

Techniques and Technologies for Monitoring Nitrate in Potable Water-A Review

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Abstract— Real time water quality detection is the key for both National as well as International Safety and Health parameter as it can basically decrease the fatality and in addition, expenses on cure those issues. Consumers expect suppliers to provide clean potable water which meets wellness standards as well as the sensuous requirements such as turbidity, color, taste. Nitrate is one of the critical parameters for the evaluation of water quality. Excessive contamination of nitrates may cause harm not only to human being but also aqua life. Nitrate in water affect the human cells carrying oxygen to the blood. It can cause methemoglobinemia or blue baby syndrome and that's why detection of nitrate is very crucial. The safety limit of nitrate detection is 10mg/l nitrate nitrogen. A variety of strategies have been proposed for detecting and monitoring nitrate in recent past (e.g. UV spectroscopy, electrochemical methodologies, and steam distillation reducing NH_3 , colorimetric pursuing reduction by Cd, hydrazine and ion chromatography). In this review, work shows electrochemical methodologies and spectroscopy methodologies for detection of nitrate. This paper basically investigates commercially available and modern research methods and gadgets worthy for detection of drinking water quality in real time and recommends advance improvements around there.

Key words: Nitrate, Electrochemical Detection, Spectroscopy Detection

I. INTRODUCTION

In 1958, the first WHO document was published as International Standards for Drinking-water. In 1984–1985, the first edition of the WHO Guidelines was published for Drinking-water Quality (GDWQ) in three volumes and they are Health criteria, Recommendations and other supporting information, control of community supplies and Surveillance^[1]. Europe WFD consists of guidelines defining categories of water quality, require component and parameter. Also, US EPA and Turkish regulation define the water quality guidelines^[2].

The earth's atmosphere contains 70 percent nitrogen. Nitrogen is present in the environment in many forms. Nitrogen changes its form and becomes a compound when nitrogen interacts with another element in the environment. Nitrates (NO_3) and Nitrites (NO_2), these are the two nitrogen compounds found in nature. Nitrates occur naturally in drinking water. Human activities such as the improper disposal of human and animal wastes and the overuse of chemical fertilizers cause high levels of nitrates in the water^[3].

High nitrate levels in water can cause methemoglobinemia or blue baby syndrome, a condition found especially in infants under six months. The stomach acid of an infant is not as strong as in older children and

adults^[4]. This causes an increase in bacteria that can readily convert nitrate to nitrite (NO_2). Do not let infants drink water that exceeds 10 mg/l $\text{NO}_3\text{-N}$ ^[5].

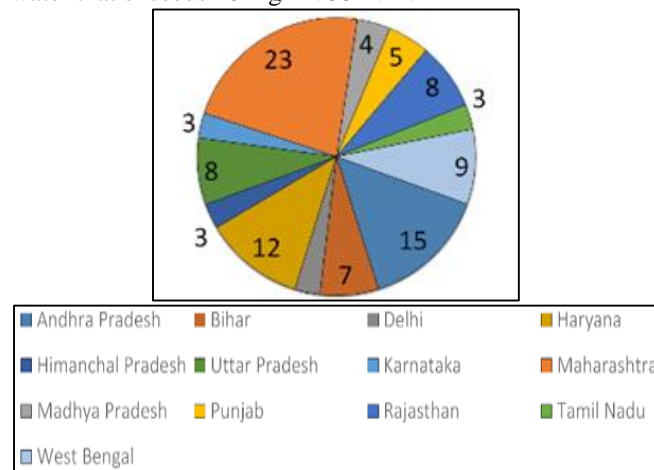


Fig. 1: State wise nitrate contamination

In India, Rajasthan, and some areas of Uttar Pradesh and Andhra Pradesh are affected with the problem of nitrate in underground water^[6-8]. This review is dedicated to the detection of important water quality parameters which poses health risks to humans in the Indian subcontinent. With the view of Indian perspective, nitrate is polluting the sources of drinking water^[9-13]. The nitrate detection is important because it can prevent its ill effects on human health. This is the motivation for the present work which is focused on the prediction of nitrate concentration in an unknown sample of water.

The purpose of this review work has been to provide a concise appraisal of the relative merits of each approach and provide a representative survey of the scientific literature covering the detection of these important analytes^[14]. A number of excellent reviews have been compiled over recent years, but each has narrowed their remit to specific matrices or techniques^[15]. Through tabulating the various analytical parameters (detection limit, range, matrix, etc.) of each system and exposing their advantages and limitations, it was hoped that the specialism divides inherent within such a diverse subject such could be bridged.

II. DETECTION METHODOLOGIES

Many methods are used for detection of Nitrate in water (e.g. UV spectroscopy, electrochemical methodologies, ion chromatography, steam distillation following reduction to NH_3 , colorimetric following reduction by Cd, Cd-Cu). But some procedures are difficult to carry or use (e.g. steam distillation after reduction to NH_3) others involve a substantial investment (e.g. ion chromatography) or pose health and environment hazards (e.g. those using hydrazine or heavy metals as reductants)^[16].

Numerous techniques have been produced for low-level detection and to overcome potential impedances that would be experienced inside the different solution. Electrochemical methods [17] consist of impedimetric electrodes, voltammetric method [18, 19], and potentiometric method [20, 22]. In Electrochemical methods, nitrate ions are converted into potential difference and current signal. These techniques are effectively performed, expending no or couple of reagents and requiring no perplexing or tedious pretreatment; also, the monitoring equipment is easily and inexpensive designed.

Spectroscopic methods consist of absorption spectrometry, Raman spectroscopy, and fluorescence spectrometry. Spectroscopic methods can reach a very low detection limit with great exactness. In spectroscopic methods, nitrate ions are converted into optical signals [23]. These methods are combined with advancement and division techniques, for example, liquid extraction, chromatography and capillary electrophoresis, the detection limit can be further decreased [24,25].

Techniques	interferences	Timing for detection	Application range
Spectroscopic Method	Min interferences	Less time-consuming	Up to 11 mgN/L
Reduction calorimetric method	Max interferences	Time consuming	0.01-1.0 mgN/L
Potentiometric method	Max interferences	Time consuming	0.14 mgN/L
Ion selective electrode	Max interferences	Time consuming	3ug/L of N-NO ₃
Voltammetric electrode	Max interferences	Time consuming	0.1 mg/L

Table 1: Comparisons of different method

A. Electrochemical Methods

Electrochemical detection methods have been examined for real-time monitoring and in situ quantitative analysis of ecological parameters. Electrochemical detection methods are divided into three categories, Ion-selective electrodes, voltammetric electrodes, potentiometric electrodes [23]. These three methods are used to detect the nitrate ions in potable water.

1) Ion Selective Electrodes

The development of electrodes responding to ions has produced a number which has found application in water analysis (including on-line analysis) [35, 36]. However, only a limited number of electrodes have proved suitable for widespread use in routine water analysis.

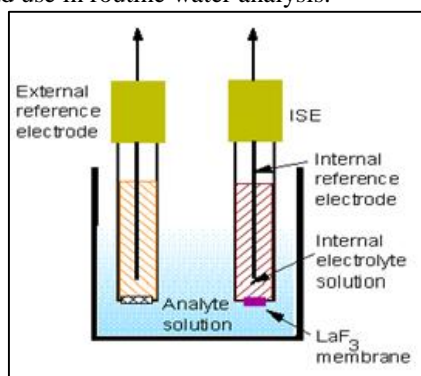


Fig. 2: Experimental Set-Up of Ion Selective Electrode

- Principle: Electrochemical half-cells also viewed as ion selective electrodes, consisting of a suitable reference electrode/reference solution system, separated from the sample by a membrane. The ions to which an electrode responds can determine the nature of the membrane. An electric potential is produced across the membrane after the electrode is placed in a solution, the magnitude of which is reliant upon the thermodynamic action of the ion to which the electrode responds. Estimation of this potential is refined by completing the electrochemical cell by means of a suitable reference electrode and connecting the electrodes to a high impedance millivoltmeter.

2) Voltammetric Electrodes

Many analytical techniques have their basis in electrochemical processes. Among these the three important used techniques are anodic stripping voltammetry (ASV), Polarography and Potentiometric stripping analysis (PSA) [24-27]. Polarography and stripping voltammetry have many variants.

- Amperometry: This technique is very extensively used to determine dissolved oxygen and determination of disinfecting agents [28-29].
- Principle - A couple of electrodes is put in the sample and after that, a constant voltage applied to them so that the determinand undergoes an electrochemical reaction at one of the electrodes. The voltage is chosen appropriately for the determinand so that the rate of reaction is limited by the diffusion of the determinand to the electrode. Under these conditions, the rate of reaction and, therefore, the current is straightforwardly relative to the grouping of the determinand.

The early 1900s, voltammetric methods have been used to detect nitrate, at that time glassy carbon electrodes were used that continuously monitor without any additional reagent consumption [30, 31]. When a potential is applied to the working electrode, voltammetric electrode provides a current signal to represent the rate of reactions on the probe surface. The potential is calculated from working electrode to avoid oxygen interference and acquire a strong electrode reaction to nitrite oxidation, including affectability and reaction time[32]. This whole system consists of three electrodes, reference electrodes, counter electrodes and working electrodes. The conversion of the working probe current to voltage requires a current-to-voltage converter and voltage amplifiers are used to amplify it to a suitable range for the analog-to-digital converter (ADC) to sample. Local instruments or remote monitors are used for display, determine, transmitted and saved the results.

3) Potentiometric Electrodes

Nitrate ions associated with organic membranes is detected by the potentiometric electrode that contains a suitable ion-exchanger or ionophore for the nitrate ion and conveys a specifically charged species from the specimen to the electrode area. A potential difference with a charged species is produced between the indicator electrodes and reference electrodes, without current flowing through the electrodes, and without any species are produced.

In recent years, potentiometric electrodes have improved by achieving very low detection limits. Signal selectivity to the analyte of interest, low detection limit and applicability to colored and turbid samples, the ability to

probe a large range of species that are not redox-active in aqueous environments, these are the main three advantages of Potentiometric Electrodes^[33]. The required instrumentation is simple to utilize, additionally easy to manufacture, inexpensive and portable. For potentiometric detection of nitrite, numerous scientists have tried to devise ion-selective electrodes, regularly secured with membranes incorporated with suitable ionophores. Obviously, neither one of the options is especially ideal. Potentiometric methods consist of several disadvantages, such as interference from different species, when the electrode approaches micrometer dimensions then unfeasible miniaturization is produced due to unstable potential, low electrode response, changes of reference potential and potential floats with time^[34].

B. Spectroscopic Methods

Spectroscopic methods are used for nitrate detection. These methods operate generally by measuring the absorption intensity of a specific wavelength influenced by nitrate. The spectroscopic method is coordinated with other enrichment and separation methods, like chromatography, capillary electrophoresis, to reduce the detection limit and to enhance detection accuracy^[37]. All spectroscopic techniques have some common features. Before we consider individual examples in greater detail, let's take a flash to think about a number of these similarities. We can divide spectroscopic analysis into 2 broad categories of techniques. In one category of techniques there's a transfer of energy between the photon and the sample.

Sr. No	Types of Energy Transfer	Region of Electromagnetic Spectrum	Spectroscopic Technique
1	absorbance	y-ray	Mossbauer spectroscopy
		UV/Vis	UV/Vis spectroscopy Atomic absorption spectroscopy
		X-ray	X-ray absorption spectroscopy
		IR	Infrared spectroscopy Raman spectroscopy
		Microwave	Microwave spectroscopy
		Radio wave	Electron spin resonance spectroscopy Nuclear magnetic resonance spectroscopy
2	Emission(thermal excitation)	UV/Vis	Atomic emission spectroscopy
3	photoluminescence	X-ray	X-ray fluorescence
		UV/Vis	Fluorescence spectroscopy Atomic fluorescence spectroscopy

Table 2: example of spectroscopic techniques involving an exchange of energy between a photon and the sample

In absorption spectroscopy, a photon is absorbed by an atom. Which undergoes a transition from a lower-energy state to a higher energy state. The type of transition depends on the Photon's energy. In second category of techniques, the electromagnetic radiation undergoes a change in phase angle, polarization, amplitude or direction of propagation as a result of its scattering, diffraction, refraction, reflection, or dispersion by the sample. Several representative spectroscopic techniques are listed in Table 2.2

2) *Raman Spectroscopy:*

This spectroscopic method is used for measurement of nitrate concentration in potable water by detecting the scattered light. A molecule excites from its ground state to a virtual energy state when a photon striking and associated with the electron bonds and cloud of that molecule. A photon is emitted from the molecule to a different vibrational state or rotational state. Measuring the intensity of in elastically scattered light is used for measurement of the sample.

Raman scattering is very weak, making it hard to partitioned powerless in elastically scattered light from extraordinary Rayleigh-scattered light. In this way, surface-enhanced Raman spectroscopy (SERS) was produced^[39, 40]. Moreover, when the excitation wavelength coordinates the electronic move of the molecule, the molecule encounters resonance Raman scattering (RRS), in which the vibrational modes connected with the energized electronic state are significantly upgraded. From this search, Raman spectroscopy has been used to detect nitrate^[41].

3) *Absorption Spectroscopy:*

In this method, measurement of the absorption of a particular substance is important for evaluating the amount of a particular substance, as energy is absorbed by the particular substance from radiation of a specific wavelength. The detection of the intensity of the radiation that passes through the substance with a specific wavelength is used to measure the absorption spectrum.

a) *Ultraviolet Spectroscopy:*

In addition, an absorption photometric method for nitrate detection is also called as ultraviolet spectroscopy method. Different ions have different absorption peaks at a

Sr. No.	Region of Electromagnetic Spectrum	Types of interaction	Spectroscopic techniques
1	X-ray	diffraction	X-ray diffraction
2	UV/Vis	refraction	refractometer
		scattering	Nephelometry turbidimetry
		dispersion	Optical rotary dispersion

Table 3: Example of spectroscopic techniques that do not involve an exchange of energy between a photon and the sample

1) *Fluorescence Spectroscopy*

In 1972, Fluorescence spectrometry was developed by Kinzo Nagasawa and Gen-Ichiro Oshima for benzidine detection^[38]. In the Fluorescence spectrometry, detection of nitrate is carried out by transmitting the light through a sample that absorbed light or other energy can be detected. Fluorescence spectrometry detection can be split into two categories: turn-off type and turn-on type.

corresponding wavelength. Hence, measurement of the absorbance at a certain wavelength is used to detect a specific ion. Other wavelengths are expected to recognize or identify interfering ions.

Ultraviolet spectroscopy method has been developed for nitrate detection. In this method, reagents yet still achieve nan molar detection limits, they require <100 ml of samples and does not require pretreatment of samples. UV spectroscopy is chosen as the analytical technique in the present work to produce the spectroscopic information but the spectroscopic technique has drawback that some species can cause interference problem [42]. These interferences can cause a considerable effect on the absorbance value of the determinant of interest. It may cause to increase or decrease the absorbance value of nitrate. Nitrate is detected in 220nm and 205 nm wavelength range [43]. Ultraviolet Spectrophotometry is used to detect arsenic, fluoride, and nitrate, arsenic and fluoride the peak of detection is observed in the visible spectrum after treating it with some reagent which results in color formation. But it was better to go for nitrate because no reagent addition was required in its detection in the UV spectrum. There is always interference hindrance in the detection of analyte as far as spectroscopy technique is concerned. There is a much need to find out the ions which interfere with nitrate in the UV range. Since the absorbance of the nitrate has to be captured it is also important to find out the concentration of nitrate up to which it obeys Beer-Lambert's law.

– Beer-Lambert's law states that:

“The optical absorbance of an analyte in a transparent solvent varies linearly with both the sample cell path length and the analyte concentration”

For measurements, the sample is held in a cuvette. The cuvette is transparent and an optically flat container.

Absorbance (A) is determine from the ratio of transmitted intensity of light energy through the sample (I) to intensity of incident light on the sample (I₀) at a given wavelength. Hence, Absorbance can be logarithmically related to transmittance as:

$$A = -\log_{10}(I/I_0)$$

Beer Law follows:

$$A = E \cdot C \cdot L$$

Here,

A= measured absorbance

I₀= Intensity of incident light at a given wavelength.

I= Transmitted intensity

C= concentration of absorbing species

E=constant known as the molar absorptivity or extinction coefficient

In an absorbance experiment, light is attenuated not only by the analyte but also by reflections from the interface between the sample and the cuvette, absorbance by the solvent and air and the sample. These are often removed by defining I₀ as the light passing through a sample "blank" or "baseline" or reference sample (for example, a cuvette filled with solvent but zero concentration of the analyte is used as the blank)[45].

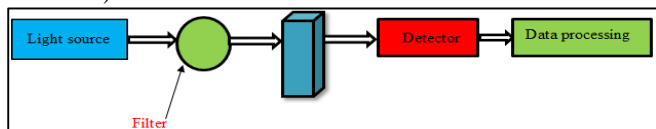


Fig. 3: Diagram of UV Spectrophotometer

b) Colorimetric Spectroscopy:

Colorimetric Spectroscopy method detects the complementary color of visible light absorbed by an analyte. The Gris diazotization reaction is widely used for colorimetric nitrate detection. In colorimetric spectroscopy method, chromogenic reagents are needed. Also, the reagents are needed for preprocessing the analyte and removing the interfering ions and impurities [46].

An optical detection system of a prototype nitrate sensor is reported by Gong Weidong and it is based on the Gris reaction with two integrated photodetectors and a green light-emitting diode (LED) light source [47]. Hydrolysis of the terminal urethane groups with hydrochloric acid produced a primary amine on polyurethane foam. A diazonium ion in the foam matrix is formed when the primary amine reacts with nitrate. A produced diazonium ion is coupled with α -naphthol, 8-hydroxyquinoline, β -naphthol, α -naphthylamine, resorcinol, or catechol. Also, a purple azo dye produced in the foam membranes. The foam membranes are then used for quantitative spectroscopy determination of nitrate [48].

III. CONCLUSION AND FUTURE PERSPECTIVES

Electrochemical methods have complex instruments. An ion selective electrodes method for nitrate detection is cost-effective and simple. But at low nitrate concentrations level an ion selective electrodes method are not reliable and suffer from other anions interference and require buffering of samples to a common ionic strength before a reliable nitrate determination can be made. Spectroscopy methods are compared with electrochemical methods, their detection limit is somewhat lower. But they are easily used and require no reagent that's why the use of spectroscopic analysis appear to be the method of choice due to the wide availability of the instrumentation involved and the simplicity of the protocols.

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