Simple design flow injection PMMA acrylic sample cell for nitrite determination

Faizar Abdurrahman, Norhana Arsad*, **Sabiran, and Harry Ramza**

Department of Electrical, Electronic and System Engineering, Faculty of Engineering and

Built Environment, Universiti Kebangsaan Malaysia 43600, UKM-Bangi,

Selangor Darul Ehsan, Malaysia

**Corresponding author: norhana@eng.ukm.my*

A polymethyl-methacrylate (PMMA) acrylic sample cell using flow injection is developed in this research for the determination of nitrite in an aqueous media. The research focuses on exhibiting direct absorbance spectrophotometry of nitrite using concentration of samples ranging from 0.1078 to 1.725 ppm. Nitrite determination is done colorimetrically using the Greiss reagent method. This method is based on the reaction of nitrite with sulphanilamide acid and N-1-napthylamine (NED) utilizing diazo coupling, and a syringe is used to administer the nitrite solution. The sample cell being used possesses a diameter of 1 mm with an overall size of 7.35×22 mm^2. To gauge the direct absorbance, a wavelength range from 400 to 650 nm has been selected for the testing, and the maximum absorbance is found to be at 545 nm. The validity of the proposed cell is explained in this letter.

OCIS codes: 300.1030, 280.4788, 120.0120.

doi: 10.3788/COL201412.043002.

Nitrites (NO_2) are natural inorganic ions, which are a part of the nitrogen cycle and are omnipresent within the environment. These ions also exist in preservatives, fertilizers, and can act as a meat curing agents[1,2]. The threshold exposure limit for the level of nitrite in drinking water is 45 $\mu g \cdot mL^{-1}$[3]. Precise measurement of nitrite compound is needed for great practical significance and fast determination of nitrite content in every related product must be done rapidly using the appropriate methods[4].

Overconsumption of nitrites that are found in food or water can be harmful to the metabolic system because they can cause methemoglobinemia, a situation where exogenous oxidizing drugs, including nitrite, reduce the carrying capacity of haemoglobin to carry oxygen[5,6]. Nitrites can also damage the nervous system, spleen liver, and cause cancerous tumours[2]. Ensafi *et al.*[7] previously reported that the formation of N-nitroso compound as a result of the reaction between nitrite and secondary amines, is known to be carcinogenic, tetratogenic or mutagenic.

Numerous researches have been conducted to find the most sensitive, effective, and rapid methods to detect and determine the concentration of nitrite, including electrochemical[8], capillary electrophoresis[9], chromatography[10], spectroscopic[11,12] and test strip sensor[13]. However these methods own several major disadvantages such that they are time consuming, heavily dependant on sophisticated equipments and skilled expertise, and are unsuitable for real time applications[14].

The most common process used in determining nitrites is based on reduction of nitrates into nitrites using various reagents such as cadmium[15], phosphomolybdenum[16] and titanium III chloride[4], followed by Griess reagent reaction to detect the presence of nitrite compound, and using spectrophotometric method for measurement.

The application of optical sensors for the detection of nitrite is proven to offer satisfactory results based on previous researches. This method has noticeably high sensitivity and selectivity while being relatively easy to handle[7] Many researches have began to employ optical sensing integrated with flow injection for nitrite determination[17].

Plastic optical fibre (POF) is a popular choice for the application[18,19]as a chemical sensor for the determination of cations and anions due to its excellent sensitivity and ease of fabrication[14]. POF also has low fragility as compared to other types of fibre, the material used in the fibre structure is solid and non toxic, plus POF only needs low power in order to operate, making it biocompatible with the human body. Hence, POF is chosen as the sensor to detect nitrites in this research.

Polymethyl-methacrylate (PMMA) is a type of polymer material that is well utilized usually for the construction of a fibre optic body. However in this experiment PMMA is employed as a sample cell due to its compatibility with organic material, while taking advantage of the material's break- resistant option, lower density of 1195 $Kg \cdot m^{-3}$ as compared to silica, and low weight to assist in the flow injection set up for the determination of nitrite within aqueous media[20].

Flow injection analysis has been employed as an analysis method for many years, which has been properly recorded. This form of analysis is done by injecting the analyte into the reaction zone and the analyte will flow through the point of detection. Any changes in absorption, electrical capacity or any other physical parameters can be detected by the movements of the analyte in the flow[16,21]. The advantages of using flow injection include accuracy, rapidity, and it only requires a small amount of sample for the measurement[17].

The nitrite sample was prepared by diluting 0.0138 gram of sodium nitrite with 200 ml of deionised water

to yield 5 samples with different concentration: 1.725, 0.8625, 0.4132, 0.2156, and 0.1078 ppm. These solutions underwent the colorimetric Griess reagent reaction process by diluting 1 mL of each sample with 1 ml sulphanilamide solution, producing 1% concentration in 5 % acid. Then, 1mL of 0.1% N-1 napthylamine (NED) is added and each solution is incubated at room temperature for 10 minutes.

The flow injection using PMMA sample cell was developed in this experiment. The sample cell would be utilized to carry out absorbance spectroscopy. It has a square geometry with two holes for SMA connectors and a 1-mm diameter hole for injecting the solution, pumped through a small pipe using a syringe to the detection area.

The experimental setup of flow injection using PMMA as the sample cell for nitrite determination is presented in Fig. 1. A unit of ultraviolet-visible-near-infred (UV-VIS-NIR) light source (DH-2000-BAL, Ocean Optics, USA) with deuterium and halogen power input was used as the light source. A 364-element CCD array Toshiba detector acted as the receiver and was connected together with an optical spectrometer (Model HR 4000, Ocean Optics, USA) for the purpose of spectral measurement. Light propagated through the sample using a POF with a diameter of 1 μm. A SMA connector was used to couple the fibre to the sample cell, through which the solution was injected to the sample cell using a syringe.

The absorption spectrum coefficients of the different nitrite samples are shown in Fig. 2. It shows the absorption of nitrite at various levels of concentrations in the wavelength range of 400–650 nm. The maximum absorbance was observed at 545 nm because nitrite ions reacting to sulfanilamide under acidic conditions to form diazonium cations in acidic solution[22]. According to previous research, reaction of nitrite ion diazotizing with colorimetric method for nitrite determination will be detected at range from 540 to 545 nm[23] due to sequence of this research presence of nitrite can be detected in small amount. The light couple directly without any media that is preclude direct interaction between the light and nitrite. So that as depicted in Fig. 2, the amount of absorption increases with increasing concentration of nitrite samples. The sensor system showed good advantage because of the following two factors. Firstly, the direct interaction between nitrite and light without any hindrance of sample cell during nitrite measurement. Secondly, the small diameter of cell could efficiently reduce the nitrite sample dispersion and simplify sample displacement to the interaction spot and generate absorbance with colorimetry method leading to improvement system and response time. This sample cell proposed to replace the conventional cuvette that's used for nitrite determination in direct absorbance.

Figure 3 shows that the absorbance varies linearly with the concentration of nitrite. According to Beer–Lambert law, absorbance increases in a direct proportional fashion with the level of nitrite. The calibration curve is an alternative form of plotting the dispersion of the sample concentration versus absorption in the targeted wavelength. The calibration curve illustrates the linear line and allows for the calculation of the correlation regression coefficient. It can be seen that the dispersion plot

does not deviate far from the linear plot line, with similar regression balancing the two parts of the upper and lower lines looking almost linear. Five concentration levels (ranged between 0.1078 and 1.725 ppm) were used to build the calibration line. The entire experiment was then repeated three times for each concentration. This
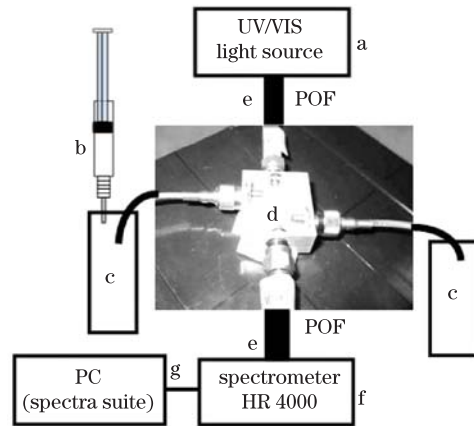

Fig. 1. Experimental setup of flow injection. a: broad band light source; b: syringe; c: nitrite sample container; d: sample cell; e: polymer optical fiber; f: optical spectrometer; g: computer.
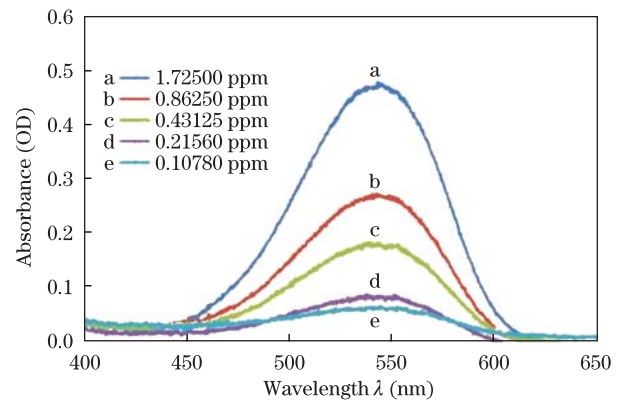

Fig. 2. (Color online) Absorbtion spectra of the presence of nitrite in aquous media: (a) 1.725, (b) 0.8625, (c) 0.43125, (d) 0.2156, and (e) 0.1078 ppm.
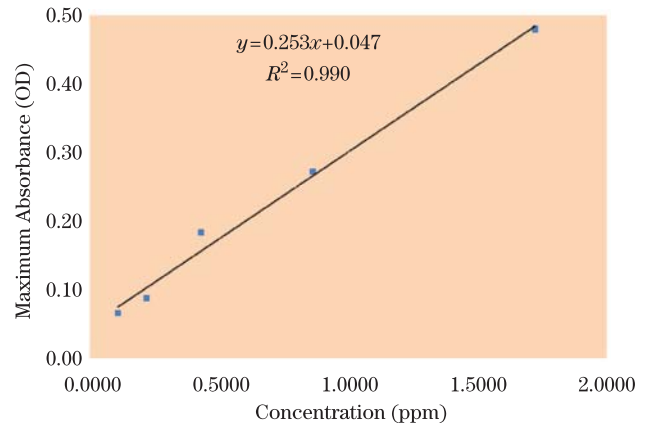

Fig. 3. (Color online) Calibration curve of nitrite concentration versus maximum absorbance.

Table 1. Optical Characteristic of Nitrite

Parameters	Unit	Characteristic
Colour	–	Purple
$\lambda_{\max}$	nm	545
Beer Law Range	μg·ml^{-1}	25–1.5625
Molar Absorptivity	LMol^{-1}·cm^{-1}	1.7620

Table 2. Regression Equation of Experiment

Regression Equation^a	$y=0.2538x+0.0479$
Correlation Coefficient	0.9902
Slope (a)	0.2538
Intercept	0.0479

subsequent process then yielded a linear calibration equation of $y = 0.2538x + 0.0479$. y-axis represents the maximum absorbance result, while x-axis represents the concentration, with a correlation coefficient of $R = 0.9902$.

As indicated in Table 1, the nitrite sample gave out a purple colour due to diazo coupling as a result of using Griess reagent reaction to form colorimetric. The maximum absorbance was found at the wavelength of 545 nm, and the molar absorptivity was found to be 1.7620 LMol^{-1}·cm^{-1}.

The correlation coefficient of 0.9902 from Fig. 3 and Table 2 shows a strong linear correlation coefficient with the value approaching, dictating an almost linear trend. Therefore, it can be said that the sensor used in this experiment almost obey the Beer-Lambert law with only a small deviation. The intercept of the regression line and the slope of the line are at 0.4252 and 0.3074, respectively.

In conclusion, we design and develope a flow injection analysis setup using PMMA acrylic as the sample cell for sensitive measurement of nitrite in aqueous media, having the sample concentration ranging from 0.1078 to 1.725 ppm. This sample cell is found to be sensitive in determining the amount of nitrite at lower concentrations. The utilization of PMMA as the sample cell is an accurate decision since this material is compatible with organic material. A broad band light source and a HR4000 spectrometer are used as the power source for this experiment. The obtained results successfully demonstrate the effectiveness of flow injection with acrylic sample cell for nitrite compound measurement in water, with the setup displays good sensitivity. This reveals the potentiality of the system for measuring nitrite concentration in drinking water and for monitoring water quality in wells and sewage system.

References

1. M. J. Moorcroft, J. Davis, and R. G. Compton, Talanta **54,** 785 (2001).
2. H. Kroupova, J. Machova, V. Piackova, J. Blahova, R. Dobsikova, L. Novotny, and Z. Svobodova, Ecotoxicol. Environ. Saf. **71,** 813 (2008).
3. V. Vishnuvardhan, R. Kala, and T. Prasada Rao, Anal. Chim. Acta **623,** 53 (2008).
4. T. Aoki and M. Wakabayashi, Anal. Chim. Acta **308,** 308 (1995).
5. D. Majumdar, Resonance **8,** 20 (2003).
6. X. Baoqing, in *Proceedings of 2010 International Conference on Mechanic Automation and Control Engineering (MACE)* 1992 (2010).
7. A. A. Ensafi and M. Amini, Food Chem. **132,** 1600 (2012).
8. P. Kalimuthu and S. Abraham John, Electroanalysis **22,** 303 (2010).
9. J. E. Melanson and C. A. Lucy, J. Chrom. A **884,** 311 (2000).
10. M. I. Helaleh and T. Korenaga, J. Chrom. B: Biomed. Sci. Appl. **744,** 433 (2000).
11. A. Kazemzadeh and A. A. Ensafi, Microchem. J. **69,** 61 (2001).
12. Z. Shiying, W. Rong, Z. Liping, H. Pingguo, and F. Dayou, Fujian Analysis & Testing **4,** 008 (2008).
13. S. Dhanya, J. Joy, and T. P. Rao, Sensor. Actuator. B: Chem. **173,** 510 (2012).
14. A. A. Ensafi and M. Amini, Sensor. Actuator. B: Chem. **147,** 61 (2010).
15. K. Horita and M. Satake, Analyst **122,** 1569 (1997).
16. L. Monser, S. Sadok, G. M. Greenway, I. Shah, and R. F. Uglow, Talanta **57,** 511 (2002).
17. G. D. Christian, Anal. Chim. Acta **499,** 5 (2003).
18. X. Cheng, W. Qiu, W. Wu, Y. Luo, X. Tian, Q. Zhang, and B. Zhu, Chin. Opt. Lett. **9,** 020602 (2011).
19. F. Chu, H. Cai, R. Qu, and Z. Fang, Chin. Opt. Lett. **6,** 401 (2008).
20. K. Peters, Smart Materials and Structures **20,** 013002 (2011).
21. G. Supriyanto, *Chromatomembrane Method Applied in Pharmaceuticals Analysis* (Logos-Verlag, Berlin, 2005).
22. D. Tsikas, J. Chrom. B **851,** 51 (2007).
23. H.-H. Perkampus, H. C. Grinter, and T. Threlfall, *UV-VIS Spectroscopy and its Applications* (Springer-Verlag, New York, 1992).