

Mass Spectrometry as a Detector in Polymer Chromatography - Scopes and Limitations

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Mass spectrometry is an extremely powerful technique in the identification and quantification of organic as well as inorganic materials and has been used for polymer characterization for quite some time now. Key to mass spectrometry is the ionization of the analytes, which can be difficult for several polymers due to their lack of ionizable groups. While direct mass spectrometric analysis can be done for polymers under certain conditions (e.g., ionizable groups, narrow molar mass distribution), often a separation of the sample into smaller fractions is beneficial.

For direct mass spectrometry of polymers MALDI (Matrix Assisted Laser Desorption Ionization) is the most frequently used technique, but it cannot directly be used in combination with chromatography as the ionization is done in high vacuum. To overcome this limitation either sample fractionation or an off-line spraying device can be used to simplify the mass spectra on one hand and to monitor the changes of chemical composition during chromatography on the other hand (Figure 1).

A further approach is the combination of adsorption-based chromatography (HPLC) and atmospheric pressure ionization mass spectrometry. Here, either electrospray (ESI) or atmospheric pressure chemical ionization (APCI) can be used to generate ions, in the first case multiply charged molecules dominate and it is applicable to polar polymers, whereas in the second case less polar materials can be ionized and are bearing dominantly a single charge.

The last approach to be discussed is the application of GC-MS for polymer characterization. Due to their high molar mass polymers cannot directly be transferred onto a GC column, but must be broken down into smaller molecules beforehand. This is usually accomplished by thermal degradation, such as pyrolysis. Pyrolysis-GC-MS is an extremely powerful technique for the identification of polymers, mixtures thereof, and even the simultaneous determination of additives such as antioxidants or plasticizers.

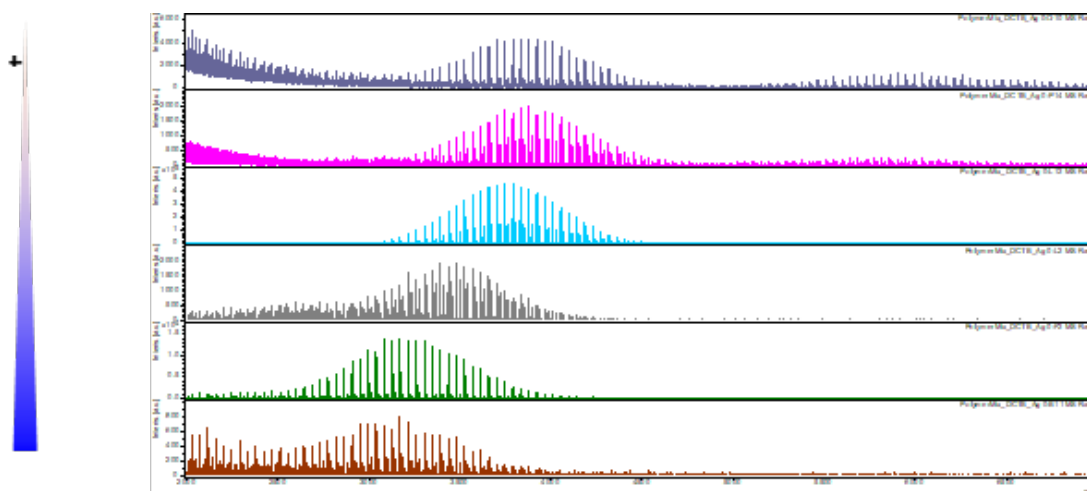


Figure 1. MALDI mass spectra of a polymer mix after size exclusion chromatography.

Speaker Bio

Clemens Schwarzinger is Professor for Chemistry at the Institute for Chemical Technology of Organic Materials at the Johannes Kepler University Linz, Austria. After finishing his PhD thesis in 2002 he worked as industrial PostDoc at Chemtech Leuna GmbH and Wacker-Chemie GmbH and was guest professor at the Petroleum

Institute in Abu Dhabi before being awarded the *venia docendi* in 2009 from the Johannes Kepler University. His research interest covers polymer synthesis but mostly polymer analysis with a focus on mass spectrometry and on a sideline scientific gemology, the science of gemstones. Current research topics are biobased polymers, functional polyesters, MALDI mass spectrometry and imaging, polymer chromatography (SEC and HPLC) in combination with mass spectrometry and thermal degradation techniques, such as pyrolysis-GC-MS and TGA-FTIR. In 2002 he was awarded the Theodor Körner Fond prize and in 2024 the Accredited Gemologists Association Research Grant, was Editor in Chief of the International Journal of Polymer Analysis and Characterization from 2019-2024 and is member of several Boards focused on polymer characterization.