Voltammetric Determination of Nitrite: Comparison of Carbon Paste and Glassy Carbon Electrodes

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Introduction

Much work has been done on the use of glassy carbon electrode in the determination of various metal ions and organic molecules[1-4]. It was reported to be more convenient than other solid electrodes[1-2]. Recently it has been used for the inverse voltammetric determination of traces of metal ions[5-9]. The present investigation studies the anodic behaviour of this electrode when applied to the determination of nitrite and some other molecules, with a view to compare it with carbon paste electrode, which has also been employed in the various determinations[10-13]. The major aim was to determine nitrite in μg amounts since very few methods are available for its determination.

Nitrites are usually determined spectrophotometrically. In some of the methods an aromatic amine is diazotized and then coupled to form an azo dye the colour of which is measured. The second line of attack is that some organic molecule is oxidized by nitrite to give a colour. This method is nonspecfic because many oxidizing and reducing agents interfere. The third method is the ASTM method developed by Rider and Mellon[14]. This procedure is sensitive but many ions interfere and stringent control of conditions is required. The reagent used in this procedure (N-(1-naphthyl) ethylenediamine dihydrochloride) is known to be carcinogenic[15].

In the present method using voltammetry stringent control of conditons is not required and the method is precise, accurate and convenient to perform.

Experimental

Equipment

All measurements were made with a potentiostatic DC polarograph[16]. As reference served a saturated calomel electrode with saturated potassium nitrate bridge solution. The glassy carbon electrode was made by sticking a carbon strip (Fac. Deutsche glascarbon, Frankfurt a.m., West Germany) with UHU PLUS in a glass tube with appropriate connection heads. The carbon paste electrode was prepared as described in earlier work[11]

Reagents

All the reagents used were of analytical reagent grade unless otherwise stated. Potassium nitrite solution was prepared in double distilled water and then standardized[14]. 1M potassium nitrate solution was prepared in double distilled water.

Cystine, thiourea, glucose and ascorbic acid were E. Merck products and desired concentrations were made in double distilled water.

Procedure

An aliqout (1ml) of the potassium nitrite solution was taken in 20 ml Metrohm cell with a self mounting plastic cell top having provision for a three electrode system and an inlet for nitrogen. The total volume was made upto 10 ml by the addition of supporting electrotyte. As indicating electrodes were used a carbon paste or glassy carbon, and a platinum wire electrode as counter electrode. A small plastic tube with perforated tip was attached to the end of refernce electrode. The electrodes were dipped in solution which was deaerated with pure nitrogen for 5 min. Then a scan with a rate of 200 mv/min. from + 0.1 to + 1.12 v was switched on. The temperature was (25+ 0.2)^{o}C. The calibration graph was constructed for both the electrodes i.e. carbon paste and glassy carbon in the concentration ranges of 10μg/ 10ml to 60μg/ and 70 μg/ 10ml to 300 μg/ 10ml respectiveiy.

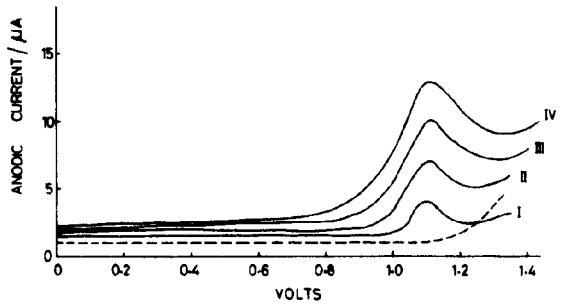

Fig. 1. Potential of Carbon Paste Electrode versus SCE/V Concentration of NO_2^-

I. 1.0×10^{-5}M
II. 2.0×10^{-5}M
III. 3.0×10^{-5}M
IV. 4.0×10^{-5}M

Scane Rate was 200 mv/min.

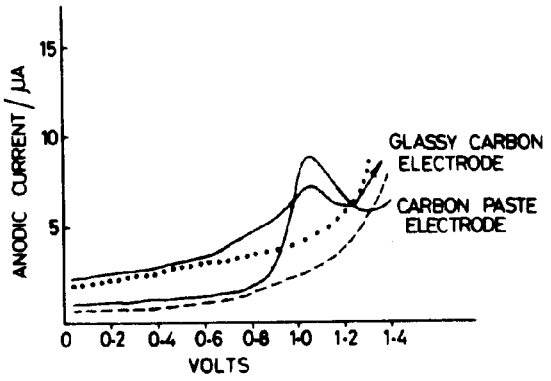

Fig. 2. Potential versusSCE/VVoltammograms 1×10^{-4} M NO_2^- 1M KNO_3 Scan Rate 200 mv/min.
--- Base Current for Carbon Paste Electrode.
.... Base Current for Glassy Carbon Electrode.

Results and Discussion

In this investigation nitrite, ascorbic acid, cystine cystein, glucose, sulfite and thiourea were tried in the positive voltage region. The main aim was to determine nitrite because this is used in the preservation of meat but at the same time it is prohibited in drinking water.

In 0.1M acetic acid and 1M potassium nitrate, ascorbic acid and thiourea were oxidized at + 0.78 and + 0.65 volt respectively with SCE as reference electrode. While cystine, cystein and glucose did not show any response in region from + 0.1 to + 1.2v with both the investigated electrodes. Nitrite is oxidized in 1.OM KNO_3 at + 1.1 volt with SCE as reference electrode.

Both the glassy carbon and the carbon paste electrodes showed oxidation peaks of similar shape, but it has been noted that the glassy carbon electrode peaks were very small with the above mentioned substances. Both the electrodes showed very small peaks for thiourea. Carbon paste electrode has been found more sensitive than glassy carbon electrode for ascorbic acid and nitrite, they could be determined as low as 1×10^{-6}M. However, with glassy carbon electrode under similar conditions 1×10^{-4} concentrations only were possible. The peak height was proportional to the concentration (Fig. 1). The results were calculated from the calibration graph (Table 1). It has been found that the base current was very high with the glassy carbon as compared to the carbon paste electrode. The potential region of the nitrite peak was the same with both the electrodes but peak slope was lower with glassy carbon as compared to

Table I. Determination of nitrite with glassy carbon and carbon paste electrodes.

Electrode	Amount taken μg/10ml	Found μg	Deviation %
Glassy Carbon	74.0	69.0	− 7.2
	144.0	149.0	+ 3.4
	288.0	280.0	− 2.7
Carbon paste	11.0	10.5	− 4.5
	33.0	32.5	− 1.5
	44.0	45.0	+ 1.1

the carbon paste electrode (Fig. 2). The base current was high with the glassy carbon electrode and because the slope of the peak for determination of nitrite was comparably low, therefore, it was not suitable for the determinations of small amounts of nitrite. Cleaning and renewing of the glassy carbon electrode was not necessary in the determination of nitrite. Four successive runs were made with glassy carbon electrode from the same solution without renewing the surface. No appreciable difference could be found in the 4 runs. However, the renewing of the paste electrode was necessary after every run.

Effect of Interferences:

In the determination of nitrite with both electrodes, sulfite, iodide and ascorbic acid interfered even when they were present half as much as nitrite. But ascorbic acid is seldom present with nitrite. Glucose and urea did not interefere.

Conclusion:

Carbon paste electrode gives well defined and higher peaks against lower base current in the determination of nitrite. It can be used for the determination of microamounts of nitrite.

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