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An automatic gas-phase molecular absorption spectrometric system using a UV-LED photodiode based detector for determination of nitrite and total nitrate

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ABSTRACT

An automatic gas-phase molecular absorption spectrometric (GPMAS) system was developed and applied to determine nitrite and total nitrate in water samples. The GPMAS system was coupled with a UV-light emitting diode photodiode (UV-LED-PD) based photometric detector, including a 255 nm UV-LED as the light source, a polyvinyl chloride (PVC) tube of 14 cm as the gas flow cell, and an integrated photodiode amplifier to measure the transmitted light intensity. The UV-LED-PD detector was compact, robust, simple and of low heat production, comparing with detectors used in other GPMAS works. For nitrite measurement, citric acid was used to acidify the sample, and ethanol to catalyze the quantitative formation of NO_2. The produced NO_2 was purged with air flow into the UV-LED-PD detector, and the gaseous absorbance value was measured. The total nitrate could be determined after being reduced to nitrite with a cadmium column. Limits of detection for nitrite and nitrate were 7 μmol/L and 12 μmol/L, respectively; and linear ranges of 0.021–5 mmol/L for nitrite and 0.036–4 mmol/L for nitrate were obtained. Related standard deviations were 1.81% and 1.08% for nitrite and nitrate, respectively, both at 2 mmol/L. The proposed method has been applied to determine nitrite and total nitrate in some environmental water samples.

1. Introduction

Gas-phase molecular absorption spectrometry (GPMAS) has been widely used for the determination of volatiles [1,2] or compounds that can be easily converted into volatile compounds [3,4]. Because of the isolation of analyte from aqueous solutions and the determination in gas-phase, the GPMAS technique is highly sensitive and with less interference from the matrix. In the previous works, atomic absorption spectrophotometer (AAS) [1–5] and UV–VIS spectrophotometer [6–9] are commonly applied as the detectors for gas absorption measurement. These optical detectors are laboratory based with high power consumption light sources and delicate monochromators, therefore, the application of the GPMAS technique to on-field monitoring or miniature instrumentation is restricted.

It has been proved that light emitting diodes (LEDs) offer significant advantages over traditional light sources, such as small size, reduced power consumption, robustness, simple optical design, long lifetime and low price [10,11]. Recently, deep-UV-LEDs with wavelengths less than 300 nm are introduced for photometric detection of solutions [12–14]. Up to data few work [15] has been reported to apply the deep-UV-LED as a gas-phase photometric detector, however, there is potential to use it for the detection of gaseous compounds that have strong absorption in the deep-UV range.

To continually monitor the nitrite and nitrate in nature water is of great importance. The World Health Organization (WHO) [16] recommends the maximum limits of nitrite and nitrate in drinking water to be 3 mg/L (65 μmol/L) and 50 mg/L (806 μmol/L), respectively. A variety of analytical methods has been reported for the determination of nitrate and nitrite, including those employing sequential injection [17], multi-pumping flow system [18], flow injection with spectrophotometric [19] or amperometric [20] detection, as well as high performance liquid chromatography with chemiluminescence detection [21]. However, the most frequently utilized method for nitrite and nitrate detection is still the spectrophotometric one based on the copperized cadmium reduction of nitrate to nitrite followed by Greiss assay [22,23]. Among the Greiss arrangements, the most common reagents are the sulfanilamide and N-1-naphthylethylenediamine dihydrochloride [22]. However, the toxicity of the potential carcinogenic compounds involved in Greiss reaction to the assay operator as well as the environmental concern due to its widespread use have encouraged the development of some alternative methods. Therefore, the GPMAS based method has been proposed [3,7,8,24]. Comparing to Greiss method, GPMAS has some advantages, including using less or none toxic

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reagents and eliminating optical interference caused by turbidity or salinity in solutions.

In most of previous GPMAS works [3,7,8], after the addition of hydrochloric acid to acidify the sample, a gaseous mixture, consisting of the main component NO, the minor components NO_2, HNO_2 and NOCl, is produced and purged into an AAS or a UV–VIS detector. However, since the absorption cross section of NO at deep-UV range is low, the detector sensitivities are not high enough for the determination of nitrite in some nature waters and the limits of detection (LODs) are usually at 0.2–7.5 mg/L (4–163 μmol/L). An improved method for rapid converting nitrite to NO_2 has been proposed by Zang [24]. It is found that via adding some organic solvents, such as methanol, ethanol and formaldehyde, to the acidified sample solution, the nitrite ion will decompose rapidly, and NO_2 becomes the main compound in the produced gaseous mixture. The possible chemical reactions among nitrite, citric acid and organic solvent (usually using ethanol) are given as follows [24]:

$$2NO_2^- + 2H^+ \rightarrow NO_2 + NO + H_2O \quad (1)$$

$$2NO + O_2 \rightarrow 2NO_2 \quad (2)$$

The ethanol is as the catalyst to accelerate the nitrite decomposition and the conversion of NO to NO_2. Utilizing the benefit of the high absorption cross section of NO_2 at 200–300 nm, the sensitivity of GPMAS method is greatly improved. With a detection wavelength at 213.9 nm, a LOD of 0.7 μg/L (0.015 μmol/L) can be obtained. However, labor-intensive manual operation is needed [24], and an AAS detector of relatively high price and energy consumption is applied.

In this work, an automatic system with GPMAS based on the flow analysis technique has been developed for nitrite and total nitrate determination. The operation process for nitrite detection involved (i) mixing the sample solution with none hazardous reagents, citric acid and ethanol; (ii) purging the produced gaseous mixture with air; (iii) passing the gas through a column filled with magnesium perchlorate to remove water; and (iv) detecting the absorbance of the gaseous mixture with an UV-LED photodiode (UV-LED-PD) based photometric detector. The nitrate could also be measured as nitrite by passing the sample solution through a copperized cadmium column to reduce nitrate to nitrite. The proposed method was used to analyze some environmental water samples with complex matrices.

2. Experimental

2.1. Reagents and solutions

All the chemicals and reagents were analytical reagent grade or higher, and supplied by Sinopharm Chemical Reagent Co., China, unless stated otherwise. All solutions were prepared with deionized water of 18.2 MΩ. Nitrite and nitrate stock solutions (both at 100 mmol/L) were prepared from sodium nitrite and potassium nitrate, respectively, which were dried at 105 °C for 1 h, and stored at 4 °C while not in use. Working standards were obtained by appropriate dilution of the stock solutions daily. A citric acid solution of 0.3 mol/L was prepared daily by dissolving 15.8 g of citric acid monohydrate in deionized water and diluted to 250 mL. Deionized water was used as the carrier solution.

For detection of total nitrite and nitrate, an ammonium chloride buffer solution of 25% (m/v) was prepared by dissolving 125 g of ammonium chloride in 500 mL water, and the pH of the solution was adjusted to 8.5 with ammonia solution. The buffer solution of 10 mL was added to every 100 mL of sample for the determination of nitrate prior to instrumental measurement. An ammonium chloride solution of 2.5% (m/v) with pH at 8.5 was prepared for on-line to clean up the cadmium reduction column, which were prepared as described in our previous work [25]. Briefly speaking, cadmium granules (40–60 mesh, GFS Chemicals, Inc., U.S.A.) were copperized with copper sulfate solution. Then 12 g of copper coated cadmium granules were filled in a glass column of 15 cm in length and 4 mm in inner diameter (i.d.), and each end of the glass column was plugged with some glass wool. The reduction efficiencies were over 90% within the study. The reduction efficiency was obtained with comparing the analytical results of a nitrate standard solution and a nitrite solution of the same concentration. Some nitrite samples were measured in both pass and bypass the cadmium column ways to check if there was an overreduction of nitrite, and the result showed no overreduction under the optimized condition. After 300 times measurement, the reduction efficiency could still be maintained at over 90%. This meant that the reduction column could be used for at least 300 times.

2.2. UV-LED-PD detector

The UV-LED-PD based detector is composed of the following parts. A black polyvinyl chloride (PVC) tube with 14 cm in length and 10 mm in i.d. was used as the gas flow cell. Two metal connectors were fixed at the perpendicular direction of the PVC tube at each end as the gas flow inlet and outlet. An UV-LED (UVTOP255-TO39BL, $\lambda = 255$ nm, full width at half-maximum = 12 nm, o.d. = 9.2 mm, Sensor Electronic Technology, Inc., U.S.A.) was jacketed with a piece of 6 mm silicone pump tube (6.4 mm i.d., 2.5 mm wall thickness, Baoding Longer Precision Pump Co., China), then forcibly inserted into one end of the PVC tube. An integrated photodiode amplifier (OPT301, Burr-Brown, U.S.A.) was jacketed with a piece of 3 mm silicone pump tube and inserted into the other end of the PVC tube. The sealing was double checked before instrumental analysis to make sure no gas leakage from the connections. The whole photometric detection module was shielded with a black PVC box to protect ambient light.

The UV-LED was driven by an adjustable constant voltage source (Long Wei Instruments Co., China) with 25 mA current. The output voltage of the photodiode was further amplified by an amplifier (AD706, Analog Devices, Inc., U.S.A.), and then the A/D conversion was operated with a data acquisition card (USB-6009, National Instruments Co., U.S.A.). The light intensity was converted to absorbance (A) according to the equation, $A = \log (I_0 - I_d)/(I - I_d)$, where I_0 was the intensity in mV when the flow cell was filled with air carrier, I_d was the dark response when the LED was turned off, and I was the monitored light intensity of the analyte. The concentrations of analytes were evaluated from the peak heights with the calibration curve obtained from the standards.

2.3. Automatic GPMAS system

Fig. 1 shows the flow manifold setup of the automatic GPMAS system. A syringe pump (SP) (NE-50X, New Era Pump Systems, Inc., U.S.A.) equipped with a 10 mL syringe (Gastight, Hamilton Co., U.S.A.) was used as the liquid driver, and an 8-position selection valve (SV) (C25Z-3188EMH, VICI, Valco Instruments Co., Inc., U.S.A.) used as a reagent and sample selector. A gas generation reactor (GGR) was adapted with a 50 mL centrifuge tube (Labcon Co., U.S.A.) via drilling holes at both bottom and cap as outlet and inlet, and line tubings were fixed to the holes with fittings and adhesive. As shown in Fig. 1, there are two gaseous and two liquid lines connecting to the GGR. A tubing for sample and solution delivery entered from the top of the GGR and reached to the bottom. A solution exit was connected the GGR bottom to a peristaltic pump (PP) (Baoding Longer Precision Pump Co., China) that was used to draw the reacted solution to waste. An air pump (AP) (Hailea Co., China) was applied to supply the carrier gas, which was metered by a mass flow controller (MFC) (Keda Yibiao Co., China) within the range 0–1.0 L/min. The

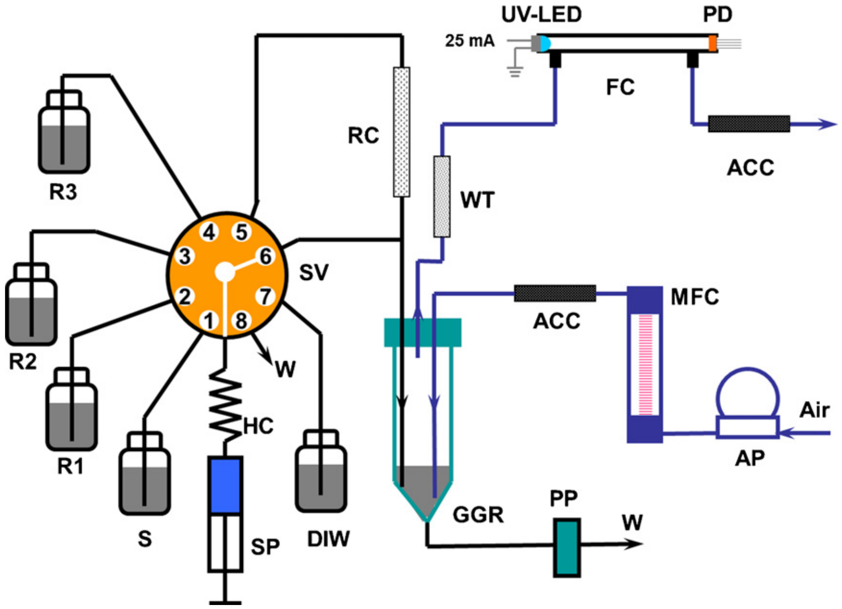

Fig. 1. Schematic diagram of the GPMAS system. S, sample or standard; R1, 0.3 mol/L citric acid; R2, ethanol; R3, 2.5% (m/v) NH_4Cl; DIW, deionized water; W, waste; HC, holding coil; SP, syringe pump; SV, 8-position selection valve; RC, Cd reduction column; GGR, gas generation reactor; PP, peristaltic pump; AP, air pump; MFC, mass flow controller; ACC, activated carbon column; WT, water trap; FC, flow cell; PD, photodiode.

carrier should pass through a column (ACC) filled with activated carbon for removing the possible impurities previous to enter the GGR. A column (WT) of 6.8 cm in length and 10 mm in i.d. filled with 4.5 g magnesium perchlorate was inserted between the GGR and the UV-LED-PD detector to trap aqueous droplet that would cause light refraction in the detection cell. Another ACC was connected to the outlet of the detector to adsorb the produced NO_2. The aforementioned reduction column (RC) was used to reduce nitrate to nitrite.

All tubings for sample and solutions were made of fluorinated ethylene propylene (FEP, 1.59 mm o.d., 0.75 mm i.d.). The holding coil (HC) volume was 5 mL. All gaseous conduit tubings were made of polyethylene (3.18 mm o.d., 2.1 mm i.d.) or polytetrafluoroethylene (PTFE, 1.6 mm o.d., 1.0 mm i.d.). The syringe pump was communicated with a laptop computer via an RS232 serial port, and the control of SV, PP and AP was achieved via the aforementioned data acquisition card. The software for GPMAS system control and data acquisition and processing was written with the LabVIEW program (National Instruments Co., U.S.A.).

2.4. System operation

To deliver the liquid solution, the SP aspirated solution into the HC and then propelled it out. Since all the delivered solution volumes were at mL level in this study, the diffusion within the small bore tubing of the HC could be neglected.

The operational procedure for nitrite measurement is explained in Table 1. The SP was set to sequentially provide 5 mL sample, 3 mL citric acid solution and 2 mL ethanol into the GGR through position 6 of the SV, and then the produced gas was purged by the AP for 2.5 min at a rate of 200 mL/min into the detector. Once the purging step was completed, the reacted solution in the GGR was discharged via the PP to waste. At the end of each analysis cycle, 10 mL of deionized water was used to wash the GGR, and the residual gas was cleaned up with the AP running for 1 min. The analytical rate for nitrite was 9 min/sample.

To buffer the sample for the measurement of nitrate plus nitrite, 25% (m/v) ammonium chloride buffer solution should be manually added into sample at a volume ratio of 1:10 (buffer:sample) before instrumental analysis. The system operational procedure is shown in Table 2. At first, 5 mL testing solution for the measurement of nitrate plus nitrite was driven at 8 mL/min to rinse the RC through position 5 of the SV, and the waste solution was discharged from the GRR. Another 5 mL of testing solution was passed through the RC at a rate of 8 mL/min, where nitrate was reduced to nitrite. Thereafter, the following processes were the same as those for nitrite measurement. Except for the cleanup of the GGR and gaseous tubing with water and air, the RC was washed with 5 mL 2.5% (m/v)

Table 1
The operational procedure for the determination of nitrite.

Step	SP operation	Flow rate (mL/min)	SV position	AP	PP	Comment
1	Aspiration 2.5 mL	8	1-S	Off	Off	Adding 5.0 mL sample into the GGR
2	Propulsion 2.5 mL	8	6-GGR	Off	Off	
3	Aspiration 2.5 mL	8	1-S	Off	Off	
4	Propulsion 2.5 mL	8	6-GGR	Off	Off	
5	Aspiration 3.0 mL	8	2-R1	Off	Off	Adding 3.0 mL citric acid into the GGR
6	Propulsion 3.0 mL	8	6-GGR	Off	Off	
7	Aspiration 2.0 mL	8	3-R2	Off	Off	Adding 2.0 mL ethanol into the GGR
8	Propulsion 2.0 mL	8	6-GGR	Off	Off	
9	Propulsion 2.5 mL	1	8-W	On	Off	Purging produced gas and cleaning up the HC
10	Aspiration 7.5 mL	8	7-DIW	On	On	Aspirating DIW and discharging reacted solution to waste
11	Propulsion 10.0 mL	8	6-GGR	Off	Off	Washing the GGR with DIW
12	Aspiration 5.0 mL	5	7-DIW	On	On	Conditioning system for next sample

Table 2
The operational procedure for the determination of nitrate plus nitrite.

Step	SP operation	Flow rate (mL/min)	SV position	AP	PP	Comment
1	Aspiration 2.5 mL	8	1-S	Off	Off	Rinsing the RC with 5.0 mL sample
2	Propulsion 2.5 mL	8	5-RC	Off	Off	
3	Aspiration 2.5 mL	8	1-S	Off	On	
4	Propulsion 2.5 mL	8	5-RC	Off	On	
5	Aspiration 2.5 mL	8	1-S	Off	Off	Collecting the RC passed sample
6	Propulsion 2.5 mL	8	5-RC	Off	Off	
7	Aspiration 2.5 mL	8	1-S	Off	Off	
8	Propulsion 2.5 mL	8	5-RC	Off	Off	
9	Aspiration 3.0 mL	8	2-R1	Off	Off	Adding 3.0 mL R1 into the GGR
10	Propulsion 3.0 mL	8	6-GGR	Off	Off	
11	Aspiration 2.0 mL	8	3-R2	Off	Off	Adding 2.0 mL ethanol into the GGR
12	Propulsion 2.0 mL	8	6-GGR	Off	Off	
13	Propulsion 5.0 mL	2	8-W	On	Off	Purging produced gas and cleaning up the HC
14	Aspiration 5.0 mL	6	7-DIW	On	On	Discharging reacted solution to waste and conditioning system
15	Aspiration 2.5 mL	8	4-R3	Off	Off	Washing the RC with 2.5% (m/v) NH_4Cl and discharging solution to waste
16	Propulsion 2.5 mL	8	5-RC	Off	Off	
17	Aspiration 2.5 mL	8	4-R3	Off	Off	
18	Propulsion 2.5 mL	8	5-RC	Off	On	
19	Propulsion 3.0 mL	8	8-W	On	On	Cleaning up the HC
20	Aspiration 7.0 mL	8	7-DIW	Off	Off	Conditioning system
21	Propulsion 10.0 mL	8	6-GGR	Off	Off	Washing the GGR with DIW
22	Aspiration 6.0 mL	8	7-DIW	On	On	Conditioning system for next sample

ammonium chloride solution for the next run. The analytical rate for nitrate was 12 min/sample.

2.5. Measurement of spectrum of gas phase

To scan the absorption spectrum of the gaseous mixture, the UV-LED-PD based detector was replaced with a quartz flow cell of 5 cm in path length and 1.8 cm in i.d. A deuterium lamp (D-2000, Ocean Optics, Inc., U.S.A.) and a high-resolution spectrometer (HR4000, Ocean Optics, Inc., U.S.A.) were used as the light source and detector, respectively. With the GPMAS system operating in a nitrite determination procedure, the absorption spectrum of the produced gas was obtained.

2.6. Application to environmental and reference samples

A seawater sample with salinity at 35 was collected from the South China Sea and stored in a polypropylene bottle. The tap water sample was collected in our laboratory. The urban sewage sample was obtained from the outlet of a wastewater treatment plant in Xiamen. The river water sample was collected from Pearl River in Guangzhou City. The mineral water was purchased from local market. A nutrient solution was the one prepared for mangrove culture in our laboratory, by adding ammonium nitrate, potassium phosphate, zinc sulfate, copper sulfate, and iron EDTA into artificial seawater with a salinity of 15.

The reference materials were purchased from Shanghai Institute of Measurement and Testing Technology (Shanghai, China). The nitrite concentration of the reference material (GBW(E)080096) was 20.00 ± 1.10 mg/L and nitrate (GBW(E)080093) was 20.00 ± 0.37 mg/L.

Each environmental sample was filtered through a 0.45 μm pore size membrane before analysis. The recovery test was operated by adding a mixture of the nitrite and nitrate standards, or adding both standards, respectively, into the sample.

3. Results and discussion

3.1. Design of the UV-LED-PD photometric detector

The mono-chromaticity of the solid state light source should be taken into account when a UV-LED-PD detector is designed. It has been pointed out [13] that there are some significant parasitic emission bands within 400–500 nm in the emission spectrum of 255 nm UV-LED. Thus, a compromised linearity could be obtained. The emission spectrum of the UV-LED used in this study is shown in the inset of Fig. 2. Different from the previous report, however, no significant parasitic emitted light was observed, probably due to the difference between LED batches. Because of the appropriate mono-chromaticity of the UV-LED, no filter was used in this study.

Initially, a quartz flow cell of 5 cm path length and 1.8 cm i.d. was used as the gas flow cell. The large volume and short path length of this flow cell led to a lower sensitivity. Then the quartz flow cell was replaced with a 14 cm length PVC tube with longer path length and smaller volume, and the sensitivity about 2.5 times higher was obtained. To simplify the optical design, no condensing lens was used in this windowless detector. However, to measure the emitted light of the UV-LED at relatively low optical power output, a sensitive detector should be equipped. The photodiode, OPT301, with sufficient response from 250 to 1000 nm, was chosen. Although a path length of 14 cm could be too long to apply to solution detection, it fitted the analysis of the produced gas, and the transmitted

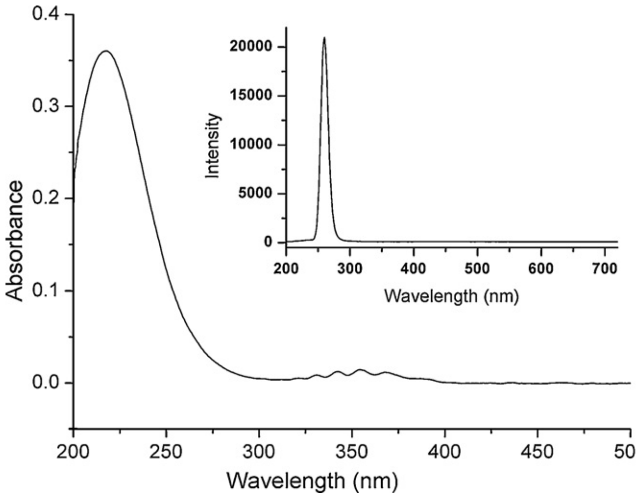

Fig. 2. Gas absorption spectrum of the produced gaseous compound, and emission spectrum of the UV-LED (inset). Nitrite concentration, 10 mmol/L; reference, air.

Table 3
Comparison of the performance characteristics for the determination of nitrite and nitrate using on-line methods.

Analyte	Determination method	Analytical range	LOD	RSD (%)	Ref.
Nitrite	FIA with gas phase molecular absorption UV spectrophotometric detection	Up to 1000 mg/L or 1000–2000 mg/L	7.5 mg/L	3.7 and 1.0	[8]
Ammonium	FIA with gas phase molecular absorption	10–650 mg/L	8 mg/L	2.0	[9]
Nitrate	Reduced to ammonium by copperized zinc column	20–800 mg/L	10 mg/L	2.9	
Nitrite	SIA and spectrophotometric detection	Total nitrite plus nitrate up to 400 μmol/L	0.07 mg/L	1.5	[17]
Nitrite	Reduced to nitrite by hydrazine		0.2 mg/L	3.1	
Nitrate	FIA with amperometric detection	0.1–2.5 mmol/L	4.2 μmol	4.7	[20]
Nitrite	FIA with spectrophotometric detection	0.05–1.6 mg/L	22 μg/L	0.96	[19]
Nitrate	Reduced to nitrite by copperized cadmium	0.05–7.0 mg/L	44 μg/L	1.02	
Nitrite	HPLC with chemiluminescence detection	0.002–2.5 μmol/L	2 nmol/L	2.6	[21]
Nitrate	Reduced to nitrite by post-column photochemical reaction	0.02–25 mmol/L	10 nmol/L	1.2	
Nitrite	Multi-pump system with spectrophotometric detection	Up to 3 mg/L	13 μg/L	0.5	[18]
Nitrate	Reduced to nitrite by hydrazine	0.039–7 mg/L	39 μg/L	1.5	
Nitrite	On-line solid phase extraction with spectrophotometric detection	2–100 nmol/L	0.3 nmol/L	3.6	[25]
Nitrate	Reduced to nitrite by copperized cadmium	5–200 nmol/L	1.5 nmol/L	4.3	
Nitrite	Gas phase molecular absorption UV spectrophotometric detection	0.021–5 mmol/L	7 μmol/L	1.81	This method
Nitrate	Reduced to nitrite by copperized cadmium	0.036–4 mmol/L	12 μmol/L	1.08	

light intensity could be measured via the photodiode coupled with multi-stage amplification.

3.2. Absorption spectrum of the analyte

The absorption spectrum of the produced gaseous compound is shown in Fig. 2. Comparing with the works of other researchers [8,13], where the absorption spectra of gaseous products including NO, NO_2, NOCl, HNO_2 and HCl are observed, and a relatively weak absorption band with 4 sharp peaks is found in the range of 195–250 nm, the spectrum of this study was quite different. In Fig. 2, there is a distinctive peak in the range 200–300 nm with a maximum absorption at 217 nm, corresponding to NO_2, via scanning and comparing the spectrum with those of the standard gases [24]. The reason of the difference could be the addition of ethanol as a catalyst, which might cause the different gaseous products.

The maximum emission wavelength of the UV-LED was found at 255 nm, where was the tail position for the absorption peak of the produced gas compound. In other words, the sensitivity of the proposed method could be lower. However, the nitrite and nitrate concentrations are relatively high in urban sewage samples, industrial and agricultural waters, so that these samples usually need be diluted sever times before assay. To fit for direct measurement of these samples, a less sensitive wavelength could be chosen. To our best knowledge, among commercially available UV-LEDs, the 255 nm one has the lowest wavelength. If UV-LEDs with farther ultraviolet light emission are available in near future, the sensitivity of this method could be greatly improved.

3.3. Measurement of nitrite

The reaction parameters affecting the nitrite measurement, including citric acid concentration, sample-to-reagent volumetric ratio, sample volume, reaction time, gas flow rate, as well as sample and reagent loading flow rate were studied and optimized with the concern of the sensitivity and sample throughput. The parameters' optimization was operated by measuring nitrite and nitrate at 2 mmol/L. Each experiment was conducted in triplicate.

(i) The effect of citric acid concentration was investigated in the range 0–0.5 mol/L. The result showed that the peak height was about constant within the range 0.1–0.5 mol/L, and a citric acid concentration of 0.3 mol/L was thus chosen. (ii) After the investigation of optimal volume ratio of sample:citric acid:ethanol with a univariate method, a volumetric ratio of sample:citric acid:ethanol of 5:3:2 was chosen. (iii) Maintaining this ratio, different sample volumes varying from 1.25 to 7.5 mL were assayed. It was found that a larger sample volume led to higher peak height, longer analysis time and wider signal peak. A sample volume of 5 mL was adopted. (iv) It was noticed that the nitrite could converse to NO_2 very quickly; therefore, right after the ethanol addition, the purge step should be performed. (v) The gas flow rate was tested in the range 100–400 mL/min. It was observed that a lower gas flow rate led to higher sensitivity, but longer analysis time and wider signal peak. If a flow rate of 100 mL/min was used, the width of the analytical peak would be prolonged to 5 min. If the flow rate was 200 mL/min, the peak width was 2.5 min. Therefore, a gas flow rate of 200 mL/min was chosen, as a compromise between determination speed and sensitivity. (vi) The flow rate of sample and reagent loading into the GGR was investigated from 4 to 8 mL/min, and no significant variation was found. To get a higher sample throughput, 8 mL/min was chosen as it was the largest flow rate could be obtained with SP.

According to the chemical reactions (1) and (2), oxygen in the purging gas might help the reaction. The results of using pure nitrogen gas or air as the purging gas had been compared. It was found that the absorbance obtained with pure nitrogen was 15% lower that with air, indicating the oxygen in purging gas could enhance the sensitivity.

3.4. Measurement of nitrate plus nitrite

Initially in the study, to avoid using toxic cadmium in the detection of nitrate, a photoreduction approach was attempted to reduce nitrate to nitrite. A low pressure mercury lamp of 30 W was used as the photoreduction light source and diethylene triamine pentaacetic acid (DTPA) as the catalyst. Although a maximum reduction efficiency of 50% was obtained for 10 mmol/L nitrate standard solution, a nonlinear behavior of the nitrate standard series at mmol/L level was found. Moreover, the photoreduction efficiency was easily influenced by foreign ions. Therefore, the traditional copper coated cadmium column was finally adopted. The nitrate reduction reaction is well known, and has been mentioned in many references [22,26].

$$NO_3^- + Cd + 2H^+ \rightarrow NO_2^- + Cd^{2+} + H_2O \qquad (3)$$

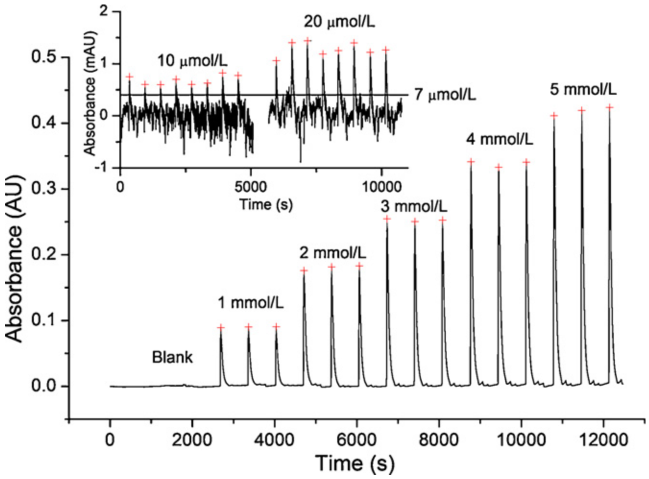

Fig. 3. Typical output signal of GPMAS system with nitrite standards. The tested nitrite were 0, 1, 2, 3, 4 and 5 mmol/L ($n = 3$), as well as 10 and 20 μmol/L ($n = 8$, inset). The line in inset represented the average peak height of 7 μmol/L, that is, the LOD value of the proposed method.

The suitable pH range for this reaction is 8.0–8.5 with higher than 90% reduction efficiency, compromising the risks of overreduction and metal precipitation [26]. The buffer solution with pH at 8.5 was chosen because it offered a relatively high buffer capacity. Even in a wider pH range (6.5–9.0), the reduction process could be operated. Considering to limit the dilution of sample by the buffer solution, a concentrated ammonium chloride solution (25% m/v) was used. After adding 10 mL of the buffer into 100 mL sample, the ammonium chloride concentration in sample was 2.3% (m/v). It was found that 10 mL 25% (m/v) ammonium chloride solution was capable to buffer 100 mL samples in complex matrix.

The flow rate for the reduction procedure was investigated from 2 mL/min to 8 mL/min. When the flow rate was too slow, an overreduction would happen, leading to low reduction efficiency. The reduction efficiency was increased with increasing flow rate. When the flow rate was higher than 6 mL/min, the reduction efficiency would keep constant. A flow rate for the reduction procedure of 8 mL/min was adopted. At this flow rate, reduction efficiency over 90% could be obtained, and the reduction approach was highly tolerable to foreign species interference.

Table 4
Interference of common ions on the determination of 2 mmol/L nitrite and nitrate (test, respectively).

Interference compound	Added concentration (mmol/L)	Nitrite recovery (%)	Nitrate recovery (%)
KCl	500	99.0	103.3
NaCl	500	98.4	97.3
$CaCl_2$	100	98.4	95.0
KBr	100	99.7	98.3
$MgSO_4$	100	97.6	91.0
$MgSO_4$	10	100.0	100.3
KNO_3	100	100.0	–
NH_4Cl	100	98.5	95.7
NaF	100	88.1	90.8
NaF	10	95.9	99.7
KI	100	24.9	33.6
KI	10	88.3	92.9
Na_2HPO_4	100	74.1	40.4
Na_2HPO_4	10	100.1	41.9
$NaHCO_3$	100	86.4	95.4
$NaHCO_3$	10	103.5	101.3
Na_2SO_3	10	60.0	48.7

Table 5
Determination of nitrite and nitrate in water samples with the proposed and reference methods [23].

Sample	Nitrite added[a] (mmol/L)	$[NO_2^-] \pm SD$ (mmol/L)		RD (%)	Nitrite recovery (%)	Nitrate added[a] (mmol/L)	$[NO_3^-] \pm SD$ (mmol/L)		RD (%)	Nitrate recovery (%)
		Proposed method ($n = 3$)	Reference method				Proposed method ($n = 3$)	Reference method		
Sea water	–	ND[b]	ND	–	–	–	ND	ND	–	–
	0.5	0.526 ± 0.013	0.517	+1.77	105.3	1.0	1.091 ± 0.010	1.033	+5.62	109.1
	1.0	1.003 ± 0.019	1.006	−0.30	100.3	2.0	2.074 ± 0.040	1.904	+8.91	103.7
Tap water	–	ND	ND	–	–	–	0.142 ± 0.004	0.139	+1.68	–
	0.5	0.510 ± 0.015	0.507	+0.53	101.9	1.0	1.187 ± 0.028	1.135	+4.53	104.5
	1.0	1.015 ± 0.014	1.006	+0.91	101.5	2.0	2.140 ± 0.027	2.006	+6.67	99.9
Urban sewage	–	ND	0.004	–	–	–	1.603 ± 0.014	1.674	−4.01	–
	1.0	1.022 ± 0.007	0.996	+2.62	102.2	1.0	2.651 ± 0.066	2.601	+2.08	104.8
	2.0	2.048 ± 0.013	2.035	+0.66	102.4	2.0	3.723 ± 0.141	3.604	+3.42	106.0
Nutrient solution	–	ND	<0.001	–	–	–	14.21 ± 0.18	13.50	+5.36	–
	1.0	0.955 ± 0.027	0.971	−1.65	95.5					
	2.0	1.941 ± 0.038	2.040	−4.81	97.1					

[a] The nitrite and nitrate standards were added, respectively.
[b] ND, not detected.

Table 6
Recoveries of mixture standards nitrate and nitrite from water samples with the proposed GPMAS method.

Sample	Mixture standard added (mmol/L)		Found (mmol/L, *n* = 3)		Recovery (%)	
	Nitrite	Nitrate	$[NO_2^-] \pm$ SD	$[NO_3^-] \pm$ SD	Nitrite	Nitrate
Seawater	–	–	ND	ND	–	–
	0.5	1.0	0.493 ± 0.007	0.984 ± 0.014	98.6	98.4
	1.0	2.0	0.980 ± 0.019	2.021 ± 0.030	98.0	101.1
Tap water	–	–	ND	0.200 ± 0.001	–	–
	0.5	1.0	0.488 ± 0.024	1.239 ± 0.016	97.6	103.9
	1.0	2.0	0.964 ± 0.063	2.179 ± 0.015	96.4	98.9
River water	–	–	ND	0.112 ± 0.001	–	–
	0.5	1.0	0.512 ± 0.008	1.120 ± 0.034	102.4	100.8
	1.0	2.0	0.995 ± 0.025	2.018 ± 0.055	99.5	95.3
Mineral water	–	–	ND	0.063 ± 0.009	–	–
	0.5	1.0	0.511 ± 0.011	1.083 ± 0.010	102.2	102.0
	1.0	2.0	0.986 ± 0.006	2.020 ± 0.026	98.6	97.8

ND, not detected.

3.5. Analytical performance

Under the optimized experimental conditions described above, the limit of detection (LOD) was 7 μmol/L and 12 μmol/L for nitrite and nitrate, respectively. The LODs were estimated from that three times the standard deviations of the 10 μmol/L nitrite and 20 μmol/L nitrate ($n = 8$), then divided by their calibrations' slopes, respectively. Standard deviation of the blank was not used for calculation, because the blank value was essentially zero with a very low standard deviation. The LODs were lower than the corresponding maximum limits of the compounds in drinking water regulated by WHO [16], indicating the potential application of the proposed method to drinking water analysis.

The calibration curves were prepared by measuring nitrite standard at concentrations of 0, 0.5, 1, 2, 3, 4 and 5 mmol/L, and nitrate at concentrations of 0, 0.5, 1, 2, 3 and 4 mmol/L, under the optimized conditions. The regression equation for nitrite was Absorbance = 8.31×10^{-2} $[NO_2^-]$ (mmol/L) + 0.0054 ($r = 0.9995$) with a liner range of 0.021–5 mmol/L, and the equation for nitrate was Absorbance = 7.88×10^{-2} $[NO_3^-]$ (mmol/L) + 0.0028 ($r = 0.9994$) with a liner range 0.036–4 mmol/L. The precision presented as relative standard deviation (RSD) was 1.81% and 1.08% for nitrite and nitrate, respectively, with both concentrations at 2 mmol/L ($n = 10$). The sample throughput rates were 6/h and 5/h for nitrite and nitrate, respectively. A typical output signal of nitrite standards of 0–5 mmol/L is shown in Fig. 3. The inset of Fig. 3 shows the response signal of eight measurements of 10 and 20 μmol/L nitrite standards. Table 3 shows a comparison of the performance characteristics using the present method with those of some previously reported on-line methods.

3.6. Interferences

The effects of some major ions existing in environmental waters on the nitrite and nitrate detection was studied. Tested concentrations of foreign ions were higher or at least equal to their concentrations in most natural waters.

Table 4 shows the results. Up to 500 mmol/L of Na^+, K^+, NH_4^+ and Cl^-, 100 mmol/L of Mg^{2+}, Ca^{2+}, NO_3^- and Br^-, and 10 mmol/L of HPO_4^{2-} and HCO_3^-, resulted in <±5% error for the measurement of 2 mmol/L nitrite. When 10 mmol/L of SO_3^{2-} and I^-, as well as 100 mmol/L of HCO_3^-, F^- and HPO_4^{2-} were, respectively, added into the sample, errors higher than 10% were found. However, these anions are usually present at μmol/L level in most natural waters, therefore, their influence can be ignored in most cases.

For nitrate measurement, more attention was paid on the reduction procedure. The pHs of all the collected samples and mixed buffer solutions for the study of foreign ion interference were assayed in the range 8.37–8.56, indicating 10 mL of 25% (m/v) ammonium chloride solution was capable to buffer the samples with high concentration of foreign components. As shown in Table 4, the cadmium column reduction is seriously affected by HPO_4^{2-}. According to the work of other researchers [26], some other effecting factors of reduction efficient of cadmium column include adsorption of high molecular organic matters on the surface of the cadmium material and the poison of some deposited metals. Thus, the sample should be filtered before analysis to remove particles and high molecular organic matters. On the other hand, the capacity of buffer solution should be large enough to control the pH value to avoid the hydrolysis of metal ions. In some cases, chelating agent, such as Na_2-EDTA, can be added to samples to eliminate the metal hydrolysis.

3.7. Validation and application of the method

The Greiss based methods [23] were used as references for comparison with the proposed GPMAS method. The samples were spiked and analyzed with both proposed and reference methods. Each sample was filtered through a 0.45 μm pore size membrane before analysis. The results in Table 5 show the relative deviations (RDs) of both methods were lower than 4.81% for nitrite and lower than 8.91% for total nitrate and nitrite. Recovery results shown also in Table 5, ranging within 95.5–109.1%, indicated that no significant matrix interference was observed for nitrite and total nitrate determination. The proposed method was highly tolerable to complex foreign components.

The nitrite reference sample (GBW(E)080096, 20.00 ± 1.10 mg/L nitrite) and nitrate reference sample (GBW(E)080093, 20.00 ± 0.37 mg/L nitrate) were analyzed using the proposed method, and the obtained results were 20.07 ± 0.15 mg/L and 20.44 ± 0.03 mg/L, respectively. It showed that the results had no significantly different from the reference values.

Real water samples were spiked with nitrite and nitrate mixture standards. The results are shown in Table 6, and the recoveries for nitrite and nitrate were found to be in the range 95.3–102.4%.

4. Conclusion

In summary, the study results showed that the GPMAS method could be applied to the determination of nitrite and nitrate in environmental water samples. The UV-LED-PD based detector was compact, robustness, simple and of low heat production. With the introduction of this kind of detectors, some on-field or portable analytical instruments can be realized. In terms of the UV-LED wavelength, with the rapid development of solid state light technology, it is expected that a new generation of UV-LED with farther ultraviolet emission light wavelength will be available in the near future, and wider analytical application should be developed.

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