Journal of the Iranian Chemical Society, Vol. 2, No. 4, December 2005, pp. 305-314.

JOURNAL OF THE
Iranian
Chemical Society

A Chemiluminescence Flow Injection System for Nitrite Ion Determination

M.K. Amini*, M. Pourhossein and M. Talebi
Chemistry Department, University of Isfahan, Isfahan 81746-73441, Iran

(Received 10 January 2005, Accepted 2 October 2005)

A chemiluminescence system is described for the determination of nitrite ion based on new designs for an ozone generator, liquid-gas separator and chemiluminescence reaction cell. The method is based on the gas-phase chemiluminescence reaction between ozone and nitric oxide, which is generated from the reduction of nitrite with iodide in sulfuric acid solution. The efficiency of the system was evaluated by investigation of the analytical performance characteristics of the system for nitrite determination in batch and flow injection procedures. Under optimal conditions, the chemiluminescence response of the system was linear against the nitrite concentration over the range 1 to 1×10^4 ng ml^{-1} in the batch procedure and 10 to 5×10^3 ng ml^{-1} in the flow injection procedure, with detection limits of 1 and 10 ng ml^{-1}, respectively. The method is highly selective and allows for the determination of nitrite in the presence of high concentrations of several cationic, anionic and nitrogen containing species. It has been successfully applied to the analysis of nitrite in natural water and soil extracts.

Keywords: Chemiluminescence, Liquid-gas separator, Nitrite, Nitric oxide, Water analysis, Ozone generator

INTRODUCTION

Due to the toxic nature of nitrite and its environmental and biological impacts, the determination of its concentration in water, the atmosphere, food and other materials is of great importance for environmental protection, food assurance, and quality control. Most health authorities, worldwide, have recognized the necessity for nitrite monitoring with legislation often levied on permissible levels in drinking water. At present, the maximum contaminant level for nitrite in drinking water is 1 μg ml^{-1} [1]. Excessive concentrations of nitrite in drinking water could be a health hazard, because of its interactions with blood pigments that may result in methemoglobinemia and the potential for the conversion of nitrite to carcinogenic nitrosamines [2,3]. Further, biologically active levels of nitrite *in vivo* can be converted to nitric oxide [4], which plays a pivotal role in numerous physiological processes [5].

Among various methods that have been reported for the determination of nitrite, chemiluminescence-based methods are of great importance for environmental monitoring, water analysis and other applications where the determination of trace amounts of nitrite, or its related compounds, is needed [6-19]. Chemiluminescence, as one of the most sensitive detection methods, offers a wide linear range, low detection limit, simple and inexpensive instrumentation and very short analysis time [20]. There are numerous reports published regarding the importance of chemiluminescence methods [21-24] and their application in the determination of a wide variety of compounds including organic [25-27], inorganic [28-30], biological [31-35], and pharmaceutical [36-41] compounds in different samples.

The chemiluminescence methods reported for nitrite determination are generally based on liquid-phase or gas-

*Corresponding author. E-mail: mkamini@sci.ui.ac.ir

phase procedures. The liquid-phase methods generally suffer from interference by a large number of other species that are commonly found in real samples [15-19]. Gas-phase chemiluminescence methods are based on the reduction of nitrite to nitric oxide (NO), which is stripped from the solution and detected *via* its chemiluminescence reaction with ozone, and as such, offer much higher selectivity compared to the liquid-phase methods. However, gas-phase chemiluminescence requires additional devices such as an ozone generator and liquid-gas separator (LGS), and thus more control over the experiment is required. Various methods have been used for the reduction of nitrite and separation of the resulting NO from the liquid-phase [6-13], but the detection of NO in all of these reports has been made with commercial analyzers. It must be noted that mixing of the reactants in the reduction step and separation of NO from the liquid-phase by a fast, efficient and reproducible method is very important, because they strongly affect the sensitivity, precision and detection limit of the measurement. Methods such as flushing the reaction flask with an inert gas [10-12,42,43], using concentric tubes of microporous PTFE membrane [9,13,44] and glass column separators [8] have been proposed for the separation of NO. Here, we were interested in designing a simple and highly efficient LGS that could also be used for the reduction reaction of nitrite in the batch mode. Further, we were also interested in building simple, small-volume devices for ozone generation and a chemiluminescence reaction chamber (flow cell) that could be assembled very easily and cheaply from the components generally found in any laboratory.

The present work describes the design and construction of a chemiluminescence system involving an ozone generator, liquid-gas separator (LGS), flow cell and detection system for the measurement of nitrite based on its reduction with iodide ion in an acidic medium. This study had three primary objectives: (a) to test the performance of the newly designed LGS and the suitability of the ozone generator for chemiluminescence determination of nitrite ion; (b) to investigate the influence of several operating parameters with regard to the response of the detection system and to obtain analytical parameters including sensitivity, linear range, detection limit, precision, accuracy and the overall performance of the proposed system for nitrite determination; (c) to investigate the influence of diverse species on nitrite determination *via* gas-phase chemiluminescence.

EXPERIMENTAL

Reagents and Chemicals

All of the chemicals used were of analytical-reagent grade from Merck, without further purification. Reagent solutions were prepared with distilled, deionized water. The stock standard solution of 1×10^3 μg ml^{-1} nitrite ion was prepared in water from sodium nitrite, already dried at 110 °C. The working standard solutions were freshly prepared by diluting the stock solution to the appropriate concentrations. A solution of 0.5 M sodium iodide in 0.5 M sulfuric acid was used as the reducing reagent in the batch procedure. Solutions of both iodide and sulfuric acid (each 0.1 M) were prepared separately for the flow injection measurements. Solutions used for the investigation of the effect of diverse species were prepared from chloride or sulfate salts of cationic species and sodium salts of anionic species. Amino acid solutions were prepared at appropriate concentrations just before use.

Apparatus

A schematic diagram of the system used in this study is shown in Fig. 1. The system was comprised of four main components including an ozone generator, LGS, reaction cell, and detection-data processing system, all of which were designed and built in our laboratory.

A schematic diagram of the ozone generator is shown in Fig. 1B. It was comprised of two concentric glass cylinders (2 and 1 cm i.d. × 10 cm length), the outside of which were covered with aluminum foil as the electrodes. As can be seen in Fig. 1B, the two electrodes were separated by a glass layer (cylinder) as the dielectric barrier. The electrodes were connected to a source of high voltage to produce a corona discharge. Ozone was generated by passing a controlled flow of oxygen through the discharge gap (~4 mm) between the electrodes at an applied voltage of 10 kV and a current of 50 mA. Ozone entered the reaction chamber through the flow meter (F_2) and the needle valve (V_2) as shown in Fig. 1A.

The LGS was made of a polyethylene tube (2 cm i.d., 10 cm height) into which was fitted to a ceramic microporous disk (10 μm pore size) (Fig. 1C). Three tubing side arms (polyethylene, 1 mm i.d.) provided sample and reagent inlets

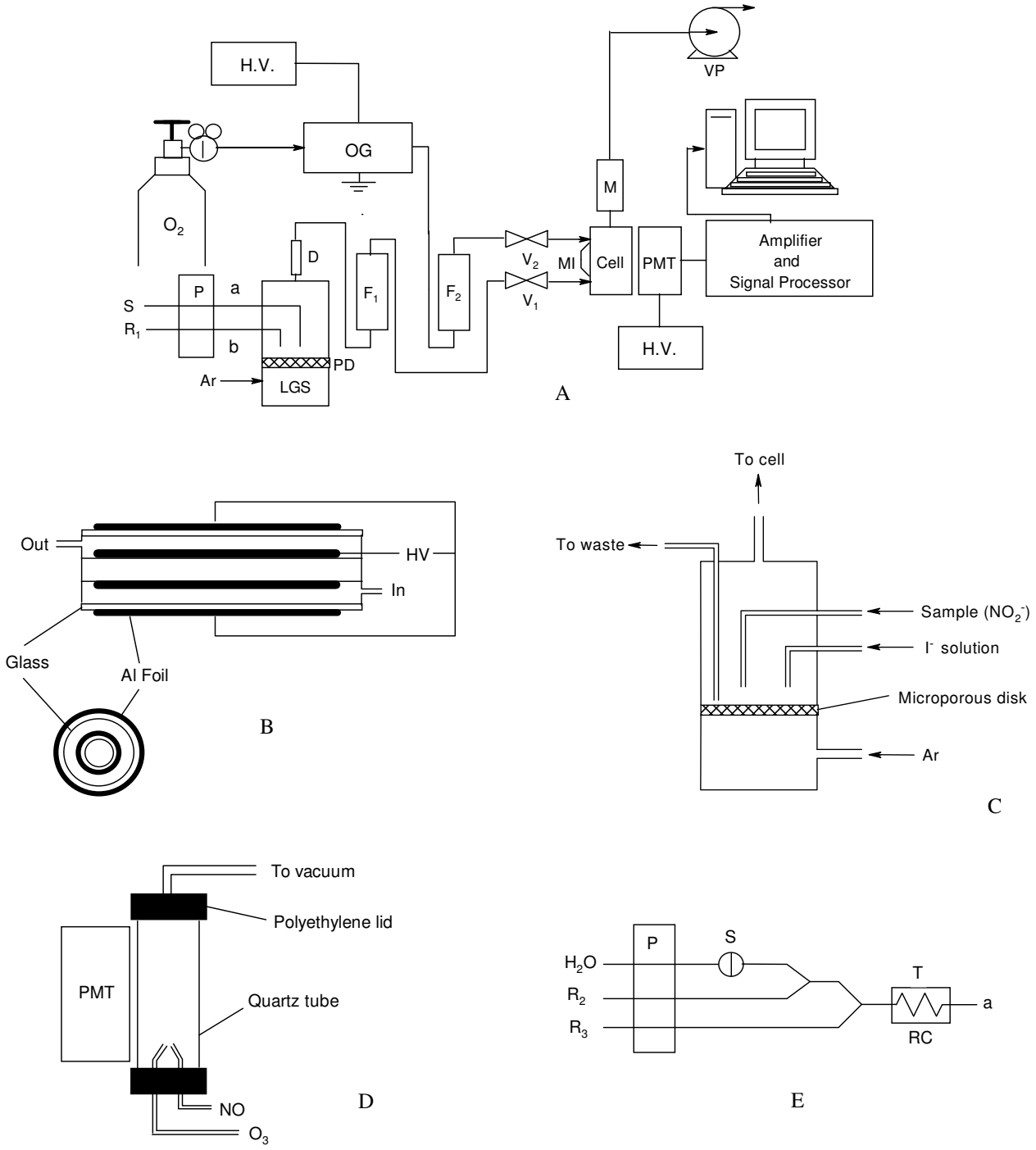

Fig. 1. Schematic diagram of the batch and flow injection systems used for the chemiluminescence determination of Nitrite: (A) the overall system, (B) ozone generator (OG); (C) LGS, (D) measuring cell, (E) flow injection manifold. S, sample; R_1, 0.5 M iodide in 0.5 M H_2SO_4 solution; PD, porous disk; D, drying tube; HV, high voltage; F_1, F_2, flow meters; V_1, V_2, needle valves; G, gold coated concave mirror; M, manometer; VP, vacuum pump; P, peristaltic pump; R_2, 0.1 M H_2SO_4 solution; R_3, 0.1 M iodide solution; RC, reaction coil; T, thermostated water bath.

above the disk and a carrier gas inlet below the disk. An outlet tube was provided at the top from which the carrier gas together with NO flowed into the measuring line. Waste reagents were removed *via* an outlet tube with the aid of the vacuum pump. Water vapor was removed to prevent interference with the detection of nitric oxide by the chemiluminescence reaction [8,13], using a column (polyethylene, 1 cm i.d., 10 cm height) containing ~10 g molecular sieve (10 Å) which was inserted between LGS and the measuring line.

The flow cell was made of a quartz tube (8 mm i.d., 4 cm height), which was covered at both ends with polyethylene lids equipped with the necessary inlets for connection to O_3 and NO, and an outlet for connection to vacuum (Figs. 1A and 1D). Operating pressure and flow rates were controlled by needle valves (V_1, V_2) and flow meters (F_1, F_2), respectively. The cell was placed in a vertical position (so that the gas would flow from the bottom upward) at a distance of ~0.5 cm in front of the photomultiplier tube (PMT). Placing a gold-coated concave mirror of appropriate focal length on the cell opposite the PMT enhanced the PMT's collection efficiency of the emitted light. The PMT and flow cell were placed in a light tight housing. All the connections were sealed with epoxy adhesive.

The chemiluminescence signal was measured with a detection system comprised of an R-298 PMT (Hamamatsu), regulated high voltage power supply, amplifier and A/D converter. Data acquisition was performed with a PC through an RS-232 interface board. Software was written to control the sampling rate and interval, and to collect and report the data as peak area. Generally, 1×10^4 data points were sampled in each measurement with a sampling interval of 10 ms.

Samples and reagents were transferred to the LGS by a peristaltic pump equipped with a liquid dispenser (Ismatec, Model ISM 404B). All connections for the liquid streams were made with 1 mm i.d. Tygon tubing. The reaction coil for the FIA procedure was a 1 mm i.d. × 2.5 m length of Tygon tubing, which was immersed in a thermostated water bath (Haake, Model FK2). The incoming NO was mixed with ozone in the reaction cell (flow cell) under low pressure (7 mm Hg, controlled with the needle valve) provided by a vacuum pump.

Preparation of Soil Samples

To 0.1 g of each soil sample, 40 ml water was added and the mixture was stirred for 30 min on a magnetic stirrer. The resulting mixture was centrifuged at 4000 rpm for 20 min and the supernatant solution was collected. The above steps were repeated on the solid residue and the supernatant solutions combined and diluted to 100 ml in a volumetric flask for the nitrite assay using the procedure described in the following section. The above procedure was also used for extraction of nitrite in the same soil samples into which known amounts of nitrite were added for the recovery test.

Procedure

Batch procedure. An appropriate aliquot of the sample or standard solution and the reducing reagent (R_1, 0.5 M iodide in 0.5 M H_2SO_4), generally 1 ml of each, were loaded over the microporous disk in the LGS by the liquid dispenser connected to the peristaltic pump (P) *via* routes a and b (Fig. 1A). The dispenser is capable of delivering exact volumes of liquids to within ±0.002 ml through the eight channels of the peristaltic pump. The generated NO was then stripped from the liquid phase by the carrier gas that flowed under the porous disk. The gases were then transported through the drying tube (D), flow meter (F_1) and needle valve (V_1) to the reaction cell. The chemiluminescence resulting from the reaction between NO and ozone was measured by the detection system. Nitrite ion standards and samples were compared using a calibration curve based on standard peak areas. The total analysis time for each sample or standard injection was approximately 2 min.

Flow injection procedure. The sample solution was loaded into a 1-ml loop and injected into a stream of water (1.1 ml min^{-1}) as the carrier. This stream was merged with the 0.1 M H_2SO_4 solution through a Y-shaped mixing element and then with the 0.1 M iodide solution through a second Y-shaped mixing element (Fig. 1E). The mixture of sample and reagents was passed through a 2.5 m reaction coil. The mixture was transferred over the microporous disk in the LGS (a in Fig. 1A). The rest of the procedure is the same as that of

the batch mode.

RESULTS AND DISCUSSION

The chemiluminescence method presented here employs a newly designed liquid-gas separator as well as new devices for ozone generation and chemiluminescence reaction cell. The ozone generator provides a silent discharge due to the presence of a dielectric barrier between the electrodes. The efficiency of ozone generation was optimized by varying the discharge gap and oxygen flow rate. The efficiency was determined by measuring the concentration of ozone in a quartz cell at 254 nm using a Shimadzu UV-160 spectrophotometer. The concentration of the ozone was estimated to be 25 mg l^{-1} in the effluent stream using Beer's law and an ε value of 3×10^3 mol^{-1} cm^{-1} (134 atm^{-1} cm^{-1}) [45]. The device has a very simple design and can be easily and cheaply assembled from components commonly found in any laboratory.

Preliminary tests showed that the LGS provides an efficient means for rapid and quantitative transport of NO produced from the reaction of nitrite with the reagent. The reagent and sample or standard nitrite solution are injected over the microporous disk inside the LGS. A controlled stream of argon, which flows under the microporous disk within the LGS, serves to efficiently homogenize the reaction mixture by bubbling into the solution and to sweep NO from the liquid phase. The $NO_{(g)}$ is then transported to the measuring system where it reacts with ozone to generate chemiluminescence. The LGS used in this work has a very simple design and can be made very easily and cheaply using a porous disk and a polyethylene tube. The system can be used for both batch and flow injection measurements. The drying tube, located between LGS and the measuring line, removes water vapor from the LGS effluent stream.

The efficiency of nitrite conversion to $NO_{(aq)}$, separation of $NO_{(g)}$ from the liquid phase, and the chemiluminescence reaction are influenced by various chemical and instrumental parameters. These were investigated by varying the iodide concentration, sulfuric acid concentration, stripping gas flow rate, ozone flow rate, reagent flow rate and reaction coil temperature.

Influence of Reagent Concentration

Optimization of the concentrations of the reagents was carried out by varying the concentration of a given reagent, while keeping the other parameters constant. The chemiluminescence intensity, obtained by integration of the peak area, was used as the criterion for the optimization process.

The reaction of nitrite with iodide ion was performed in the presence of sulfuric acid because of its low volatility. The influence of the sulfuric acid concentration was studied in the range of 0.01 to 1.8 M. The chemiluminescence intensity increased with an increase in the concentration of H_2SO_4 and became almost constant above 0.5 M (Fig. 2). As a result, 0.5 M was selected as the optimum concentration of this reagent.

The effect of the iodide concentration on the chemiluminescence intensity was studied in the range 0.01 to 1.0 M, as shown in Fig. 3. Based on the results of this study, we chose 0.5 M as the optimum concentration of iodide for subsequent measurements. Consequently, a mixture of 0.5 M iodide in 0.5 M H_2SO_4 solution was used as the reagent for nitrite reduction in the batch procedure. Optimum values of sulfuric acid and iodide in the flow injection procedure were obtained by pumping various concentrations of these solutions

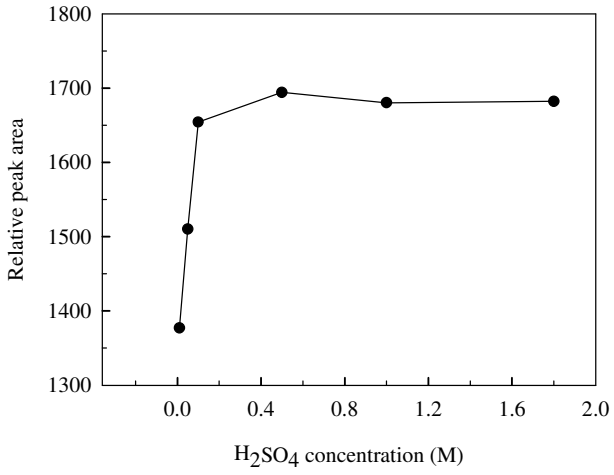

Fig. 2. Effect of sulfuric acid concentration on the chemiluminescence intensity. NO_2^-, 1 μg ml^{-1}.

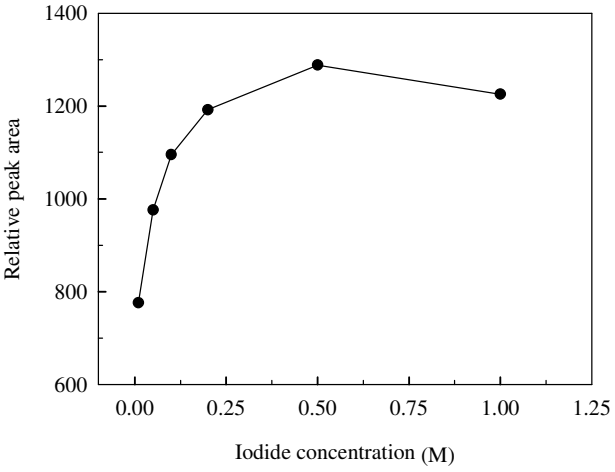

Fig. 3. Effect of iodide concentration on the chemiluminescence signal. H_2SO_4, 0.5 M; NO_2^-, 1 μg ml^{-1}.

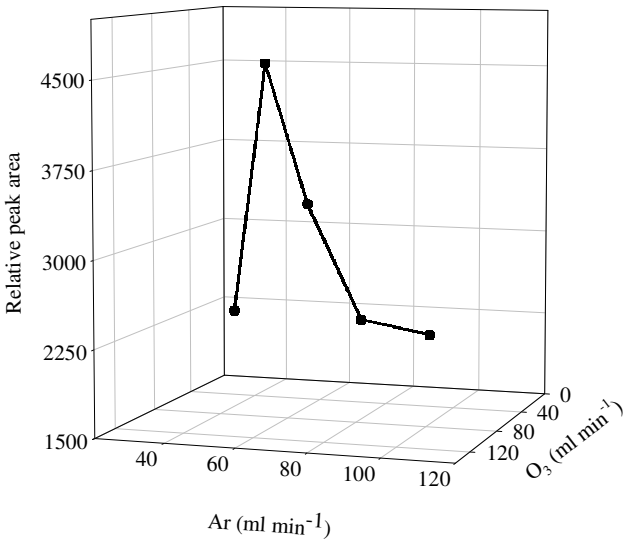

Fig. 4. The influence of argon and ozone flow rates on the chemiluminescence response. H_2SO_4, 0.5 M; NO_2^-, 1 μg ml^{-1}.

according to the procedure described in the experimental section. Optimum values of both reagents in the flow injection procedure were found to be 0.1 M.

Effect of Gas Flow Rates

Preliminary investigations showed that the chemiluminescence strongly depended on both the O_3/Ar flow rate ratio and their total flow rate. The flow rate ratio was first optimized in the range 0.8 to 2.8 with a constant argon flow rate. Maximum chemiluminescence for a 1 μg ml^{-1} NO_2^- solution was observed at an O_3/Ar flow rate ratio of 1.15. The total flow rate of these streams was optimized by simultaneously changing both flow rates, keeping their ratio constant at 1.15. The results, shown in Fig. 4, indicated the optimum total flow rate to be 101 ml min^{-1} (*i.e.,* 54 and 47 ml min^{-1} for ozone and argon, respectively).

Flow Rate of Reagent Solution

The influence of iodide and sulfuric acid flow rates on the chemiluminescence intensity in the flow injection procedure was examined in the range 0.5-2.2 ml min^{-1} using a 0.5 μg ml^{-1} solution of NO_2^- (Fig. 5). The results show that the chemiluminescence signal increases with an increase in flow rate and reaches its maximum at 1.1 ml min^{-1}. Therefore, we used this flow rate for the reagents throughout the experiment.

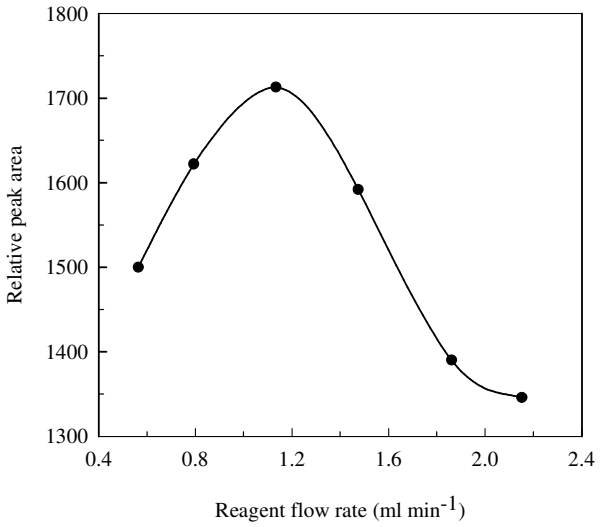

Fig. 5. Effect of flow rate of reagents in the flow injection procedure. H_2SO_4, 0.5 M; NO_2^-, 0.5 μg ml^{-1}.

Reaction Coil Temperature

The effect of temperature on the reaction of nitrite with iodide in the flow injection procedure was determined by

placing the reaction coil in a thermostated water bath at various temperatures. Maximum chemiluminescence was achieved with a bath temperature of approximately 20 °C. Therefore, the reaction of nitrite with the reagents was generally carried out at room temperature with no temperature control.

Analytical Performance Characteristics

Under the optimum operating conditions given in Table 1, the integrated peak area was plotted against the NO_2^- concentration. Typical chemiluminescence traces recorded at several nitrite concentrations (after curve smoothing) are shown in Fig. 6. The calibration plot thus obtained was linear in the concentration range of 1 to 1×10^4 ng ml^{-1} with the regression equation of $y = 1.046 \times 10^4 x + 5.974$ (where y is the integrated peak area and x is ng ml^{-1} NO_2^-) and a correlation coefficient, r, of 0.9999 (n = 12) in the batch procedure (Fig. 7).

The linear range in the flow injection procedure was 10 to 5×10^3 ng ml^{-1}, with the corresponding regression equation of $y = 2.839 \times 10^3 x + 1.553$, r = 0.9995 (n = 10). The detection limits, at a signal to noise ratio of 3, were found to be 1 ng ml^{-1} for the batch and 10 ng ml^{-1} for the flow injection systems. The lower detection limit in the batch mode indicates that the newly designed LGS behaves efficiently as the vessel for the reduction of nitrite in this mode, in addition to its main role of separating NO from the liquid-phase. The response time from injection of the solutions to the point where the chemiluminescence reaches its peak intensity was ~70 s; the time required for the peak to settle back to the baseline was ~140 s. Therefore, the sampling frequency is 25 samples h^{-1}.

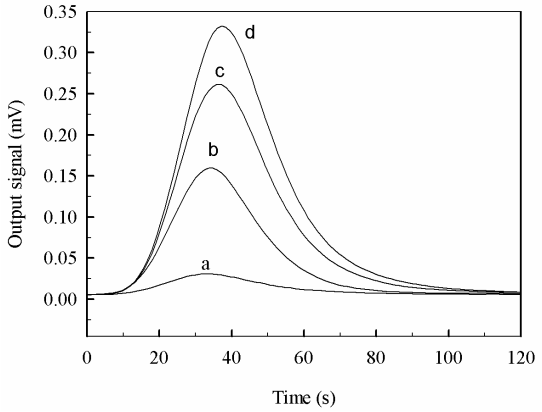

Fig. 6. Typical smoothed curve of chemiluminescence signals recorded at (a) 0.10, (b) 0.50, (c) 0.80 and (d) 1.0 µg ml^{-1} NO_2^- at optimized conditions.

Interferences

The influence of various ions and molecules that may be

Table 1. Optimized Parameters and Analytical Conditions for Nitrite Determination

Parameter:	Batch procedure	FIA procedure
Sulfuric acid (M)	0.5	0.1
Iodide (M)	0.5	0.1
Reagent flow rate (ml min^{-1})	–	1.1
Reaction coil temperature (°C)	–	20
Ozone flow rate (ml min^{-1})	54	54
Argon flow rate (ml min^{-1})	47	47
Analytical Characteristics:		
Calibration equation	$Y = 1.046 \times 10^4X + 5.974$	$Y = 2.839 \times 10^3X + 1.553$
Correlation coefficient (r)	0.9999 (n = 12)	0.9995 (n = 10)
Linear range (ng ml^{-1})	$1–1 \times 10^4$	$10–5 \times 10^3$
Detection limit (ng ml^{-1})	1	10
Precision (average RSD%)	1.1	1.8

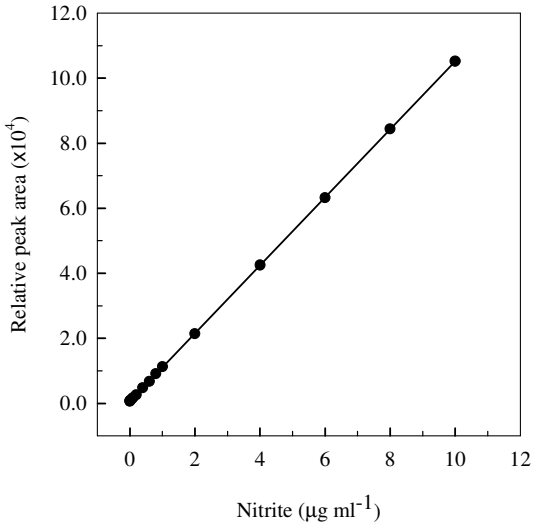

Fig. 7. Calibration plot obtained in the batch procedure.

present in real samples was investigated. Solutions containing 0.1 μg ml^{-1} nitrite and various excess amounts of foreign ions or molecules were treated as described in the procedure. The tolerance limit was taken to be the amount of interference that caused an error of not more than 5% in the measured chemiluminescence intensity. The error was calculated by comparing the peak area of the resulting chemiluminescence signal with that obtained by injecting an aqueous solution of nitrite containing no foreign ions as a reference. The results of this study are summarized in Table 2.

The results show that alanine, histidine, aspartic acid, caffeine, glycine, urea, NH_4^+, $S_2O_3^{2-}$, NO_3^-, Zn^{2+}, Co^{2+}, Ca^{2+}, Cl^-, and Fe^{3+} at 1×10^5 fold, CN^- at 5×10^4 fold, Cu^{2+} at 1×10^4 fold, hydroxylamine at 5×10^3 fold, cysteine, SO_3^{2-} and CO_3^{2-} at 1×10^3 fold have no influence on the determi-nation of 0.1 μg ml^{-1} NO_2^-. It is interesting to note that, some of these compounds, especially amino acids that can be found in natural waters, would interfere in some of the methods based on the reduction of nitrite with metal ions or in the presence of metal ion catalysts, probably by chelating the catalyst [13,46]. However, the results obtained in the present study show that amino acids and some other nitrogen containing compounds such as ammonia and urea can be tolerated at very high concentrations. High tolerance limits for NO_3^-, Cl^-, NH_4^+ and caffeine have been reported previously [9].

Table 2. The Influence of Foreign Species on Nitrite Determination, Expressed as Tolerance Weight Ratio (Species/Nitrite)

Species	Tolerance ratio
Alanine, Histidine, Aspartic acid, Glycine, Caffeine, Urea, NH_4^+, $S_2O_3^{2-}$, NO_3^-, Cl^-, Zn^{2+}, Co^{2+}, Ca^{2+}, and Fe^{3+}	1×10^5
CN^-	5×10^4
Cu^{2+}	1×10^4
Hydroxylamine	5×10^3
Cysteine, SO_3^{2-}, and CO_3^{2-}	1×10^3

Methods based on liquid-phase chemiluminescence for nitrite, which are mostly carried out *via* the peroxynitrous acid route, generally suffer from severe interference by most cationic and some anionic species and, as such, these species must be separated before measuring the chemiluminescence [15-19]. However, the present gas-phase chemiluminescence method offers a high degree of selectivity with respect to several cationic, anionic and nitrogen containing species. This can be attributed to three discriminating steps of the method: selective conversion of nitrite to NO; relatively selective separation of the volatile NO from aqueous solution; selective reaction of NO with ozone to generate chemiluminescence.

Precision and Accuracy

The precision of the method was estimated by repeated injection of solutions containing 0.1 to 1.0 μg ml^{-1} nitrite. The average relative standard deviations were 1.1% and 1.8% (n = 5) for batch and flow injection procedures, respectively. In fact, an efficient and reproducible process for stripping NO from solution, and constant concentration of ozone are the most critical factors in determining the precision of the method. The high precision obtained in this work can be related to the efficient mixing of the reaction mixture and efficient separation of NO from the liquid phase in the LGS, as well as efficient and the reproducible behavior of the ozone generator.

The accuracy of the method was checked by applying the

Table 3. Results of Real Sample Analysis

Sample	NO_2^- (ng ml^{-1})		
	Added	Found	Recovery (%)
Well water	0	5.2 ± 0.7	
	9.0	14.2 ± 0.4	100.4
Rain water	0	35.1 ± 0.8	
	46.0	79.4 ± 1.0	96.3
River water[a]	0	76.1 ± 0.8	
	50.0	124.7 ± 1.1	97.2
Snow	0	210.0 ± 1.5	
	20.0	230.2 ± 1.4	101.0
Lake water	0	70.7 ± 1.5	
	20.0	91.7 ± 1.4	105.0
Soil (1)[b]	0	45.3 ± 0.9	
	43.0	86.7 ± 1.1	96.3
Soil (2)[b]	0	25.2 ± 0.4	
	32.0	55.3 ± 0.7	94.1

[a] Zayandeh Rood. [b] Sample weight, 0.1 g; see experimental section for sample preparation.

proposed method to the determination of nitrite in a variety of natural water samples, including river, rain, well, lake and snow, and two soil samples. These samples were spiked with nitrite standards for the recovery test. From the results presented in Table 3, it is evident that the sensitivity of the method is high enough to enable direct analysis of nitrite in test samples. The spike recoveries were between 94.1 and 105%, indicating that nitrite could be quantified accurately in various water samples and soil extracts without special pretreatments except for a simple extraction of nitrite from soil samples with water.

CONCLUSIONS

A chemiluminescence system was developed for the determination of nitrite by batch and flow injection procedures based on a simple ozone generator and a simple method for stripping NO from the solution. These devices are very simple in construction and can be easily and cheaply built in any laboratory. The system is highly efficient for the determination of nitrite and besides its high sensitivity, precision and accuracy, offers very high selectivity over a number of cations, anions and molecular species. The detection limit and precision obtained for nitrite are of the same order as those reported previously [8,13,42-44], but the linear range is at least an order of magnitude better than the previous reports. The proposed method was successfully applied to the determination of other nitrite in natural waters and soil samples. The system can be easily adapted for the determination other nitrogenous species.

ACKNOWLEDGMENT

The authors gratefully acknowledge the support of this work by the Office of Graduate Studies of the University of Isfahan.

REFERENCES

[1] Drinking Water Standards and Health Advisories, EPA 822-R-04-005, U.S. Environmental Protection Agency, Washington DC, 2004.

[2] C.S. Bruning-Fann, J.B. Kaneene, Vet. Hum. Toxicol. 35 (1993) 521.

[3] A.D. Eaton, L.S. Clesceri and A.E. Greenberg, Standard Methods for the Examination of Water and Waste Water", 19th Edition, American Public Health Association, Washington DC, 1995.

[4] L. Jia, J. Bonaventura, J.S. Stamler, Nature 380 (1996) 221; A. Samouilov, P. Kuppusamy, J.L. Zweier, Arch. Biochem. Biophys. 357 (1998) 1.

[5] S.H. Synder, D.S. Bredt, Sci. Am. 266 (1992) 68; P.L. Feldman, O.W. Griffith, D.J. Stuer, Chem. Eng. News 20 (1993) 26; P. Biban, T. Zangardi, E. Baraldi, N. Dussini, L. Chiandetti, F. Zacchello, Life Sci. 68 (2001) 2789.

[6] C.A. Lucy, C.R. Harrison, J. Chromatogr. A 920 (2001) 135.

[7] M. Yamamoto, H. Kosaka, Anal. Chem. 66 (1994) 362.

[8] T. Aoki, S. Fukuda, Y. Hosoi, H. Mukai, Anal. Chim. Acta 349 (1997) 11.

[9] A.J. Dunham, R.M. Barkley, R.E. Sievers, Anal. Chem.

67 (1995) 220.
[10] R.M. Bateman, C.G. Ellis, M.D. Sharpe, S. Mehta, D.J. Freeman, Clin. Chem. 47 (2001) 1847.
[11] R.D. Cox, Anal. Chem. 52 (1980) 332.
[12] R.M. Bateman, C.G. Ellis, D.J. Freeman, Clin. Chem. 48 (2002) 570.
[13] Y. Kanda, M. Taira, Anal. Sci. 19 (2003) 695.
[14] B.K. Oh, M.E. Meyerhoff, Biomaterials 25 (2004) 283.
[15] C. Lu, F. Qu, J.M. Lin, Y. Yamada, Anal. Chim. Acta 474 (2002) 107.
[16] P. Mikuska, Z. Vecera, Anal. Chim. Acta 495 (2003) 225.
[17] P. Mikuska, Z. Vecera, Anal. Chim. Acta 474 (2002) 99.
[18] C. Lu, J.M. Lin, C. W. Huie, M. Yamada, Anal. Chim. Acta 510 (2004) 29.
[19] P. Mikuska, Z. Vecera, Z. Zdrahal, Anal. Chim. Acta 316 (1995) 261.
[20] A. Roda, M. Pazzagli, L.J. Kricka, P.E. Stanley, Bioluminescence and Chemiluminescence Prospectives for the 21st Century, Wiley, Chichester, 1999.
[21] M.J. Navas, A.M. Jimenez, G. Galan, Atmos. Environ. 13 (1997) 3603.
[22] X.R. Zhang, W.R.G. Baeyens, A.M. Garcia-Campana, J. Ouyang, Trends. Anal. Chem. 18 (1999) 384.
[23] M.J. Navas, A.M. Jimenez, Food Chem. 55 (1996) 7.
[24] C. Dodeigne, L. Thunus, R. Lejeune, Talanta 51 (2000) 415.
[25] S. Tsukada, H. Miki, J.M. Lin, T. Suzuki, M. Yamada, Anal. Chim. Acta 371 (1998) 163.
[26] B. Li, Z. Zhang, M. Wu, Talanta 51 (2000) 515.
[27] M.C. Ramos, M.C. Torijas, A. Navas Diaz, Sensors Actuat. B 73 (2001) 71.
[28] W. Qin, Anal. Chem. 70 (1998) 3579.
[29] W. Qin, Z. Zhang, C. Zhang, Analyst 122 (1997) 685.
[30] X. Zheng, Z. Zhang, Sensors Actuat. B 84 (2002) 142.
[31] Y.F. Mestre, L.L. Zamora, J.M. Calatayud, Anal. Chim. Acta 394 (1999) 159.
[32] L. Zhang, N. Teshima, T. Hasebe, M. Kurihara, T. Kawashima, Talanta 50 (1999) 677.
[33] B. Li, Z. Zhang, Sensors Actuat. B 69 (2000) 70.
[34] K. Tsukagoshi, M. Yamamoto, R. Nakajima, Anal. Sci. 16 (2000) 1357.
[35] Z. Song, X. Zhou, Spectrochim. Acta A 57 (2001) 2567.
[36] B. Li, Z. Zhang, L. zhao, C. Xu, Anal. Chim. Acta 459 (2002) 19.
[37] Z. Song, S. Hou, Talanta 57 (2002) 59.
[38] B. Li, Z. Zhang, M. Wu, Microchem. J. 70 (2001) 85.
[39] Y. Zhao, W.R.G. Baeyens, X. Zhang, A.C. Calokerinos, K. Nakashima, G. Van Der Weken, Analyst 122 (1997) 103.
[40] H. Han, Z. He, Y. Zeng, Anal. Sci. 15 (1999) 467.
[41] A.C. Calokerinos, N.T. Defteros, W.R.G. Baeyens, J. Phar. Biomed. Anal. 13 (1995) 1063.
[42] R.C. Doerr, J.B. Fox, Jr.L. Lakritz, W. Fiddler, Anal. Chem. 53 (1981) 381.
[43] R.S. Braman, S.A. Hendrix, Anal. Chem. 61 (1989) 2715.
[44] T. Aoki, M. Wakabayashi, Anal. Chim. Acta 308 (1995) 308.
[45] T.J. Manning, B. Little, J. Purcell, A. Feldman, W. Parker, K. Register, B. Sumner, C. Schibner, Chemical Educator, 7 (2002) 278.
[46] M.T. Downes, Water Res. 12 (1978) 673.