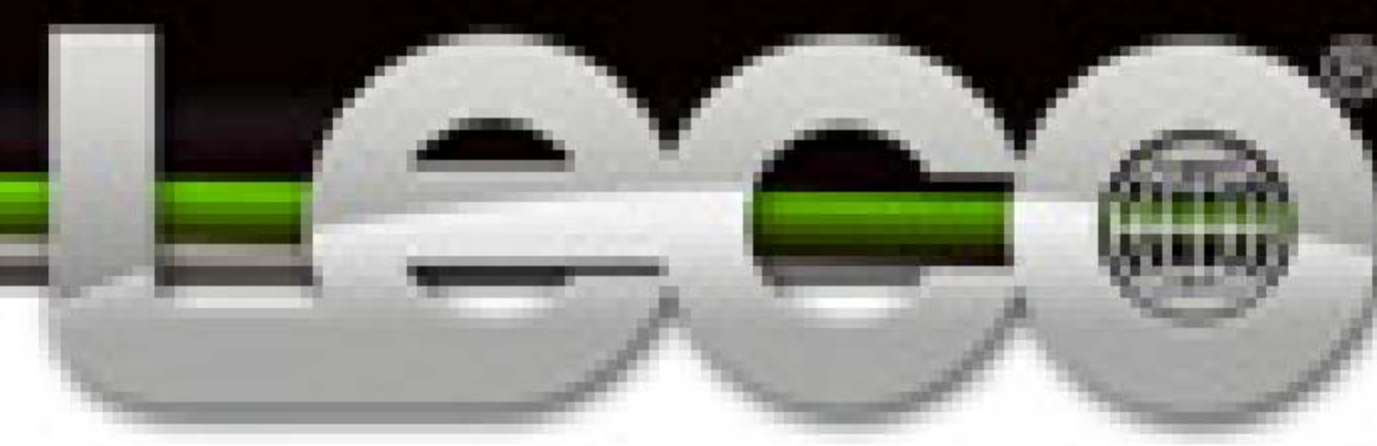




Fragmentation Trees for Automated de novo Interpretation of Impure Electron Ionization Spectra from Gas Chromatographic Complex Mixture Analysis—Chemical Deconvolution

Kevin Siek¹; Vasily Makarov²; Viatcheslav Artaev¹; Dmitry Mazur³; Albert T. Lebedev³ | ¹LECO Corporation, Saint Joseph, MI USA; ²Mass Spectrometry Consulting Ltd., Bar, Montenegro; ³Moscow State University, Moscow, Russian Federation

Introduction

- Impure spectra contain signals from multiple analytes or signals unrelated to the main analyte, due to propinquitous coelution that confounds purely mathematical de-coelution. Some such spectra are expected in complex sample analysis.
- Impure spectra may impede manual or automated interpretation and beget false assignments or other failures.
- Chemical information within high-resolution spectra can assist mathematical de-coelution and facilitate analyte identification.

Methods

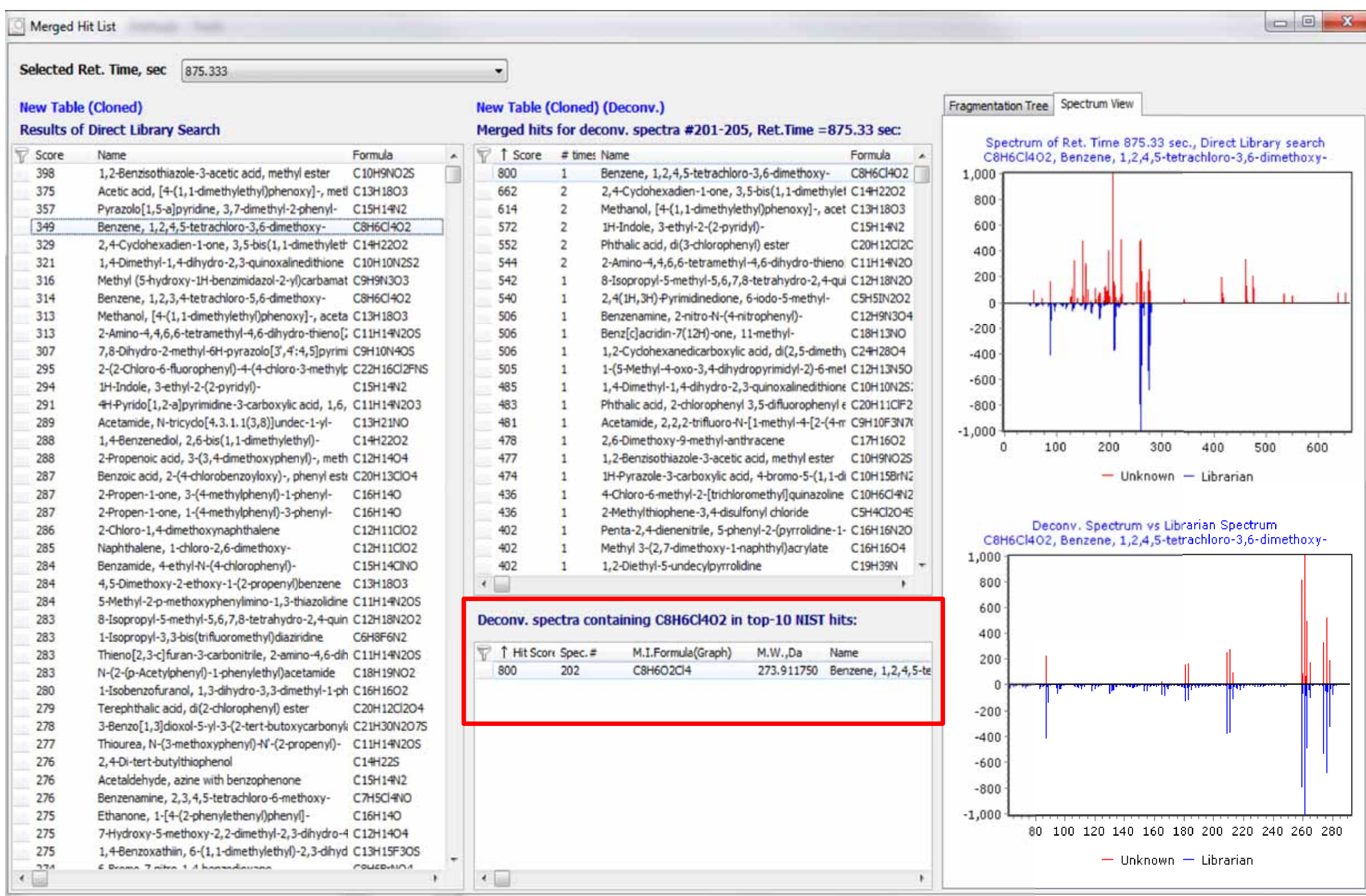
- Samples were prepared using conventional practices and analyzed by a Pegasus® GC-HRT (see handout for details).
 - Lake Ontario fish tissue
 - Municipal wastewater
 - Nigerian crude oil
- The wastewater sample was subsequently analyzed by Pegasus GC-HRT 4D to confirm results (details in handout).
- Chromatographic feature finding was performed using commercially available software (ChromaTOF-HRT® 1.81).
- Peak tables were sent to chemical deconvolution software.

Results Summary

- False signals rejected from 40 hand-selected impure spectra
 - 40 spectra with total of 64 spurious signals at high m/z and intensity
 - 55 of these 64 spurious signals were orphaned
 - 5 of these 64 were joined to a separate minor fragmentation graph
 - 4 of these 64 joined to the principal analyte's fragmentation graph
- Fish tissue example coelution
 - Incurred tetraCl-diMeO-benzene under fish fat and siloxane peaks
 - CD separated analyte's fragmentation graph from matrix graphs
 - Filtering library hits by formula yields only the one correct hit
- Wastewater example coelution
 - Full spectrum reflects only benzothiazole, overlooking other analytes
 - CD reports 3 analytes and 1 matrix component within this peak
 - In GC-HRT 4D analysis, same 3 analytes separate in 2nd dimension
- Crude oil example coelution
 - Coelution of 5 analytes sorted correctly
 - CD generally finds chemically distinct analytes, as in the example
 - CD generally fails for chemically similar analytes, as expected

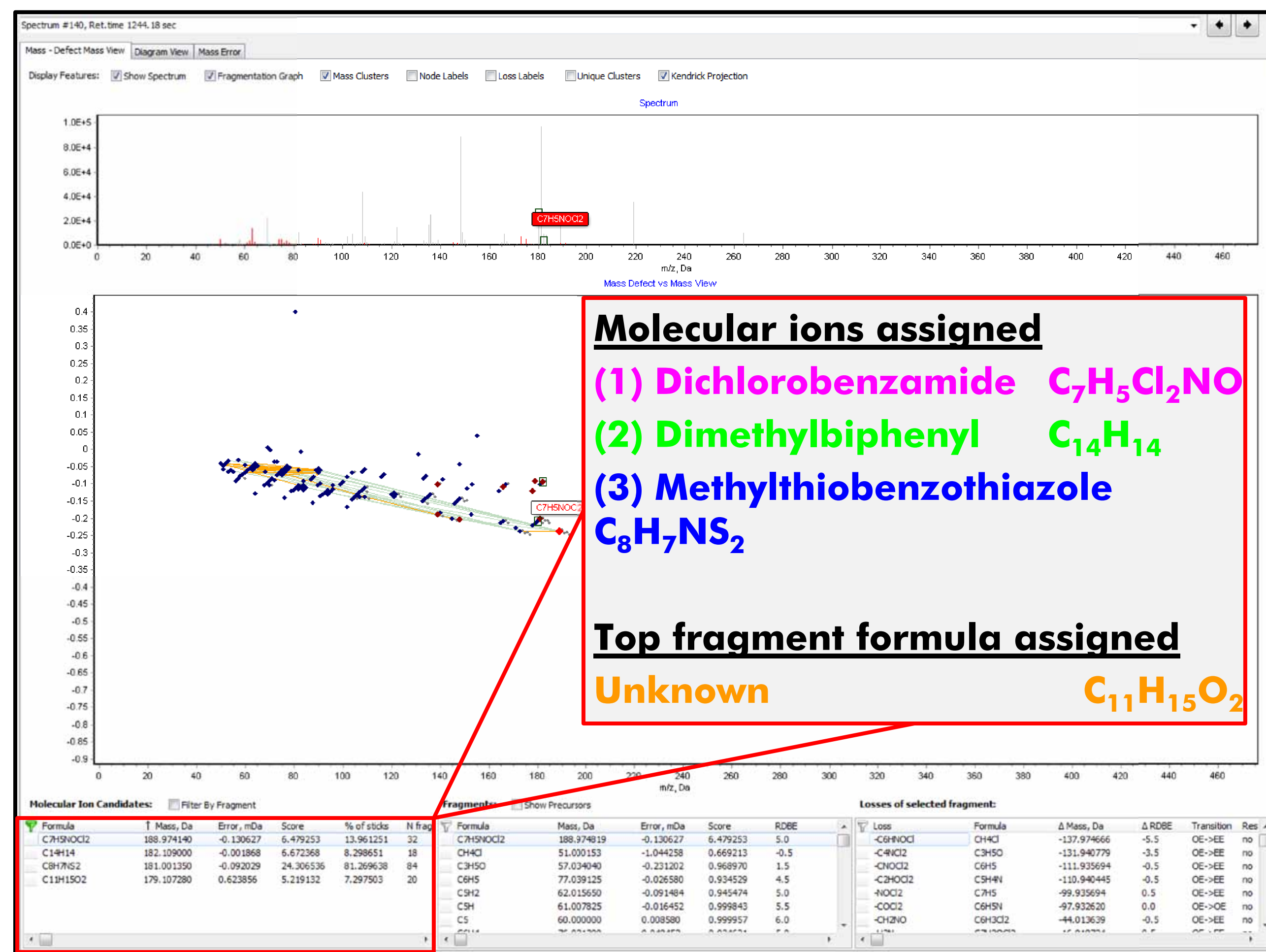
Results Example I: 3x Coelution in Fish Tissue Matrix

CD returns the one correct hit after filtering by formula;
matrix (low m/z) + siloxane (high m/z) interference removed:

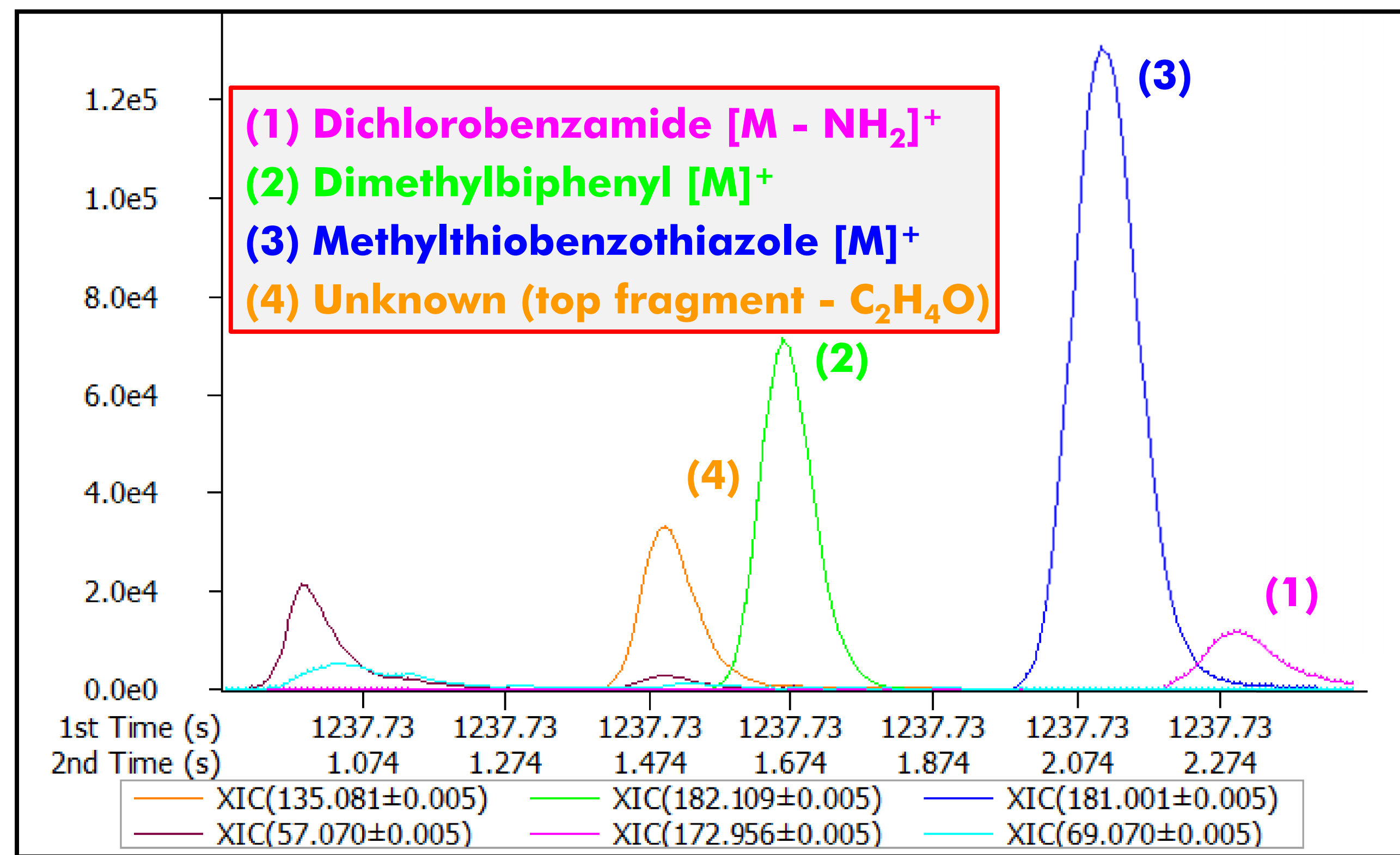


Results Example II: 4x Coelution in Wastewater

CD distinguishes 3 molecular ions and 1 top fragment:

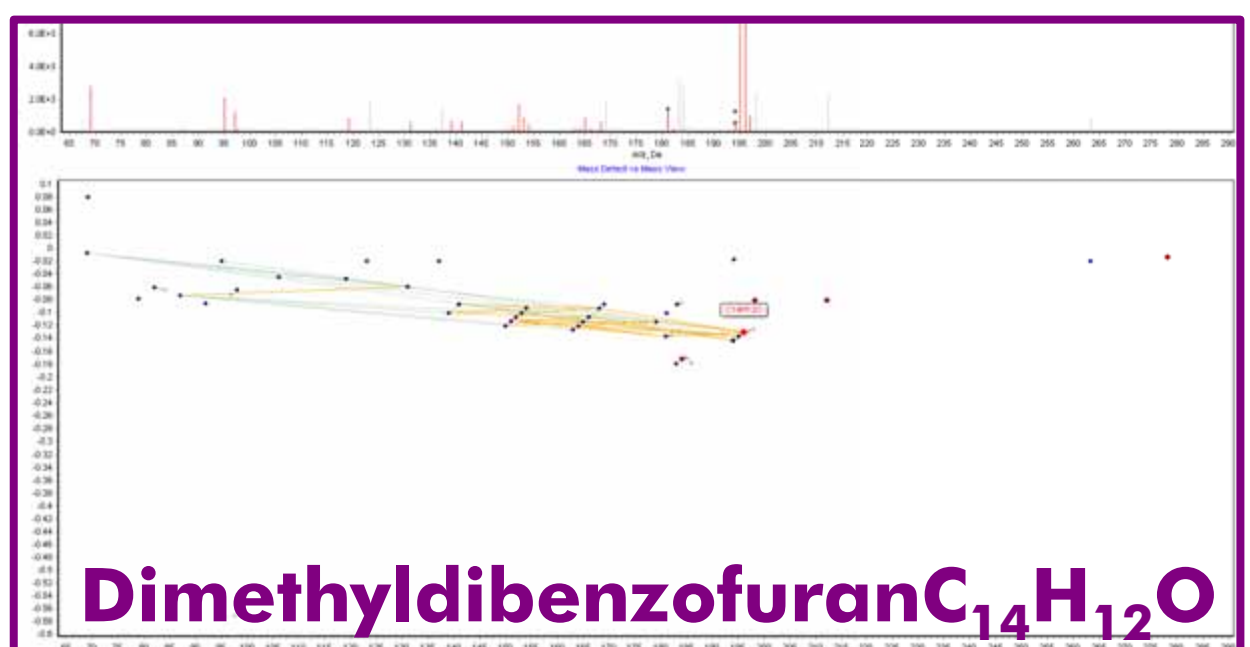
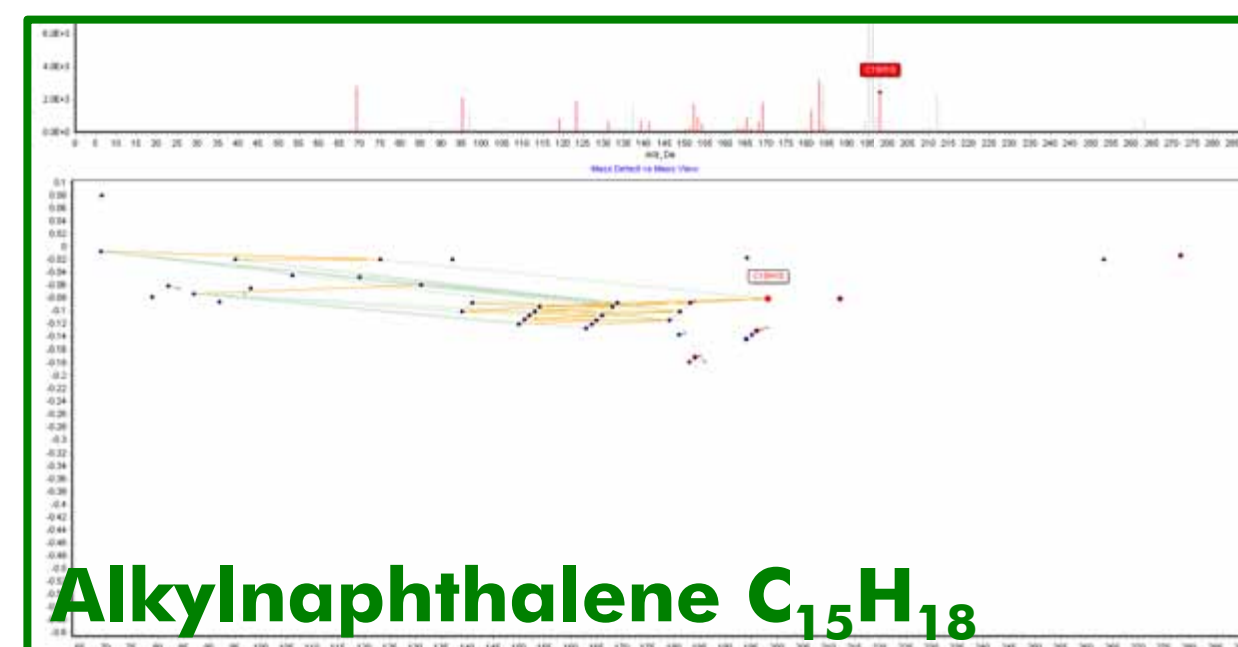
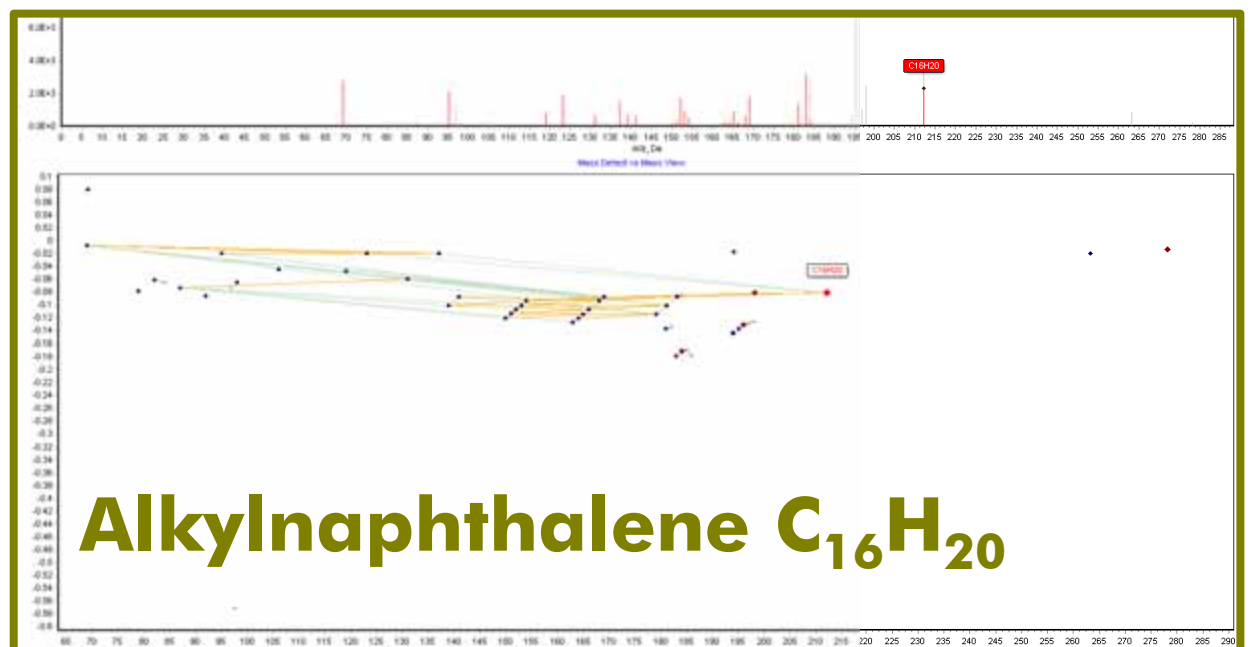
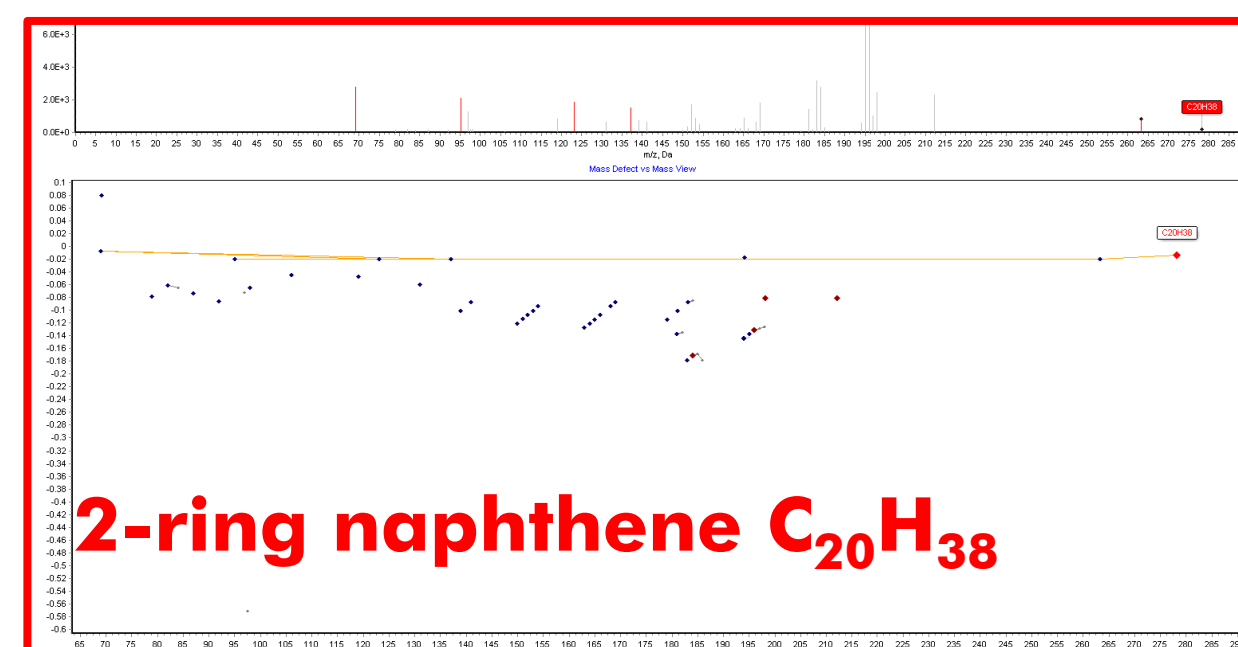
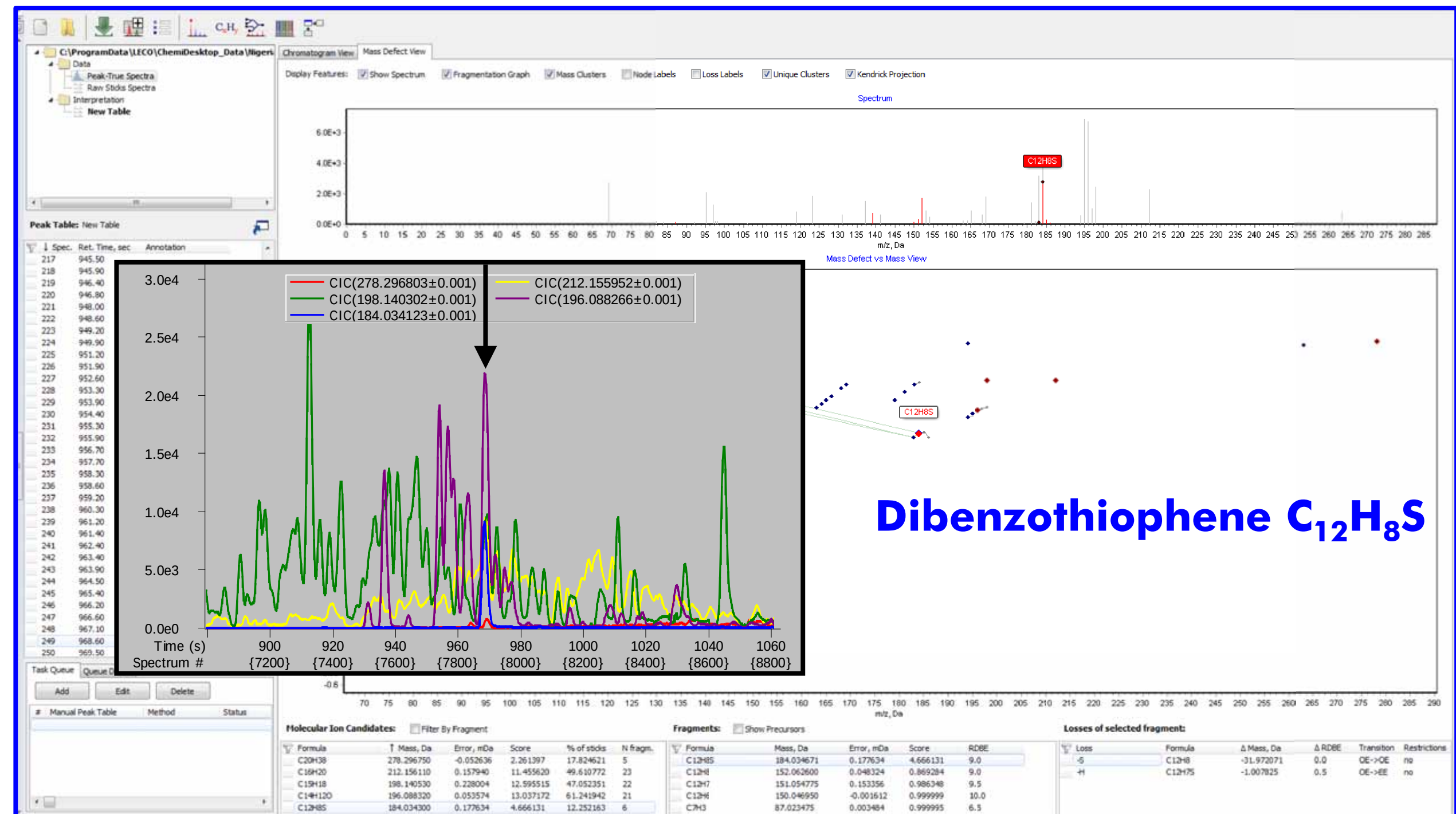


Same analytes found in subsequent GC-HRT 4D analysis:



Results Example III: 5x Coelution in Crude Oil

Five separate molecular ions found in coelution at ≈ 969 s:



Conclusions

- Chemical deconvolution algorithms accurately reported independent components of dead coelutions where such components belong to distinct chemical classes.
- Present algorithms fail to distinguish chemically similar analytes such as branched and linear alkanes, thus chemical deconvolution is not a substitute for GCxGC.
- Chemical deconvolution algorithms accurately rejected more than 80% of spurious signals from manually curated spectra found to be contaminated with unrelated signals.