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Indirect Spectrophotometric Determination of Nitrate Ion in Groundwater Using an Organic Reagent

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ABSTRACT: Low river water levels in summer and low rainfall in winter have led to desertification, leading to widespread use of groundwater in many areas of Iraq, especially in the southern and central regions. Groundwater is considered an alternative solution to address desertification, but in reality, many health problems have emerged due to the ions present in groundwater, which cause numerous diseases. Among these ions studied in this research is the nitrate ion (NO_3^-). This spectroscopic method was proposed to determine the concentration of nitrate ions in groundwater. Eriochrome Black T (EBT) colorimetric detector was used as a spectroscopic detector after complexing the detector with silver nitrate to determine the nitrate ion in groundwater. Several parameters and optimal conditions for this reaction were studied, and the assessment of nitrate levels was found to be consistent with the linear equation of the Beer-Lambert law in the range of 0.5–5.0 mg/L at a wavelength of (530) nm. When plotting the calibration curve, good linearity was recorded ($R^2 = 0.9979$). The limits of detection (LOD) and quantification (LOQ) of the method were determined to be 0.269 and 0.816 mg/L, respectively, based on the standard deviation values. The precision measured in terms of relative standard deviation (RSD) over the specified time period at five concentration levels was less than 6.7%. The recovery rate was satisfactory, ranging from 96 to 103, Sandell's sensitivity equal to (0.0263) $\mu g.cm^{-2}$. The rationale for using spectrophotometric methods lies in their simplicity of operation, low cost, and applicability in laboratories with limited resources, as opposed to more advanced techniques such as HPLC or LC-MS. Based on these results, the method was approved for the determination of nitrate ions.

Keywords: Organic reagent Eriochrome Black T (EBT); Groundwater; Silver Nitrate; Spectrophotometer.

1. INTRODUCTION

When studying the molecular formula of the negatively charged nitrate ion (NO_3^-), we notice that it consists of three oxygen atoms bonded to a single nitrogen atom. It occurs naturally in soil as salts, as well as in water, especially in contact with soil, such as groundwater. It is also found in many foods and pharmaceuticals. Nitrates are essential chemical compounds for plants and animals to survive and grow. The human body can obtain nitrate naturally through the nitrogen cycle within the body, which occurs in several stages, including the oxidation of nitrite (NO_2), which in turn produces nitric oxide (NO_3^-), which is produced in the cells lining the blood vessels by a special enzyme called nitric oxide synthase. The NO_2^- is then oxidized to NO_3^- in both the blood and plasma.

Nitrates play an important role in many chemical industries, especially in the agricultural fertilizer industry, which works to increase plant growth and increase production. Among these fertilizers are ammonium nitrate, sodium nitrate, and potassium nitrate. The widespread use of these types of nitrogen fertilizers, coupled with the lack of experience of farmers, has led to a serious problem due to the accumulation of nitrate ions in the soil. Direct contact of this nitrate-rich soil with groundwater or excessive irrigation has led to its high dissolution with many other negative ions. When humans use this type of water, especially groundwater, it has caused many diseases that affect human health, ranging from minor to very serious. Among these diseases are those that affect children, such as "blue baby syndrome," Nitrates cause a serious illness that affects young age groups, especially newborns, as they cause the formation of what is known as methemoglobinemia and increase the risk of spontaneous abortion, in addition to the possibility of congenital malformations if the nitrate value exceeds 10 mg/L [1], especially in pregnant women.

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Also, incurable and serious diseases that affect the digestive system, such as cancer, the emergence of thyroid problems, and respiratory diseases that affect residents near polluted industrial plants that produce this type of nitrogen oxides, as high levels of nitrate concentration led to cancer, cardiovascular diseases, and this is linked to the occurrence of high blood pressure. It is noted that the presence and formation of nitrosamines directly affect the nervous system [2, 3, 4]. On the other hand, nitrates are positively used in many therapeutic drugs, such as various skin treatments such as the skin disease acne.

Chemically, nitrate is classified as an inorganic ion (NO_3^-) and is a part resulting from a series of reactions of nitrogen with oxygen gas, where the final product is the oxidation of nitrite, which is high in both surface and groundwater. The nitrate ion has physical properties that vary from one compound to another according to the nature of the other ion, which ultimately gives salts of these many properties, including taste and smell. In most of its compounds, it is in the form of solid white salts, and it is stable at normal temperatures. All types of its salt compounds have a high solubility in water, which leads to its high presence in groundwater. The nitrate ion can be detected by special laboratory experiments [2].

The high level of nitrate ions in water in general, and particularly in groundwater, depends on the nature of the area through which the water passes. It also depends on the nature of the soil and whether it contains environmental pollutants or industrial waste or pesticides, which contain nitrate ions in their chemical composition, and which are present around well water. According to (WHO) and (IHO) reports No. 416/1990 [5], the normal level of nitrate in water is 50 mg/L. It is 50 mg/L in drinking water. To estimate nitrate ion levels in water, rapid and accurate chemical methods are required, such as spectrophotometric methods. This requires the interaction of the nitrate ion with organic reagents, such as the EBT reagent or the nitrogen coupling reaction [6, 7, 8]. These are well-known methods that are sensitive to low concentrations.

Another common method for estimating nitrate ions is to react them with salicylic acid in the presence of sulfuric acid, making the medium acidic [9]. Another known method for estimating nitrates is to use trivalent vanadium instead of cadmium derivatives, as it reduces nitrite to nitrate [10]. This is a spectroscopic method.

There are a number of dyes, especially organic reagents, for the nitrate ion deposition. UV spectroscopic methods can be used to estimate the nitrate ion from its aqueous solutions at a wavelength of (222) nm, or using colored chemical compounds such as sulfanilic acid and N-(1-naphthyl) ethylenediamine (NED), as well as using visible light in spectroscopic methods. In addition to using spectroscopic and colorimetric methods to estimate nitrates, other methods have been used, including precise chromatographic methods. These methods include ion chromatography using electrochemical or spectroscopic detectors, and gas chromatography after converting nitrate to nitrate oxides and forming volatile compounds that can be easily quantified by chemical or spectroscopic detection. Electrical methods using ion-selective electrodes have also been used for nitrate determination, and these are capable of directly detecting nitrate in solutions. Voltametric methods have also been used to determine nitrate in complex samples based on the potential change at very low concentrations of nitrate ions. It has also been observed that nitrate can be determined using wet analytical chemistry, cadmium (Cd) reduction, and gas atomic absorption spectroscopy. Biosensing methods use enzyme-based devices, such as nitrite reduction, to convert nitrate to quantifiable compounds. Some of these methods were not sensitive and stable to the analyte under study.

The organic reagent Eriochrome Black T (EBT) Figure (1) was used to estimate the nitrate ion after forming a colored complex with the silver ion, which gave a color product that could be estimated using spectroscopic devices.

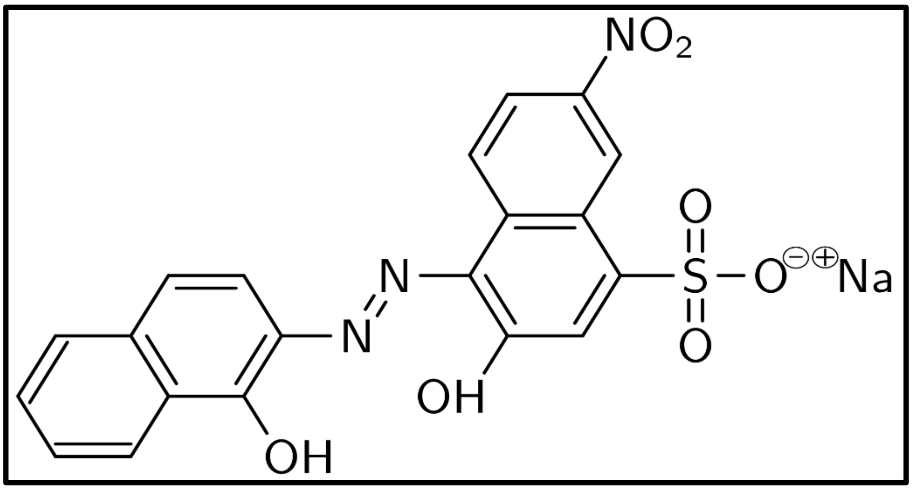


Figure (1): Chemical structure of reagent Eriochrome Black T (EBT).

2.Materials and Methods

2.1 Reagents.

Analytical chemicals were used in this study. Silver nitrate ($AgNO_3$, 99.0%, sourced from China), Eriochrome black T (EBT, sourced from Germany), glacial acetic acid (sourced from India), hydrochloric acid (HCl, 37%, UK), and nitric acid (HNO_3, 69%, India) were obtained from certified suppliers. Deionized water was used to prepare all solutions.

2.2. Instruments and Apparatuses.

A dual-beam UV-Visible spectrophotometer (Biochrom, UK) equipped with 1 cm path length quartz cuvettes was used to record the absorbance values. pH measurements were performed using a calibrated digital pH meter with a glass electrode. Adjustable micropipettes (10–100 µL and 100–1000 µL) and various sizes of filter paper were used during solution preparation and analysis.

2.3. Solution Preparation.

The effect of pH on complex formation was studied using buffer solutions prepared from acetic acid and sodium acetate, with the pH adjusted to range from 3.8 to 6.0. The pH was adjusted and maintained during each measurement to ensure reproducibility.

2.3.1. Formation of Ag-EBT complex.

To prepare the EBT -Ag complex, equimolar solutions (1.0×10^{-3} M) of $AgNO_3$ and EBT were mixed in a 1:1 volume ratio and diluted with deionized water to a final concentration of 5.0×10^{-5} M. This solution was used in subsequent spectrophotometric investigations.

2.4. Effect of nitrate on theEBT- Ag complex.

At this stage, the interaction of nitrate with EBT -Ag was studied, where the concentration of nitrate was changed while maintaining the concentration in the EBT- Ag complex and vice versa, which led to the formation of the ternary complex (EBT- Ag- NO_3) and a change in color from blue-violet to dark red in an acidic medium.

2.5. Dye selection.

Several dyes were examined to determine their ability to form stable silver complexes suitable for spectroscopic analysis. The method conforms to the Beer- Lambert’s law. Among these, Eriochrome black T (EBT) showed the most reliable and reproducible results and was therefore chosen as the complex ligand for this study.

2.6. Reaction Time Optimization.

To determine the optimal time for maximum complex formation, the stability of the Ag-EBT complex was monitored over a period ranging from 10 minutes to 48 hours [11]. The absorbance was recorded at defined intervals to assess the stability and reaction kinetics of the complex.

2.7. Effect of pH on Complex Formation

The influence of pH on complex formation was investigated using buffer solutions prepared from acetic acid and silver acetate, adjusting the pH in the range of 3.8 to 6.0. The pH was adjusted and maintained during each measurement to ensure reproducibility.

2.8. Stoichiometry of the Ag-EBT-Nitrate Complex

The stoichiometry of the complex was determined using two classical approaches: the method of continuous variation (Job's method) and the molar ratio method. Equimolar concentrations (5.0×10^{-5} M) of $AgNO_3$ and EBT were mixed in varying volume ratios (1:9 to 9:1) to maintain a constant total volume of 10 mL. These experiments were conducted under optimized acidic conditions to determine the stoichiometric ratio of nitrate to the Ag-EBT complex.

2.9. Method Validation.

To evaluate the reliability of the spectrophotometric method for nitrate quantification in groundwater, validation was performed according to standard analytical parameters, including linearity, limit of detection (LOD), limit of quantification (LOQ), precision, [12,13] and accuracy.

2.9.1. Limit of Detection and Limit of Quantification

The LOD and LOQ were calculated using the standard formulas:

$$LOD = 3.3 \times (\sigma/S)$$

$$LOQ = 10 \times (\sigma/S)$$

Where: σ = standard deviation of the y-intercept of the calibration curve, S = slope of the calibration curve.

LOD is the lowest concentration of nitrate that can be reliably detected, while LOQ is the lowest concentration that can be measured with acceptable accuracy.

2.9.2. Precision and Accuracy.

Precision was assessed by analyzing five replicates of a known nitrate concentration under the same experimental conditions. The results were expressed as relative standard deviation (RSD%).

Accuracy was evaluated by performing recovery experiments. Known concentrations of standard nitrate solutions (0.5, 1.0, 1.5, 2.0, and 2.5 mg/L) were spiked into groundwater samples. The recovery percentage was calculated using the following formula:

$$\%\text{Recovery} = \left(\frac{\text{Measured concentration}}{\text{Added concentration}}\right) \times 100$$

2.10. Interference study.

Soil contains different types of salts that are transferred to groundwater. These ions are numerous and varied, such as chloride, fluoride, sulfate, and sodium. Their concentrations vary depending on the nature and type of soil. High concentrations of these ions, approximately ten times the main concentration, were taken to observe their effect on the estimation of the nitrate ion.

2.11. Calculating the nitrate ion concentration in a groundwater sample.

A sample of groundwater was taken after undergoing a dilution process using an analytical method called " spike " to verify the accuracy of the method used by determining the recovery rate in the sample and ensuring no interference with other ions. Two samples were prepared, one part being analyzed directly, and the other to which a known amount of nitrate was added.

3. RESULTS AND DISCUSSION

3.1. Optimization of Parameters

3.1.1. Selection of dye.

To obtain stable complexes with silver ions for spectroscopic measurements, several reagents were tested and studied, such as Solochrome dark blue, xylenol orange, Solochrome black, and Eriochrome black T (EBT). The latter reagent was found to produce more stable, reliable, and reproducible results. This reagent also has the ability to react with silver cations to form Ag-EBT complexes [14].

3.1.2. Determine the wavelength of the resulting color complex.

Determining the wavelength of the resulting Ag-EBT-$NO3^-$ complex requires the use of a dual-band spectrophotometer. By observing the absorbance values, we establish the wavelength, which was (530) nm, which differs from the wavelengths of both the EBT detector and the detector with the silver ion, Figure (2), which gave a red shift [15, 16].

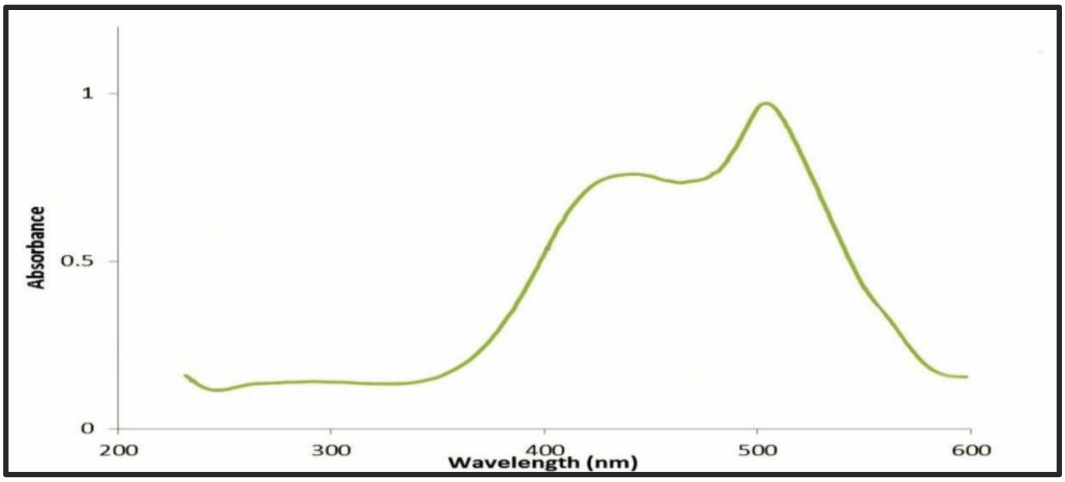
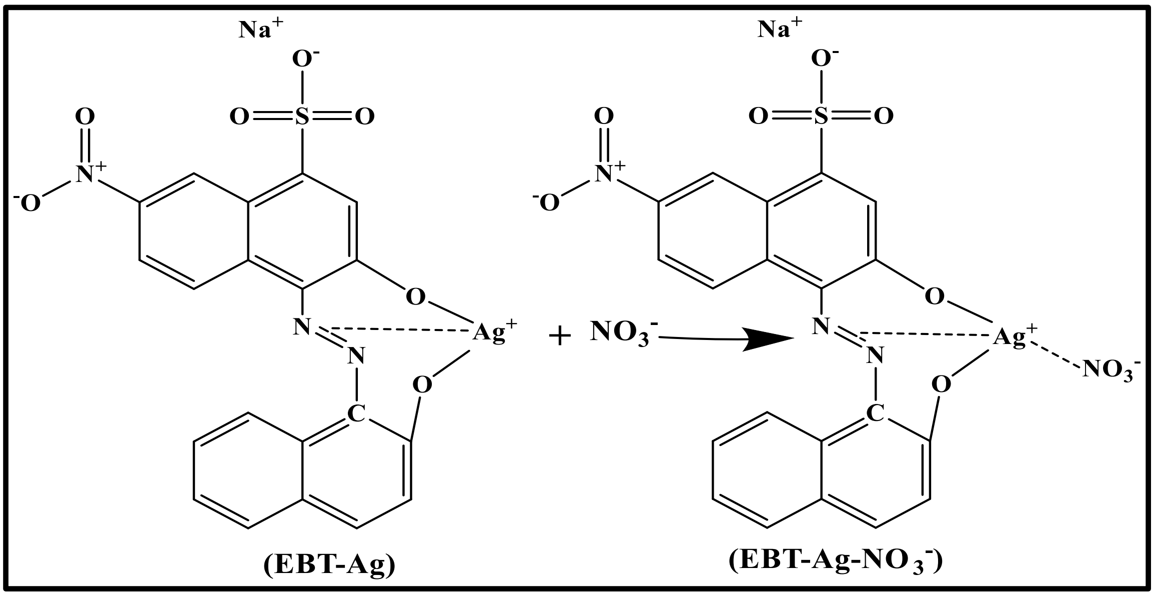


Figure (2): UV-VIS spectrum of (EBT-Ag-$NO3^-$) complex in water.

3.1.3. The reaction step of the nitrate ion with the Ag-EBT complex product.

Increasing the nitrate ion concentration increases the color intensity when the nitrate ion reacts with the EBT-Ag complex prepared in the previous step, resulting in a dark red color. This supports the interaction between the silver complex and the nitrate ion. Adding more nitrate ions increases the color stability of the complex. This is due to the color change and increased stability of the complex resulting from the structural rearrangement of the hydroxyl and sulfonate groups after the nitrate ion is added to the EBT-Ag complex and the formation of the ligand.

The reaction mechanism can be suggested in the diagram shown in Scheme (1).



Scheme (1) **Suggested mechanism for product (NO3^{-}) with (EBT-Ag).**

3.1.4. Improving the reaction time.

Reaction time positively affects the product produced when nitrate ions are determined and the EBT-Ag-NO_3^- complex is formed. The figure below shows absorbance values over different time intervals. The highest absorbance was recorded after 15 hours, followed by a steady state with increasing stability of the complex after 24 hours.

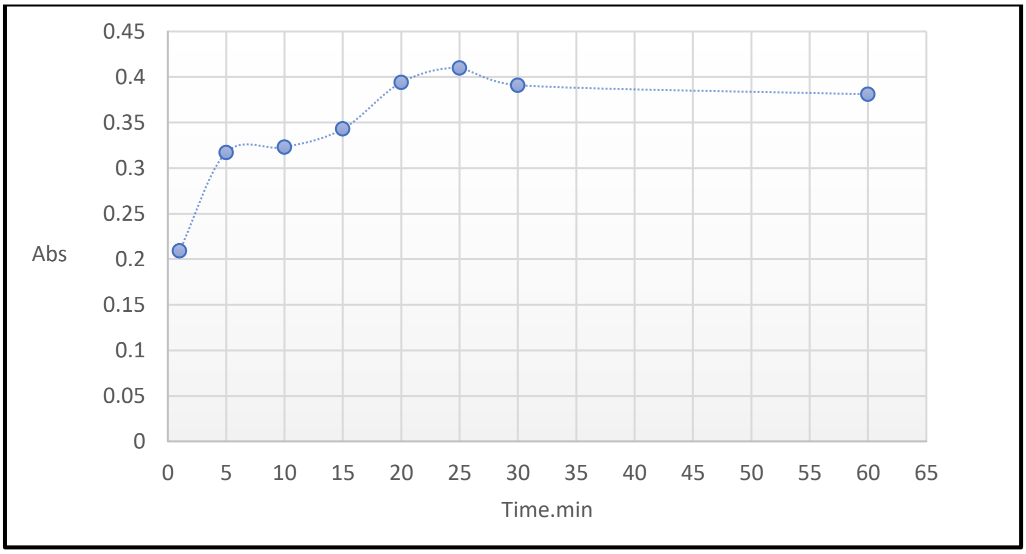


Figure (3): **The effect of time on the stability of the colored complex**

3.1.5. Improvement of pH.

In order to obtain a suitable acidic medium for the stability of the resulting complex with the nitrate ion and the completion of the reaction process, it is necessary to study several acids ranging from 4 to 6. From observing the absorbance values in Figure (4), we can see the extent of the effect of pH. The highest absorbance value was recorded at a pH of 5.

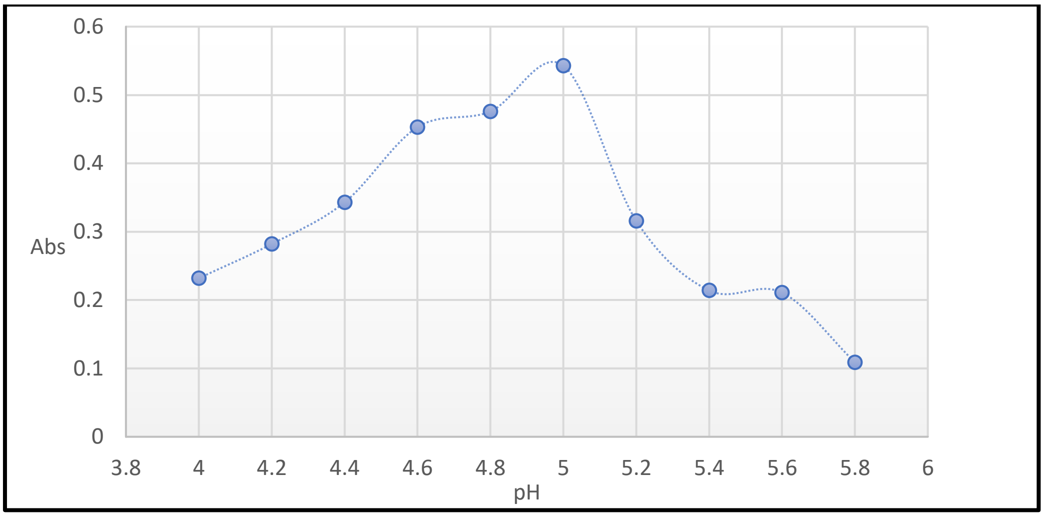


Figure (4): pH value for nitrate ion determination.

3.1.6. Stoichiometric Analysis Using Molar Ratio and Continuous Variation (Job's) Methods

To determine the stoichiometric composition of the resulting metal-ligand complex, both the molar ratio method and Job's method (continuous variation) were employed. These methods were applied to investigate the binding interaction between the nitrate ion (NO_3^-) and the silver–Eriochrome Black T (Ag–EBT) complex. As shown in Figures 5 and 6, the maximum absorbance was observed at a 1:1 molar ratio, indicating the formation of a stable 1:1 stoichiometric complex between Ag^+ and EBT in the presence of nitrate.

The observed increase in color intensity (deep red) with increasing nitrate concentration suggests the formation of a ternary complex (EBT- Ag- NO_3), possibly through an additional coordination interaction. It is proposed that the oxygen atom in the EBT ligand donates a lone pair of electrons to the vacant orbital of the Ag^+ ion, forming a coordinate (dative) bond. This interaction may enhance the electron density around the central silver ion and stabilize the overall complex structure.

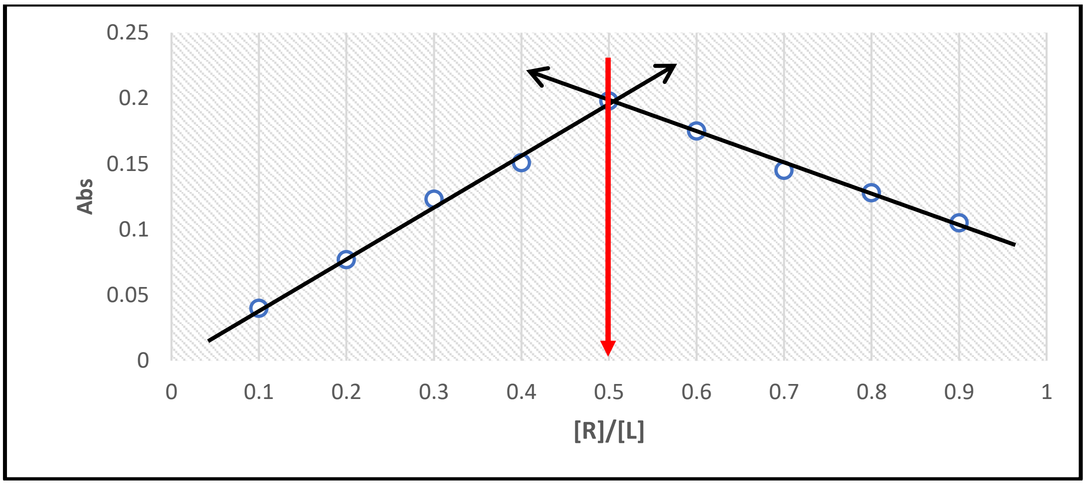


Figure (5): Continuous variation plot (Job's method) for the Ag–EBT complex.

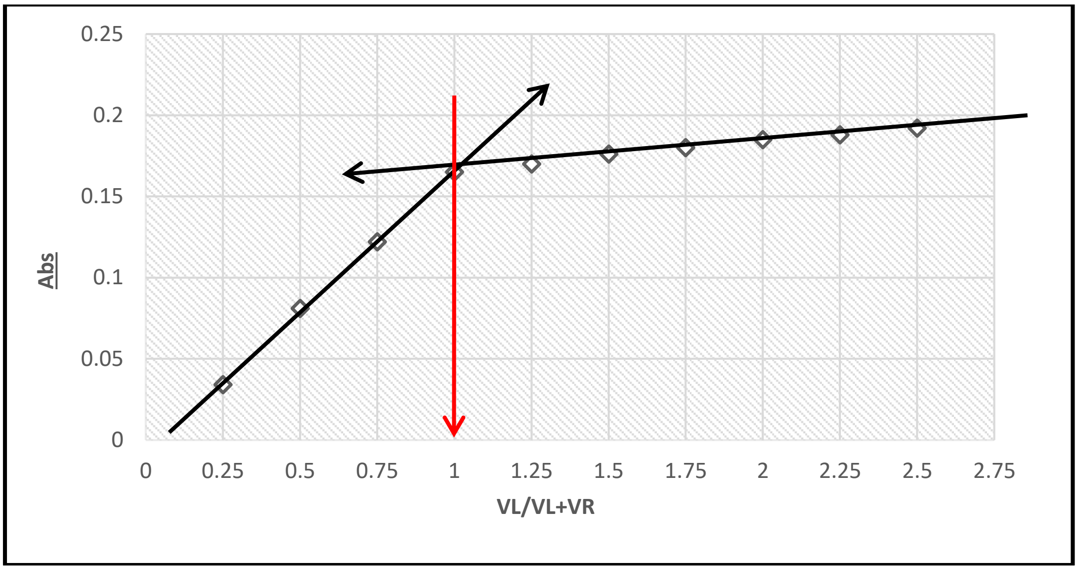


Figure (6): Molar ratio plot for the interaction between silver ions and EBT ligand.

3.1.7. Study of negative interference ions in groundwater

To evaluate the selectivity of the proposed spectrophotometric method in practical applications, the effect of common anions in groundwater, namely chloride (Cl^-), fluoride (F^-), sulfate (SO_4^{2-}), and carbonate (CO_3^{2-}), was evaluated. A constant nitrate concentration of 1.5 mg/L was analyzed in the presence of high and varying concentrations of interfering ions.

The recovery percentage was calculated using the following equation:

$$\text{Recovery (\%)} = \left(\frac{\text{Measured concentration}}{\text{True concentration}}\right) \times 100$$

The absorbance values obtained under these conditions showed negligible interference from the added anions. Recovery percentages remained within acceptable limits (typically 96%–104%), confirming that the method maintains its accuracy and selectivity even in the presence of high concentrations of common interfering species. These findings are in agreement with previously published spectrophotometric studies [17, 18], supporting the method's applicability for the accurate determination of nitrate in complex environmental matrices.

Table (1): Effect of interferences on the determination of Nitrate ($NO3^{-}$ $^-$).

Interference	Abs.
Cl^{-1}	0
F^{-1}	0
SO_4^{-2}	0
CO_3^{-2}	0

3.2. Determination of Nitrate.

3.2.1. Calibration curve.

A calibration curve was plot for the resulting-colored complex between absorbance and concentration to estimate nitrate in the groundwater sample Figure (7) at a concentration between (0.5-5) mg/L, after setting the optimal conditions studied in the previous steps, and at a wavelength of (530) nm. Ten concentrations were prepared against a blank solution for each concentration, where the equation of the straight line was as follows: $y = 0.147X + 0.0379$. Sandell's sensitivity was calculated using a specific absorption coefficient of (0.0263) $\mu g.cm^{-2}$ and a good linearity coefficient $R^2 = 0.9979$. The high correlation coefficient confirms the suitability of the calibration model for determining quantitative nitrate.

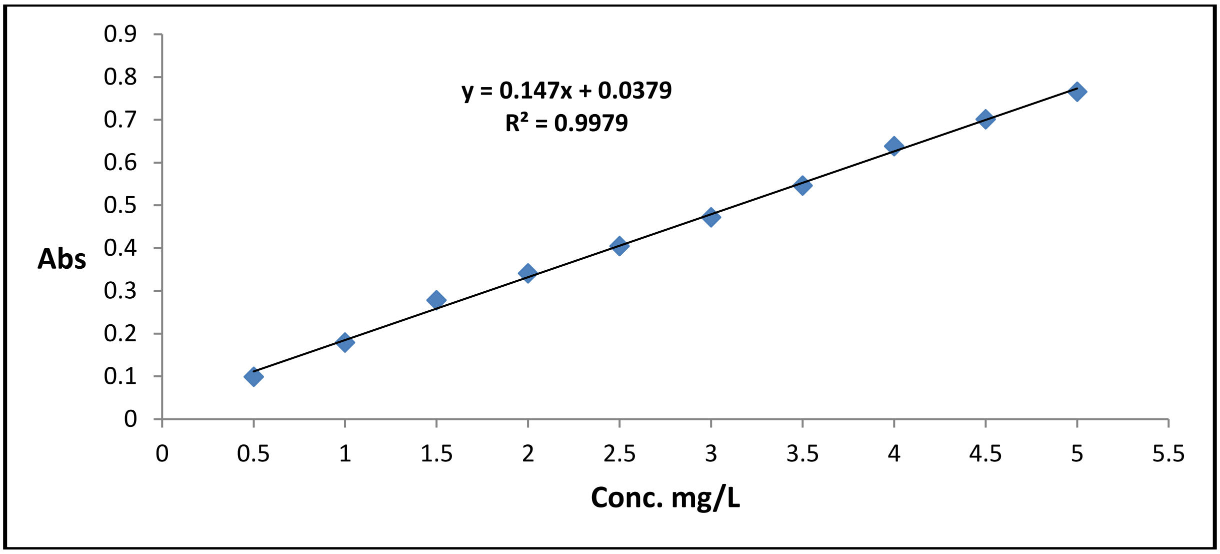


Figure (7): **Calibration curve for nitrate determination at 530 nm**

3.2.2. Method Accuracy Study.

The accuracy of the proposed spectrophotometric method for the determination of nitrate ions in groundwater was evaluated by analyzing five different concentration levels: 0.5, 1.0, 1.5, 2.0, and 2.5 mg/L. The study was conducted over a period of 48 hours to assess both intraday and interday precision. Each concentration was measured in triplicate under identical conditions to ensure reproducibility.

Accuracy was expressed in terms of the relative standard deviation (RSD%), calculated for each concentration level. As shown in Table 2, all RSD values were below 6.7%. The low RSD values (<6.7%) confirm the method's precision and its suitability for nitrate analysis in groundwater

Table (2): **Reproducibility and intraday / interday precision data for nitrate determination using the developed spectrophotometric method.**

Levels of NO_3^- in mg/L	Intraday (%RSD)	Interday (%RSD)
0.5	4.91	4.51
1	5.78	6.05
1.5	6.94	6.98
2	7.93	8.01
2.5	7.75	8.18
Range	Intraday %RSD: 4.91% – 7.93%	Interday %RSD: 4.51% – 8.18%

3.3. Calculating the recovery value using real samples

To calculate the recovery value, five solutions of different concentrations were prepared and compared to the standard solutions prepared in the previous steps using the same preparation method. Table (3) below shows the recovery rates for each concentration. Reading the results of the table, we note that the sample recovery rate in the groundwater under study ranged between (96 and 103), demonstrating the effectiveness of the proposed method for estimating nitrate ions.

Table (3): **Analytical results of groundwater sample analysis via spiking (n= 5).**

Sample type	Nitrate standard spiked (mg/L)	This method, NO_3^- found (mg/L) in sample waters after dilution	Nitrate found (spiked + sample water)	Recovery %
Sample-1	0.25	5	5.24	96
Sample-2	0.5	5	5.51	102
Sample-3	0.75	5	5.74	98.67
Sample-4	1.00	5	6.03	103
Sample-5	1.25	5	6.21	96.8

3.4. Calculation of linear range, limit of detection (LOD), limit of quantification (LOQ) and Sandell's sensitivity.

Calculation of Linear Range, Limit of Detection (LOD), Limit of Quantification (LOQ), and Sandell's Sensitivity

The analytical performance of the developed spectrophotometric method was evaluated by determining the linearity, limit of detection (LOD), limit of quantification (LOQ), and Sandell sensitivity for the determination of nitrate ions in groundwater. A calibration curve was plotted over a concentration range of 0.5–5.0 mg/L, showing good linearity with a correlation coefficient (R^2) of 0.9979 and a standard deviation of 0.012 mg/L. The limits of detection and LOQ were calculated using the following standard formulas:

$$\mathrm{LOD} = \frac{3.3 \times \sigma}{S}, \quad \mathrm{LOQ} = \frac{10 \times \sigma}{S}$$

where σ is the standard deviation of the y-intercept, and S is the slope of the calibration curve. The calculated LOD and LOQ values were (0.269) mg/Land (0.816) mg/L, respectively.

Sandell's sensitivity was determined to assess the method's capability to detect small amounts of nitrate per unit area, yielding a value of [0.0263] µg/cm². These results indicate that the method provides reliable sensitivity and a wide linear response range for nitrate analysis in groundwater samples.

$$\text{Sandell's Sensitivity(SS)} = \frac{Concentration(\mu g/mL) \times 0.001}{Absorbance}$$

When compared to previously reported spectrophotometric methods, the current approach demonstrated comparable or superior sensitivity and detection limits, as shown in Table 4. Therefore, the proposed method can be considered a simple, cost-effective, and efficient tool for the routine determination of nitrate in environmental water samples.

Table (4): **Analytical parameter for complex (EBT-Ag-NO3⁻).**

parameter Value	Value
Wavelength (λ_{max}) nm	530
Beer's law limit (mg/L)	0.5-5
Molar absorptivity (L.mol-^{1}.cm-^{1})	2.37
Sandell's sensitivity(µg.cm^{-2}) [19]	0.0263
Detection limit (mg/L) [20]	0.269
Quantitation limit (mg/L) [21]	0.816
Linearity coefficient(R^2)	0.9979
Slope (b)	0.147
Intercept (a)	0.0379

4.CONCLUSION.

The importance of studying negative ions in groundwater lies in their excessive use as drinking water and their potential to cause many serious diseases. The easiest way to estimate these ions is through spectroscopic methods, which form colored compounds. Their concentrations can be determined based on the Beer-Lambert law, within the range of 0.5-5.0 mg/L. A colored complex is formed using the EBT reagent. The results were for both the detection limit of 0.269 mg/L and the quantification limit of 0.816 mg/L. Recovery rates were also calculated in groundwater samples.

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