

# Coulometric Analysis of Nitrite Using Electrochemically Activated Carbon Felt Electrode

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In this study, we report the development of an absolute determination method based on potential-controlled coulometric analysis using carbon-felt-electrode-introduced nitrogen-containing functional groups fabricated by the electrode oxidation of ammonium carbamate solution for measuring nitrite. The potential-controlled coulometric cell was constructed by using a working electrode consisting of a carbon felt electrode that was electro-oxidized at +1.1 V (vs Ag/AgCl) in 0.1 M ammonium carbamate solution. When the applied potential of the sensor cell was +0.75 V, the oxidized current of nitrite was immediately observed by adding 10  $\mu\text{L}$  of 1 mM nitrite. In addition, the electron number of the electrode reaction was two electron paths from the estimation of the electrical charge of nitrite detection. This finding indicates that the proposed determination method resulted in the absolute quantity analysis of nitrite. The current vs time curves indicate that the determination of nitrite was finished completely in a relatively short time ( $\sim 30$  s). The relative standard deviation (RSD) for ten successive measurements of 1 mM nitrite was 2.2%. This indicates that our coulometric method can be used for the absolute determination of the nitrite concentration in practical applications.

## 1. Introduction

In recent years, carbon materials have attracted growing interest from many researchers because of their various allotropes of carbon [graphite, diamond, diamond-like carbon (DLC), fullerenes, carbon nanotube, graphene, and so forth], various microtextures (more or less ordered) due to the degree of graphitization, various types of dimensionality from 0 to 3D, ability to exist under different forms (from powders to fibers, foams, and composites), and being environmentally friendly.<sup>(1)</sup>

More recently, researchers have been very highly interested in using electrodes made of carbon materials [such as glassy carbon (GC) and carbon felt electrodes] because of their accessibility, inexpensiveness, chemical stability in different solutions (from very acidic to basic), ability to perform in a wide range of temperatures,<sup>(1)</sup> and being widely used as sensing

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electrodes of electrochemical detection because of a wide potential window, a low background current, and good stability as compared with a metal electrode.<sup>(2–11)</sup> Such other implementations are sensing, actuation, computation, and communication into composites.<sup>(12)</sup>

The electrochemical activation of a carbon surface has been performed for applications including electroanalytical chemistry and electrocatalysis.<sup>(13–15)</sup> Recently, we have proposed that nitrogen atoms containing functional groups can be easily introduced onto the surface of a GC electrode by the electrode oxidation of ammonium carbamate in an aqueous medium at a highly positive electrode potential, and we named this electro-oxidized GC electrode as an aminated GC electrode.<sup>(15–17)</sup> In this electrochemical surface modification, not only the primary amine group (for example, aniline-like aromatic amine moiety) but also other nitrogen-containing functional groups (for example, the secondary amine-like moieties containing pyrrole-type nitrogen and quaternary amine-like moieties containing graphitic quaternary nitrogen) can be introduced onto a GC electrode surface.<sup>(18,19)</sup> Our group has reported that the observed hydrogen redox wave is related to the mutual redox reactions between hydrazino, diazene, and diazo groups bonded to the electrode surface.<sup>(19)</sup>

In addition, an electrocatalytic redox wave between a hydrogen ion ( $H^+$ ) and a hydrogen molecule ( $H_2$ ) was observed after the long-term electrochemical reduction of nitrogen atoms containing functional groups introduced onto a carbon electrode surface in a strong acid electrolyte. During the electrode reduction of the electro-oxidized carbon electrode in the sulfuric acid electrolyte, the platinum ion dissolved from the platinum wire counter electrode was electrodeposited on the nitrogen atom surface containing functional groups introduced into a carbon electrode.<sup>(20)</sup>

Sodium nitrite can be used in various industries including agricultural, basic chemical, and chemical industries. In addition, this substance can be found in the environment, food, foodstuff additives, physiological systems,<sup>(21)</sup> dye synthesis, and corrosion inhibition.<sup>(22)</sup> The disadvantages of nitrite are as follows: it is highly toxic at high concentrations and harmful to human health and the environment.<sup>(21,23–26)</sup> For example, nitrite probably reacts with amines to form highly carcinogenic nitrosamines<sup>(27)</sup> and may induce a reduction in the oxygen transport capacity of blood that leads to methemoglobinemia.<sup>(27–30)</sup> However, the quantitative determination of the amount of nitrite has been considered to have huge importance for environmentally related issues up to now. For this reason, our group focuses on the importance of finding a friendly and economical method of measuring nitrite.

Electroanalytical methods are a part of analytical chemistry that studies an analyte by measuring the potential, current, and electrical charge to determine the analyte concentration or characterize the analyte chemical reactivity.<sup>(31)</sup> There are several categories that depend on which aspects of the cell are controlled and measured. Those methods can be divided into the following four major categories: potentiometry (measures the potential of a solution between two electrodes), voltammetry (involves a constant and/or varying potential at an electrode surface and measures the resulting current with a three-electrode system), amperometry (measures the current as a function of an independent variable that is typically a time or electrode potential), and coulometry (measures the concentration of an unknown analyte in solution by converting the analyte from one oxidation to another).<sup>(31)</sup>

There are several advantages in using electrochemical methods to analyze nitrite, such as high sensitivity, operational simplicity, and applicability to a large number of target substances.<sup>(32–38)</sup> Although nitrite can be determined by either reduction or oxidation, the electrochemical oxidation of nitrite is usually favored over reduction to avert the major interferences from oxygen molecules and nitrite.<sup>(34,35)</sup> In our previous study, we proposed a simple electrochemical method for the detection of nitrite by amperometry measurement using an aminated GC electrode.<sup>(21)</sup> Basically, the use of amperometry for nitrite detection is profitable. However, in practice using the amperometric method, the sensor requires calibration for detecting an analyte.

In this study, we propose the potential-controlled coulometry of nitrite using an aminated carbon felt electrode. In coulometry, the concentration of an analyte can be directly obtained by only one experiment, differing from the other analytical methods that require calibration, such as amperometry, because the Faraday constant (coulomb/mole) can convert the electrical charges flowing during a complete electrolysis for analytes.<sup>(39,40)</sup> Another reason is that the potential-controlled coulometry has a very simple sensor cell structure.<sup>(40)</sup>

## 2. Material and Methods

### 2.1 Chemicals and materials

A carbon felt (GF-20-5F, 20 mm diameter, 5 mm thickness) was obtained from Nippon Carbon Co., Ltd. Ammonia carbamate ( $\text{H}_2\text{NCOONH}_4$ ) was purchased from Merck KGaA., Darmstadt, Germany, and used without further purification. Sodium nitrate ( $\text{NaNO}_2$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ), sodium acetate ( $\text{CH}_3\text{COONa}$ ), and potassium hexacyanoferrate ( $\text{K}_3[\text{Fe}(\text{CN})_6]$ ) were obtained from Wako Pure Chemical Industries, Ltd., Japan. Acetic acid buffer solution (pH 4.0) was prepared using 0.1 M ( $\text{M} = \text{mol dm}^{-3}$ ) sodium acetate and acetic acid. The cation exchange membrane used was from Asahi Glass Engineering, Japan. All aqueous solutions were prepared using distilled water obtained with a Millipore Milli-Q system (Millipore, Japan). All the experiments were conducted at room temperature.

### 2.2 Apparatus

An ultrasonic bath was purchased from Branson Ultrasonic, Emerson Japan, Ltd. A potentiostat/galvanostat (HA-151B, Hokuto Denko Co., Ltd., Japan) was used to perform a controlled potential electrolysis. The cyclic voltammetric measurements were carried out using an automation polarization system (HZ-3000, Hokuto Denko Co., Ltd., Japan) with a three-electrode cell consisting of a working carbon felt electrode, an aqueous  $\text{Ag}/\text{AgCl}$  (3 mol/L  $\text{NaCl}$  electrolyte) as a reference electrode, and a platinum wire as the counter electrode. The coulometry measurement used a digital coulomb meter (Nikko Keisoku Co., Ltd., Japan) and a digital recorder (GR-3500, Keyence Co., Ltd., Japan).

### 2.3 Preparation of aminated carbon felt electrode

The carbon felt (GF-20-5F, 20 mm in diameter, and 5 mm in thickness) was mixed with ethanol and distilled water, then treated in an ultrasonic bath for 1 h. The purpose of using an ultrasonic bath is to eliminate all traces of contamination that are firmly or merely attached to the surface of the carbon felt.

As previously reported, nitrogen atoms containing functional groups can be easily introduced onto a GC electrode surface by the electrode oxidation of ammonium carbamate in an aqueous medium at a highly positive electrode potential, and we named this electro-oxidized GC electrode as an aminated GC electrode.<sup>(15–17)</sup> The GC or carbon felt electrode covalently attached with nitrogen-containing functional groups was fabricated by electrolysis. As described, the carbon felt was electro-oxidized in 0.1 M ammonium carbamate aqueous solution at a constant potential of 1.1 V for 1 h (60 min). The reference electrode used was Ag/AgCl and a platinum wire was employed as the counter electrode. All experiments were carried out at room temperature.

### 2.4 Cyclic voltammetry

We observed the following two types of carbon felt as working electrodes: an aminated carbon felt electrode and an unmodified carbon felt electrode. The electrolyte solution used was 0.1 M acetic acid buffer solution (pH 4.0) with or without one droplet of 10 mM NaNO<sub>2</sub>. An aqueous Ag/AgCl (3 M NaCl electrolyte) reference electrode, a magnetic stirrer, and a platinum wire used as a counter electrode were also employed. The potential scan range was 0.4 to 1.1 V, the number of potential cycles was 100, and the potential scan rate was 20 mV/s. All experiments were observed at temperature room.

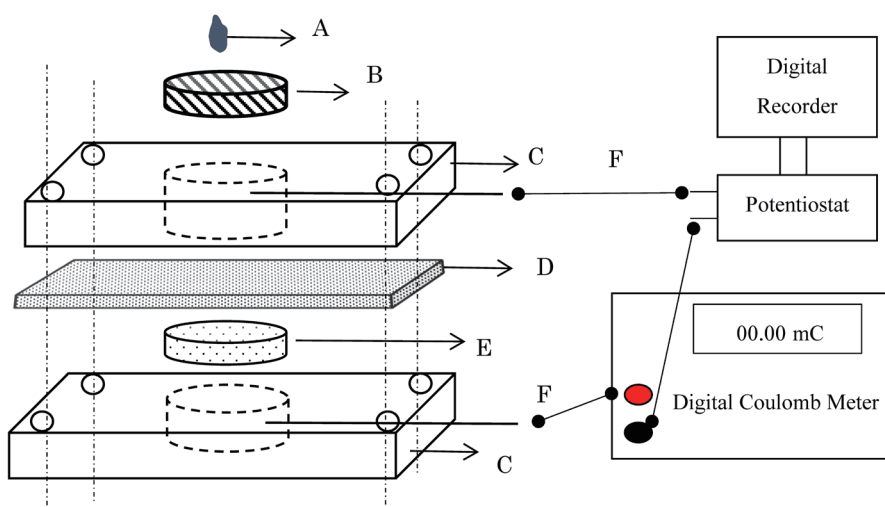


Fig. 1. (Color online) Schematic of coulometric measurement. A: sample addition; B: aminated carbon felt electrode; C: acrylic plate; D: ion exchange membrane; E: unmodified carbon felt electrode; F: Pt lead wires.

## 2.5 Coulometric determination of nitrite

The schematic of the constructed potential-controlled coulometric cell is shown in Fig. 1. The modified/aminated carbon felt electrode (20 mm in diameter, 5 mm in thickness) was used as a working electrode. The unmodified carbon felt electrode without any electrochemical modification treatments was used as a counter carbon felt electrode. The aminated carbon felt was separated from the counter carbon felt electrode by the cation exchange membrane. A platinum wire (0.5 mm diameter) was used as a lead wire. The aminated carbon felt electrode was immersed in 0.1 M acetic buffer (pH 4.0). A saturated aqueous solution of potassium hexacyanoferrate (III) was used as a counter solution soaked in the counter carbon felt electrode.

In addition, we measured the electrical charge (mC) and response time (s) by adding one droplet of 1 mM  $\text{NaNO}_2$  for three measurements and the average value was calculated. The applied potential used was from 0.3 to 1 V. However, the best applied potential sensor cell was used for all measurements in the potential-controlled coulometry. One droplet of 1 mM  $\text{NaNO}_2$  was added for ten repetitive measurements in the 0.1 M acetic acid buffer solution, and the sample volume was 10  $\mu\text{L}$ . The various added sample volumes were from 0 to 100  $\mu\text{L}$ . The high to low concentration and low to high concentration used were from 0.1 to 10 mM  $\text{NaNO}_2$ .

## 3. Results and Discussion

### 3.1 Electrocatalytic performance of nitrite using aminated carbon felt electrode

Figure 2 shows the cyclic voltammograms obtained using aminated carbon felt electrodes with (solid line) and without (dotted line) 10 mM  $\text{NaNO}_2$  in 0.1 M acetic acid buffer solution (pH 4.0). We observed that, without the addition of nitrite in the aminated carbon felt electrode, no oxidation wave was generated from nitrite in the potential range from 0.4 to 1.1 V. However, with the addition of nitrite using an aminated carbon felt electrode as a working electrode, we observed an oxidation wave generated in the measurement using cyclic voltammetry. Then, we

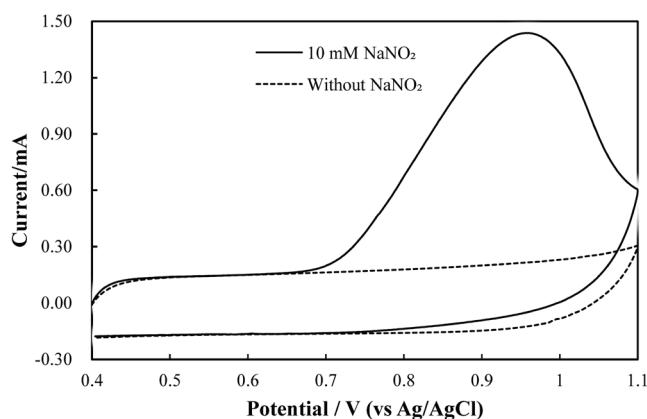


Fig. 2. Cyclic voltammograms of aminated carbon felt electrode in acetic acid buffer solution (pH 4.0) with (solid line) and without (dotted line) 10 mM  $\text{NaNO}_2$ . The scan rate is 20 mV/s.

found that the anodic peak potential was 0.95 V and that the oxidation peak current was 1.44 mA. We also confirmed the induction of the electrocatalytic activity of nitrite in this process. This cyclic voltammogram shows the electro-oxidation product in the electro-inactive species. Then, these results suggest that the nitrite ion is oxidized to the nitrate ion according to Eq. (1).

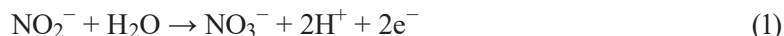


Figure 3 shows the cyclic voltammograms of the aminated carbon felt electrode (solid line) and unmodified carbon felt electrode (dotted line) with 10 mM NaNO<sub>2</sub> in 0.1 M acetic acid buffer solution (pH 4.0). This result indicates that the aminated carbon felt electrode exhibits an oxidation peak current compared with the unmodified carbon felt electrode. The oxidation peak current of the aminated carbon felt electrode was 1.44 mA and that of the unmodified carbon felt electrode was 0.18 mA. The oxidation peak current of the aminated carbon felt electrode was about sevenfold larger than that of the unmodified carbon felt electrode. This increase in oxidation peak current has been reported by Wang *et al.*<sup>(21)</sup> In their study, the increase in oxidation peak current was twofold larger when using an aminated GC electrode as a modified carbon electrode and a GC electrode as an unmodified carbon electrode in 0.1 M acetic acid buffer solution (pH 4.0) containing 100 μM NaNO<sub>2</sub>.<sup>(21)</sup> The multiple increases in oxidation peak current indicate the presence of a nitrogen atom containing functional groups in the aminated carbon felt electrode and also aminated GC electrode as a modified carbon electrode.

### 3.2 Analytical performance for potential-controlled coulometry using aminated carbon felt electrode

A correlation was observed between the applied potential and the electrical charge at various applied potentials during the coulometric measurement of nitrite. The electrical charge (solid line) and response time (dotted line) are shown in Fig. 4.

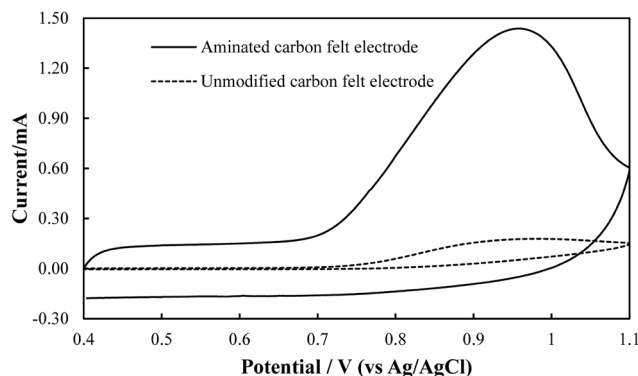


Fig. 3. Cyclic voltammograms of aminated carbon felt electrode (solid line) and unmodified carbon felt electrode (dotted line) in acetic acid buffer solution (pH 4.0) with 10 mM NaNO<sub>2</sub>. The scan rate is 20 mV/s.

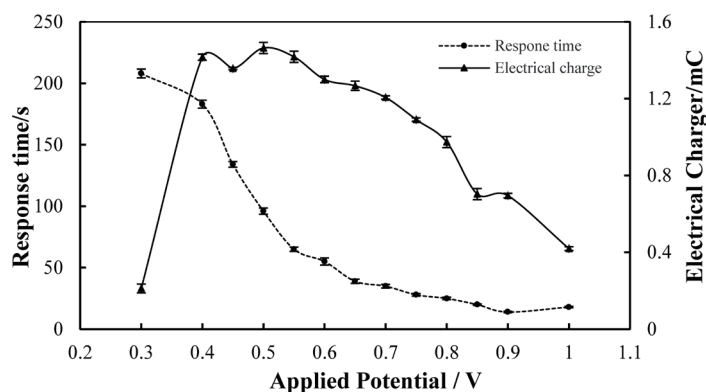


Fig. 4. Response time and electrical charge vs applied potential with 1 mM  $\text{NaNO}_2$  in acetic acid buffer solution (pH 4.0). The sample volume is 10  $\mu\text{L}$ .

Response time is the time required to return into the baseline and remain constant, when adding a sample to the electrolyte solution in the potential-controlled coulometry. In the applied potential range from 0.3 to 0.9 V, the response was fast. However, in the applied potential range from 0.9 to 1.0 V, the response was slightly slow.

The amount of substance (mole) of the analyte corresponds to the electrical charge through the Faraday constant. This means that the number of electrons can be estimated from the electric charge under the measurement to determine the concentration of the analyte. From the electrical charge results in Fig. 4, we know that the electron number of the electrode reaction was two electron paths from the estimation of the electrical charge of nitrite detection. The high point of the electrical charge is when the applied potential is 0.5 V. However, in the applied potential range from 0.5 to 0.8 V, the electrical charge decreased. On the other hand, the electrical charge decreased significantly when the electrode potential exceeded 0.8 V. This result indicates that the catalytic site on the aminated carbon felt electrode surface was destroyed by electrode oxidation. With all the reasons mentioned above, we assume that the optimal applied potential for measuring the electrical charge is 0.75 V.

Figure 5 shows the relationship between the typical current and the time curve obtained by the repetitive measurement of 1 mM  $\text{NaNO}_2$  in 0.1 M acetic acid buffer solution (pH 4.0). The response time of the electro-oxidation current was short ( $\sim 30$  s) and no detectable residual current fluctuation appeared after the electrolysis had been completed. The relative standard deviation (RSD) for the tenth successive measurement was 2.2%.

The relationship between the electrical charge flowing through the electro-oxidation process of nitrate and the added sample volume is shown in Fig. 6. This result indicates that the electrical charge corresponds to the added sample volume in the range from 1 to 100  $\mu\text{L}$  with good linearity. Moreover this result also indicates that the electrolysis efficiency is close to 100% because the determination is very quickly realized.

The relationship between the current and the time at various concentrations of  $\text{NaNO}_2$  in acetic acid buffer solution (pH 4.0) is shown in Fig. 7. We observed the high to low concentration of  $\text{NaNO}_2$  with a sample volume of 10  $\mu\text{L}$ . From this result, we consider that



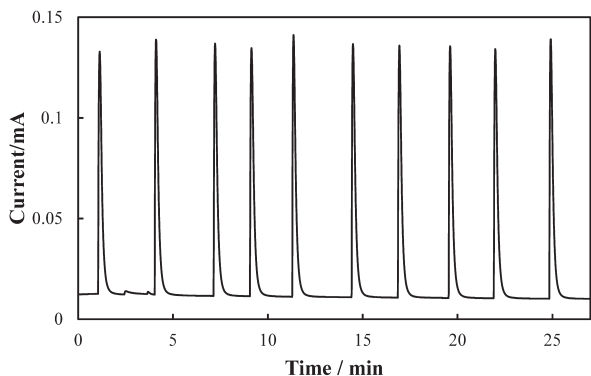


Fig. 5. Current vs time curve obtained for repetitive measurement of 1 mM  $\text{NaNO}_2$  in acetic acid buffer solution (pH 4.0). The sample volume is 10  $\mu\text{L}$ .

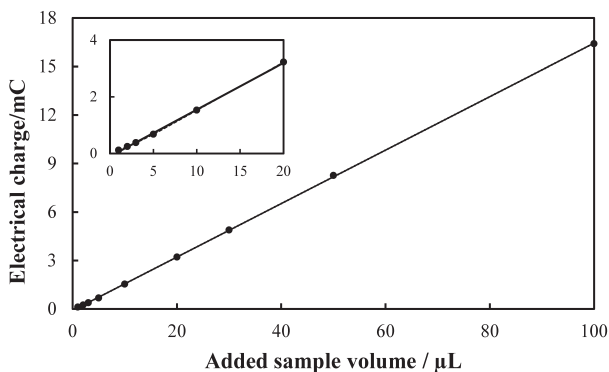


Fig. 6. Relationship between electrical charge and added sample volume.

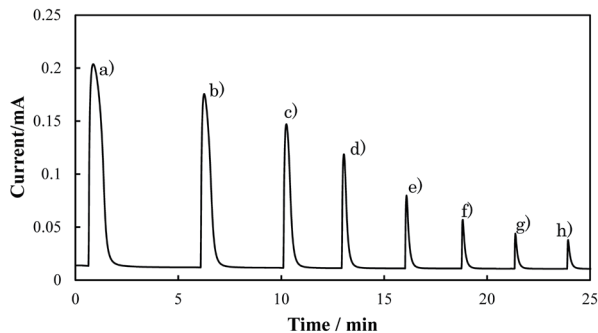


Fig. 7. Current vs time curve obtained by measurement of  $\text{NaNO}_2$  in acetic acid buffer solution (pH 4.0). (a) 5 mM; (b) 3 mM; (c) 2 mM; (d) 1 mM; (e) 0.5 mM; (f) 0.3 mM; (g) 0.2 mM; (h) 0.1 mM. The sample volume is 10  $\mu\text{L}$ .

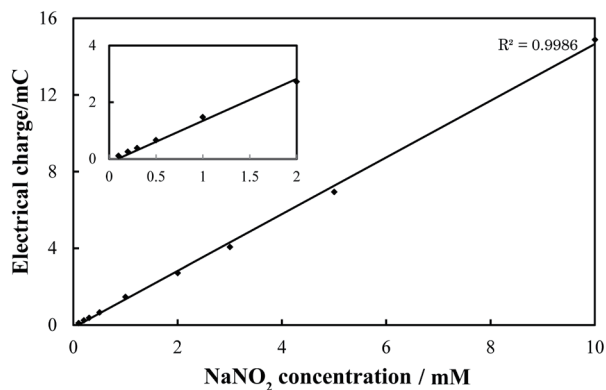


Fig. 8. Various concentrations of  $\text{NaNO}_2$  in acetic acid buffer solution (pH 4.0) at applied potential of 0.75 V. The sample volume is 10  $\mu\text{L}$ .

the calibration curve changes with the addition of  $\text{NaNO}_2$  at various concentrations. It can be described that the high-concentration solution (a) has a slow response. In contrast, the low-concentration solution (h) has a fast response.

Figure 8 shows the relationship between the electrical charge and the  $\text{NaNO}_2$  concentration. We used various  $\text{NaNO}_2$  concentrations ranging from 0.1 to 10 mM in acetic acid buffer solution (pH 4.0); 10  $\mu\text{L}$  of the sample was dropped into the aminated carbon felt electrode. The obtained result indicates that the electrical charge correlates with the  $\text{NaNO}_2$  concentration in the range from 0.1 to 10 mM with good linearity. Therefore, the potential-controlled coulometry described here must be a very useful analytical method because the accurate and rapid measurement of the nitrite concentration is easily performed.



## 4. Conclusions

We have prepared nitrogen atoms containing functional groups that can easily be introduced to the surface of a modified carbon felt electrode, called the aminated carbon felt electrode. Potential-controlled coulometry can be used for the analysis of nitrite because it does not require calibration, it is inexpensive, and accurate and rapid measurement can easily be performed. We also have succeeded in determining the optimal applied potential of 0.75 V for analytical performance in a coulometric sensor, especially using the electrolyte 1 mM NaNO<sub>2</sub> in acetic acid buffer solution (pH 4.0). In this coulometric sensor, we can determine the high to low sample concentration. Thus, we proposed coulometric sensing as a promising method for nitrate detection.

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