

TANDEM MASS SPECTROMETRY IN THE CHARACTERIZATION OF CONVERTED BIOMASS

Hilkka I. Kenttämä

Department of Chemistry, Purdue University

Street address

West Lafayette, IN, USA

hilkka@purdue.edu

Tandem mass spectrometry has been proven to be an invaluable tool in the field of complex mixture analysis and the identification of unknown molecules directly in mixtures due to its high sensitivity, selectivity, versatility and speed. This presentation focuses on the development of ionization techniques, novel instrumentation, HPLC methods and tandem mass spectrometric methodologies for the identification of unknown compounds in complex mixtures generated by conversion of lignocellulosic biomass. For example, characterization of catalytically converted lignin is best carried out by using high performance liquid chromatography (HPLC)/multiple stage high-resolution tandem mass spectrometry using hydroxide-doped electrospray ionization. Eleven model compounds were used to identify the optimal elution gradient and stationary phase for HPLC separation. Electrospray ionization (ESI) doped with hydroxide ions allows the ionization of all model compounds without fragmentation. Elemental compositions of the deprotonated analytes can be determined by high-resolution analysis in the Fourier-transform ion cyclotron resonance part of the tandem mass spectrometer used. Detailed structural information for the analytes is obtained by multi-stage tandem mass spectrometry (MS^n) experiments on the deprotonated analytes in the linear quadrupole ion trap part of the instrument. In addition to the acquisition of full mass spectra for the ionized compounds eluting from HPLC (MS^1), fragment ions formed from these ions, and those formed from their fragment ions, and so on, were subjected to consecutive isolation and collision-activated dissociation (CAD) experiments until no further fragmentation products were observed. This approach provided valuable structural information for the components of real lignin degradation product mixtures. Further, tandem mass spectrometry experiments that combine CAD and ion-molecule reactions often give much more valuable structural information than each individual experiment by itself. These two reaction processes should be performed in separate and clean environments as their efficiency and information value is otherwise compromised. Unfortunately, commercial instruments allow these experiments to be performed only up to MS^3 . Hence, a new tandem mass spectrometer was built by combining two commercial linear quadrupole ion trap (LQIT) mass spectrometers with differentially pumped ion trap vacuum chambers. This instrument allows many stages of clean tandem mass spectrometry experiments involving both CAD and ion-molecule reactions. The utility of this approach is demonstrated using several examples.