Chromatography and ionization on a single surface

R. Dubrow, G. Siuzdak, and colleagues at the Scripps Research Institute, Mass Consortium Corp., George Washington University, and Nanosys have developed a new surface for integrating chromatography and matrix-free desorption/ionization. The new platform consists of arrays of single-crystal silicon nanowires (SiNWs) and can be used to study small molecules, metabolites, and peptides in biofluids at attomole levels.

After growing SiNWs on silicon wafers with gold colloid particles as catalysts, the researchers treated the structures with a silylating reagent. Silylation has been shown to increase the sensitivity of desorption/ionization on silicon (DIOS) MS, a related technology that uses porous silicon surfaces. The randomly oriented SiNWs grew up to 100 μm long, with diameters of 10–60 nm.

When Dubrow, Siuzdak, and colleagues performed desorption/ionization on the SiNWs, they observed that the S/N levels and mass ranges varied with NW length and density. Signal properties did not change, however, with varying NW diameter. SiNW desorption/ionization required less laser energy than other surface desorption/ionization methods, such as MALDI and DIOS. From calculations of the internal energies of several analyte molecules, the researchers concluded that the SiNW surfaces efficiently transferred energy to analytes.

Dubrow, Siuzdak, and colleagues observed that SiNWs have strong fluid wicking properties due to capillary forces in the spaces between the NWs. The capillary forces allowed the separation of analyte mixtures. The researchers separated cocaine and its metabolite from human serum, two drug molecules from each other, and *N*-acetylethanolamines from mouse spinal tissue with SiNWs. After separation on the SiNWs, the analytes were desorbed, ionized, and analyzed by MS. SiNWs enable researchers to perform many steps for peptide and metabolite analysis on a single surface. (*Anal. Chem.* **2005**, *77*, 1641–1646)

In-capillary proteolysis

Extraction and purification procedures frequently lead to losses of proteolytic peptides. To overcome this problem, Gottfried Pohlentz and colleagues at the University of Münster (Germany) have developed an in-capillary proteolytic digest method.

In the new approach, native proteins are incubated with endoproteases in the electrospray capillary. The resulting peptides are analyzed directly by nanoelectrospray MS during the proteolytic digest. Because no proteins are lost during the purification steps, maximal structural information can be obtained. According to the researchers, the method allows for direct determination of kinetic data and can be used on mixtures. However, the method is limited to proteins in solution and only the most abundant proteins. Less-abundant proteins will still require additional purification steps. (*Proteomics* **2005**, *5*, 1758–1763)