

FLOW INJECTION DETERMINATION OF NITRITE BY GRAPHENE QUANTUM DOTS

Habibollah Eskandari*, Mandana Amiri, Somayyeh Baghi Sefidan

Department of Chemistry, Faculty of Basic Sciences, University of Mohaghegh Ardabili, Ardabil
56199-11367, Iran

Abstract

A simple, rapid and sensitive flow injection based spectrophotometric method has been applied for the determination of nitrite. The method is based on the fast reaction of nitrite with metoclopramide hydrochloride in acidic solutions to produce a diazonium cation which is subsequently coupled with graphene quantum dot, and forms a yellow colored azo product. The product absorbs electromagnetic radiation at 423 nm (λ_{max}). The dependency of absorbance to various instrumental and chemical parameters was investigated and the optimum condition was selected to prepare nitrite calibration graph. Beer's law was obeyed in the range of 0.02-7 $\mu\text{g mL}^{-1}$. Various concentrations of nitrite were selected, and precision and accuracy of the method were evaluated. The obtained relative standard deviations and recoveries as percent were in the range of 1.5-6.1% and 97.8-99.2%, respectively. The method was successfully applied on the determination of nitrite in various water, sausage and cheese samples.

Key words: nitrite, flow injection analysis, graphene quantum dot, metoclopramide

1. INTRODUCTION

Nitrite is a universal economically chemical reagent which has been widely used in various industries related to textile, photography, dye and food preservation. Nitrite is an important intermediate in biological nitrogen cycle and diffused to environment due to human industrial activities. Nitrite is also produced during activities of some micro-organisms (Manzoori, Sorouraddin & Haji-Shabani 1998). Secondary amines are converted to carcinogenic nitrous amines in the presence of nitrite (Ensafi, Rezaei & Nouroozi 2004).

A wide range of techniques have been applied for the determination of nitrite. Some of the monitoring methods are based on chemiluminescence (Kanda & Taira 2003), electrochemical techniques (Biagiotti et al. 2007; Liu et al. 2007), ion chromatography (Andrade et al. 2003), fluorescence (Noroozifar et al. 2007) and spectrophotometry (Fernandez-Arguelles et al. 2004; Abbas & Mostafa 2000; Baeza, Bartoli & Alonso 2005). The simplest and most frequently applied methods utilize spectrophotometric detection, based on the Griess reaction because of its fairly low cost and good sensitivity (Tsikas 2007). The Griess reaction involves formation of a diazonium salt by treatment of an aryl amine with nitrous acid that followed by reaction with aromatic compounds containing electron donating groups. However, environmental safety is not guaranteed by some of the methods, because they use large volumes of toxic reagents such as 1-naphthylamine. The toxicity of the reagents used and the amount of wastes produced are the most important features, during the development of a new analytical method. Hence, there is a great need to develop methods which may be less harmful to humans and to the environment (Anastas & Kirchhoff 2002).

Graphene quantum dots (GQDs) are a kind of zero-dimensional nano-materials, which can be regarded as incredibly small pieces of graphene (Shen et al. 2012; Zhu et al. 2012; Zhang et al. 2012; Li et al. 2013). The GQDs exhibit new phenomena due to quantum confinement and edge effects (Li et al. 2013). Compared with organic dyes and semi-conductive quantum dots, GQDs are superior in terms of their excellent properties in photo stability, against photo bleachers and blinkers. They are biocompatible and have low cytotoxicity (Shen et al. 2012; Zhu et al. 2012; Li et al. 2013). Unlike their cousins, carbon dots, GQDs clearly possess a graphene structure inside the dots with some of the unusual properties of graphene (Zhang et al. 2012; Li et al. 2013). For these reasons, GQDs have attracted attention of researchers. Graphene quantum dots have scarcely been used in analytical chemistry. The few, recent exceptions involve the determinations of humidity (Alizadeh & Shokri

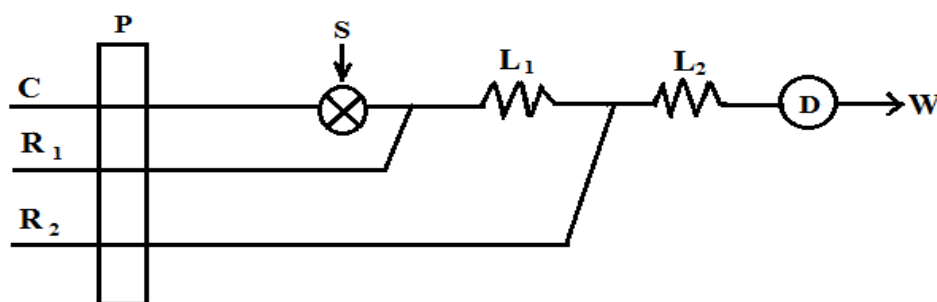
2016), glucose (Razmi & Mohammad-Rezaei 2013), free chlorine (Dong et al. 2012), Cd(II) (Li et al. 2012), TNT (Fan et al. 2012), Fe(III) (Wang et al. 2012), pyrocatechol (Yang et al. 2012), glutathione, uric acid and tryptophan (Mazloum-Ardakani et al. 2015), immunoglobulin G (Zhao et al. 2013), and sequencing of DNA (Zhao et al. 2011).

In this approach, we report a new analytical application of GQDs as a reagent. GQDs were coupled with diazotized metoclopramide in acidic media for the determination of nitrite. A flow injection (FI) manifold was applied and the fast formed colored product was monitored spectrophotometrically. An excellent rapid, sensitive and selective nitrite determination procedure was developed.

2. EXPERIMENTAL

2.1. Apparatus

The flow system used in this work is given in Scheme 1.



Scheme. 1. Schematic diagram of the flow-injection system used for the determination of nitrite.

Condition: C, carrier (H_2O); R_1 , metoclopramide hydrochloride ($2 \times 10^{-3} \text{ mol L}^{-1}$) in $3 \times 10^{-1} \text{ mol L}^{-1} \text{ HCl}$; R_2 , graphene quantum dots (5-fold diluted); P, peristaltic pump; i. d. of tubes = 0.8 mm; S, sample injection unit; length of L_1 = 16 cm; length of L_2 = 34 cm; D, detector; wavelength = 423 nm; W, waste.

The absorbance was measured with a Cecil model CE 1021 spectrophotometer, equipped with a flow-through cell of 20 μL inner volume and 1.0 cm optical path. An 8-channel peristaltic pump (Gilson, Miniplus 2) with three silicone rubber tubes (0.8 mm i.d.) was used. PTFE mixing joints were used. Nitrite containing sample solutions were injected with a 6-port Rheodyne sample injector. A Shimadzu 1650 PC spectrophotometer with 1.0 cm matching quartz cells was used for obtaining the sample spectra.

Surface morphology of the prepared GQDs was studied by LEO 1430VP SEM. The TEM investigations were performed by a Zeiss-EM10C instrument. The FT-IR spectra were obtained by a Perkin Elmer Spectrum RX I apparatus.

2.2. Reagents

Citric acid anhydrous, hydrochloric acid and sodium hydroxide were purchased from (Merck, Germany). Metoclopramide hydrochloride was purchased from (Fluka). Sodium nitrite and N-(1-naphthyl)-ethylene diamine dihydrochloride (NED) were purchased from (Loba-Chemie, India).

All chemicals used were of analytical grade and all solutions were prepared in distilled water.

2.3. Synthesis of GQDs

GQDs were selectively and successfully synthesized by controlling the degree of carbonization of citric acid and dispersing the carbonized product into alkaline solution, according to the procedure reported (Dong et al. 2012). In a typical procedure, 2.0 g of citric acid was heated in a 250 mL beaker to 200 °C. After 30 min, the color of the melted product became orange, hinting the formation of GQDs. After dissolution in sodium hydroxide, the GQDs were used for nitrite determination.

2.4. Sample manipulation

For treatment of sausages, about 10 g of sausages were weighed, minced and transferred into a 250 mL beaker. Then 20 ml of water was added and the mixture was heated to 80°C for 15 min. Then, the mixture was transferred to a 100 mL volumetric flask. Appropriate hot water was added to bring the volume to about 75 mL. The flask was transferred to a steam bath for 2 h. The mixture was cooled to room temperature, and 2 mL of Carrez(II) solution was added. The volume was adjusted to 100 mL with water, and centrifuged for 25 min to be cleared. The solution was analyzed by the method recommended by the AOAC (Horwitz 1980).

Cheese samples were minced and smoothed. An amount of 30 g of the slurry of cheese was weighed exactly, placed in a 100 mL beaker and digested following the method recommended by the AOAC (Horwitz 1980).

3. RESULTS AND DISCUSSION

3.1. Characterization of GQDs

The scanning electron microscopic image of the synthesized GQDs is shown in Fig. 1(I).

The SEM image shows that GQDs are relatively spherical with diameters less than 30 nm. The obtained TEM micrograph was also used for more accurate size determination of GQDs. The TEM image is given in Fig. 1(II). The size of GQDs is mostly distributed in the range of 10–20 nm, and an average size about 15 nm was calculated.

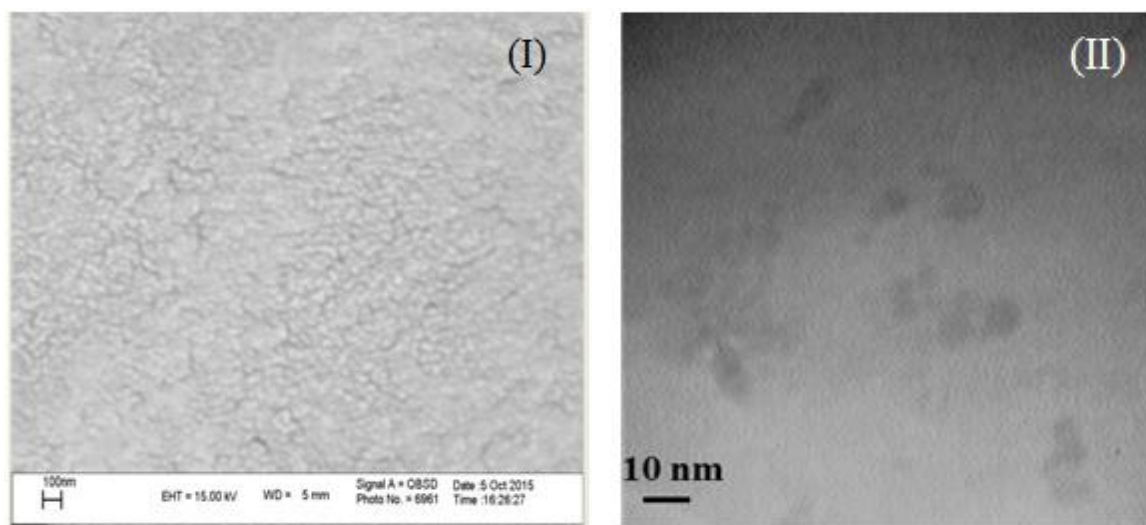


Fig. 1. SEM (I) and TEM (II) images of the synthesized GQDs.

Fig. 2 shows the FT-IR spectrum of GQDs. As expected, it can be seen that GQDs contain the functional groups of OH and COOH. The strong and broadened peaks at wave number range of 3000–

3500 cm^{-1} (assigned to OH stretching) and the strong paired peaks at 1634 and 1554 cm^{-1} (respectively, assigned to asymmetric and symmetric stretching of carboxylate functional groups) can be clearly distinguished in the spectrum. These evidences show that the prepared GQDs possess a large density of hydrophilic functional groups such as hydroxyl and carboxylate groups (Alizadeh & Shokri 2016).

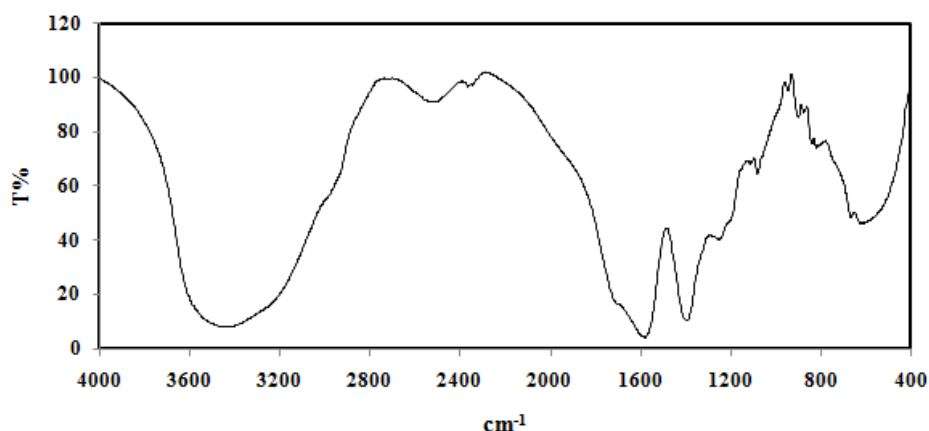


Fig. 2. FT-IR spectrum of the synthesized GQDs.

3.2. Absorption Spectra

The colorimetric nitrite determination method is based on the diazotization of metoclopramide hydrochloride in an acidic medium prior to coupling with GQDs. The product of the azo coupling reaction gives an absorption maximum at 423 nm, as can be seen in Fig. 3. At this wavelength the blank is sufficiently small, and makes reproducible absorbance measurements. Hence, monitoring of absorbance was performed at 423 nm for all of the nitrite monitoring experiments.

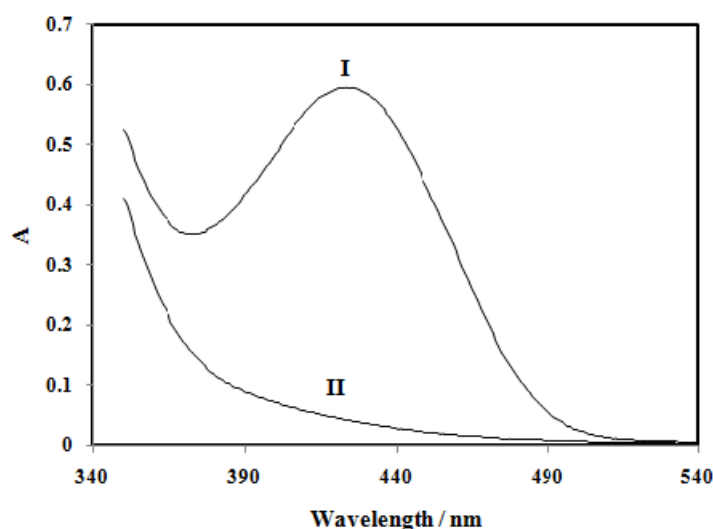
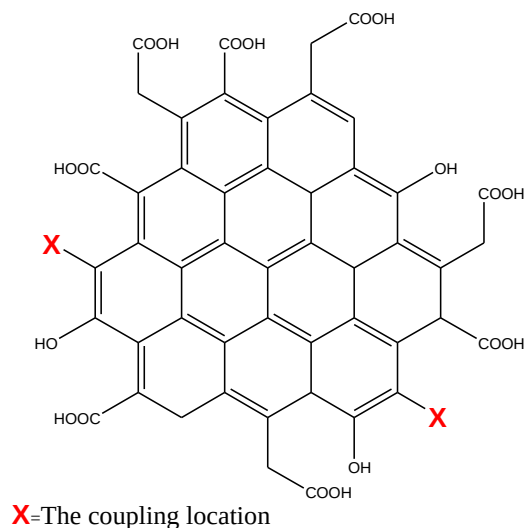


Fig. 3. (I) Absorption spectra of azo dye produced ($1 \mu\text{g mL}^{-1}$ nitrite) against water, and (II) blank against water.

The most probable reactive sites of GQDs (for azo coupling reaction) have been shown in Scheme 2.



Scheme 2. GQDs structure and its azo coupling reactive sites (have been assigned as X).

3.3. Optimization

Preliminary tests showed that a 3-way FI manifold provides the method to be analytically efficient. A one at a time protocol was obeyed for optimizing the affecting parameters.

The effect of metoclopramide concentration on the sensitivity was investigated by varying the concentration of metoclopramide hydrochloride in the range of 0.02-2.0 mmol L⁻¹. The results of the study are given in Fig. 4. As can be seen, metoclopramide as 2 mmol L⁻¹ shows the maximum sensitivity, in the tested range. Therefore, metoclopramide as 2 mmol L⁻¹ was selected for the next studies.

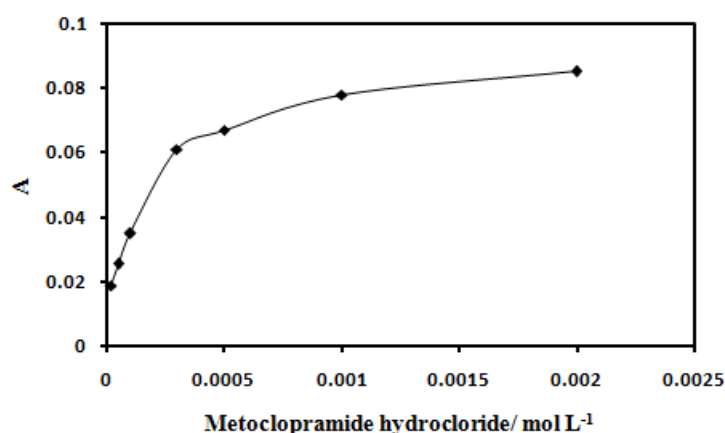


Fig. 4. Effect of metoclopramide concentration on the sensitivity of the method.

Condition: hydrochloric acid, 0.1 mol L⁻¹; GQDs, 5-fold diluted; nitrite, 1 µg mL⁻¹; flow rate, 1.1 mL min⁻¹; length of L₁, 16 cm; length of L₂, 34 cm; sample injected volume, 50 µL.

The effect of concentration of hydrochloric acid on the sensitivity was also investigated by varying the concentration of the acid in the range of 0.03-0.4 mol L⁻¹. The results in Fig 5 showed that the rate of the diazotization reaction reaches to a maximum and constant amount for hydrochloric acid concentrations greater than 0.3 mol L⁻¹. Hence, hydrochloric acid as 0.3 mol L⁻¹ was selected for the next studies.

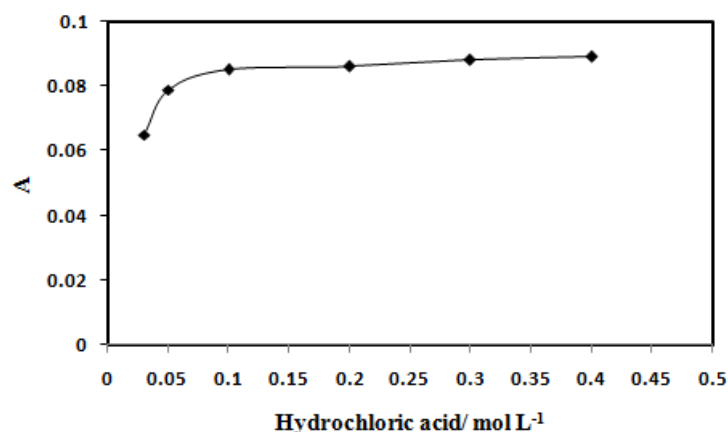


Fig. 5. Effect of hydrochloric acid concentration on the sensitivity.

Condition: metoclopramide hydrochloride, 2×10^{-3} mol L⁻¹; GQDs, 5-fold diluted; nitrite, 1 μ g mL⁻¹; flow rate, 1.1 mL min⁻¹; length of L₁, 16 cm; length of L₂, 34 cm; sample injected volume, 50 μ L.

Concentration of GQDs is an important parameter. The prepared stock solution of GQDs in sodium hydroxide was diluted with water to prepare GQDs solutions with different dilution. The prepared solutions has been used as the third stream in FI manifold, and sensitivity of the method was monitored. The results are given in Fig 6. The horizontal axis of the figure is the dilution factor which has been involved to the stock solution of GQDs. As can be seen, a 5-fold dilution has produced the best sensitivity. The 5-fold dilution on the stock solution of GQDs, was chosen for further investigations.

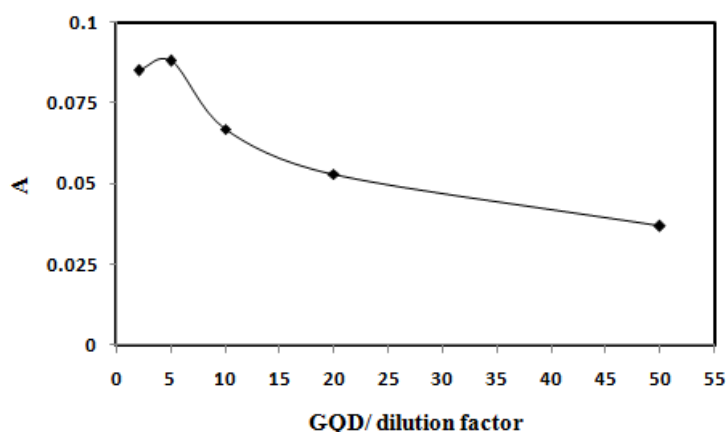


Fig. 6. Effect of GQD concentration on the sensitivity.

Condition: metoclopramide hydrochloride, 2×10^{-3} mol L⁻¹; hydrochloric acid, 0.1 mol L⁻¹; nitrite, 1 μ g mL⁻¹; flow rate, 1.1 mL min⁻¹; length of L₁, 16 cm; length of L₂, 34 cm; sample injected volume, 50 μ L.

The reaction of nitrite and metoclopramide in the presence of hydrochloric acid is occurred in L_1 reaction coil. When length of L_1 increases the diazotization reaction time is increased. But, by increasing the length of L_1 , the more dispersion is occurred; therefore, sensitivity is decreased. As can be seen in Fig 7, length of L_1 as 30 cm has produced the best sensitivity. Therefore, L_1 with a length equal to 30 cm was selected for the next studies.

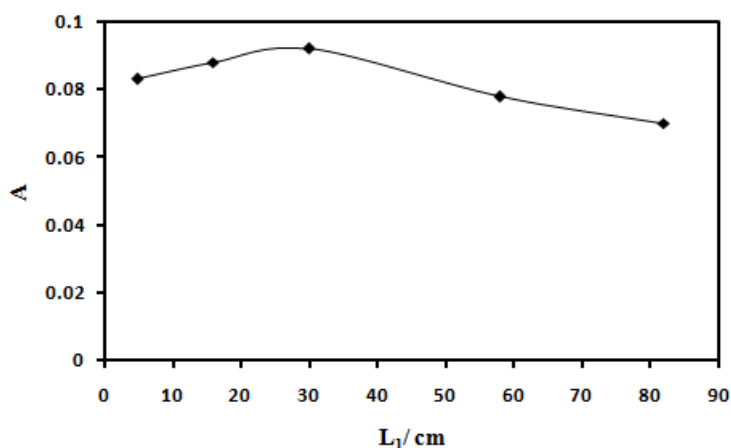


Fig. 7. Effect of length of L_1 on the sensitivity of the method.

Condition: metoclopramide hydrochloride, $2 \times 10^{-3} \text{ mol L}^{-1}$; hydrochloric acid, 0.3 mol L^{-1} ; nitrite, $1 \mu\text{g mL}^{-1}$; flow rate, 1.1 mL min^{-1} ; GQDs, 5-fold diluted; length of L_2 , 34 cm; sample injected volume, $50 \mu\text{L}$.

Investigation on the effect of length of L_2 (in the range of 27-45 cm) indicated a decrease in sensitivity, when the length of coil L_2 was increased. More dispersion is occurred when longer L_2 is used. Therefore, the selected length for coil L_2 was 27 cm.

The injected volume of the samples was varied, and sensitivity was monitored. Both peak height and peak width increased by increasing the sample volume. Therefore, both sensitivity and time of analysis have been increased by increasing the injected sample volume. However, sensitivity was not increased noticeable for injection volumes more than $250 \mu\text{L}$. Therefore, injected sample volume as $250 \mu\text{L}$ was selected to obtain appropriate sensitivity and rate of analysis.

Flow rate also must be optimized. Various pump speed were applied to reach different flow rates. The results of the study are given in Fig 8. As can be seen, flow rate as 2.0 mL min^{-1} has produced the most sensitivity. When flow rate increased dispersion is lowered but the reaction times are decreased. For the next studies, flow rate as 2.0 mL min^{-1} was selected.

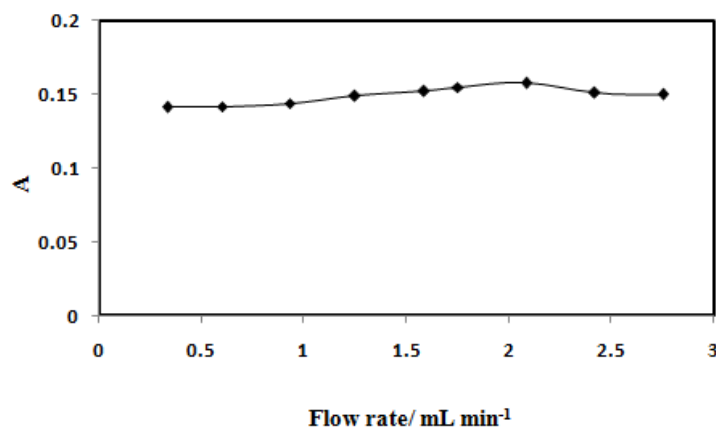


Fig. 8. Effect of flow rate on the sensitivity.

Condition: metoclopramide hydrochloride, 2×10^{-3} mol L⁻¹; hydrochloric acid, 0.3 mol L⁻¹; nitrite, 1 μ g mL⁻¹; flow rate, 1.1 mL min⁻¹; GQDs, 5-fold diluted; length of L₁, 30 cm; length of L₂, 27 cm; sample injected volume, 250 μ L.

The temperature of water bath was varied in the range of 20-50°C. In all cases variation of the temperature had no effect on the peak heights. Therefore, 20 °C was selected as an optimum temperature.

3.4. Analytical figures of merit

The optimal conditions for the established method were applied and a calibration graph was obtained at 423 nm. One linear range was observed. The calibration equation was $\text{Abs} = 0.1592 \times C_{\text{Nitrite}} + 0.0018$ ($R^2 = 0.9975$) in the range of 0.02-7.0 μ g mL⁻¹.

The accuracy and precision of the nitrite determination method were investigated. Nitrite concentrations as 0.05, 2.0 and 6.0 μ g mL⁻¹, were analyzed by the method ($n=10$), and the absorbances were evaluated by the obtained linear calibration curve. The recoveries and relative standard deviations as percent for 0.05, 2.0 and 6.0 μ g mL⁻¹ of nitrite were found 99.2 and 6.1, and 97.5 and 2.2, and 97.8 and 1.5, respectively.

3.5 Effect of foreign species

Interference study was carried out using various foreign cations, anions and organics. The study presents the selectivity of the method. Known concentrations of the species were added, individually, to a solution containing 0.4 μ g mL⁻¹ of nitrite. The tolerance limit was defined as the concentration of the species, when caused an error in the range of $\pm 7\%$ for nitrite. Maximum tolerable amounts of the foreign chemicals are given in Table 1.

Table 1. Effect of foreign species on the determination of nitrite as $0.4 \mu\text{g mL}^{-1}$.

Species	Tolerance limit ($W_{\text{Ion}}/W_{\text{Nitrite}}$)
K(I), Na(I), Cr(III), Sr(II), Hg(II), Al(III), Sn(II), Li(I), Mn(II), Zn(II), Pb(II), Cu(II), Ni(II), Co(II), Mg(II), Ba(II), Cd(II), Ce(III), NH_4^+ , NO_3^- , Br^- , CN^- , H_2PO_4^- , $\text{C}_2\text{O}_4^{2-}$, IO_3^- , CH_3COO^- , F^- , SCN^- , ClO_4^- , Cl^- , SO_4^{2-} , I^- , HCO_3^- , Tartrate, Sucrose, Glucose, EDTA	$> 500^*$
BrO_3^-	500
Fe(III)	60
Ascorbic acid	30

*: Maximum concentration which has been tested.

4. APPLICATIONS

The presented procedure was successfully applied to the determination of nitrite in various water, cheese and sausage samples. Water samples were examined directly using the procedure proposed without any pretreatment. The results are shown in Tables 2, 3, and 4. A standard nitrite determination method was also applied (Horwitz 1980).

Table 2. Determination of nitrite in water samples.

Sample	Nitrite, $\mu\text{g mL}^{-1}$ (n=8)		Recovery%
	Taken	Found	
River	-	0.055	-
	0.050	0.103 ± 0.002	96.000
	0.100	0.152 ± 0.006	97.000
Well	-	ND*	-
	0.050	0.048 ± 0.003	96.000
	0.100	0.107 ± 0.006	107.000
Lake	-	0.056	-
	0.050	0.105 ± 0.003	98.000
	0.100	0.152 ± 0.006	96.000

*: Non-determinable

$\pm$ means standard deviation.

Table 3. Determination of nitrite in cheese samples.

Sample	Nitrite, ($\mu\text{g g}^{-1}$) (n=5)		Recovery%
	Taken	Found	
Cheese 1	--	0.34	-
	2.00	2.31 $\pm$ 0.03	98.50
Cheese 2	-	0.31	-
	2.00	2.42 $\pm$ 0.03	105.50

$\pm$ means standard deviation.

Table 4. Determination of nitrite in sausages.

Sample	Nitrite, ($\mu\text{g g}^{-1}$)	
	Proposed method (n=5)	Standard method (n=5)
Beef sausage1	7.92 $\pm$ 0.27	7.66 $\pm$ 0.02
Beef sausage 2	21.70 $\pm$ 0.42	20.80 $\pm$ 0.14

$\pm$ means standard deviation.

5. CONCLUSION

In this research we develop a new analytical application for GQDs. GQDs were applied as an azo coupling reagent. The produced azo dye was monitored to establish an efficient method which was successfully used for the determination of nitrite in water, cheese, and sausage samples. Simplicity, reliability, reproducibility, time saving, low reagent consumption, need of small sample volume, large dynamic range and high samples throughput (up to 30 samples h^{-1}) are the most valuable features of the proposed method.

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