The Xpose Algorithm: A New Tool to Simplify Comparative Sample Analysis

Uncover and characterize subtle spectral distinctions in your LC-MS and GC-MS workflows

Introduction

High-resolution accurate mass LC-MS and GC-MS analyses can provide a great depth information, but the complexity of many samples can make the discernment of minor variabilities challenging. Such subtle differences in spectral features can reveal important formation variations to support competitive product research or safeguard product integrity. Components leaching from packaging material, readily extractable compounds, or degradation products may represent only a small percentage of the total product picture, but their characterization can be critical.

Bruker's Xpose algorithm has been developed to allow the subtraction of high resolution, high density data files to expose hidden compounds in your samples. With this approach, the resulting clean (simplified) MS and MS/MS spectra help to facilitate identification and structural elucidation of these unique targets.

Detection and Identification, Additive Characterization, Polymer Analysis

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Experimental

Detection and Characterization of a Polymer Product Additive

Two proprietary polymeric samples, one control (Figure 1, blue trace) and one novel sample containing an unknown additive (Figure 1, red trace), were subjected to MS and MS/MS analysis on a Bruker impact II QTOF system following separation on a Bruker Elute UHPLC system.

For both the sample and control, 20 µL were injected onto a C4 Waters Acquity column (BEH300 C4, 1.7 µm 2.1 X 100mm) at a flow rate of 400 µL/min. Mobile Phase A was water/methanol (99:1) with 5 mM ammonium formate and 0.01% formic acid. Mobile Phase B was acetonitrile with 10% THF. A gradient was applied according to Table 1.

Full Scan MS and Auto MS/MS data were collected in positive ion mode from m/z 50 – 5000. The MS spectra rate was 2 Hz. The capillary voltage was 4500 V, and the nebulizing gas was set at 1 bar. The dry gas rate was 4.0 L/min, and the dry temperature 300°C.

Following data collection, sample and control data sets were selected in the Xpose menu (Figure 2). Application of the Xpose algorithm results in the generation of a new Base Peak Chromatogram. (Figure 3, top) At

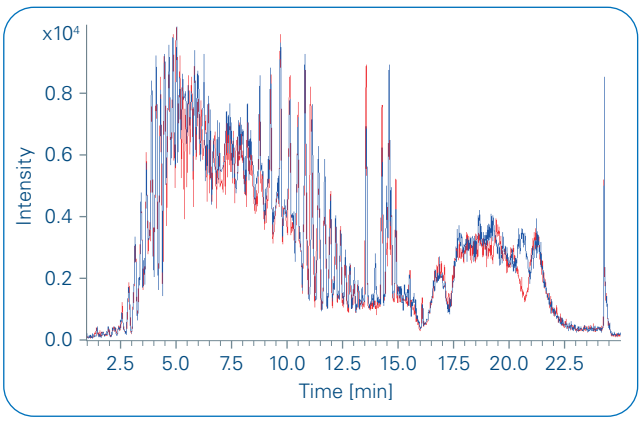

Figure 1: Overlay of Base Peak Chromatograms for the two tested polymeric samples, as shown in Bruker Compass DataAnalysis (DA) software. DA is a powerful tool for qualitative analysis, viewing chromatograms, mobilograms, and spectra, and for assisting with compound identification and structural elucidation. All views, including formulae, structures, and other annotations, are easily transferrable for the creation of specific data presentation or publication, and customizable report templates enable rapid, uniform data documentation.

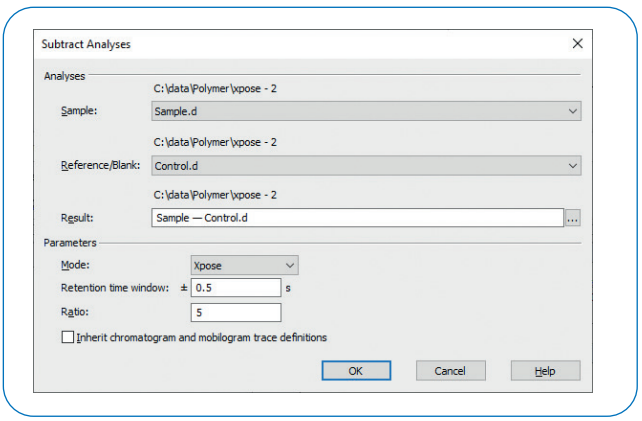

Figure 2: Xpose menu. For this sample set, the default algorithm parameters were used. If desired, retention time window and ratio parameters may be adjusted, and/or the resulting data set renamed.

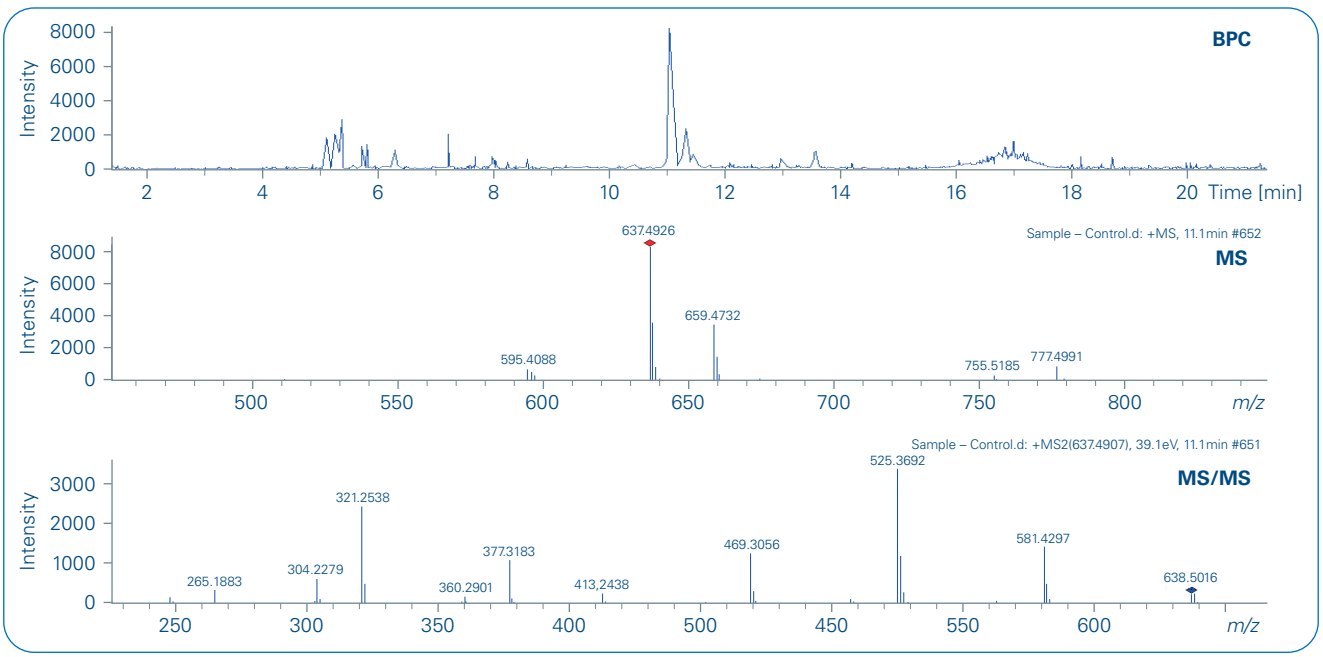

Figure 3: Subtractive spectral views of the Base Peak Chromatogram and (single time point) MS and MS/MS data resulting from the application of the Xpose algorithm, revealing a unique additive at m/z 637.4926.

elution time 11.1 minutes, clean MS and MS/MS spectra of the unknown additive (Figure 3, center and bottom, respectively) can be clearly seen.

Using Bruker's SmartFormula with the generated spectra, potential molecular formulae are calculated (Figure 4) The best match is $C_{40}H_{65}N_2O_4$, based on ppm deviation (2.1 ppm) and mSigma value scoring (6.1) (Figure 4). The mSigma value indicates the quality of the match to theoretical isotope ratios in both intensity and distance. Using scale from 0 to 1000, lower values signify a better match.

MS and the MS/MS fragment data were combined in Bruker's SmartFormula3D to generate a more accurate molecular formula proposal (Figure 5). The best match (again $C_{40}H_{65}N_2O_4$) was sent to Compound Crawler, enabling a broad search of online structural databases, including ChemSpider, PubChem, and ChEBI, which suggested the unknown sample additive was the antioxidant Irganox® 1098 (BASF) (Figure 6).

Table 1: LC Gradient

Time (min)	%A	%B
0.0	90	10
0.5	90	10
20.0	0	100
23.0	0	100
23.1	90	10
25.0	90	10

Conclusion

The detection and characterization of minor sample components can have major implications for product utility, stability, and safety. This task can be accelerated using the Xpose algorithm, even within complex data sets as are typically collected on Bruker's family of high-resolution QTOF instruments. With Xpose, differentiating spectral elements are clearly visualized, facilitating rapid characterization of hidden compounds, including additives, impurities, or degradation products. This approach can provide significant analytical advantages in a wide variety of research and development and quality control applications.

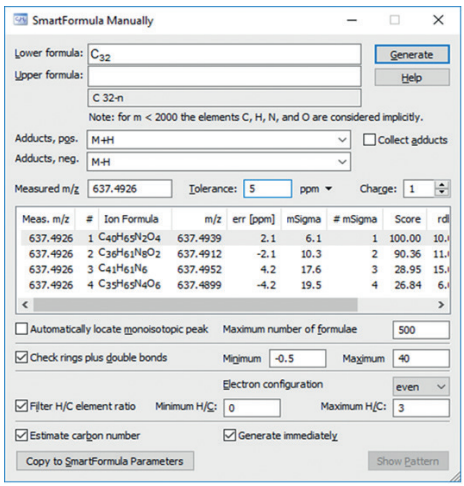

Figure 4: SmartFormula results, indicating calculated (potential) elemental formulas and error parameters for evaluation of candidates.

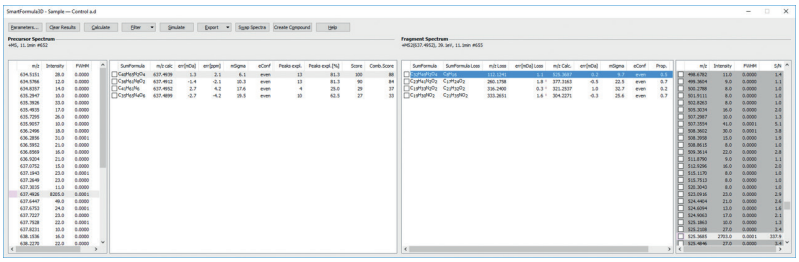

Figure 5: SmartFormula3D results, combining SmartFormula MS with available MS/MS fragmentation data to reduce the number of candidate formulae.

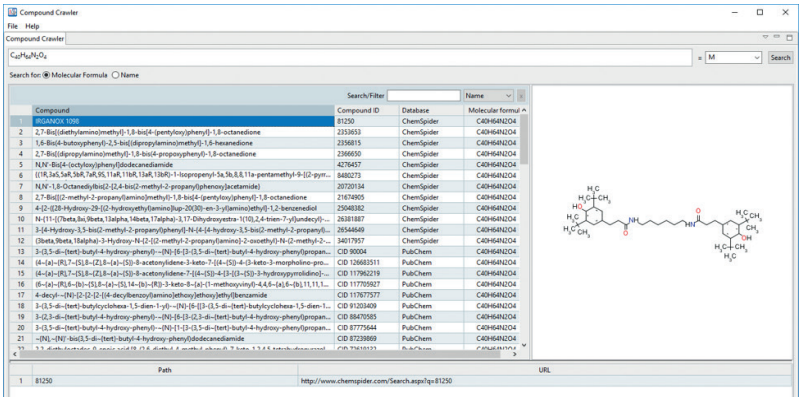

Figure 6: CompoundCrawler search results, indicating the likely structure of the antioxidant additive.

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