Study and Application of a Porous Flow-Through Electrode Electrospray Emitter

Gary J. Van Berkel[1]; Vilmos Kertesz[1]; Michael C. Granger[2]

[1]Oak Ridge National Laboratory, Oak Ridge, TN; [2]ESA, Inc., Chelmsford, MA

Keywords: Electrochemistry; Electrospray Ionization (ESI); Ionization, Electrospray; Oxidation

Novel Aspect: First study and use of a porous flow-through electrode emitter in electrospray.

Introduction

Our prior work has shown that progression from a simple tubular electrode emitter [1] to a planar, flow-by electrode geometry [2] increases the efficiency of hetereogenous redox reactions of the analytes in the electrospray (ES) emitter. The flow-by electrode device also allowed us to begin to explore the known role of electrode material in influencing electrochemical reactions. In this report we investigate and use the first porous flow-through electrode electrospray emitter for efficient analyte oxidation in ES-MS at flow rates up to at least 50 microliters/min.

Methods

Experiments were performed on a PE Sciex API 165 single quadrupole mass spectrometer (MDS Sciex, Concord, Ontario, Canada). A syringe pump was used to continuously infuse the analyte solution. Spectra were acquired with a modified TurboIonSpray source. This porous electrode emitter was mounted in the TurboIonSpray source by simple exchange of this unit for the zero-dead volume union that connects the solution flow into the source to the normal emitter capillary electrode.

Preliminary results

Our new emitter electrode was a porous electrode in a cylindrical sandwich assembly comprised of stainless steel inlet and outlet endcaps and a PEEK cell body. The electrode was composed of porous graphitic carbon (PGC) (40% total porosity, 99% open porosity, mean pore size = 0.8 µm) 0.51 mm dia. x 0.36 mm thick. The calculated surface area of the electrode was 170 square millimeters. We tested the efficiency of the system for analyte electrolysis at various flow rates from 2.5 to 200 microliters/min. Using reserpine as a test case, we found that ES currents were slightly higher and the efficiency of analyte electrolysis substantially higher than previously reported with our planar flow-by electrode emitter. At flow rates up to 50 microliters/min, the efficiency of electrolyis was 100%. This is at least double the flow rate at which 100% analyte oxidation efficiency could be maintained with our other electrode designs. One of our practical goals has been to obtain an electrode emitter geometry that provides 100% analyte electrolysis efficiency at solution flow rates of 40-50 microliters/min, thereby allowing the emitter system to be coupled with microbore chromatography. Now having this capability we will show this coupling and the enhanced analyte signals from species that are not usually observable in conventional ES-MS analysis. The main examples will be “electrochemically-ionizable” derivatives [3] of compounds not normally amenable to analysis by ES-MS.

1. Kertesz and Van Berkel, J. Mass Spectrom., 2001, 36, 204.
2. Van Berkel, et al., Anal. Chem., 2002, 74, 5047.
3. Van Berkel, et al., Anal. Chem. 1997, 70, 1544.

Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC05-00OR22725 with Oak Ridge National Laboratory managed and operated by UT-Battelle, LLC.