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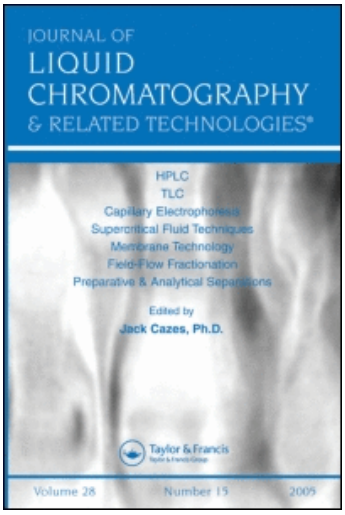

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Enhancement of LCEC Response by Use of Rectrochemically Pretreated Glassy Carbon Electrodes

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ENHANCEMENT OF LCEC RESPONSE BY USE OF ELECTROCHEMICALLY PRETREATED GLASSY CARBON ELECTRODES

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ABSTRACT

A simple electrochemical pretreatment procedure has been shown to increase the selectivity of LCEC detection by lowering the required operating potential compared to that needed at conventional untreated glassy carbon. The effect of a conditioning procedure consisting of sequential application of brief positive and negative potentials to a polished glassy carbon surface was examined for a group of model LCEC analytes including p-hydroquinone, dopamine, dihydronicotinamide adenine dinucleotide (NADH), ascorbic acid, and hydrazine. The lowering of the potential required for detection of these species was greatest for the irreversibly oxidized systems which exhibit the largest overvoltage at untreated glassy carbon--namely, NADH, ascorbic acid, and hydrazine. For these species at pretreated electrodes, comparable detector response was achieved using potentials 0.2 to 0.5 V less than that otherwise needed for optimum response. The improved performance of the electrochemically pretreated electrodes was maintained over a wide range of pH conditions and mobile phase compositions and dramatically facilitated the determination of the latter set of compounds in physiological matrices.

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INTRODUCTION

In recent years, electrochemical measurement techniques have been shown to offer a useful approach for the detection of numerous easily oxidized or reduced compounds following high performance liquid chromatography (1,2). In practice, of course, the success with which such liquid chromatographic/electrochemical detection (LCEC) methods can be applied is determined primarily by the electrode potential required to effect oxidation or reduction of the compound of interest. Thus, LCEC has found its principal applications for the determination of easily oxidized species such as catechols and aromatic amines which require the use of modest positive potentials where the typical background current is low and few electrolyzable interferences are likely to be encountered. Unfortunately, many other compounds of considerable analytical interest undergo electrolysis only at activation-controlled rates and, as a result, at potentials drastically exceeding their thermodynamic redox potentials. For these compounds, detection by LCEC cannot provide optimum levels of sensitivity and selectivity and, in extreme cases, can provide no useful quantitation at all.

Consequently, considerable effort has been directed toward the development of electrode systems which exhibit enhanced response towards these activation-controlled systems. In this regard, both chemical modification of the native electrode surface by attachment of catalytic mediator molecules (3,4) and electrode conditioning by chemical (5), thermal (6), and electrochemical (7-13) treatment have been utilized. Of these possibilities, the electrochemical pretreatment procedures, most of which consist of the imposition of alternating oxidizing and reducing potentials at carbon electrodes, represent the simplest and most widely applicable approach. In this laboratory, such an electrochemical conditioning sequence has been shown to make LCEC detection of simple hydrazines attractive, lowering the potential required for their detection by 0.5 to 1.0 V and yet permitting detection limits two to three orders of magnitude lower than previously achieved at conventional untreated

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electrodes (14). However, aside from this one instance, the potential of electrochemical pretreatment procedures to improve LCEC detection has not been seriously considered. Accordingly, in this paper, we will investigate the general utility of electrochemical pretreatment for use in LCEC. The effect of electrode pretreatment on the LCEC determination of a series of standard compounds including dopamine, p-hydroquinone, ascorbic acid, hydrazine, and dihydro-nicotinamide adenine dinucleotide (NADH) will be characterized; and it will be shown that this simple procedure can significantly decrease the potential required for detector operation. The effect is most pronounced for electrochemically irreversible analytes such as ascorbic acid, hydrazine, and NADH which exhibit a high overvoltage at the ordinary electrode surface. As a result, LCEC quantitation of these species in real sample matrices containing a complex spectrum of possible interferents can be significantly simplified.

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MATERIALS AND METHODS

Chemicals

NADH (Grade III), ascorbic acid, and dopamine hydrochloride were obtained from Sigma Chemical Co. (St. Louis, MO). Hydroquinone was obtained from Fisher Scientific Co. Practical grade n-octylamine was obtained from Eastman Kodak Co. (Rochester, NY). All were used as received without any further purification. Deionized water was used for all solution preparation.

The buffer medium used during electrode pretreatment usually consisted of a solution of 0.1 M KNO_3 and 0.01 M Na_2HPO_4 with the pH adjusted to 7 with 0.015 M HNO_3. When other buffers were used for pretreatment or for cyclic voltammetry (CV), they were prepared from KH_2PO_4 and Na_2HPO_4 according to reference 15.

To inhibit sample degradation, ascorbic acid, dopamine, and hydroquinone sample solutions always contained 0.05 M $HClO_4$. In addition, fresh standards were made each day. Urine samples were

filtered through a 0.27-μ Gelman glass filter and, for ascorbic acid determinations, were diluted with an equal volume of 0.05 M $HClO_4$ prior to chromatographic analysis.

Instrumentation

CV experiments and electrode pretreatment were performed with a Bioanalytical Systems (West Lafayette, IN) Model CV-1B potentiostat and Model MF-2012 glassy carbon working electrode. A three-electrode cell was employed with an Ag/AgCl reference and a Pt counter electrode. The pretreatment procedure used was similar to that reported by Engstrom (12). First, the electrode was polished three times with a 5-μ alumina slurry for one minute and rinsed thoroughly each time with deionized water. To eliminate the possibility of Al_2O_3 catalysis as reported recently by Kuwana (16), the electrode was then thoroughly sonicated in deionized water. The electrochemical pretreatment itself consisted of holding the electrode first at +1.75 V vs. SCE for five minutes and then at -1.2 V for ten seconds. Unless otherwise indicated, the electrode was immersed in pH 7 phosphate buffer during this potential sequence.

The liquid chromatograph employed consisted of a Waters Associates Model M-600 or a Perkin-Elmer Model LC-10 pump, a Rheodyne Model 7125 injector, a Waters Associates Model 440 UV detector, and an IBM Model EC-230 electrochemical detector with a Bioanalytical TL-5 thin layer glassy carbon electrode assembly. All chromatography was performed on an octadecylsilane column of 10-μ, irregular particles (Alltech Associates, Deerfield, IL). A home-made silica (Adsorbosil, Mesh 200/425, Alltech Associates) presaturation column was placed between the pump and the injector in order to prevent the neutral mobile phase from attacking the analytical column. A octadecylsilane guard column (Brownlee Labs, Santa Clara, CA) was used when urine samples were injected. Unless otherwise specified, the flow rate used in all chromatographic experiments was 1.0 ml/min.

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RESULTS AND DISCUSSION

Five compounds were selected for use as test systems to evaluate the effectiveness of electrode pretreatment to enhance the analytical performance of LCEC: dopamine, p-hydroquinone, ascorbic acid, hydrazine, and NADH. All of these species can be oxidized at glassy carbon electrodes and have previously been the objects of LCEC analysis. Of this group, dopamine and hydroquinone are oxidized quasi-reversibly at low positive potentials and thus represent ideal candidates for LCEC. The other three systems are electrochemically irreversible; and, although LCEC has been employed with some success for each, significant improvements might be expected to result from prior electrochemical conditioning of the sensing electrode.

Cyclic voltammetry (CV) was employed to survey the effect of electrochemical pretreatment on all five systems. The results obtained for CV performed in pH 7 buffer both before and after pretreatment of the glassy carbon electrodes are summarized in Table 1. In general, this data is consistent with results previously obtained at pretreated glassy carbon electrodes by Engstrom (12) and in our own laboratory (14). All of the oxidations were shifted to lower potentials; and, in general, the CVs exhibited sharper peaks which resemble more closely the shapes expected for ideal reversible electrode processes. The shifts in peak potential (ΔE_p's) were more pronounced for the irreversible systems displaying the highest overvoltage at the untreated electrode. Thus, the hydrazine oxidation changed from a broad, poorly defined wave at +0.85 V vs. Ag/AgCl at untreated glassy carbon to a sharp, well-shaped peak at +0.30 V at the pretreated electrode. It was these consistent and sometimes dramatic shifts to lower potentials which initially attracted our attention to the possible advantages of employing electrochemical pretreatment procedures in LCEC.

If the pretreated electrodes are to be employed in practical chromatographic applications, it is necessary that the performance

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TABLE 1

Effect of Electrode Pretreatment on Cyclic Voltammetry Response

Analyte	Ep (Oxidation), V vs. Ag/AgCl		ΔE_p,mV
	Before Pretreatment	After Pretreatment	
Hydroquinone	+0.18	+0.11	70
Dopamine	+0.21	+0.19	20
Ascorbic Acid	+0.30	+0.00	300
NADH	+0.56	+0.41	150
Hydrazine	+0.85	+0.30	550

enhancements of Table 1 are retained under a variety of solution (or mobile phase) conditions. It has already been demonstrated that the effects of pretreatment are unaltered by the presence of significant proportions of organic solvents such as methanol and acetonitrile in the electrolysis medium (14). However, as all previous work with the pretreated electrodes has been carried out only in neutral solutions, their performance in solutions of various pH also needed to be examined. Accordingly, the voltammetric behavior of several of the test systems at electrodes pretreated as above in pH 7 buffer was further characterized by obtaining the CVs in solutions of different pH and comparing the results with the behavior under the same conditions at untreated electrodes. The behavior at electrochemically conditioned electrodes, summarized for dopamine and ascorbic acid in Table 2, was again directly analogous to the well-known redox behavior of these compounds at the untreated surfaces. In all cases examined, pH-dependent shifts in the peak potentials observed for the oxidations at the untreated electrodes were paralleled by shifts in the same direction and of roughly the same magnitude at the pretreated surfaces. At the same time, the enhancement resulting from the pretreatment procedure occurred uniformly over the entire pH range employed as evidenced by the roughly constant ΔE_p's observed at each pH. Thus, for example, ascorbic acid oxidation at both electrode surfaces showed little or no change in potential between pH 7 and 4 but shifted, as expected, to more positive

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Table 2

Effect of Solution pH on Treated and Untreated Electrode Response

pH	DOPAMINE[a]		ASCORBIC ACID	
	E_p Before Pretreatment, V vs. Ag/AgCl	E_p After Pretreatment, V vs. Ag/AgCl	E_p Before Pretreatment, V vs. Ag/AgCl	E_p After Pretreatment, V vs. Ag/AgCl
7.0	+0.21	+0.19	+0.30	+0.00
6.1	+0.30	+0.25	+0.26	-0.05
5.0	+0.42	+0.34	+0.30	+0.06
4.3	+0.46	+0.38	+0.31	+0.07
3.1	+0.54	+0.44	+0.38	+0.13

[a]Data is given here for the oxidation only.

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potentials at lower pH values. But, over the entire pH range, ΔE_p for the oxidation between the two surfaces remained relatively constant (240 to 300 mV). For hydrazine at untreated glassy carbon, the hydroxide-catalyzed oxidation shifted rapidly to more positive potentials as the solution was made more acidic. The effect was so great that, at pH values less than 5, the hydrazine oxidation consisted only of an extremely broad and greatly reduced wave whose plateau occurred at potentials well in excess of +1.0 V but whose "peak" position could not be clearly resolved. At the pretreated electrode, pH decreases likewise resulted both in severe broadening of the hydrazine oxidation and in shifts to higher potentials. However, even at pH 4.1, the plateau position occurred at a potential of only +0.61 V.

In view of the encouraging performance of electrochemically pretreated glassy carbon in decreasing the overvoltages observed in CV for the test analytes, the identical electrode conditioning operations were subsequently applied in LCEC and evaluated for the same set of compounds. The mobile phase composition employed for each compound was selected individually on the basis of previously reported chromatographic analyses (14,17-19) and is summarized in Table 3. No attempt was made to utilize identical chromatographic conditions for all systems because the direct application to a variety of already established procedures was deemed to provide

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TABLE 3

LCEC Response at Treated and Untreated Electrodes

Analyte	Mobile Phase	$E_{plateau}$, V vs. Ag/AgCl		Detection Limit (ng injected)	
		Before Pretreatment	After Pretreatment	Before Pretreatment	After Pretreatment
Hydroquinone	pH 7 buffer/ 20% methanol	+0.60 V	+0.50 V	0.30	0.30
Dopamine	pH 3.8 phosphate-citric acid buffer/ 5% acetonitrile	+0.60 V	+0.45 V	0.20	0.20
Ascorbic Acid	pH 5 acetate buffer, 1 mM octylamine, 200 mg/l EDTA	+0.60 V	+0.35 V	0.12	0.06
NADH	pH 7 buffer/ 5-20% methanol	+0.80 V	+0.60 V	1.2	0.70
Hydrazine	pH 7 buffer	>+1.0 V	+0.50 V	--	0.01

a better test of the practical utility of the electrode pretreatment approach as a general means of providing enhanced LCEC response. Typical responses obtained for NADH and ascorbic acid are shown respectively in Figures 1 and 2. Each of the chromatograms was recorded using a detector potential of +0.30 V vs. Ag/AgCl both for the polished but untreated and the electrochemically conditioned glassy carbon surfaces. With both analytes, greatly increased current levels were observed for the surfaces which had been subjected to the pretreatment process. Further, the response enhancement was quite long-lived as was evidenced by the chromatograms obtained for ascorbic acid at the same pretreated surface over the 5-hour observation period employed (Figure 2).

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The LCEC data presented in Table 3 match closely the behavior expected for the pretreated electrodes on the basis of the CV data of Table 1. Again, lower potentials were required for detection of each of the test analytes--with the decrease greatest for the irreversible systems showing the largest overvoltage at the untreated electrode. As shown in Figure 3, hydrodynamic voltammograms (HDVs) observed upon pretreatment for dopamine and hydroquinone showed only comparatively small shifts which were of relatively minor importance since both compounds are already detectable before pretreatment at modest detector potentials. On the other hand, the shifts observed for the other systems were sufficiently large that significant reductions in the potentials required for optimum LCEC analysis resulted. The most dramatic example was, of course, hydrazine for which electrode pretreatment has been shown to decrease the potential required from +1.0 V vs. Ag/AgCl to +0.5 V (14).

In general applications, we expect that the most important advantage resulting from the use of pretreated electrodes for LCEC analysis will be increased selectivity due to the greatly decreased number of interferents at the lower values of applied potential made possible by the pretreatment procedure. For hydrazine, this selectivity improvement was accompanied by a

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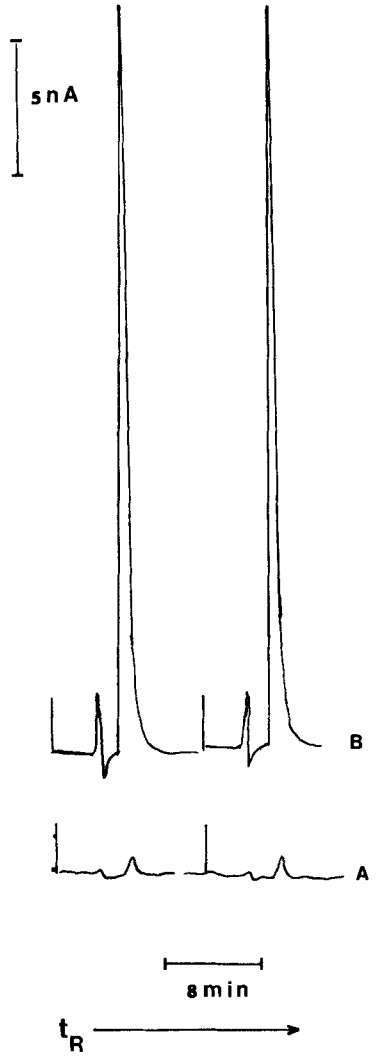

FIGURE 1. Chromatograms obtained at +0.30 V vs. Ag/AgCl for repeated injection of 30 ppm solution of NADH at (A) untreated and (B) electrochemically pretreated glassy carbon electrodes. Injection volume: 20 µl; flow rate: 2.0 ml/min.

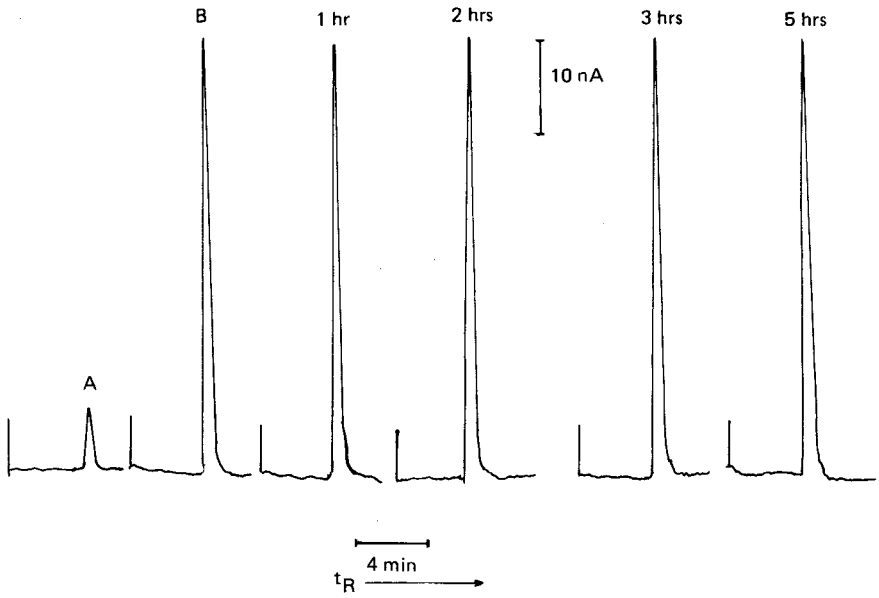

FIGURE 2. Chromatograms obtained a +0.30 V vs. Ag/AgCl for repeated injections of 10 ppm ascorbic acid solution at (A) untreated electrode and (B) electrochemically pretreated electrode. Injection volume: 6 μl.

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decrease in the detection limit by a factor of more than 100 (14). However, as expected from the similar current levels attained at the HDV plateaus for both the pretreated and untreated surfaces in Figure 3 and shown by the actual detection limits reported in Table 3, absolute sensitivities for the other analytes were enhanced by a factor of 2 at best by the electrochemical conditioning.

Additional examples demonstrating the increased selectivity for the detection of NADH and ascorbic acid are provided in Figures 4 and 5. In the first example, NADH was added at the 50 ppm level to the urine of a healthy volunteer; and chromatograms were recorded under a variety of detector conditions. The only sample treatment performed prior to injection consisted of filtration through a 0.27-μ glass filter. Curves 4B and 4D illustrate the results obtained at both untreated and electrochemically pretreated

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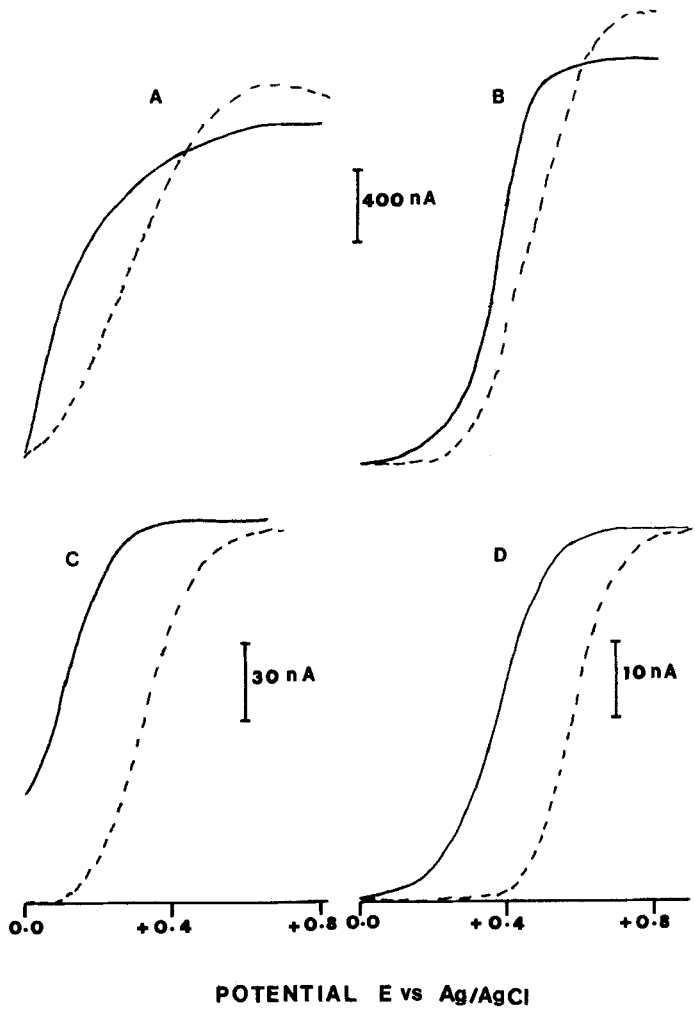

FIGURE 3. Hydrodynamic voltammograms for (A) hydroquinone (60 ppm), (B) dopamine (100 ppm), (C) ascorbic acid (10 ppm), and (D) NADH (20 ppm) at untreated (---) and electrochemically pretreated (——) glassy carbon electrodes. See Table 3 for chromatographic conditions.

electrodes at +0.80 V vs. Ag/AgCl, the potential ordinarily prescribed for optimum detection of NADH by LCEC (19). In both cases, the quantitation of the NADH was impractical as the NADH signal (retention time of 16 minutes) was severely obscured by the large background currents due to the numerous early eluting sample components oxidizable at this relatively high potential. When the background signals were reduced to a more manageable level by lowering the applied potential to +0.30 V, no NADH peak at all could be observed at the untreated surface (curve 4A). At the pretreated electrode, however, a smaller but nevertheless quite usable peak, now largely resolved from the background, was still in evidence.

In the second example, the chromatographic response upon injection of a urine sample doped with 10 ppm ascorbic acid is shown for several LCEC situations (Figure 5). In all cases shown, the chromatographic background was greatly reduced compared to that seen in Figure 4 because this urine sample had been obtained from a volunteer who had been fasting for the preceding 24-hour period. The chromatographic conditions employed were the same as those suggested by Kissinger (18) and detailed for ascorbic acid in Table 3, and the only sample treatment consisted of filtration and dilution with 0.05 M $HClO_4$. The chromatograms in Figures 5A and 5B represent the results obtained using a standard LCEC approach employing an untreated glassy carbon electrode held respectively at +0.30 V and +0.60 V vs. Ag/AgCl. The ascorbic acid peak, occurring at a retention time of about five minutes, was observed at both potentials but, as expected from the HDV provided earlier for the compound in Figure 3, was severely reduced at the lower potential. A second, more slowly eluting peak, observed only at the higher potential, was identified as being due to uric acid (which undergoes oxidation at about +0.4 V). Since the ascorbic acid and uric acid peaks fortuitously were well resolved under these chromatographic conditions, this potential could in fact have been employed successfully for ascorbic acid quantitation. However, had the two species possessed more similar retention properties, a

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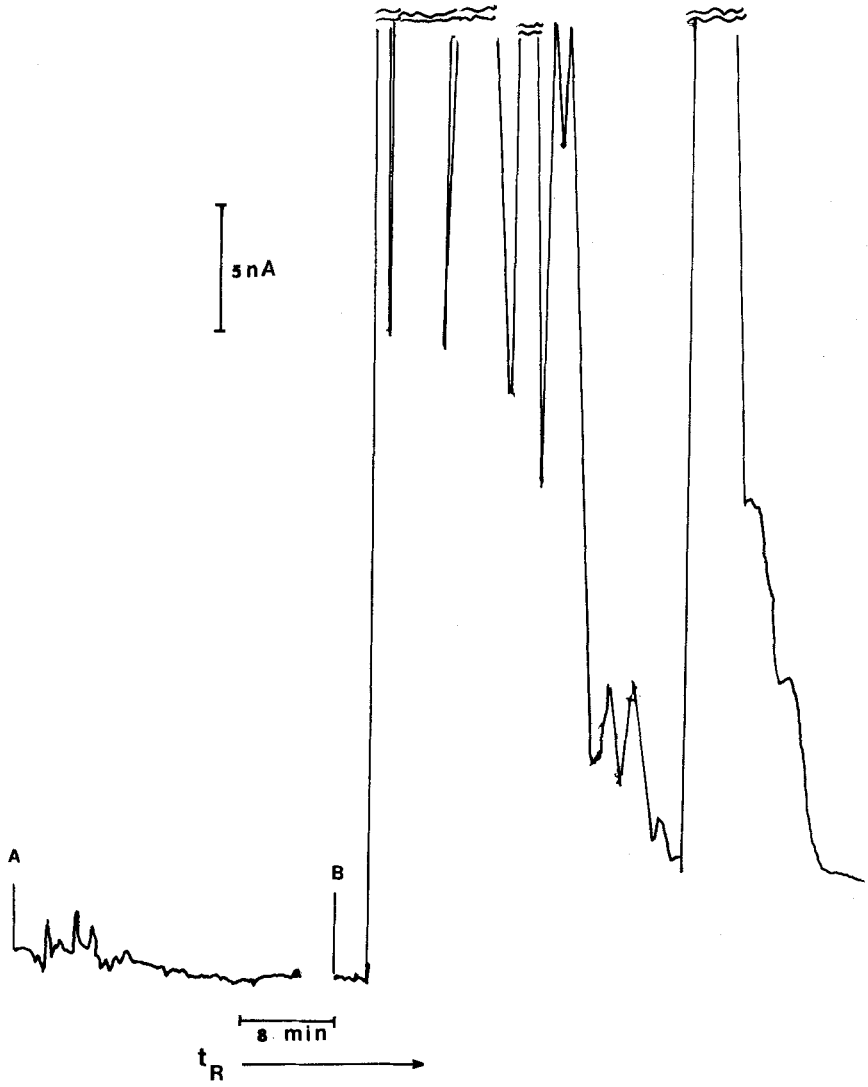

FIGURE 4. Effect of electrochemical pretreatment on LCEC response for a urine sample doped with 50 ppm NADH. (A) untreated electrode at +0.30 V; (B) untreated electrode at +0.80 V; (C) pretreated electrode at +0.30 V; (D) pretreated electrode at +0.80 V. All potentials are reported vs. Ag/AgCl. Injection volume: 20 µl.

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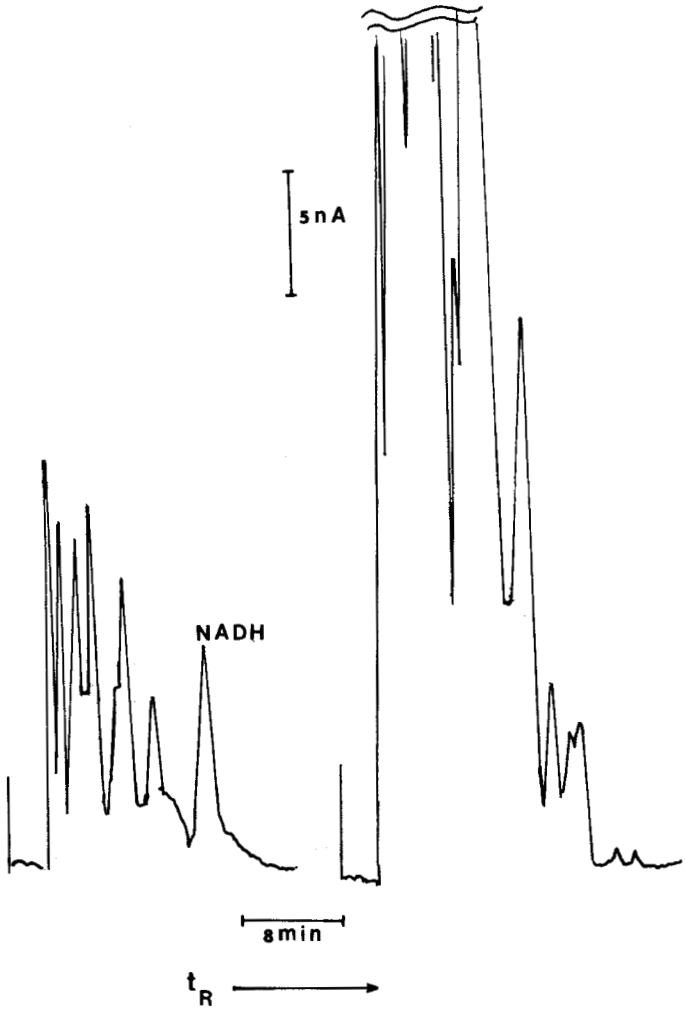

FIGURE 4 (continued)

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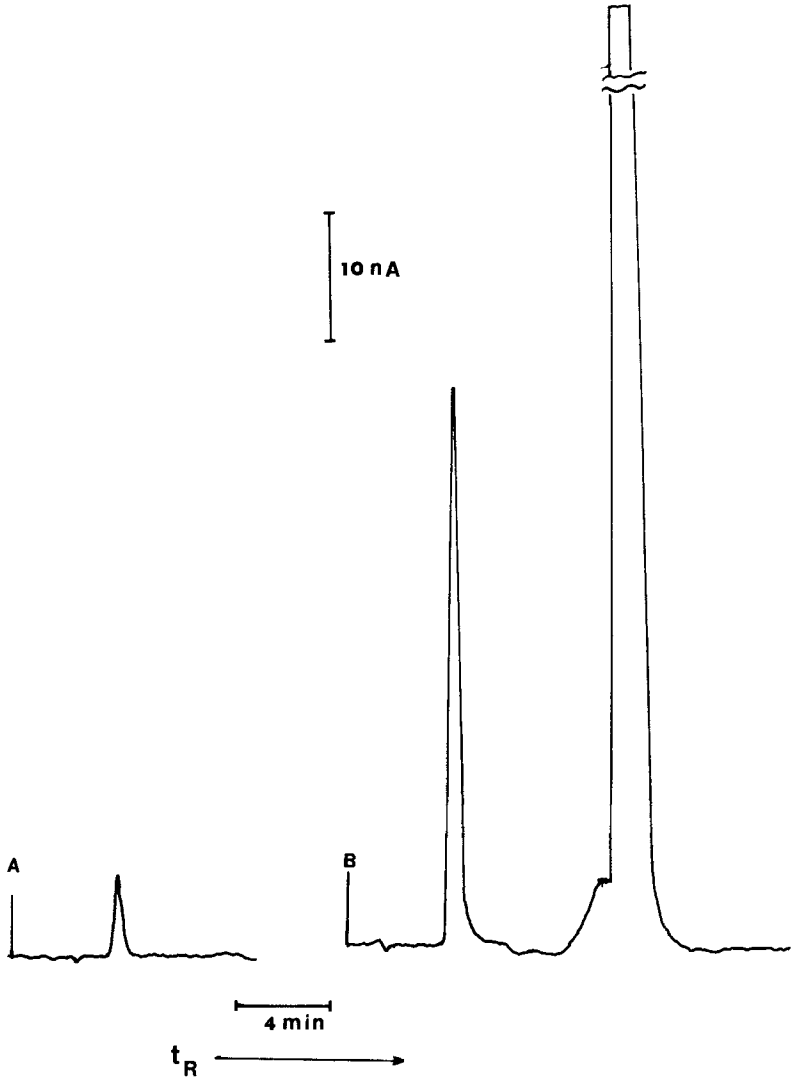

FIGURE 5. Effect of electrochemical pretreatment on LCEC response for a urine sample doped with 10 ppm ascorbic acid. (A) untreated electrode operated at +0.30 V; (B) untreated electrode at +0.60 V; (C) pretreated electrode at +0.30 V; (D) pretreated electrode at +0.60 V. All potentials are reported vs. Ag/AgCl. Injection volume: 6 μl.

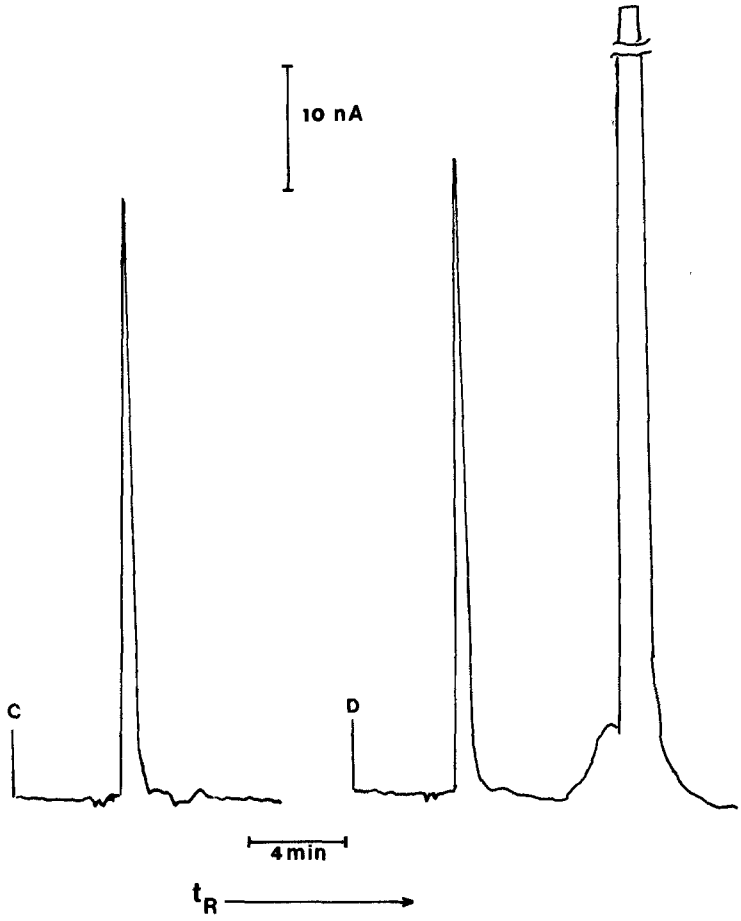

FIGURE 5 (continued)

serious interference would have resulted. Figures 5C and 5D show equivalent chromatograms obtained at electrochemically pretreated glassy carbon. The response at +0.60 V was virtually the same as that seen in curve 5B for the conventional electrode. But the chromatogram taken at +0.30 V (which corresponds to the HDV plateau for ascorbic acid at the pretreated electrode) not only showed no response for the uric acid but also exhibited nearly as much current response for ascorbic acid as was observed for the

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untreated electrode at +0.60 V. Thus, quantitation of ascorbic acid could be accomplished at the pretreated surface with no significant loss of sensitivity without concern over the presence or retention behavior of the uric acid. In fact, the ascorbic acid peak observed even at +0.10 V was reduced by only approximately 30%. Operation at this extremely low potential thus offers a unique route to analysis which is both acceptably sensitive and, at the same time, tremendously selective.

An additional advantage of the electrochemical pretreatment approach is the ease with which the electrode modification involved can be performed in practice. As described in the experimental section, the pretreatment process itself required only about five minutes to carry out and could even be performed in situ while the electrode was simply set up as usual for LCEC and exposed to the chromatographic mobile phase. Further, the performance enhancements which resulted were particularly long-lived as the glassy carbon electrodes, once conditioned, generally showed no observable decrease in detector current even over 8 to 10 hours of continuous chromatography. In addition, the process was quite versatile, showing little sensitivity to the particular medium in which the pretreatment was conducted. Although all of the examples cited previously were performed with electrodes pretreated in pH 7 phosphate buffer, virtually no limitations on the pretreatment medium were observed in our work. Identical enhancement in electrode performance was obtained regardless of whether the electrode was immersed in solutions ranging from pH 3 to 7.

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CONCLUSION

Relatively simple electrochemical pretreatment has been shown to comprise a generally applicable approach to achieve enhanced analytical response in LCEC determinations employing glassy carbon working electrodes. The primary effect produced by such pretreatment procedures consisted of a shift of the electrode processes examined to less extreme potentials than were otherwise required. Although the resulting increases in selectivity and

sensitivity depended greatly on the specific nature of the analyte system under consideration, significant improvements were found for systems which exhibited extremely irreversible behavior at the conventional untreated electrode surface. In addition, the enhancements resulting from electrode pretreatment occurred over a wide range of pH and solution conditions similar to those usually employed in reverse-phase HPLC.

This study is not meant to suggest that electrochemical pretreatment can be expected to produce dramatic improvements in LCEC response for all species currently determined by this technique. Rather for well-behaved electrochemical systems such as dopamine and hydroquinone which are oxidized at relatively low potentials at untreated glassy carbon, only modest improvements at most are to be anticipated. However, considering the practically insignificant investments in time, equipment, and experimental convenience required by the electrode conditioning procedures employed here, we believe that anyone involved in glassy carbon LCEC should at least consider their use.

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