Tr. J. of Chemistry
21 (1997) , 21 – 29.
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Analytical Applications of Organic Conducting Polymer Electrodes*

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Received 10.1.1997

Electrodes modified by he electrodeposition of conducting polymers were used for the detection and quantitative determination of some inorganic, organic, and biological molecules. Monomers used were five membered ring heterocycles or crown ethers and their derivatives. The polymer films were deposited on glassy carbon or platinum substrates. The resulting electrodes were used in the amperometric mode or in the potentiometric mode for flow injection and chromatographic analyses. The results showed that the proposed modified surface catalyzes the oxidation of organic and biological compounds. The detection of electroinactive inorganic anions, such as F^-, Cl^-, Br^-, NO_2^- and NO_3^- was also possible using a Cu(II)-containing poly(3-methylthiophene) working electrode for the single-column ion chromatography. The development of a novel type of poly(crown ether) electrode that is capable of selectively determining some 1,2-dihydroxybenzenes will also be discussed.

Introduction

The development in the area of synthetic organic conducting polymers has attracted the attention and involvement of scientists in different research areas[1]. These "materials" have been proposed, and applied, in wide variety of technical applications such as solid state batteries and energy storage, electrochromic displays, rectification, microelectronics, and photovoltaic devices[2]. Recently, we and many other research groups became interested in the modification of electrode surfaces with films of conducting polymeric materials[3]. Film-coated electrodes have been used in different detecting modes such as to immobilize redox-mediators, for the measurements in liquid chromatography, and for preconcentration[4]. We have been interested in both electrochemically grown[5] and chemically synthesized[6] poly(heterolenes). Among the several materials studied in our laboratories is the poly(3-methylthiophene), poly(crown) ethers, and Cu-containing poly(heterolene) composites[7]. On the other hand, electrode materials most commonly used in amperometric systems are glassy carbon, platinum and gold electrodes[8], which have reversibiliy limitations.

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* This work is presented at 35th IUPAC-İstanbul Congress as an invited lecture.

Moreover, several limitations are encountered in the application of mercury electrodes in flowing solutions such as their mechanical unstability[9], or the lack of inherent selectivity and adsorption of unwanted species from solution including other interfering Faradaic processes at other "conventional" surfaces. The behavior of electrodes modified with conducting poly(thiophene) film and their derivatives have been of great interest due to both their stability and their conducting properties[10]. The selective response of this class of polymers towards dissolved ions[11] and to some organic molecules[12] made them useful in various applications as new "generation" of electrochemical sensors.

The work presented here describes a compilation for the applicability of using organic conducting polymer electrodes in different analytical detecion and sensing modes. Among the main applications discussed here are: (i) the voltammetric behavior of some organic molecules of biological interest and their amperometric detection in a flow through system using the conducting polymer electrode, (ii) the detection and determination of some inorganic and organic molecules in the potentiometric mode for both stationary and flow-injected ionic or molecular species at polymer coated platinum electrode, and (iii) the conductivity monitoring of inorganic anions with a Cu(II)-containing poly(3-methylthiophene) electrode in single-column ion chromatography. The electrocatalytic properties, selective voltammetric or potentiomeric determination, and sensitivity for this class of electrode materials will also be discussed and compared.

Experimental

Procedure and Apparatus

Electrochemical polymerization was carried out in a one compartment well containing deaerated acetonitrile, 0.1 M tetrabutylammonium tetrafluoroborate and 0.05 M 3-methylthiophene or dibenzo-18-crown-6. Either a potentiostatic or cycling (between two potential limits) mode was adapted for films growth. Cyclic voltammetry and potentiometry was done with films grown at a constant potential of 1.6 - 1.8 V for 30 - 45 s, unless otherwise stated. After the polymerization, all films were kept at -0.20 V for 10 minutes to electrically neutralize the film. A platinum (MF2013, BAS, West Lafayette, Indiana USA, or a glassy carbon (MF2012, BAS) electrodes, coated or otherwise were used for the voltammetric measurements. These measurements were conducted with a BAS-100 electrochemical analyzer and voltammograms were recorded with a DMP-40 digital plotter from Houston Instrument. A thin layer detector cell with dual Pt-Pt electrodes (MF1012, BAS) was used for flow injection/HPLC-amperometric detection of analytes. The mobile phase was driven by an Altex model 100 double reciprocating pump with a flow rate of 1.0 mL/min. A 20 μL sample injection loop was used throughout the experiment. The electrode potential was controlled by a BAS model CV-1B cyclic voltammetry unit and signals were recorded with a Fisher Series 5000 recorder. Potentiometric measurements were made with an Orion Model 601A ionalyzer using an Orion Model 90-02 double-junction reference electrode with 10% KNO_3 solution in its outer chamber. As the ion selective electrodes respond to ionic activity, and as the readout is to be proportional to the analyte concentration, it is important that the activity coefficient, which relates these factors, is kept constant. In this respect, all the studied solutions contained 1×10^{-3} M KNO_3 as an ionic strength adjuster. These experiments were normally carried out at 23.0 ± 0.5 °C. In all potentiometric measurements a stepwise addition method was used for the calibration.

Chemicals and Solvents

Tetraalkylammonium salts were purchased from Aldrich and were used as received. Organic and biological salts were purchased from Sigma. All other salts, buffer solutions, HPLC-grade solvents, and reagents were obtained from Fisher Scientific. However, solvents used in the electropolymerization were distilled, purified as described in standard methods[13] and kept over molecular sieves, type 4A, prior to use. Aqueous solutions were prepared by dissolving a preweighed sample in conductivity water.

Results and Discussion

Oxidation Kinetics and Detection at Poly(3-methylthiophene) (PMT)

Figure 1 shows the cyclic voltammetric behaviors of ascorbic acid, catechol, dopamine and p-aminophenol at PMT electrode. Except for ascorbic acid, these and other test substances all displayed reversible behavior in 0.1 M H_2SO_4 electrolyte. As will be discussed further in this manuscript, the oxidation peak potential positions of these substances are more important than their reversibility characteristics in the sensor application. The enhanced electron transfer abiliy of the PMT electrodes are presented in Table 1 by tabulating the anodic peak potentials of test substances at three different electrodes (PMT, platinum and glassy carbon). Glassy carbon (GC) electrodes are often preferred for the analysis of biological systems owing to their relatively high electrocatalytic effeciency and resistance towards surface fouling[14]. However, the anodic peak poentials of all the compounds studied were always much higher than those obtained at platinum electrodes, as can be noted from Table 1. Detailed Discussion of the voltammogram shown in Figure 1 can be found elsewhere[15].

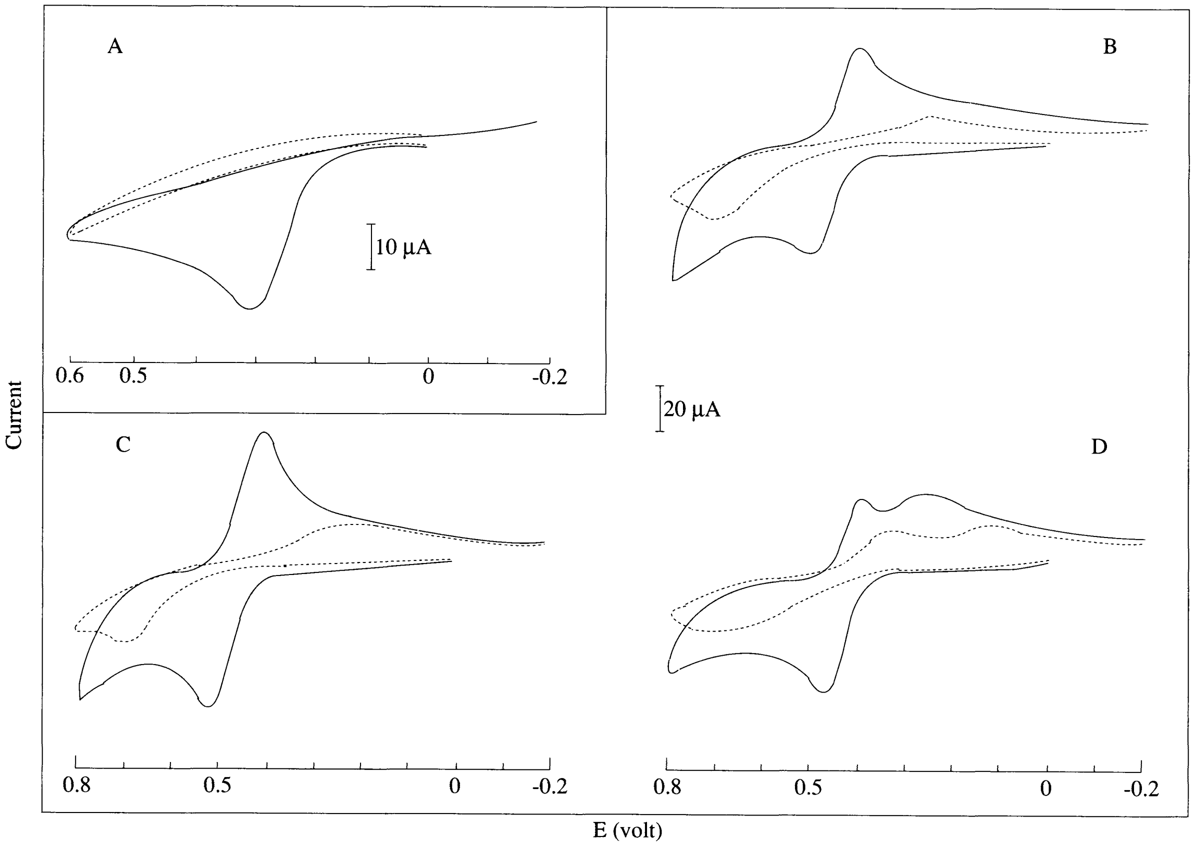

Figure 1. CV behavior of 5 mM each of Ascorbic Acid (A), Dopamine (B), Catechol (C), and p-Aminophenol (D) in phosphate buffer at PMT (solid) and Pt (dashed).

Table 1. Oxidation Peak Potentials of Some Biological Compounds at Three Different Electrodes.

Compound	Epa (mV)		
	PMeT	Pt	GC
Acetaminophen	492	600	904
p-Aminophenol	471	620	900
Ascorbic Acid	296	–[b]	981
Catechol	520	689	849
Dopamine	510	690	831
Epinephrine	440	735	940
Hydroquinone	492	567	729
Fe^{2+}/Fe^{3+}	317	437	568

[a] Values are obtained from the positive scan of first voltammetric cycle
Electrolyte: 0.01 M H_2SO_4; analyte concentration 5 mM. Scan rate 50 mV/s.

[b] No peak was observed in the potential window studied.

The importance of the PMT electrode was manifested in its use for the differential electrochemical analysis of a mixture of ascorbic acid, which is an interferent, and other biological molecules such as dopamine (3b, 12). It was suggested that differential electroanalysis of ascorbic acid in the presence of dopamine at polypyrrole electrodes was achieved due to favorable interaction between an anion, the ascorbate, and a polymer containing fixed positive charges. It is apparent from Figure 2 that the peak position of the solute at the PMT electrodes shows variation with the type of the second analyte in the mixture. This phenomenon is not confined to ascorbic acid; it was observed that peak posiions of individual solute types were not necessarily the same when they were mixed. In order to demonstrate another advantage of the PMT electrode over ca GC; Figure 3A shows the differential pulse voltammogram at a glassy carbon electrode of an equimolar mixture of ascorbic acid, p-aminophenol and catechol, which is, as expected, a single overlapped peak. However, the separation is easily achieved at PM-coated GC, as shown in Figure 3B. This separation was not achieved before, to the best of our knowledge, for one experiment at the same surface. The pH and film thickness effects on the film response was discussed earlier (3b). In conclusion, judicious control of the film polymerization conditions seems to be essential for sensitivity of the electrode and the repeatability of the results.

Amperometric measuremens under flow injections or liquid chromatography conditions are particularly important, especially in routine and batch analysis methodologies. Flow injection and chromatographic analyses, followed with amperometric detection, for catechol, ascorbic acid, dopamine, epinephrine, NADH, p-aminophenol and acetaminophen were performed using Sörensen buffer as mobile phase (in the case of FIA), or as in published procedures (in case of HPLC/EC)[12]. Figure 4 shows the chromatogram obtained for a sample which is a mixture of norepinephrine and dopamine using PMT electrode. The conditions for the separation and detection were as follows: column; PARTISIL 5 ODS-3, mobile phase; 0.15 M monochloroacetic acid, 50 mg SOS, pH 3.0, flow rate; 1.5 mL/min, electrochemical detector; the PMT electrode at an applied potential of 0.55 V (vs. Ag/AgCl). Equimolar amounts of the four analytes were used, namely 1.00×10^{-4} M. Comparison of this chromatogram to that shown in Figure 5 where glassy carbon electrode was used reveals the following facts: (i) the current signals obtained in the case of using glassy carbon, (ii) the base line of the first chromatogram shows a relatively higher stability when compared to that obtained in Figure 5. The calibration curves obtained for the PMT electrode showed higher sensitivities when compared to those obtained at GC electrode. Limits of detection for the different compounds studied were : 0.153, 0.137, 0.105, and 0.218 ng/mL for norepinephrine, Ldopa, epinephrine, and dopamine, respectively.

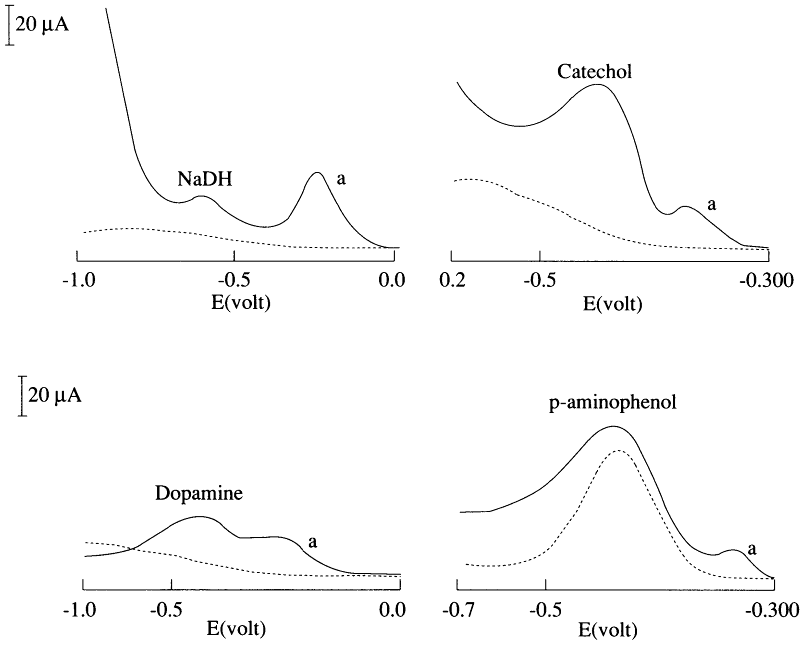

Figure 2. Simultaneous determination of Binary Mixtures in phosphate buffer (pH = 6.9) Square wave voltametry, (a) Ascorbic Acid. Analyte concentration, 5mM.

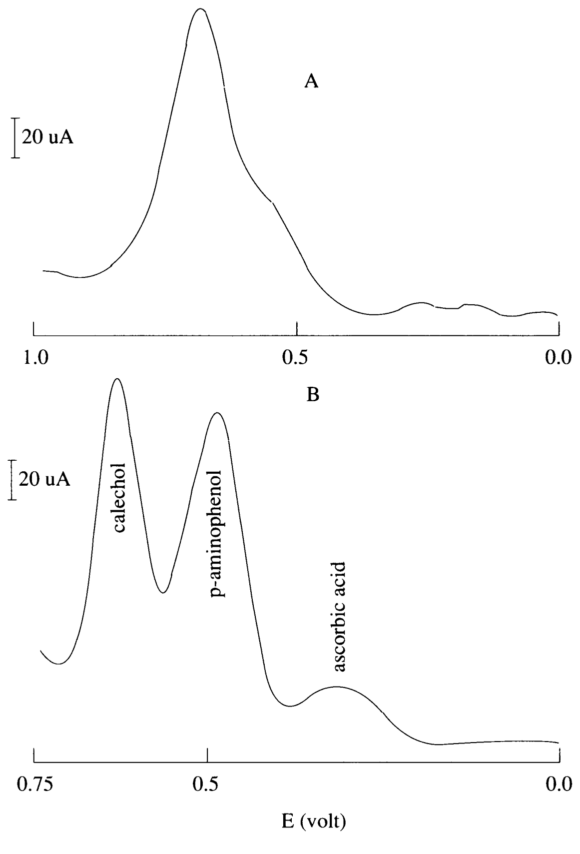

Figure 3. Separation of ternary mixture of 5 mM each ascorbic acid, p-aminophenol, and catechol in phosphate buffer, at GC (A) and PMT (B) electrodes

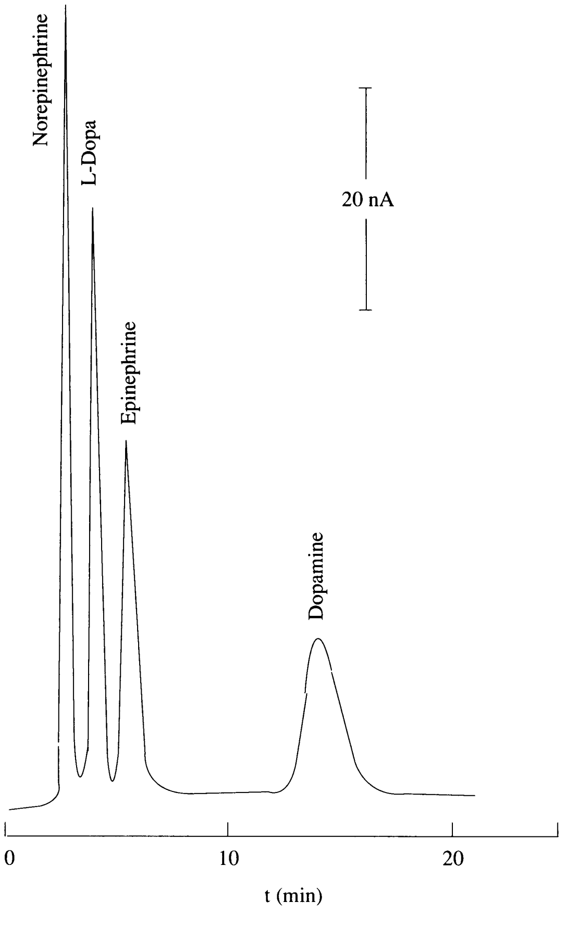

Figure 4. Chromatogram of catecholamines mixture, using PMT electrode as detector in amperometric mode.

The PMT and GC electrodes were examined for the analysis of catecholamines over an extended period of time of over 60 days. The electrodes were also tested for a successive injection in the flow analysis mode for over 20 injections. In general, the PMT electrode showed higher stability over that observed for the GC. Moreover, the same electrode were tested and compared for their stability in the presence of surface active agents such as albumin or gelatin. The signal obtained at the GC was attenuated and relatively unaffected in the case of using he PMT electrode.

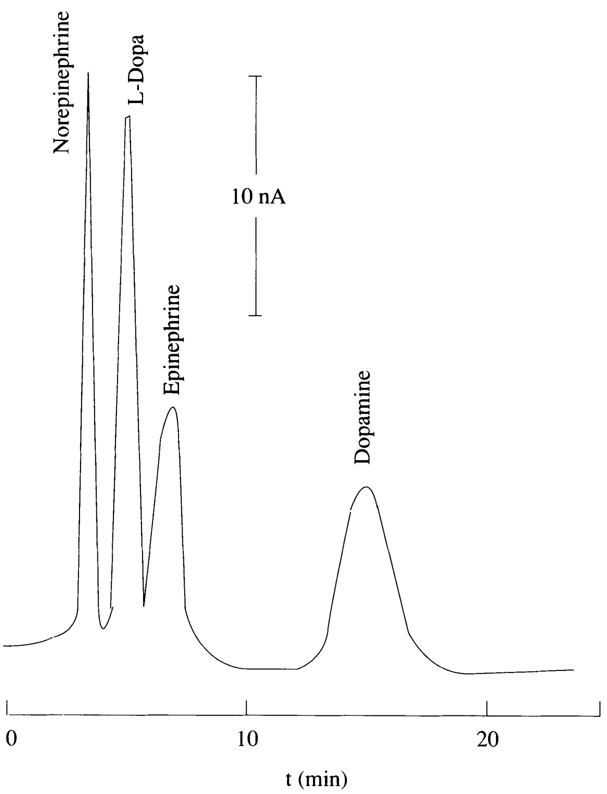

Figure 5. Chromatogram of catecholamines mixture, using GC electrode as detector in amperometric mode.

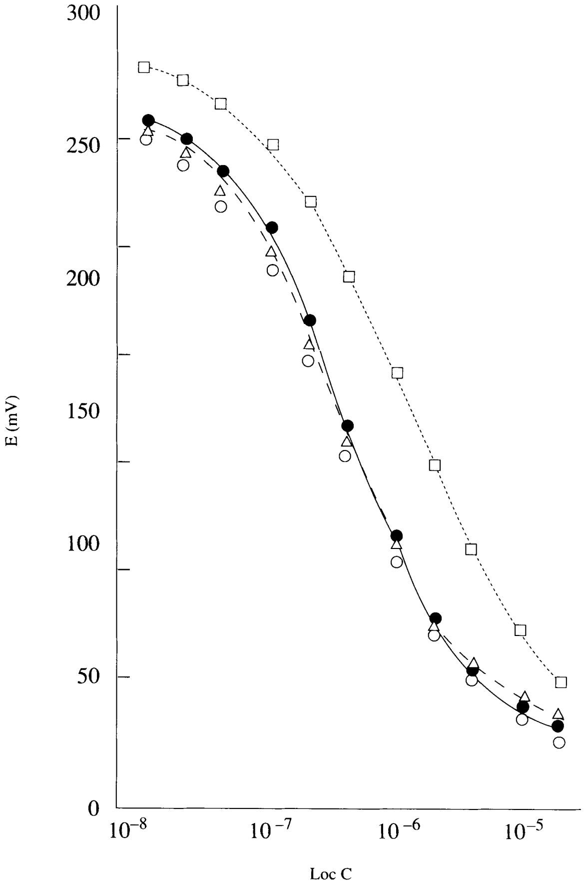

Figure 6. Calibration curves of polycrown ether electrode for catecholamines. •, Dopamine; Δ, Norepinephrine; ○, Epinephrine; □, L-dopa.

Potentiometric Analyses of Inorganic and Biological Molecules at Conducting Polymer Electrodes

A new potentiometric electrode was constructed by means of electrochemical polymerization of the binaphthyl-20-crown-6 on a platinum electrode for the determination of catecholamines. The synthesized polymer was employed as the sensing element. A typical calibration curve of the polycrown ether electrode for catecholamine is shown in Figure 6. The general characteristics of the calibration curves of dopamine, epinephrine, and norepinephrine are similar. However, the calibration curve of L-Dopa has better linearity than that of catecholamine. The polycrown ether electrode has a linear response range of 1×10^{-7} M to 5×10^{-4} M and a super-Nernstian response slope of 110-130 mV/decade with a detection limit of 3×10^{-8} M for the catecholamines. The "usable" analytical dynamic range of the various calibration curves was about 1.5×10^{-8} M to 2×10^{-5} M. It was known that binaphthyl-20-crown-6 could complex with potassium ions due to the size matching of the potassium ion (1.33 Å) and the crown cavity (1.35 Å)[16]. In the present case, high concentrations of potassium (up to 0.1 M) were used to make the phosphate buffer solution. However, all the interferences that might be caused by the interaction of potassium (control cation) and other inorganic cations are negligible compared to the dopamine response[17]. Anions tested were: Cl^-, F^-, Br^-, NO_3^-, NO_2^-, HCO_3^-, Ac^-, $B_4O_4^{2-}$, ClO_4^-, SCN^-, SO_4^{2-} $S_2O_3^{2-}$ and I^-, which all showed virtually no response. All alkyl derivatives of catecholamines and similar compounds[17] were tested for their response behavior and the results indicate that the electrode responded to those compounds having a common factor in their chemical structure; that is, the presence of a 3,4- dihydroxyphenyl moiety. Moreover, the presence or absence of the amino group in the compound did not significantly affect the electrode response.

The poly(dibenzo-18-crown-6) was also employed as a potentiometric detector in the FIA of catechol in the presence of ascorbic and/or uric acids. Table 2 shows the potentiometric flow injection analyses of catechol in the presence of uric acid. The same polymer electrode was found to selectively response to Sr^{2+} ion concentration in aqueous solution with a detection limit of about 2.9×10^{-5} M with a Nernstian slope of 59 mV/decade, after special pretreatment[18]. The slope value is contrary to that expected for a divalent cation.

Table 2. 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

On the other hand, poly(3-methylthiophene) was used as potentiometric sensor for the detection of iodide in aqueous solution. The polymer film was deposited electrochemically on a platinum or carbon substrate, then was subjected to different chemical and/or electrochemical pretreatment in iodide containing electrolytes[11]. The polymer elecrode pretreated using a "hybrid" technique of electrochemical and chemical treatment proved to have an extended lifetime of the iodide selectivity. The working temperature range, the selectivity coefficients, and response time of this sensor electrode are comparable to those commercially available.

Conductivity Monitoring by an Amperometric Detector wih a Cu(II)-Containing Poly(3-methylthiophene) Electrode

The analytical application of an electrode consisting of a pressed disk of Cu(II) PMT in a cavity of a Kel-F block for the detection of some inorganic anions in the flow injection and HPLC/EC analyses has been described[18,20]. The detector was shown to sense the ionic analytes on the basis of conductivity changes upon the passage of sample plugs. The Cu(II) PMT electrode also exhibits significantly greater signal stabiliy than either bare Pt or stainless steel (SS) electrode used in the same detector unit, for example for CN^- detection. The electrode response was further examined under true ion chromatographic (IC) conditions. It was seen that chromatograms of a test mixture of electroinactive (that is, at the potential applied to the working electrode) anions obtained with the amperometric unit employing the Cu(II) PMT electrode and with a commercial conductivity detector were virtually identical with regard to relative peak heights. The fact that platinum and SS electrodes used in the same cell configuration do not produce similar responses suggests that copper ions in this electrode surface play a special role in generating the observed responses. Figure 7 depict the chromatograms obtained with the amperometric unit with the Cu(II) PMT electrode had the commercial conductivity detector (a.c. conductivity system from LDC/Milton Roy Conducto Monitor III with a cell constant of 10 cm^{-1}). The response of the detector is comparable for the mixture of ions (10^{-3} M each) in the p-hydroxybenzoic acid using the Cu(II) PMT electrode or the conductivity detector. The present results strongly suggest that the observed current signals are associated with the analyte conductance changes caused by the passage of the analyte plug through the detector rather than any Faradaic process of the polymer.

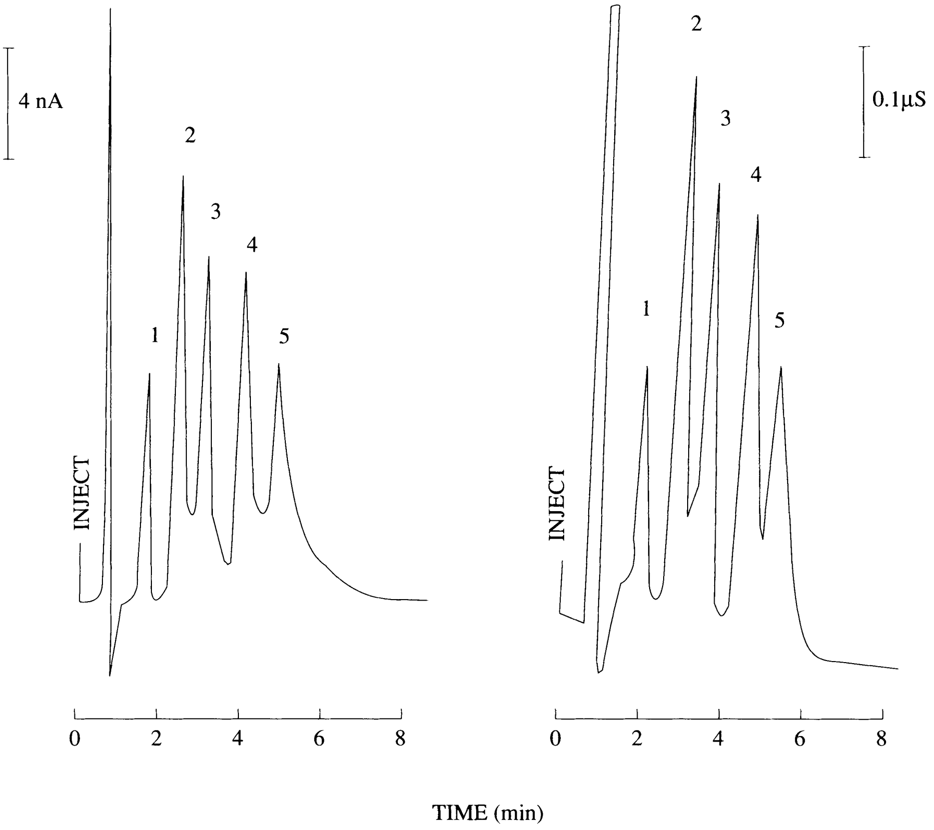

Figure 7. Chromatograms with (A) amperometric-Cu(II)PMeT and (B) conductivity detection of a standard anion mixture 10^{-3} M each): 1. F^-: 2, Cl^-; 3. NO_2^-: 4, Br^-; 5. NO_3^-. Eluent: 4×10^{-3} M PHBA at 2 ml min^{-1}.

In conclusion, we have demonstrated that conducting poly(heterolenes can be used successfully for diverse analytical applications. The polymer electrodes showed beter sensitivity and noticeable resistance against surface fouling when compared to platinum or glassy carbon electrodes. Moreover, this new class of sensor electrodes can be used in different modes such as voltammetry, potentiometry, d.c. conductivity, or amperometry. The polymer electrodes also showed good stability for usage over extended periods of time.

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