

# Assigning double bond position using ozonolysis: On-line mass spectrometric approaches

Michael C. Thomas

Supervisor: Dr. Stephen Blanksby

*School of Chemistry, University of Wollongong*

## **Abstract**

Despite rapid developments in instrumentation in recent years, determining double bond position by mass spectrometry (MS) alone remains challenging. In certain cases, Collision Induced Dissociation (CID) provides informative fragments ions that allow assignment of double bond position; however, fragmentation is often excessively complex making double assignment difficult. Derivatisation prior to analysis can be used to simplify CID spectra, although, this is time consuming and therefore not desired.

Lipid analysis and natural product structural characterisation represent two areas where assigning double bond position is of major importance. For lipid analysis, electrospray ionisation tandem mass spectrometry (ESI-MS/MS) can provide a near complete structural characterization of lipids present within complex mixtures. Unfortunately, current ESI-MS/MS methods cannot distinguish isomeric phospholipids that differ only in the position of double bonds. This is a critical limitation as positional isomers are present in biological systems and can have distinct biochemical functions. For natural products, a combination of high resolution MS and NMR in most cases allows the complete characterisation of molecular structure. However, locating double bond position within long alkene chain is sometimes impossible, even with the aid of two-dimensional NMR experiment. Therefore, alternative methods for assigning double bond position are required.

Two on-line mass spectrometric techniques for determining double bond position have been developed. Both of these methods utilise ozone to cleave C-C double bonds to form chemically induced fragment ions indicative of double bond position. Ozonolysis can either be performed in the electrospray source or within the ion trapping region of an ion-trap mass spectrometer. These two on-line techniques will be discussed and examples of lipid and natural product structural characterisation will be presented.