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The Determination of Catechols in the Presence of Ascorbic Acid and Uric Acid by Flow Injection Analysis Employing a Potentiometric Dibenzo-18-crown-6 Electrode Detector

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THE DETERMINATION OF CATECHOLS IN THE PRESENCE OF ASCORBIC ACID AND URIC ACID BY FLOW INJECTION ANALYSIS EMPLOYING A POTENTIOMETRIC DIBENZO-18-CROWN-6 ELECTRODE DETECTOR

KEY WORDS: Catechol, Catecholamines, Electrochemistry, Potentiometric Detector, Flow Injection Analyses, Modified Electrode, Interferents: Ascorbic Acid and Uric Acid

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ABSTRACT

A polished platinum disc was modified by electropolymerization of dibenzo-18-crown-6 (DB-18-C-6) onto the surface. This DB-18-C-6 electrode has been used as a detector for catechol and catecholamines in a potentiometric-flow injection mode. The potentiometric-flow injection response of the DB-18-C-6 modified electrode exhibited a linear response for catechol and catecholamine concentrations from 10^{-2}-10^{-6} M achieving detection limits as low as 0.5 x 10^{-6} M.

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An interference study was carried out with ascorbic acid and uric acid which are serious interferents using amperometric detectors. No significant interference was observed for the presence of either of these two or mixture of these two common interferents until they were in greater than a 10-fold excess.

INTRODUCTION

The analyses of catecholamines (neurotransmitters) is a very important problem in biomedical studies.[1-4] Electroanalytical techniques are very attractive for such analyses as these species are readily oxidized. However, biological samples containing these species usually contain either ascorbic acid or uric acid (or both) which are oxidized at more negative potentials. Therefore, simple amperometric and voltammetric methods cannot be used without prior separation for flow injection analysis (FIA).[5,6]

A promising class of potential sensing elements for ion selective electrodes includes many immobilized synthetic macrocyclic host compounds in liquid or polymer matrices. These macrocyclic compounds have diversity in structure and, subsequently, chemical recognition function as well as high chemical stability which makes them ideal as detectors. A large number of reports has been published on a series of crown ether derivatives for potentiometric cation selective electrodes.[7-16] A crown ether modified electrode based on the electropolymerization of binaphthyl-20-crown-6 has been employed recently as a selective potentiometric electrode for the catechol moiety.[16]

In the present study we describe a DB-18-C-6 modified platinum electrode as potentiometric sensor for catechols in the flow injection mode. The performance of this detector is evaluated for catechol analyses and for catechol samples containing either ascorbic acid or uric acid (or both). The degree of interference of these species is described.

EXPERIMENTAL

Reagents

Unless otherwise stated, the chemicals used were ACS reagent grade which were used without further purification. The water was distilled in house and then further purified with a Sybron/Barnstead NANO Pure II system. The mobile phase was 0.1 M potassium phosphate buffer and the Ph was adjusted to 9.4 using a potassium hydroxide solution.

Apparatus and Procedures

A platinum disc electrode-Teflon block purchased from Bioanalytical System (BAS: West Lafayette, IN) was used. The platinum disc was polished with alumina polishing solution using a BAS (MF-1056) polishing kit. The electrode was rinsed with HPLC grade acetonitrile and air dried. The polymerization of the crown ether onto the platinum disc electrode was carried out by a three electrode system. A platinum wire coil was the auxiliary electrode and an Ag/AgCl (BAS MF-2063) was the reference electrode. A PAR 275 Potentiostat/Galvanostat performed the electrochemical polymerization using an applied potential of + 3.2V vs. Ag/AgCl for five minutes in the monomer

solution. The monomer solution consisted of 0.025 M dibenzo-18-Crown-6 and 200 mM tetrabutylammoniumtetrafluoroborate (TBATFB) as the supporting electrolyte. The polymerized electrode was then rinsed with HPLC grade acetonitrile, air dried and immersed in a monomer free (TBATFB) solution. A potential of + 0.5 V vs. Ag/AgCl was applied for approximately twenty-five minutes.

The monomer modified electrode-Teflon block and Ag/AgCl reference electrode were incorporated into a standard BAS thin layer flow cell. The flow injection system consisted of an Altex Model 100A double reciprocating pump followed by an Altex injection valve (Cat. No. 905-42). A 20 μl sample loop was used throughout the experiments. The potentiometric measurements were carried out with an Orion Model 601A Ion-analyzer and the recorder was a Fisher Recordall Series 5000. A flow rate of 1.0 ml/min was used throughout.

RESULTS AND DISCUSSION

The potentiometric-FIA response was found to depend on the catechol concentration. Figure 1 illustrates the potentiometric FIA response of the DB-18-C-6 crown ether modified electrode which was linear over four decades of catechol concentrations (10^{-2} - 10^{-6} M) with detection limits as low as 0.5 x 10^{-6} M. Similar results were obtained for the neurotransmitters.

In the biomedical field there is great concern about common interferents such as ascorbic acid and uric acid in the determination of catechols. It was found that ascorbic acid did not significantly hinder the potentiometric response to catechol as long as the catechol/ ascorbic acid concentration ratio was 1/10 or

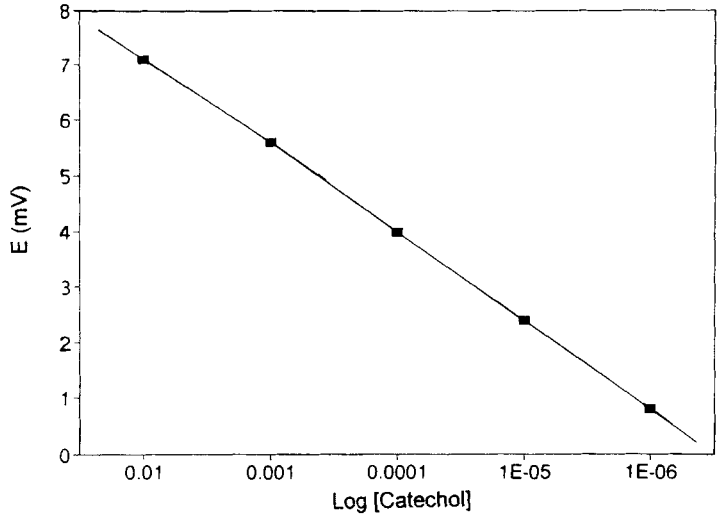

FIGURE 1. Flow injection-potentiometric detection calibration curve of the dibenzo-18-crown-6 (DB-18-C-6) modified electrode for catechol. Sample size: 20 μl; mobile phase: potassium phosphate buffer (pH=9.4); flow rate: 1.0 ml/min. Correlation coefficient: 0.999.

less as shown in Table I. Table I also shows that as the concentration of ascorbic acid is 10-fold greater than the concentration of catechol, the signal then increases.

Figure 2 shows the typical FIA signal responses obtained in the absence of ascorbic acid and in the presence of the interferent in equal concentrations. This demonstrates that at equal concentrations of catechol to ascorbic acid the FIA response signal remains the same as in the absence of ascorbic acid. It can be seen that the response time of this potentiometric electrode is faster than the rate of flow of the sample slug past its surface. It also shows the typical reproducibility of peak heights obtained. Table II shows that uric acid acts in a

TABLE I. Potentiometric Flow Injection Analyses of Catechol in the Presence of Ascorbic Acid. ΔPotential is the difference between signal peak height and base line potentials.

CATECHOL (M)	ASCORBIC ACID (M)	ΔPOTENTIAL (mv)
10^{-2}	0	13.2
10^{-2}	10^{-1}	15.2
10^{-2}	10^{-2}	13.2
10^{-2}	10^{-3}	13.2
10^{-2}	10^{-4}	13.2
10^{-2}	10^{-5}	12.8
10^{-3}	0	10.4
10^{-3}	10^{-1}	16.0
10^{-3}	10^{-2}	12.8
10^{-3}	10^{-3}	10.4
10^{-3}	10^{-4}	10.4
10^{-3}	10^{-5}	10.4
10^{-4}	0	6.8
10^{-4}	10^{-1}	12.4
10^{-4}	10^{-2}	10.0
10^{-4}	10^{-3}	8.0
10^{-4}	10^{-4}	6.4
10^{-4}	10^{-5}	6.4
10^{-5}	0	4.8
10^{-5}	10^{-1}	12.0
10^{-5}	10^{-2}	9.2
10^{-5}	10^{-3}	7.2
10^{-5}	10^{-4}	6.4
10^{-5}	10^{-5}	4.8

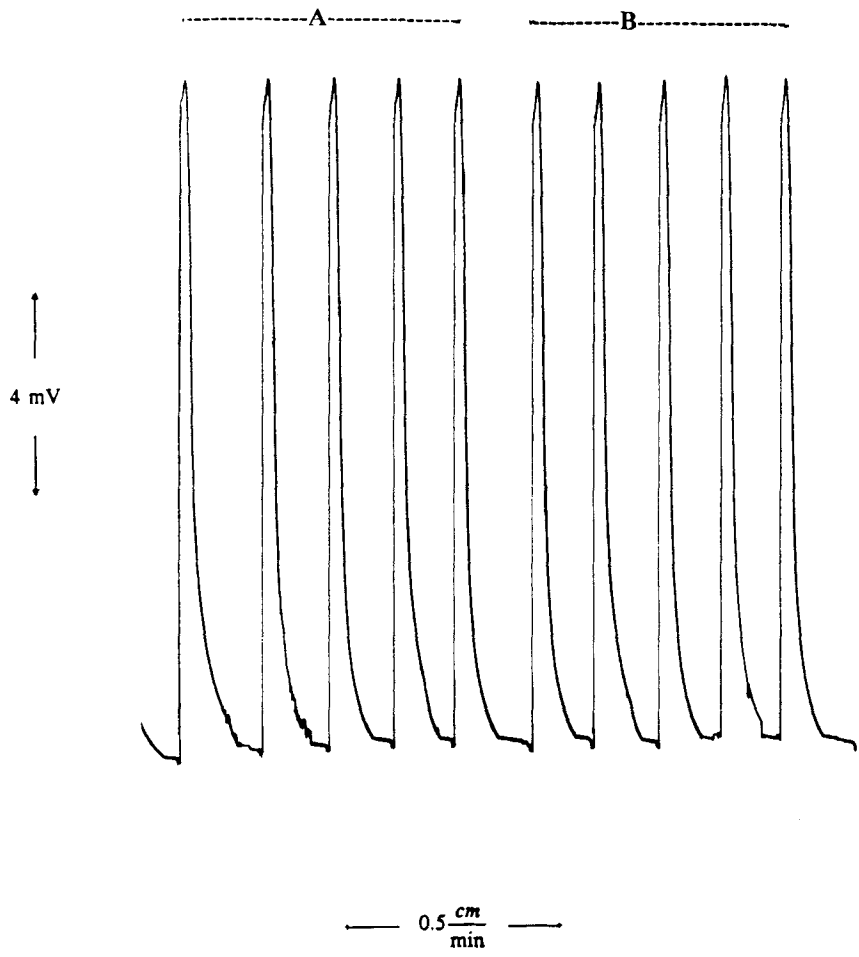

FIGURE 2. **Examples of FIA signals obtained on the modified DB-18-C-6 electrode. Sample size: 20 μl; mobile phase: potassium phosphate buffer (pH=9.4).**

A) 10^{-2} M Catechol

B) 10^{-2} M Catechol + 10^{-2} M Ascorbic Acid

Table II. Potentiometric Flow Injection Analyses of Catechol in the Presence of Uric Acid

CATECHOL (M)	ASCORBIC ACID (M)	ΔPOTENTIAL (mv)
10^{-2}	0	13.6
10^{-2}	10^{-1}	25.2
10^{-2}	10^{-2}	13.6
10^{-2}	10^{-3}	14.0
10^{-2}	10^{-4}	13.2
10^{-2}	10^{-5}	13.6
10^{-3}	0	8.8
10^{-3}	10^{-1}	2.3
10^{-3}	10^{-2}	16.8
10^{-3}	10^{-3}	8.0
10^{-3}	10^{-4}	7.6
10^{-3}	10^{-5}	7.6
10^{-4}	0	5.6
10^{-4}	10^{-1}	18.0
10^{-4}	10^{-2}	8.8
10^{-4}	10^{-3}	6.0
10^{-4}	10^{-4}	5.6
10^{-4}	10^{-5}	5.6
10^{-4}	0	6.8
10^{-4}	10^{-1}	16.8
10^{-4}	10^{-2}	13.6
10^{-4}	10^{-3}	5.6
10^{-4}	10^{-4}	5.6
10^{-4}	10^{-5}	5.6

Table III. Potentiometric Flow Injection Analyses of Catechol in the Presence of Both Ascorbic Acid and Uric Acid.

CATECHOL (M)	ASCORBIC ACID (M)	URIC ACID (M)	ΔPOTENTIAL (mv)
10^{-4}	0	0	6.8
10^{-4}	10^{-1}	10^{-1}	16.8
10^{-4}	10^{-2}	10^{-2}	13.6
10^{-4}	10^{-3}	10^{-3}	5.6
10^{-4}	10^{-4}	10^{-4}	5.6
10^{-4}	10^{-5}	10^{-5}	5.6

similar manner to ascorbic acid as an interferent. For the lower concentrations (10^{-3} - 10^{-5} M) of uric acid present, the potential response was the same as that of the catechol response (10^{-4} M) without uric acid present.

A combination of ascorbic acid and uric acid present in the determination of catechol show similar interferent properties as shown in Table III. The signal response does diminish by a few tenths of a millivolt for comparable total concentration or less interferents to catechol concentration compared to that in the absence of these two interferents.

CONCLUSION

The classical problem encountered in the biomedical field in the determination of catechols by amperometric detectors is the problem of the presence of the interferents ascorbic acid and uric acid present in the natural biological media.

This study demonstrates that the DB-18-C-6 potentiometric-FIA modified electrode significantly minimizes the problem of these interferents allowing the determination of catechols by FIA directly without separation. As preliminary studies of other crown ether compounds (various number of oxygens as well as open versus cyclic structure) show significant differences in response to potentiometric catechols, it is felt that ascorbic acid and uric acid interferences can be reduced even further with some of these polymers. Also sensitivity limits can be improved. These studies are presently underway.

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