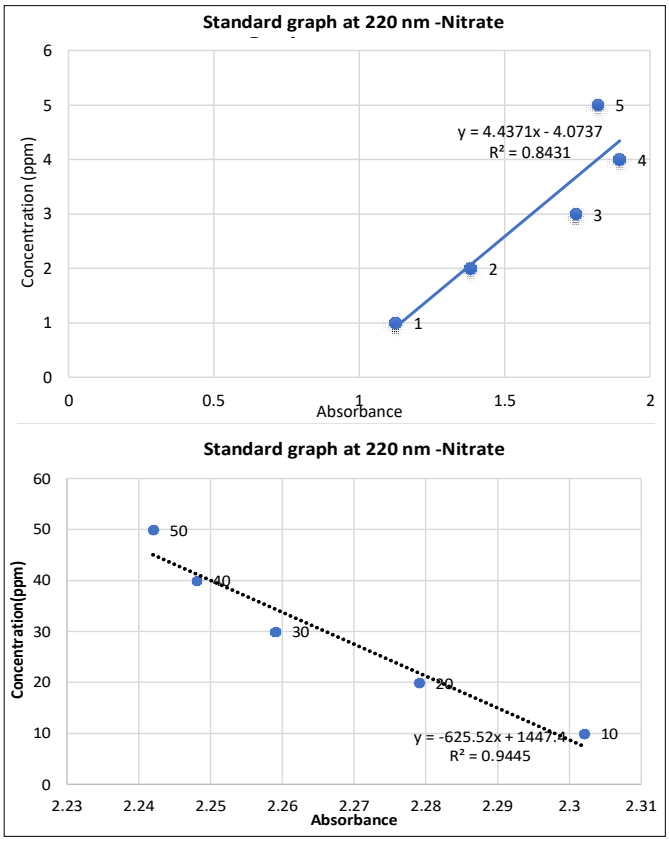


Fig 1: Standard graph and R^2 value at 220 nm for nitrite.

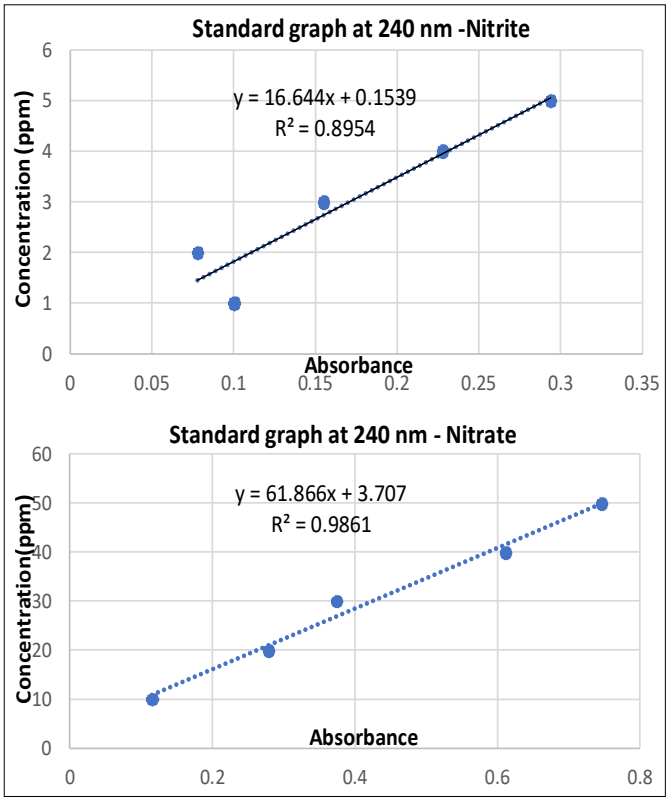


Fig 2: Standard graph and R^2 value at 240 nm for nitrate.

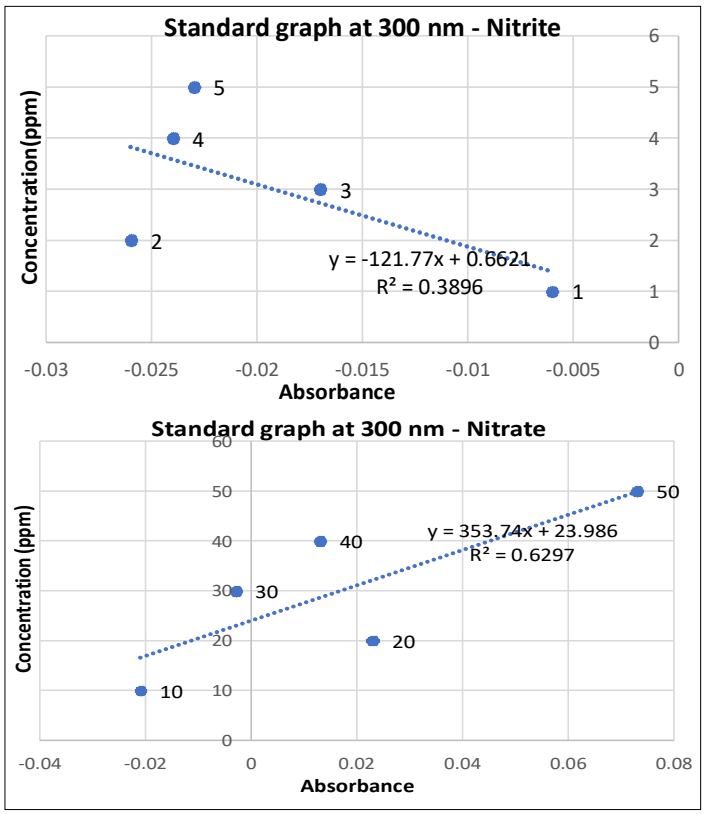


Fig 3: Standard graph and R^2 value at 300 nm for nitrate.

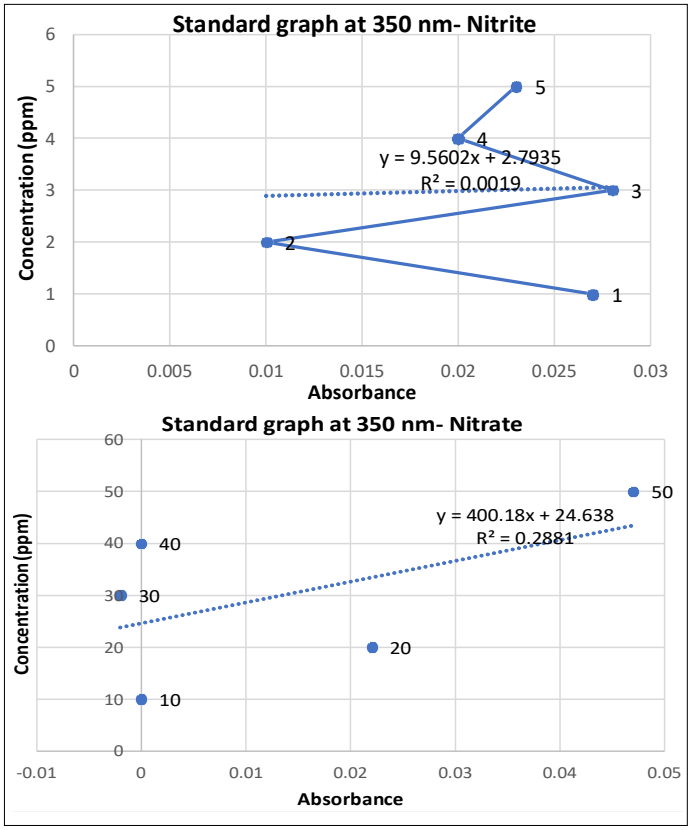


Fig 4: Standard graph and R^2 value at 350 nm for nitrate.

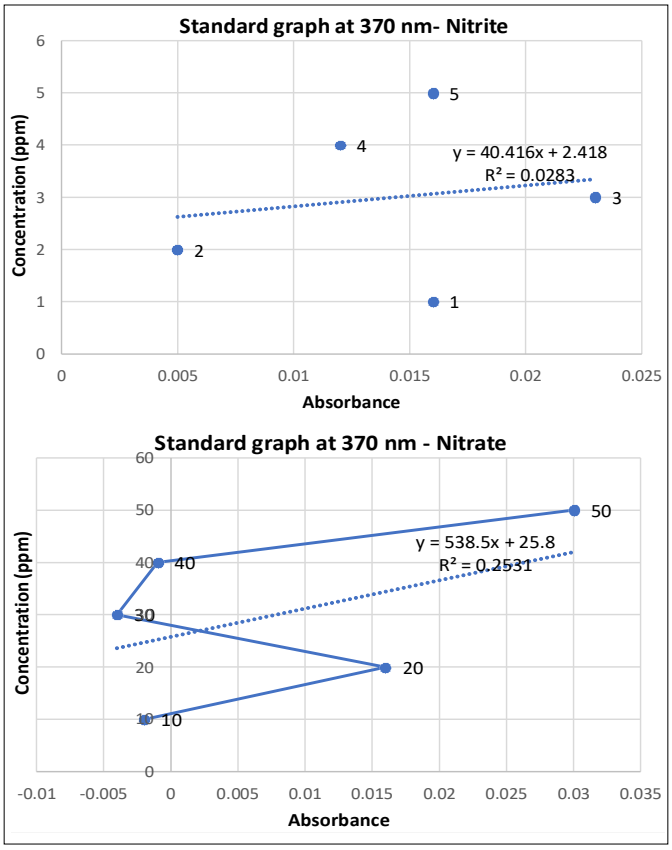


Fig 5: Standard graph and R^2 value at 370 nm for nitrate.

Table 2: NO_2^- (240 nm).

Sample	Absorbance	Concentration (ppm)
S1	0.002	0.383
S2	0.057	0.996
S3	0.007	0.128
S4	0.057	0.999
F1	0.067	1.116
F2	0.049	0.848
F3	0.036	0.635
F4	0.051	0.896
F5	0.052	0.910
WB	0.138	2.407

Table 3: pH and TDS (ppm).

Samples	pH	TDS (ppm)
S1	7.7	670
S2	8.4	673
S3	8.6	1114
S4	8.8	986
F1	8.8	700
F2	8.3	973
F3	8.6	461
F4	8.6	723
F5	8.7	762
WB	9.1	1382

For nitrite concentration, the samples F1 (1.116 ppm) and the WB (West Bengal) sample exceeded the permissible limit of 1 ppm (BIS). Other samples had nitrite within the permissible limit.

Naturally occurring nitrate levels do not exceed 4 to 9 mg/l of nitrate and 0.3 mg/l of nitrite in United States (USEPA, 1987). Hence, except S3, all other samples have nitrite concentration above 0.3 mg/L or ppm it shows that some external contamination but their nitrate values within the permissible limit.

As expected, the pH and TDS of the ground water sample from West Bengal had the highest values of 7.7 and 1382 ppm respectively compared to the samples from Coimbatore, Tamil Nadu.

CONCLUSION

Based on the above study it was found that among the various detection wavelengths analysed, 240 nm was found to be appropriate for measurement of both nitrate and nitrate in the ground water samples using optical spectrophotometric method. This is in accordance with the findings of Chen *et al.* (2021) who reported that the nitrate absorption spectrum lies within the range or 220 to 260 nm.

The groundwater from the borewells located inside the Karunya Campus and the nearby settlements are not subjected to nitrate pollution. But the nitrite content in almost all the samples were found to be slightly higher.

The ground water sample collected from the state of West Bengal is higher in nitrate, nitrite, pH and TDS compared to the samples from Coimbatore indicating external contamination.

Conflict of interest

All authors declare that they have no conflicts of interests.

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