The introduction of desorption electrospray ionization mass spectrometry (DESI MS) by Cooks and coworkers in 2004 brought, for the first time, widespread attention to the concept of open air surface analysis under ambient conditions. Contemporary with the disclosure of DESI, work carried in parallel by other research teams explored a similar philosophy in chemical analysis. Examples include the patent on the ion source named Direct Analysis in Real Time (DART) filed in December 2003, Shiea’s work on open air laser based ion sources, and work by the Van Berkel group at Oak Ridge National Laboratory on surface sampling probes (SSPs) for direct sampling of thin layer chromatography plates first published in 2002. DESI, DART, and other ambient MS techniques enabled an exciting new perspective on ways to perform both qualitative and quantitative chemical investigations on samples not typically amenable to direct MS analysis. As a bonus, direct analysis on native surfaces could be done, in most cases, without sample preparation. The field of ambient MS was thus born, reigniting the interest in finding new ways of making ions for posterior mass spectrometric analysis. Our group and others have classified ambient MS techniques based on their intrinsic desorption/ionization mechanisms. The sub-divisions that we propose are as follows: (1) one-step techniques where desorption occurs by solid-liquid extraction followed by ESI, APPI, sonic spray, or CI ion production mechanisms; (2) one-step plasma-based techniques involving thermal or chemical sputtering neutral desorption followed by gas-phase chemical ionization; (3) two-step techniques involving thermal desorption or mechanical ablation in the first step followed by a second, separate step where secondary ionization occurs; (4) two-step techniques involving laser desorption/ablation followed by an independent secondary ionization step; (5) two-step methods involving acoustic desorption approaches; (6) multimode techniques combining two or more ambient MS techniques; (7) one-of-a-kind techniques that make use of other principles for desorption or ionization which do not belong to any of the previous categories. In this presentation we will provide an overview of each of these classes of ambient MS techniques, with an emphasis on the strengths and weaknesses that each one may have for different types of applications.

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