

COMPARISON OF GC-MS AND GCXGC-MS ANALYSIS OF WHISKY VOLATILES.

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Introduction

Gas chromatography coupled with mass spectrometry (GC-MS) or high-resolution mass spectrometry (GCxGC-HRMS) is widely used to identify differences between similar samples. Comprehensive two-dimensional gas chromatography combined with high-resolution mass spectrometry (GCxGC-HRMS) uses two columns with different phases to achieve greater separation of complex mixtures. Each separation method has its strengths and weaknesses with respect to hardware setup and information content. Chemometric analysis of GCxGC-HRMS data provides an additional challenge because of the complexity of the data set. Traditionally, data processing for GC-MS and GCxGC-MS analysis requires separate software packages. Here we show a unified data analysis software package that supports both GC-MS and GCxGC-MS data, and we compare the information and data analysis for identical sample sets analyzed by both GC-MS and GCxGC-MS using a high-resolution time-of-flight mass spectrometer.

Methods

An Agilent 8890 gas chromatograph fitted with a Zoex ZX-2 thermal modulator was interfaced with a JMS-T2000GC (AccuTOF GC-Alpha, JEOL USA, Inc) reflectron time-of-flight mass spectrometer. An HTA HT2800T All-In-One autosampler was mounted on the gas chromatograph and used for headspace SPME measurements of Scotch whisky samples.

Data analysis for both GC-MS and GCxGC-MS data was carried out with AnalyzerPro[®] XD software (SpectralWorks Ltd.).

Mass spectrometer: JEOL AccuTOF GC-Alpha

- High data acquisition speed (50 Hz) well suited for GCxGC
- High mass resolving power to separate isobaric peaks (30,000)
- High mass and isotopic accuracy for elemental composition determination
- Multiple ion sources (EI, CI, PI, FI), probes, and sample introduction methods
- Easy ion source maintenance and fast ion source pumping

Chromatography -- GC-HRMS:

Advantages:

- Easy hardware setup and data analysis
- Generally shorter analysis times than GCxGC-MS
- Chromatographic deconvolution useful when components are not completely separated
- Better suited than thermal modulation GCxGC for small volatiles (C3-C3)

Considerations:

- Components in truly complex mixtures cannot be separated using a single GC column
- Not ideal for mixtures of both polar and nonpolar compounds

Chromatography -- GCxGC-HRMS:

Benefits:

- Powerful tool for separating highly complex mixtures
- Separation by two physical properties (e.g. boiling point and polarity)
- The 2D chromatogram shows separation by compound class
- Ideal for mixtures of both polar and nonpolar compounds

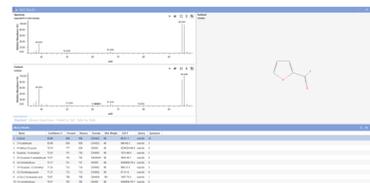
Considerations:

- Complex and more expensive hardware setup
- Requires fast MS detection (TOF is ideal)
- Traditionally require specialized data analysis software
 - AnalyzerPro XD offers a unified data analysis approach
- Flow and thermal modulators have different properties
- Thermal modulation does not focus small volatiles (C3-C7)

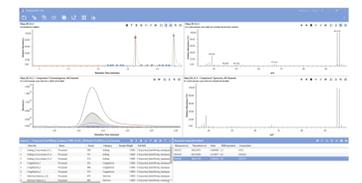
Procedure:

- Measure at least 3 replicates for each of 5 whiskies by GC-HRMS
- Measure at least 3 replicates for each of 5 whiskies by GCxGC-HRMS
- Set up a sequence in AnalyzerPro XD for each data set
- With the exception of differences in the optimal peak detection and modulation parameters, the data analysis procedure in Analyzer Pro XD is identical for GC-HRMS and GCxGC-HRMS data.
- AnalyzerPro XD carries out chromatographic deconvolution and peak detection with database searching for compound identification
- Statistical analysis and PCA reveals differences between samples
- *Note: GC and GCxGC-HRMS analysis was carried out at different times: four whiskies were common to both.*

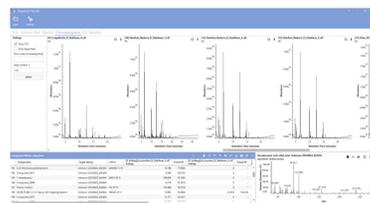
Data Analysis Examples



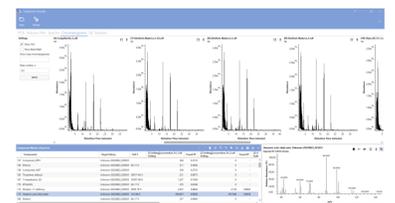
Database search for furfural in GCxGC-HRMS data



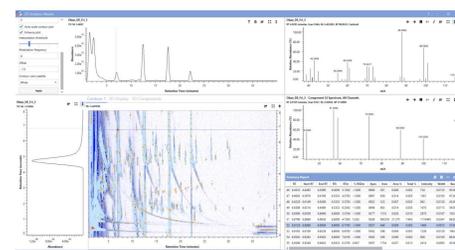
Elemental compositions from exact masses in furfural in GCxGC-HRMS data



GC-HRMS Reconstructed Total Ion Current Chromatograms (unmodulated, good separation for early eluters)

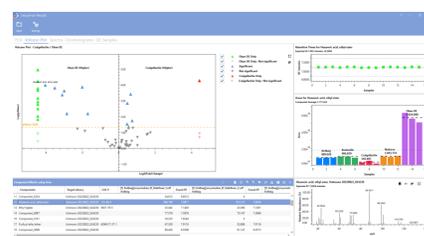


GCxGC-HRMS Reconstructed 1D Total Ion Current Chromatograms (modulated, poor thermal focusing for early eluters)

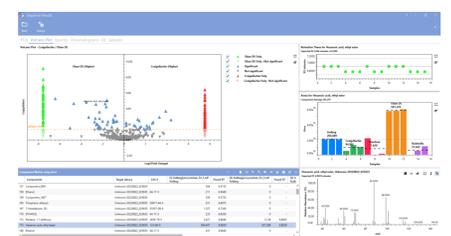


2D Chromatogram for one of the whisky samples in the GCxGC-HRMS data, with ethyl hexanoate highlighted

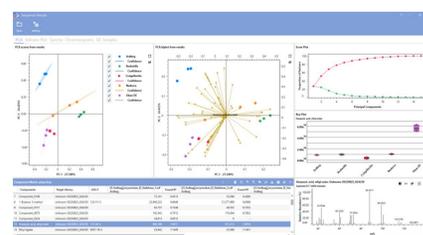
Statistical analysis shows the same trends by GC-HRMS and GCxGC-HRMS for a selected compound: ethyl hexanoate (fruity, sweet apple flavor)



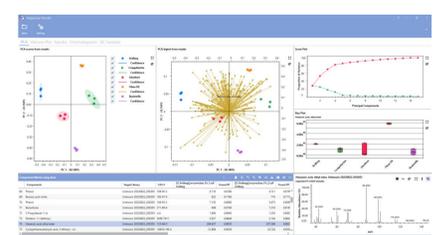
Volcano plot comparing headspace volatiles from two whisky samples analyzed by GC-HRMS



Volcano plot comparing headspace volatiles from two whisky samples analyzed by GCxGC-HRMS



Principal Component Analysis for headspace volatiles from five whisky samples analyzed by GC-HRMS



Principal Component Analysis for headspace volatiles from five whisky samples analyzed by GCxGC-HRMS

Results

- The AccuTOF GC-Alpha is capable of acquiring high-resolution accurate-mass mass spectra with high-quality database matches for both GC and GCxGC sample introduction.
- AnalyzerPro XD provides a single data processing application that can be applied to both one-dimensional gas chromatography coupled with high-resolution mass spectrometry (GC-HRMS) and comprehensive two-dimensional gas chromatography coupled with high-resolution mass spectrometry (GCxGC-HRMS).
- AnalyzerPro XD provides a direct link of the statistical plots to the specific MS component with visualization and/or library search results as well as ultimately the high-res elemental composition.
- If library search does not result in a clear match, the chemist is then able to pass the found formulae to ChemSpider/PubChem for additional investigation.