Phenolic Impurities In Industrial Processes

In recent years liquid chromatography/electrochemistry has been applied to many trace organic analyses in biological samples. Examples are described in other notes in this series. Industrial chemists are also considering LCEC as a method for their analytical problems. The outstanding selectivity of LCEC can be exploited for the analysis of a phenolic starting material in a large amount of an electrochemically inactive product.

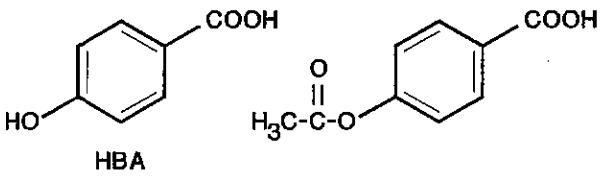

Figure 1. Structures of 4-hydroxybenzoic acid (HBA) and 4- acetoxybenzoic acid.

4-Hydroxybenzoic acid (HBA) or related compounds are acetylated with acetic anhydride to form acetates. In this process the extent of contamination of the product by the remaining starting material is of interest. LCEC is a suitable method for this determination. The phenolic acids can be oxidized at approximately +1 V (vs. Ag/AgCl).

Since the acetates are not electrochemically active, little sample preparation is necessary, making an LCEC method potentially useful for pilot and production plant operations. For this example a 100 mg sample of the acetate was dissolved in 100 mL of methanol. 25 µL aliquots were injected into an LC-154 analyzer equipped with an LC-4B/17 amperometric detector and a glassy carbon working electrode. The BAS 400 Liquid Chromatograph and the BAS 200 Problem Solver also are suitable instruments for this analysis.

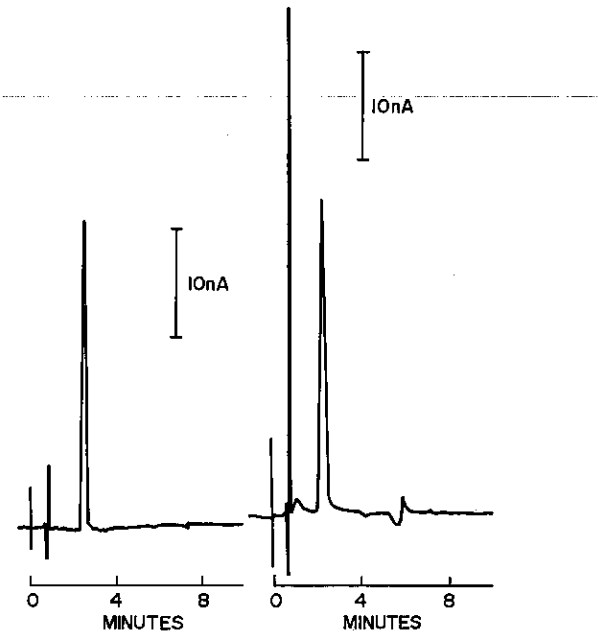

Figure 2. (A) Standard solution of 4-hydroxybenzoic acid, 17 ng injected. (B) 100 mg 4-acetoxybenzoic acid per 100 mL of methanol, 25 µL injection. Peak height indicates 18 ng.

F2 shows chromatograms of samples of HBA and 4-acetoxybenzoic acid supplied by a customer. 0.72 mg of HBA per gram of 4- acetoxybenzoic acid remains unreacted. The LCEC technique can also be easily used to analyze HBA for phenol, a decomposition product.

Conditions

System: LC-154 or either the BAS 400 or 200
Detector: LC-4B/17 with glassy carbon electrode
Mobile phase: 25% Methanol, 75% 0.05 M sodium perchlorate, 0.01 M sodium citrate, pH = 4.0
Stationary phase: Biophase ODS 3µm (100 mm x 4.6 mm)
Applied potential: +1.00 V (vs. Ag/AgCl)
Flow rate: 1.5 mL/min.