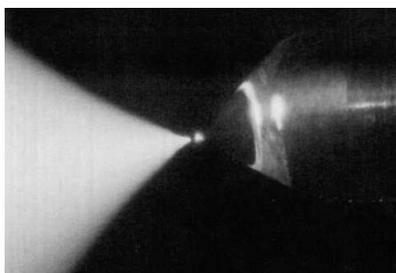


IONIZATION OF VAPORS BY AN ELECTROSPRAY CLOUD (SESI)



So-called secondary electrospray ionization (SESI) involves bringing in contact a vapor-containing gas and an electrospray cloud (the white feature to the left of the photo). The charge originally contained in the spray drops is then transferred to polar vapor molecules in the gas, turning them into ions suitable for mass spectrometric or other analyses. The approach is also effective in ionizing involatile materials present in air as suspended microscopic particles. The method was first described in 1986 by John B. Fenn and colleagues [1]. Their original ideas have not been published in the form of archival articles, but have been summarized by Fuerstenau et al as follows [2].

At the 34th (1986) ASMS Conference we reported that: "On several occasions strange peaks in observed ESPI mass spectra have been traced to contaminants in the nitrogen bath gas. To elucidate these observations we have effected deliberate contamination of the bath gas by injecting small quantities of such species as acetone, dioxane, methyl amine and tri-ethylene glycol. Strong peaks comprising protonated parent molecules were obtained even at a concentration level estimated at ppb....When...(the sprayed methanol-water mixture contained even greater amounts of the same materials)...no corresponding peaks were found in the resulting spectra. We concluded that the ionization mechanism

must involve charge exchange or chemi-ionization interactions between gas phase molecules and charged species produced in the ES process." [1] In later experiments some species at ppb levels or less in the counter current drying gas produced ions identical with those from the same species as solutes in the sprayed solution. We concluded that in those later experiments the gas phase molecules were collected by ES droplets, then emitted as ions as the droplet evaporated just as if they had been solutes in the sprayed solution. It seems likely that in the earlier results the droplets had already evaporated before they came in contact with the "contaminants" in the bath gas. Recently, in exploring mobility analysis for ES ions Hill et al. [3] rediscovered this phenomenon, dubbing it "Secondary Electrospray Ionization" or SESI and attributing it to gas phase proton exchange between ES ions of small solutes and neutral molecules, as we did in our first experiments. Hill et al also suggested that gas phase interactions between ES droplets and neutral molecules might provide even more effective ionization, i.e. the mechanism we assumed in our later studies.

[1] C.M. Whitehouse, F. Levin, C.K. Meng, and J.B. Fenn, Proc.34th ASMS Conf. on Mass Spectrom. and Allied Topics, Denver, 1986, p. 507

[2] S. Fuerstenau, P. Kiselev, J.B. Fenn, ESIMS in the Analysis of Trace Species in Gases, *Proceedings of the 47th ASMS Conference on Mass Spectrometry Allied Topics*; Dallas, TX, June, 1999; ThOE 3:00

[3] C. Wu, W.F. Siems, H.H. Hill, Proc. 46th ASMS Conf. on Mass Spectrometry and Allied Topics, Orlando, June 1998