New development of optical fibre sensor for determination of nitrate and nitrite in water

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ABSTRACT

A novel ultraviolet optical fibre sensor is developed for the determination of nitrate and nitrite in water samples. The absorptivity spectra of nitrate and nitrite are determined at analytical wavelengths of 302 nm and 356 nm. Nitrate and nitrite are measured in the concentration range from 0.0 mg/L to 50 mg/L. The obtained results indicate that a linear relationship between the absorbance with the concentration of nitrate and nitrite in water. The other chemical species present in water do not much interfere with ultraviolet absorbance measurement of nitrate and nitrite. Detection limits are investigated by optical fibre sensor for nitrate is 0.0017 mg/L and nitrite is 0.0014 mg/L. Regression equations for the determination of nitrate and nitrite are presented and successful applied which require the determination concentration nitrate and nitrite in environmental water samples.

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1. Introduction

Nitrogen is an inert diatomic non-metal gas. Nitrogen is colourless, neutral, and constitutes 78% of Earth's atmosphere which is an element of all living creatures [1]. Nitrogen can exist in different forms, naturally existing in the environment as gas nitrogen, ammonia nitrogen, nitrates, nitrites and organic compounds [2]. Nitrogen becomes one of the measurement standards in the determination of water quality especially in wastewater management because nitrogen can cause diverse effects on the environment. The majority sources of nitrogen in environment are originally from urban sewage, manufacturing waste, and artificial fertilizers. The nitrogen is presented in the form of nitrogen oxides and it reacts with water become acid rains and fall back to the ground [3]. Human activities such as agricultural practices, combustion, transportation, and other alterations have increased the input of nitrogen compound into biochemical cycles [1]. Nitrogen compound enrichment or eutrophication can cause the losses of component species and loss of ecosystem function. Therefore, determination of the concentration of nitrogen in water is critical to follow the environmental regulatory limits.

Nitrate is a renowned pollutant in water and soil. Nitrates are mainly determined by the spectrometric, colorimetric and ion chromatography methods [4]. Nitrate is used mostly as a nitrogen fertilizer [5]. Besides that, nitrate is used in numerous industrial processes as an oxidizing agent and blasting agents. A most important use is in the manufacture of medium and high quality glass, such as optical and artistic glass, television and computer screens, and fibreglass. Furthermore, nitrates are an ingredient in the manufacture of charcoal briquettes. In rubber vulcanization and in petrochemical industries, enamels and porcelain are produced and used in formulations of heat-transfer salts for heat-treatment baths for alloys and metals. Besides that, nitrate organic compounds are used in management of water, cleaning compounds and explosive, pharmaceutical production. In the refining of some alloys, nitrates are used for the recovery of lead, production of uranium and leaching of copper ore [6]. Recently, many researches determine nitrate by using the typical reagents. Several reported spectrophotometric methods are involved since 1950-an, the basic of common reactions, such as ion chromatography, nitration reactions, specific ion electrodes, a reduction reaction followed by diazotization and others. The familiar spectrophotometric methods for the determination of nitrate are based on the nitration of phenolic compounds, brucine, 2,6-xylenol, 2,4-xylenol, 3,4-xylenol, phenoldisulfonic acid, chromophoric acids and phenol 4-aminoazobenzene. Besides that, nitrates are determined by using sensitive spectrophotometric methods as extractable ion associates of the nitrate ion with basic dyes [7].

Nitrites are intermediates in the nitrogen cycle which are unstable and can be transformed into nitrates or ammonia depending on the conditions. Their existence in water can be a consequence

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of water processing as corrosion inhibitors. Nitrites are frequently used in preservatives. Nitrites are origin from urban wastes, manufacturing wastes, removal wastes and flowing with water from synthetically fertilized fields [8]. Due to the increasing interest in the pollution issues of natural and sewage water, an index of organic pollution of nitrite level in water when correlated with other forms of nitrogen in water which making the determination of exact concentration of nitrite in water more desirable [9]. Various instrumental methods such as polarography, voltammetry, fluorimetry, biamperometry and flow injection spectrophotometry have been used for nitrite determination [10–14]. According to Kumar, nitrite was determined spectrophotometrically based on diazo coupling which provide a much lesser detection limit and enhanced sensitivity of the reaction [15,16].

The major resource of inorganic nitrogen ions for human is through drinking water and food. An approximated daily amount of nitrates for human intake reaches 75 mg to 100 mg per day, which 80% to 90% come from vegetables and 5% to 10% come from water [17]. In most of the countries, the admissible concentration in drinking water is controlled at 50 mg/L for nitrates and 0.5 mg/L for nitrites. Due to the toxicity of nitrogen for human, the limit concentrations of nitrogen in drinking waters are strictly given by guideline [18].

In the present study, a simultaneous measurement and quick method was reported for the determination of nitrate and nitrite by using fibre optic sensor. Fibre optic sensors are fibre-based devices used to sense quantity measurements, typically temperature or mechanical strain, and occasionally used for vibrations, pressure, acceleration, or concentrations of chemical species. Fibre optic sensors exhibit a number of advantages compared with other types of sensors which including absolute measurement, excellent resolution and range, resistant to electromagnetic interference, water and corrosion. In addition, fibre optic sensor can be develop multiplexed in parallel or in series and passive operation which is intrinsically safe, small size, light weight, and modest cost. These characteristics make the optical sensor fibre sensors safe and suitable to remote operation [19].

From previous study, majority of methods are slow measurement, laborious and require the use of toxic and expensive reagents. The new specific methods and detector was developed and studied for economic of analyses, cheap apparatus and quick, and hence a possibility of use in most laboratories. In this research, the main advantages of optical fibre sensor included the small volume samples analysis, quick for analyses, high sensitivity and selectivity without reagents used. The new specification optical fibre sensor was developed as a possibility of simultaneous separation and determination of nitrate and nitrite in water samples.

2. Material and method

2.1. Spectrophotometric determination of nitrate and nitrite

2.1.1. Preparation of nitrate and nitrite

All chemicals salts used were of analytical reagent grade which were purchased from MERCK (Darmstadt, Germany) and distilled water was used for the preparation of all solutions used in experiments. Nitrate and nitrite solution (1.0 g/L) were prepared by dissolving 1.371 g of sodium nitrate and 1.500 g of sodium nitrite, respectively in distilled water. One pellet of sodium hydroxide and 1 mL of chloroform were added to slow down bacterial growth and to prevent liberation of nitrous acid, respectively [20]. Nitrate and nitrite solution were diluted to 0.100 g/L concentration, respectively. Working standard solution was prepared daily by appropriate diluting the stock solution. All of the samples were prepared in 50 different concentrations. There were three types
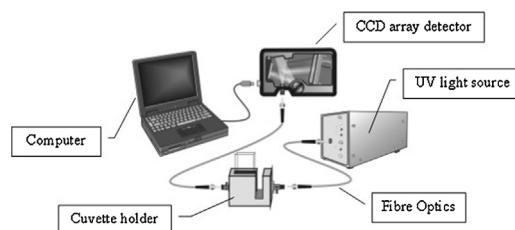

Fig. 1. The configuration and respond of the charge-coupled device array spectrometer for typical absorbance setup. (*Source*: Ocean Optics, 2008).

of variables to be determined which included nitrate, nitrite, and nitrate plus nitrite. In this spectrophotometric method, no reagents were used and all samples were conducted in a dark room at standard ambient temperature.

2.1.2. Apparatus and procedures

Spectroscopic measurement can be implemented through different techniques which included transmittance, absorbance and reflectance. All measurements were presented by using Channel 0 of the Jaz Spectrometer (Ocean Optics, U.S.A.) which using spectra ranged between 200 nm to 850 nm. The detector used in the Jaz spectrometer has a high-sensitivity of 2048-element charge-coupled device (CCD) array (Sony, product number ILX511B). The sensitivity of the detector can sense up to 75 photons/count at 400 nm and 41 photons/count at 600 nm. The deuterium tungsten halogen light (Ocean Optics, U.S.A.) was used as light source in the research. The light source combined with the continuous spectrum of a resonant frequency excited deuterium UV light source and a tungsten halogen VIS–NIR light source in a single optical path. Quartz cuvettes (1 cm path length) were used for the sample testing in the whole research study. The aqueous solution sample (2 mL) was pipetted into quartz cuvette, then placed into the CUV-ALL-UV 4-way cuvette holder and measurement was taken. The configuration and respond of the charge-coupled device array spectrometer was shown in Fig. 1.

The analytical potential of the method was investigated by applying it to the determination of spiked amounts of nitrate and nitrite in water samples collected. There were three types of water samples collected and tested which included lake water sample, sewage water sample, and leachate water. In the research, the known concentrations of nitrate and nitrite solution were added to real water samples in which volume was fixed. Each test was repeated for 30 times with different of known concentration of nitrate and nitrite. The added concentration of nitrate and nitrite were measured by the proposed methods and regression.

2.2. Standard chemistry analytical determination of nitrate and nitrite

2.2.1. Preparation of real samples for analysis

In the present research, proposed method was applied to real samples in which water samples from lake, sewage, and leachate were tested. Lake water was taken from Tasik Harapan in USM (Pulau Penang, Malaysia). Sewage water was also collected from sewer in USM (Pulau Penang, Malaysia). Meanwhile, leachate water was taken from landfill site at Pulau Burong (Pulau Penang, Malaysia). Nitrate and nitrite sample which randomly diluting to different known concentration was added to these real water samples. Same volumes of the real water samples were added to 30 different concentrations of nitrate and nitrite solution.

2.2.2. APHA method 4500-NH₃ B. Preliminary distillation step
2.2.2.1. *Preparation of reagents for analysis.* Borate buffer solution were prepared by adding 88 mL of 0.1 N sodium hydroxide