CAPSULES
preliminary notes and applications from Bioanalytical Systems, Inc.

Electrode Pretreatment

Purpose
Improve detection limits and selectivity of electroactive compounds by electrochemically pretreating the electrode.

Advantage
The electrode is cycled between two potentials (negative and positive), while out of the LCEC system, in a determined buffer. This pretreatment increases selectivity in the LCEC system by lowering the required potential needed to oxidize an analyte. This lowers, and in some cases removes, the response due to interfering compounds that are generally present in a complex matrix. In general, pretreatment does not lower detection limits. In the case of hydrazine, however, a simple pretreatment improves detection by 2 to 3 orders of magnitude.

Notes
Electrode pretreatment is not a widely used procedure, but we have had a few inquiries about it. We will therefore list the procedures and the references, with some selected data.

Method
A three-electrode cell configuration was employed during the preconditioning period.

Pt Electrodes

Ref. 1. Measuring H_2O_2: Step the potential between +1.0 V and -0.4 V vs. Ag/AgCl 100 times with a 100 msec hold at each potential.

Ref. 2. Measuring H_2O_2: Cycle in 1 M H_2SO_4 from -0.8 V to +0.8 V vs. Ag/AgCl several times. The cycling is stopped at +0.8 V and the electrode washed with distilled water.

Glassy Carbon Electrodes

Ref. 3. Measuring Hydrazine: 5-min preanodization at +1.75 V vs. standard calomel electrode followed by a 10-sec precathodization at -1.2 V. The supporting electrolyte/buffer consisted of 0.1 M KNO_3 and 0.01 M Na_2HPO_4 which was adjusted to pH 7.0 with 0.015 M HNO_3.

Ref. 4. Same as above.

Summary
Again, it looks like electrode pretreatment could give a selectivity advantage in LCEC, but generally not a detection-limit advantage. The effect appears to be most pronounced for electrochemically irreversible analytes such as ascorbic acid, hydrazine, NADH, nalbuphine, nicotine, etc. Pretreatment can conveniently be carried out with a CV-27 by stepping between E1 and E2, a CV-1B or an LC series electrochemical detector. Of course a BAS-100A could also be used. While such procedures occasionally will be beneficial, they are very empirical and BAS recommends avoiding their use if at all possible. The electrode surface chemistry is not well controlled in such cases and drift following the pretreatment is not uncommon.

References

1. C.E. Lunte, Current Separations, Vol. 6, No. 1, 1984, pg 14-15.

2. G. Sittamalam and G. S. Wilson, Anal. Chem. 55(1983) 1608-1610.

3. K. Ravichandran and R.P. Baldwin, Anal. Chem. 55(1983) 1782-1786.

4. K. Ravichandran and R. P. Baldwin, J. Liq. Chromatogr. 7(1984) 2031-2050.

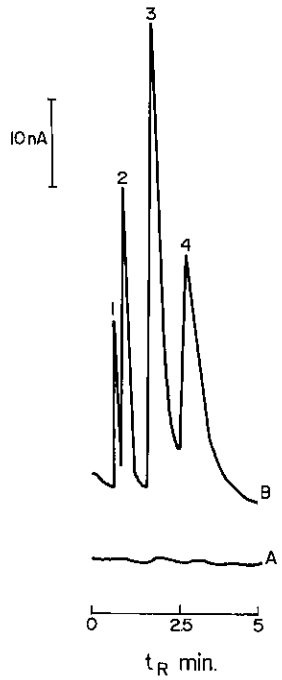

Figure 1. Chromatogram of a hydrazine mixture at 0.10 V. vs. Ag/AgCl using an untreated (A) and a pretreated (B) glassy carbon electrode. Redrawn from Ref. 3.

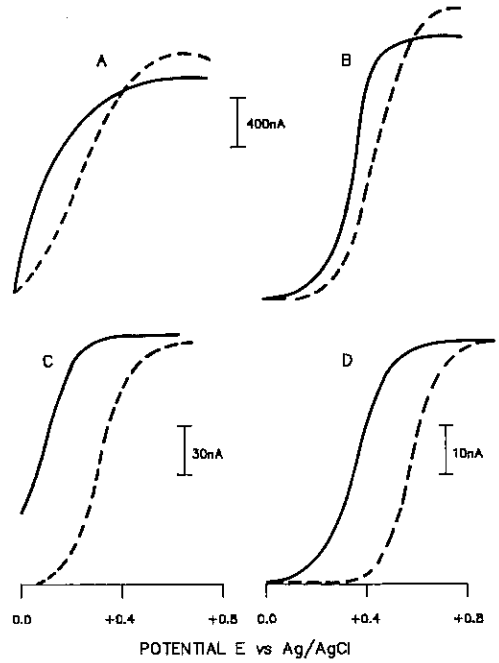

Figure 2. Hydrodynamic voltammograms for (A) hydroquinone, (B) dopamine, (C) ascorbic acid, and (D) NADH at untreated (- -) and pretreated (—) glassy carbon electrodes. Redrawn from Ref. 4.

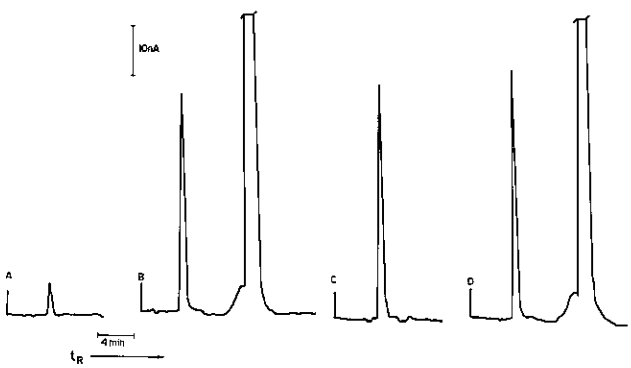

Figure 3. Effect of electrochemical pretreatment on LCEC response for a urine sample spiked with ascorbic acid. (A) untreated +0.3 V, (B) untreated +0.6 V, (C) pretreated +0.3 V, (D) pretreated +0.6 V. All potentials are vs. Ag/AgCl. Redrawn from Ref. 4.