# WHAT DO WE DO WITH ALL THAT DATA? COMPLEMENTARY DATA PROCESSING METHODS FOR TWO-DIMENSIONAL GAS CHROMATOGRAPHY AND MASS SPECTROMETRY

Robert B. (Chip) Cody
JEOL USA, Inc., 11 Dearborn Rd., Peabody MA 01960 USA

## 1. Introduction

Comprehensive two-dimensional gas chromatography combined with mass spectrometry generates a great deal of information. The different data analysis packages offer complementary features with different strengths, depending on the questions to be answered. A combined approach using different software systems is often needed to obtain a comprehensive view of the sample composition. This is illustrated for GCxGC-HRTOFMS analysis of coffee aromas.

The first step in data analysis is often determination of the types of compounds that are present. Although this is traditionally done by database searching, it is helpful to make use of other data, such as accurate mass measurements and retention index matching. For samples that have repeating units such as petrochemicals, polyhalogenated compounds, and polymers, soft ionization such as field desorption or photoionization is helpful, with or without chromatographic separation. In fact, measurements made without chromatographic separation can reveal compounds that are not suitable for gas chromatography. It's important to know what we're missing! Modified Kendrick Mass Defect plots can provide an overview of the compound classes present, and that information is helpful to guide the examination of the GCxGC-MS data with dedicated GCxGC software and identify the regions on the 2D chromatogram where different compound classes may be found. Chemometric analysis such as offered with SpectralWorks' AnalyzerPro XD software is a powerful approach to identifying differences between samples.

## 2. Methods

Headspace aromas from two single-varietal roasted coffee beans purchased from local coffee roasters and two blended coffees from Starbucks and Illy were analyzed by GCxGC-HRTOFMS. Coffee beans were ground to a fine espresso grind and approximately 10 grams of each freshly ground coffee were placed into a 20 mL headspace vial. Aroma compounds were sampled by using solid-phase microextraction (SPME) with a Supelco divinylbenzene/Carboxen SPME fiber.

A SepSolve INSIGHT thermal modulator was used for comprehensive two-dimensional gas chromatography with a normal-phase column set. Mass spectra were acquired with a JEOL AccuTOF GC-Alpha high-resolution time-of-flight mass spectrometer and a combination electron ionization (EI) and photoionization (PI) ion source. Molecular ions were present for most compounds in the EI data, so PI data were not acquired. A combination EI/FI (field ionization source) was also used to acquire FI data for one of the coffees.

Data analysis was carried out using several software packages: SepSolve ChromSpace for controlling the thermal modulator and visual comparison of GCxGC-MS data, SpectralWorks AnalyzerPro XD software for chemometric analysis, GC Image software for data analysis and figure creation. JEOL msFineAnalysis AI software was used for qualitative analysis. Mass Mountaineer software was also used for Kendrick Mass Defect Analysis of the summed GCxGC-FI mass spectral data (not shown – see our other poster).

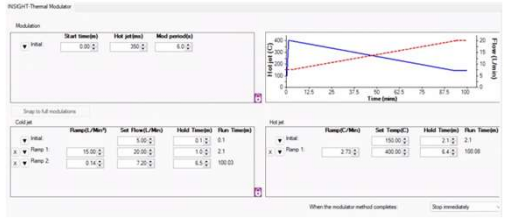
MS Acquisition
- Range: *m/z* 10-600
- Spectral acquisition: 50 Hz
- Resolving power: 30,000

Temperature Control

Temperature ON

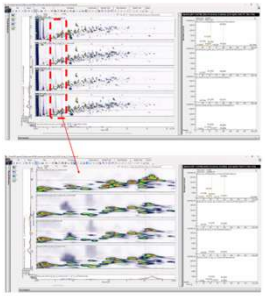
| | Rate [°C/min] | Temperature [°C] | Hold Time [min] |
|---|---|---|---|
| Initial | | 40.0 | 2.000 |
| Step 1 | 3.000 | 320.0 | 5.000 |

Total Time [min] 100.333

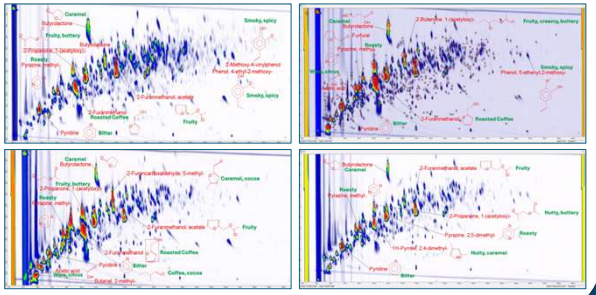


## 3. Chromatograms

ChromSpace comparison of samples from each coffee
The selected component is discussed in subsequent figures.

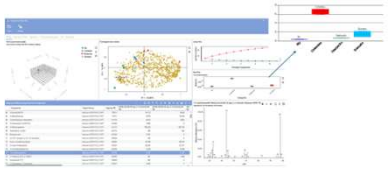


GC Image annotation with text and structures for selected compounds



## 4. Chemometrics

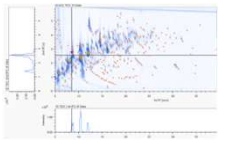
AnalyzerPro XD is useful for 1DGC-, 2DGC-, and direct analysis-MS
Chemometric analysis shows a component unique to Colombian coffee



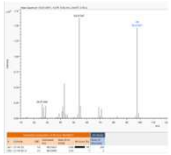
## 5. Unknown Identification

msFineAnalysis AI for nontargeted analysis

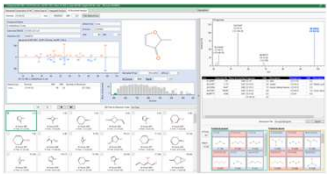
Unknown compound | Top database match

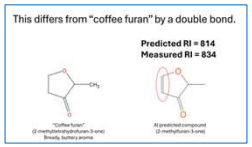


Top database match has wrong composition!



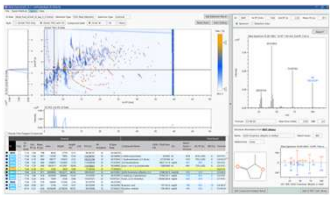
Next best DB match has poor RI match.






**msFineAnalysis structure analysis suggests a reasonable structure**

"Coffee Furan" is also present



## 6. Conclusions

Over 500 compounds were detected in the headspace volatiles for each coffee. Chemometric analysis revealed differences in the presence and relative abundances of the volatile compounds that contribute to the aromas. Chemical differences most likely relate to chemotaxonomic differences as well as differences in processing (roasting) methods.

A compound that was uniquely abundant in the Colombian coffee was identified using all the available information: elemental compositions from accurate-mass and isotope data, retention index matching, and fragment ion coverage. The top database match was inconsistent with the elemental composition of the molecular ion. Of the database matches with the correct composition, none had a database retention index in good agreement with the measured value.

**The msFineAnalysis AI structure analysis function identified a previously unreported compound that is not registered in the NIST and Wiley databases. This compound has a structure that is consistent with all measured GCxGC-HRMS data, and its structure is closely related to a well-known coffee aroma compound.**