Electrolytic Induced pH Changes in nano-ESI: Implications for the Appearance of Mass Spectra

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Nano-electrospray ionization (nano-ESI) typically refers to an electrospray emitter that operates at a flow rate between 10 to 100 nanoliters/min. Nano-ESI possesses all the advantages of a traditional (macro) electrospray source for mass spectrometry and additionally is very useful for the analysis of "precious" samples available only in limited volumes. A nano-ESI emitter usually consists of a glass capillary with a tip pulled to a narrow internal diameter. The electrospray voltage is applied to the solution by either a metal coating on the outside of the capillary or a metal wire inside the capillary. The particular nano-spray geometry, as well as the metal used to make electrical contact, can affect the electrolytic reactions that occur to maintain charge balance in the ESI solution [1]. Under different experimental conditions it is possible for either analytes, the ESI metal contact, or the solvent to undergo redox chemistry.

Electrolytic Oxidation of Water. When using a high voltage metal contact that is not easily oxidized, oxidation of water (eq.1) supplies the charge-balancing current [2], viz., $2H_2O \Leftrightarrow O_2 + 4H^+ + 4e^-$ (eq. 1). The concentration of protons added to the solution due to this reaction is given by eq. 2, viz. $[H+]_{elec} = i_{ESI}/nF\nu_f$ (eq. 2), where i_{ESI} is the ESI current, F is Faraday's constant, and n_f is the solution flow rate. Figure 1 shows time lapse photographs of a nano-electrospray tip containing a water solution of the pH indicator congo red with a Pt wire contact. The initial pH of this solution is 5.5. After electrospraying continuously for 70 min, a color change to blue is observed at the wire tip showing that the pH of the solution exiting the capillary is now ~ 3. With time the blue form of the dye is observed toward the back of the nano-spray tip as illustrated by the picture taken at 90 min. This indicates that either protons or the blue form of the indicator migrate upstream. This is somewhat surprising since the blue form of this dye is positively charged in solution. Figure 2 shows the pH of the ESI solution at the wire tip as a function of time. Each point on the graph was obtained with a different pH indicator dye. After 2 hours of electrospraying the pH of the solution using a Pt wire contact is 1.0, a change of 6 pH units! Either adding a buffer such as ammonium acetate to the solution or using a stainless steel wire instead of Pt (Figure 2) reduces the magnitude of the pH change. The stainless steel wire acts as either a redox buffer [2] or supplies the major charge balance via corrosion. For many analytes the gas-phase abundance of ions in an ESI mass spectra qualitatively reflect the abundance of these

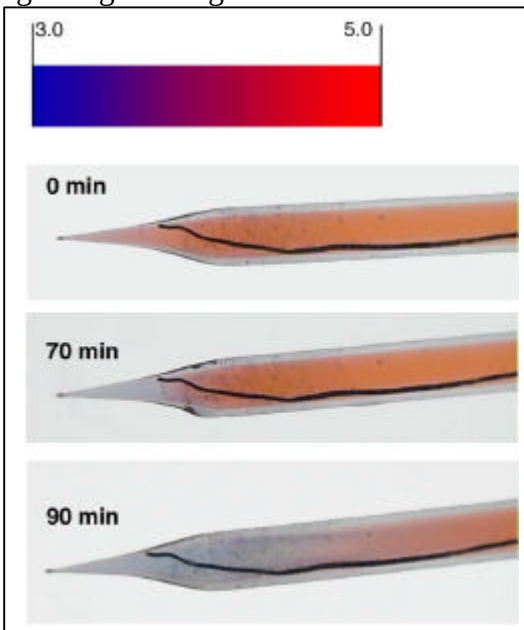

Figure 1.

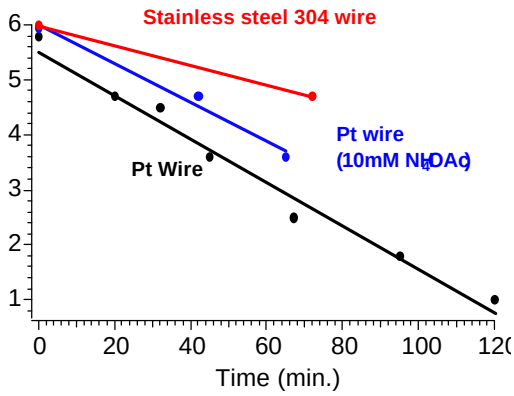

Figure 2

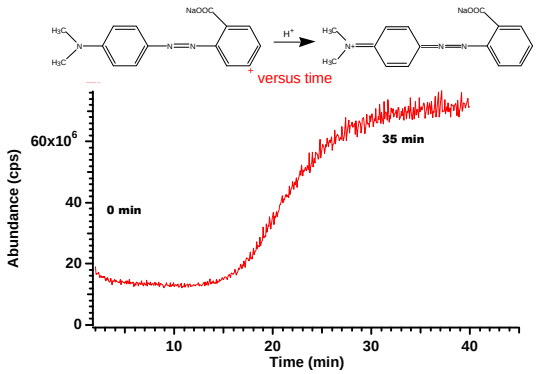

Figure 3

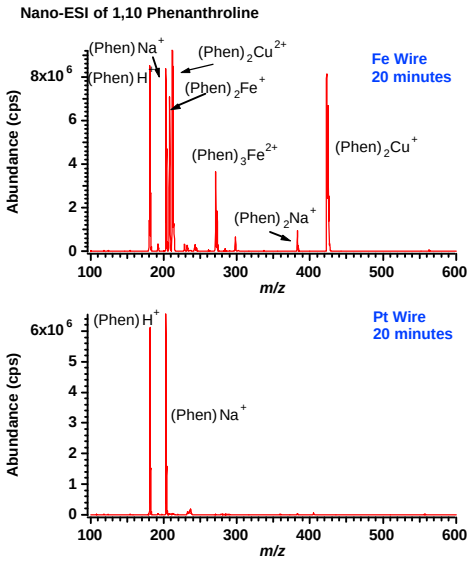

Figure 4

ions in solution. Thus, for samples in which the equilibrium distribution of ions in solution is a function of pH, the electrochemically induced pH change of bulk solution in a nano-electrospray tip can significantly affect the abundances of these ions in a mass spectrum. This is illustrated in Figure 3 for the indicator dye methyl red. After about 16 minutes into the experiment, the intensity of the molecular ion increases dramatically (the charged form of the (M + Na) ion is predominant in solution at low pH). Because the redox reactions occur at the wire tip, it takes time for the product to reach the end of the nano-spray tip and ultimately the mass spectrometer. Inserted in Figure 3 are pictures of the solution in the nano-ESI tip after spraying 0 minutes (orange color) and 35 minutes (pink color).

Electrolytic Reactions of the ESI metal contact. Figure 4 shows nano-ESI mass spectra of 1,10-phenanthroline with an iron wire (top) and a Pt wire (bottom). Anodic corrosion of the iron wire contact is the source for the metal ion complexes observed in the top spectra. Three 1,10-phenanthroline molecules combine with an iron (II) ion in solution to form a complex which is red in solution. After electrospraying for 20 minutes the solution in the nano-spray tip turns red (data not shown). In contrast to the pH indictor experiments, a color change is observed along the entire wire solution interface. Iron is relatively easy to oxidize (E^o = -0.44 vs. SHE) compared to water and the interface potential is high enough along the entire wire to oxidize iron but only high enough at the wire tip to oxidize water (E^o = -1.223 vs. SHE).

[1] Van Berkel, G. J.; Zhou, F. *Anal. Chem*. **1995**, *67*, 2916.

[2] Van Berkel, Zhou, F., Aronson, J. T. *Int. J. Mass Spec. Ion Proc*. **1997**, *162*, 55.

P. D. S. acknowledges support through an appointment to the ORNL Postdoctoral Research Associates Program administered jointly by ORISE and ORNL. ES-MS instrumentation was provided through a cooperative research and development agreement with PE-SCIEX Instruments (CRAD No. ORNL96-0458). This work was supported by the division of Chemical Sciences, Office of Basic Energy Sciences, United States Department of Energy under contract DE-AC05-96OR2464 with ORNL. ORNL is managed by Lockheed Martin Energy Research Corp.