

Mitigation of Artifactual Ion Formation and Signal Variation in Electrospray Mass Spectrometry

Michael C. Granger¹, Gary J. Van Berkel², Paul Gamache¹ and Wayne R. Matson¹

¹ ESA Inc., Chelmsford, MA 01824

² Organic and Biological Mass Spectrometry Group, Chemical Sciences Division,
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6131

Introduction:

Its ease of use and the spectrum of chemical classes that are amenable to ESI can account for the ESI ion source becoming a ubiquitous interface between liquid phase analytes and MS. However, the nature of electrospray ion formation provides a mechanism by which compounds can undergo harsh electrolysis in the emitter resulting in artifactual ion formation and unnecessarily complicated MS spectra – or an incoherent spectrum in the case of many biologically relevant molecules that demonstrate a facility for electrochemical oxidation. This phenomenon can lead to time consuming or incorrect spectral interpretation, particularly in the case of non-targeted analyses. In this paper we demonstrate that artifactual ion formation can be largely overcome by accurately controlling the potential of the emitter using an in-source electrochemical cell. Using a three-electrode electrochemical cell as part of the ES emitter we were able to lessen or prevent the occurrence of electrochemical analyte alteration of several catechol estrogens.

Methods:

Mass spectrometric analysis was performed on either a PE Sciex API 365 or API 4000 (Concord, Ontario, Canada) triple quadrupole mass spectrometer. Spectra were acquired with a modified TurbolonSpray source. Standards of several catechol estrogens were made up as 20 μ M solutions in methanol/water (50% v/v) with 5mM ammonium acetate as supporting electrolyte. The analytes were then either infused or injected into the ES-MS through our modified emitter. The emitter consisted of an axisymmetric, highly efficient three-electrode electrochemical cell whose outlet was a 3cm long silica pulled-tip capillary. An electrically floated CouloChem III potentiostat (ESA Inc., Chelmsford, MA) was used to control the interfacial potential of the emitter electrode.

Preliminary Data:

Using a traditional metal ESI source a portion of all the catechol estrogens appeared to be oxidized in the emitter leading to several peaks for each analyte in the resulting spectra. Comparable observations were made when the emitter was modified with our non-energized porous three-electrode electrochemical cell. However, energizing the cell and holding the potential of the modified emitter at a value lower than the oxidation potential for the catechol/quinone transition resulted in a marked decrease in the product distribution of the analytes. The nature of the product could also be completely changed by applying a large enough positive potential to ensure complete oxidation of the analyte. Having demonstrated the utility of the device we will report on an expanded set of chemical classes for which it functions, namely oxidative stress markers (e.g., 8-hydroxy-2'-deoxyguanosine), amino acids (e.g., methionine) and peptides (e.g., glutathione).

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