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Background Currents and Baseline Noise

INTRODUCTION

For the most part, the background current measured in an HPLC-electrochemical detector (ECD) system equates with baseline noise (see also Frequently Asked Questions on ESA's web site <http://www.esainc.com>). Background current can be either faradaic (i.e., obeys Faraday's Law) or non-faradaic. Electrolysis of contaminants in the mobile phase is a typical source of faradaic current. Non-faradaic currents include charging currents (i.e., when applied potential is changed), electronic noise, antenna effects, earth-loop effects, line noise, noise from connections, and thermal effects.

Background currents are therefore dependent upon many factors including:

- The applied potential. The greater the applied potential, the greater the background current and noise. Carbon-based working electrodes have an upper potential window of around 1000 mV. Mobile phases with high organic content will typically have lower background current for a given potential than highly aqueous mobile phases. Those with high concentration of electrolytes will typically have higher background currents. Make sure that all mobile phase components are compatible with the applied potential being used. For example, EDTA is a commonly used chelating agent. However, above 400 mV it can be a significant contributor to background currents.
- The quality of water used in mobile phase production. It is essential to use ultrapure water (conductivity typically >18 M Ω -cm, <5 ppb total organic carbon). In some cases further purification of HPLC-grade water may be necessary. (See Tech Note 94.)
- The quality of the organic modifier (e.g., methanol, acetonitrile). Make sure that the highest quality is used and that contaminants (e.g., formation of peroxides from ethers, etc.) are kept to a minimum. (See Tech Note 95.)
- The quality of the salts used in mobile phase production (the highest quality with minimal transition metal contamination must be used). Electroactive impurities of as little as 0.001% means that the resulting background current will adversely affect high sensitivity analyses.
- System components. All fluidic components should be inert with minimal metal surfaces. Many typical HPLC components contain metal surfaces that can bleed redox active transition metals into the mobile phase causing high background currents, auto-oxidation of labile analytes and sometimes irreparable damage to the EC cell. Such components **MUST** be routinely passivated (follow manufacturer's instructions for passivation).

- The analytical column. New columns **MUST** be flushed to waste overnight before attaching the electrochemical cell in order to remove metal contaminants resulting from the end frits, column body and remaining catalysts from the synthesis of column particles. Test the contribution of the column by monitoring the background current after using a union to replace the column.
- The cleanliness of glassware used to make the mobile phase. Make sure glassware is totally dry. Cover open vessels with aluminum foil to prevent entry of dust, etc. Do not use soap as any residue left on the glassware surface can dissolve into the mobile phase and act as an ion-pairing agent.
- The growth of microbes in mobile phases that contain low levels of organic modifiers. Use lithium salts or if unavailable, use Reagent MB (P/N 70-1025) (typically 100 µL/L of mobile phase) when preparing mobile phases with <3% organic modifier to prevent microbial growth.
- Recycling. Especially when measuring dirty biological samples and/or the use of high concentration standards.
- Not degassing the mobile phase sufficiently. This becomes a problem at higher oxidation and reduction potentials.

It is a good idea to use a Guard cell (ESA Model 5020, P/N 55-0417) to help screen EC-active impurities.

Please prepare the mobile phase correctly (see Tech Note 95) and degas prior to use. **DO NOT** use a lowpressure gradient system for on-line mixing of supporting electrolyte, organic modifier, and water. For gradient conditions use supporting electrolyte in each mobile phase.

Marked changes in the background current is a good indication that something is wrong with the HPLC system. Do not ignore changes in background current—troubleshoot the system to identify the cause (e.g., contaminated mobile phase, column bleed, the need for system passivation) and then correct the problem.

Do everything possible to minimize background currents. The lower the background currents the better; the greater the sensitivity (lowered s/n ratio) and the longer the life of the working electrode.

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