Indirect Voltammetric Method for Determination of Nitrogen Dioxide in the Ambient Atmosphere

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Abstract

A hydrodynamic voltammetrric method was developed to determine the concentration of atmospheric nitrogen dioxide. Air samples were collected in 0.1M NaOH scrubbing solution which converts NO_2 to NO_2^- and NO_3^- in a fixed stoichiometric ratio. The produced NO_2^- ion was analyzed by hydrodynamic voltammetry at a rotating disk gold electrode. A calibration curve was established by plotting the anodic steady state current (i_s) versus NO_2^- concentration. The calibration curve showed a remarkable linearity between the steady state current for NO_2^- oxidation and NO_2^- ion concentration (correlation coefficient = 0.9975). The Validity of the method was checked against spectrophotometric determination of NO_2^- . The agreement between the two methods was confirmed (R^2 = 0.9965). The applicability of the method to real-life analysis was established by estimation of NO_2 concentration in ambient air of three districts in Amman. The results indicated that the atmospheric concentration of NO_2 in the three districts conforms to the international and national atmospheric clean air standards.

Keywords: Atmospheric nitrogen dioxide analysis; Hydrodynamic voltammetric analysis; Rotating disk gold electrode.

Introduction

Nitrogen dioxide is considered as one of the five main pollutants in the atmosphere. This pollutant has adverse effects on plants, animals and human beings [1-3] and it contributes to acid rain and photochemical smog [4-5] phenomena.

Different methods have been developed for the analysis of nitrogen dioxide in ambient atmosphere. These methods include spectrophotometric [6-8] and chromatographic [9] techniques. In these methods, expensive, unstable, and environment unfriendly chemicals are usually used. The development of a simple method which uses inexpensive and harmless chemicals is inevitable.

The aim of this work is to develop a voltammetric method for determination of atmospheric nitrogen dioxide. The latter is converted to nitrite ion by bubbling air into a 0.1M NaOH collection solution. Chemical analysis of nitrite at a rotating disk electrode

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(RDE) has been reported [10]. The produced nitrite ion is determined by recording the steady state current at a rotating disk gold electrode.

Materials and Methods

Instrumentation

The air sampling system was a 7-bubbler sampler connected in series (Research Applied Company, USA). The airflow rate was measured using a flow rate meter with three metering tubes covering the range 0.05 – 2400 L/h supplied from Karl Kolb Scientific Technical Supplies (Germany).

A scanning potentiostat (EG & G model 362) and An X-Y recorder (Philips model PM 8120) were used for collection of hydrodynamic voltammetric data. A conventional, three-electrode cell equipped with a multiple-inlet system for admission of supporting electrolyte and for purging and blanketing the solution with oxygen-free nitrogen was used. The working electrode was a rotating gold disk electrode. The rotating disk electrode and the speed controller were supplied by Pine Instruments (USA).

The reference electrode was a $Ag/AgCl/[Cl^-]=1.0$ mol L^{-1}. The reported potentials were measured and reported against $Ag/AgCl/[Cl^-]=1.0$ mol L^{-1} and all measurements were carried out at ambient temperature (25 ^{o}C). The auxiliary electrode was a spiral shape platinum wire(purity = 99.95%) supplied by Johnson Matthey (USA).

Spectrophotometric comparative results were obtained by using a Varian (Model Carry 1) UV-VIS spectrophotometer. All measurements were conducted under complete control of Cary UV software.

Materials

All the reagents used were of analytical reagent grade and were used as received from the suppliers without further purification. The nitrogen gas used was CP-grade product supplied by National Gas and it was passed through Oxosorb cartridge (Supelco) for removal of residual traces of oxygen. All solutions were prepared by dissolving their respective reagents in triply distilled water. A little amount of sodium hydroxide and potassium permanganate was added to the second distillation flask. Potassium permanganate in a basic medium is supposed to eliminate traces of organic impurities.

Procedures

The air sampling system was subjected to three tests: the flow-rate calibration, the pump stability and the nitrogen dioxide collection efficiency. A flow-rate metering tube graduated in millimeters equipped with a floating corundum cone was used for measurement of the flow rate of sampled air. Calibration of the flow-rate meter to read in L/h was achieved through equations which involved air density, air viscosity, mass density and diameter of the corundum float which are supplied by the metering tube manufacturer [11]. Pumping stability was tested by running the pump continuously for 24 h with monitoring the bubbling action in the bubbler and the pump pressure gauge.

The bubbling action was consistent and the pressure gauge amounted to a fixed value during the test period.

Collection efficiency of atmospheric NO_2 was tasted by generating a well-known amount of NO_2 by reacting 10 mL of pure nitric oxide gas with 5 mL of pure oxygen in a graduated syringe then the generated NO_2 was drawn into the sampling system by the pumping action. Nitrogen dioxide evolves according to Equation 1.

$$2NO_{(g)} + O_{2\,(g)} \longrightarrow 2NO_{2\,(g)}$$ 1

The evolved NO_2 gas was withdrawn by the sampling system into collection solution containing 0.1M sodium hydroxide to convert NO_2 to nitrite ion at 2:1 ratio as indicated in Equation 2.

$$2NO_{2\,(g)} + 2NaOH_{(aq)} \longrightarrow NaNO_{2(aq)} + NaNO_{3(aq)} + H_2O_{(aq)}$$ 2
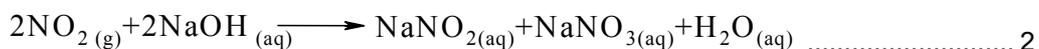
The nitrite concentration was determined spectrophotometrically by measuring the absorbance using the proper reagents at 540 nm , and also by hydrodynamic voltammetry at a rotating gold disk electrode. The limiting anodic current for nitrite oxidation was determined by recording the voltammogram at a scan rate of 10 mV/s and a rotation speed of 900 rpm. The spectrophotometric method and the voltammetric method gave collection efficiencies of 95.0 and 93.1% respectively.

Results and Discussion

Cyclic Voltammetryic Response of Nitrite Ion at the Disk Gold Electrode:

In the present work, cyclic voltammetric experiments were carried out in order to characterize the peak of the anodic current of the nitrite ion in the supporting electrolyte solution used. It was also decided to determine the working potential range, and to recognize the potential region controlled by mass transfer. Each cycle of an experiment was commenced by obtaining a verified-clean gold surface as indicated by its characteristic voltammogram[12].

Figure 1. shows a cyclic voltammogram at a disk gold electrode in 0.5M H_2SO_4 supporting electrolyte solution. The voltammogram shows two distinct current peaks, anodic current peak ($i_p{}^a$) due to oxide formation and a cathodic current peak ($i_p{}^c$) due to reduction of the oxide species formed at the surface.
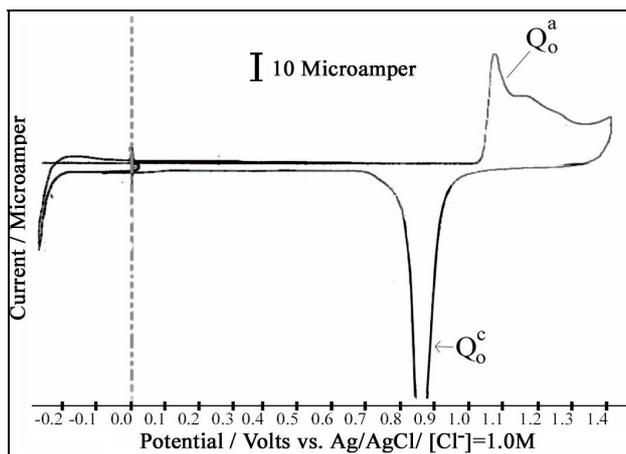
Figure 1: Cyclic voltammogram of a polycrystalline gold electrode in 0.5 M H_2SO_4. dE/dt = 100 mV/s.

Figure 2. shows a set of representative cyclic voltammogras for the disk gold electrode in 0.1M $NaClO_4$ and 1mM $HClO_4$ solution which contained variable concentrations of nitrite ion. The voltammograms show anodic peaks for NO_2^- ions centered at +0.76V. The calibration plot for the anodic peak current extracted from the cyclic voltammograms vs. NO_2^- concentration was established (Figure 3). The calibration plot indicates an excellent linearity between the concentration of NO_2^- (C_{NO2}^-) and the peak current (correlation coefficient = 0.9975). The regression equation is

$$i(\mu A) = 33.757 C_{NO2}^- + 6.2667 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 3$$

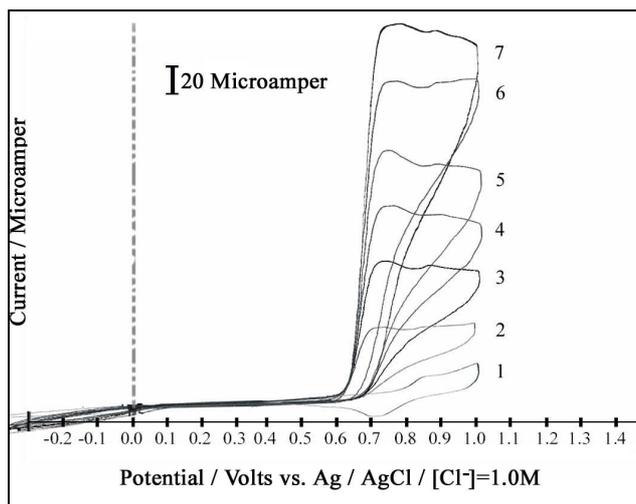This experiment indicates the applicability of voltammetry to analysis of NO_2^- at polycrystalline gold electrodes.

Figure 2: Cyclic voltammetric curves for the oxidation of nitrite ion at a gold disk electrode in 0.10 M $NaClO_4$ + 1.0 mM $HClO_4$ solution containing (1) 0.00 (2) 1.0 (3) 2.0 (4) 3.0 (5) 4.0 (6) 5.0 (7) 6.0 mM $NaNO_2$. dE/dt = 50 mV/s.
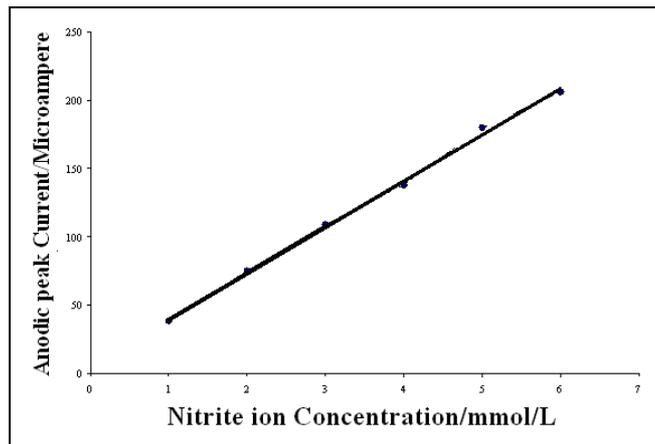
Figure 3: A plot of peak current (i_p) extracted from cyclic voltammograms of nitrite ion at a gold disk electrode vs. nitrite ion concentration. Experimental conditions are given in Figure 2.

Hydrodynamic Voltammetry of Nitrite Ion at a Rotating
Gold Disk Electrode:

Hydrodynamic voltammetric analysis is known to be more sensitive than cyclic voltammetry. For this reason analysis of NO_2^- at a rotating gold disk electrode was attempted. Figure 4 shows a sample voltammogram at a gold disk rotating electrode in a solution of 0.10 M $NaClO_4$ and 1.0 mM $HClO_4$ containing (a) 0.0 (b) 0.4 mM NO_2^-. The limiting anodic current appears at +0.76V. The limiting current, i_l was obtained from the voltammograms and plotted against the concentration of NO_2^- (C_{NO2}^-) in the solution. Figure 5 shows the extracted limiting anodic currents (i_{la}) for a variable concentration of NO_2^- ions in 0.1 M $NaClO_4$ and 1mM $HClO_4$ solution.
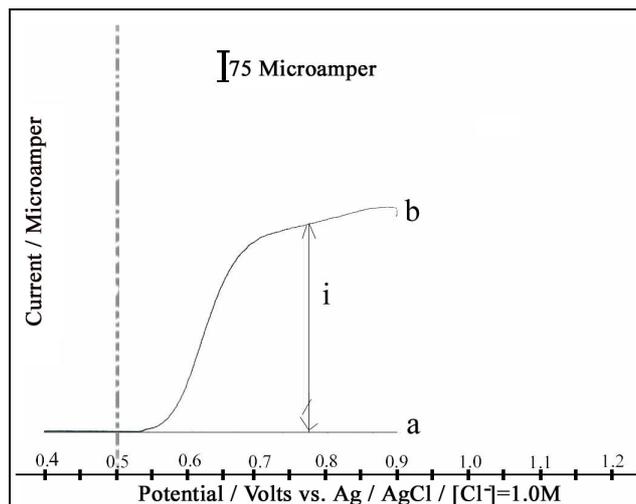

Figure 4: The voltammogram of a rotating disk gold electrode in 0.10 M $NaClO_4$ + 1.0 mM $HClO_4$ solution containing (a) 0.0 and (b) 0.4 mM $NaNO_2$ f = 900 rpm, dE/dt = 10 mV/s.
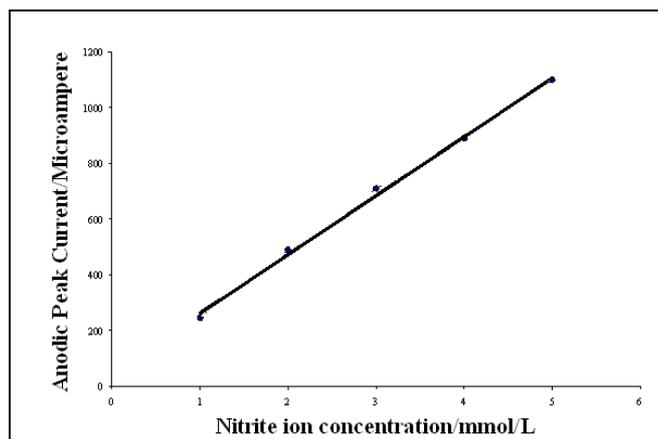
Figure 5: Calibration curve for the limiting current (i_{la}) of nitrite at a rotating gold disk electrode vs. nitrite ion concentration. Experimental conditions are given in Figure 4.

The calibration plot indicates a linear relationship with a regression equation of

$$i(\mu A) = 211C_{NO2^-} + 54 \quad \text{... 4}$$

and a correlation coefficient of 0.9972. The sensitivity of the hydrodynamic technique results is nearly one order of magnitude greater than that of the cyclic volammetric results. For this reason, hydrodynamic voltammetry was used in the present work for analysis of NO_2^- which results from scrubbing of atmospheric NO_2 in sodium hydroxide solutions.

Analysis of NO_2 concentration in ambient atmosphere

The applicability of the developed method was tested by analysis of atmospheric NO_2 in three regions in Amman: Raghadan, Asharaq Al-Awasat circle and Al-Abdali regions. In parallel to the voltammetric analysis, NO_2 samples collected from the same regions were analyzed photometrically. The results are given in Table 1. Application of t-test to these results indicated that the null hypothesis is correct and that there is no significant difference between the two methods which attests to the validity of the developed method. The lowest detection limit based on 8-hour sampling time is 4.0 ppb NO_2^- which amounts to a minimum detectability of 0.015 mg m^{-3} NO_2^-. The minimum detectability is lower than the internationally acceptable concentration of NO_2 in ambient atmosphere (0.15 mg m^{-3}).

Table 1: Concentrations of NO_2 in ambient air samples in three selected regions in Amman determined by (1) spectrophotometrically and (2) the developed electrochemical method.

Sample Name	Flow Rate (L/hour)	Volume of Air Pumped to Bubbler (m^3)	Concentration of NO_2 gas (mg/m^3)
1 :*Raghadan* Transport Station	16.9	5.07×10^2	1.82
2 : *Raghadan* Transport Station	16.9	5.07×10^2	1.72
1: *Alabdali* Transport Station	19.5	5.85×10^2	1.67
2: *Alabdali* Transport Station	19.5	5.85×10^2	1.50
1: The *Alsharq Alawsat* Transport Station	17	5.10×10^2	3.62
2: The *Alsharq Alawsat* Transport Station	17	5.10×10^2	3.51

Interferences

Figure 6 shows the voltammograms obtained at a rotating gold disk electrode upon scanning the potential in solutions containing SO_3^{2-}, CO_3^{2-}, NO_3^-, and SO_4^{2-}. From the voltammograms, the only species which was found to interfere with the nitrite analysis is the sulfite ion, SO_3^{2-}. The interference problem of sulfite was eliminated by adding dilute hydrogen peroxide to the solution containing SO_3^{2-}. It is clear from Figure 7 that the signal of the SO_3^{2-} ion was eliminated while the wave which is due to NO_2^- is not affected.
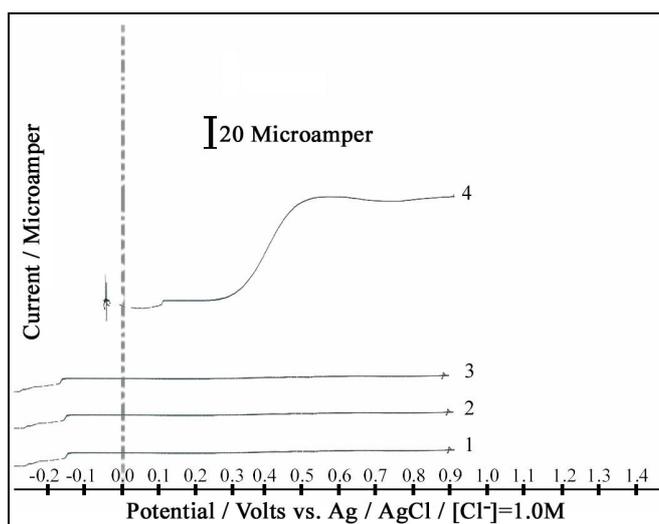

Figure 6: Hydrodynamic voltammetry curves for a rotating gold disk electrode in a 0.1M $NaClO_4$ in 1mM $HClO_4$ solution containing (1) 2.0 mM $NaNO_2$ (2) 2.0 mM Na_2SO_4 (3) 2.0mM Na_2CO_3 (4) 2.0 mM Na_2SO_3 : f = 900 rpm, dE/dt = 10 mV/s.
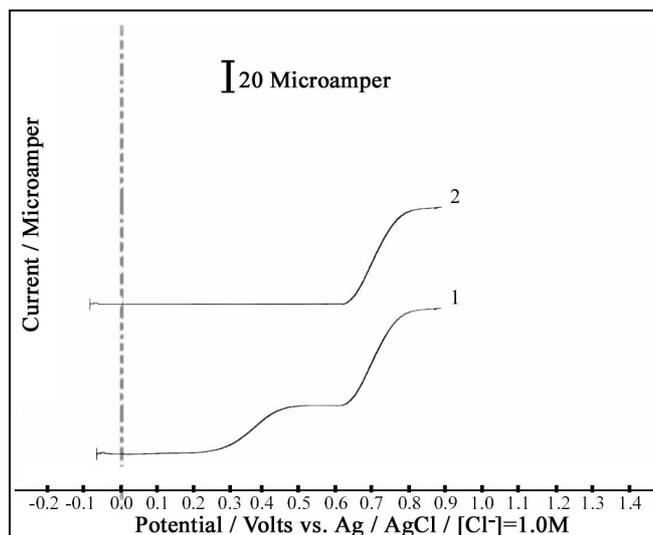
Figure 7: Hydrodynamic voltammetric curves for the oxidation of nitrite ion on a rotating gold disk electrode in a 0.1M NaClO$_4$ in 1mM HClO$_4$ solution containing (1) 2.0 mM Na$_2$SO$_3$ and 2.0 mM NaNO$_2$ (2) 2.0 mM Na$_2$SO$_3$; 2.0 mM NaNO$_2$ and 2mL of diluted H$_2$O$_2$: f = 900 rpm, dE/dt = 10 mV/s.

Conclusions

The proposed method is based on using dilute sodium hydroxide solution as a scrubbing medium for NO$_2$ gas when pumped from the ambient atmosphere. This method can be considered as an environment friendly method where no organic solvents or harmful reagents are used. Moreover, the proposed method utilizes simple and inexpensive instrumentation. The sampling efficiency and the total efficiency of the analytical method were not less than most of the analytical methods for analysis of gases. The lowest detection limit (0.015 mg.m^{-3}) for the proposed method, is remarkable and below the international standard (0.15 mg.m^{-3}) [13]. This method also has a wide dynamic range (0.017 – 1211 mg.m^{-3}) of NO$_2$ gas. The method showed high accuracy as proved by independent analysis data where the percent difference on average doesn't exceed 5%.

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