Potential Benefits of Comprehensive Two-Dimensional Gas Chromatography – High Resolution Time-of-Flight Mass Spectrometry (GC×GC-HRTOFMS)

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Introduction

- GC×GC systems, both commercial and non-commercial, vary in performance. There are two key performance characteristics that determine the performance of a GC×GC system—injection peak width and modulation speed. For typical column configurations (30–60 m first column) an injection peak width with σ <10 ms and a modulation period as short as 1 second are required. If either of these are less than optimal, the peak capacity and resolution in the first and second dimensions will be compromised.
- To obtain the best results from a high performance GC×GC system, the detector must be capable of high data acquisition rates. For a typical GC×GC column configuration, a data acquisition rate of approximately 200 spectra/s is required. Slower detectors are used with sub-optimal GC×GC systems and/or sub-optimal column sets and conditions to match the peak width with the data acquisition rate.
- GC×GC-TOFMS with nominal mass resolution has demonstrated its high performance in various application areas over the past several years and is considered one of the most powerful techniques for targeted and non-targeted analysis of complex volatile and semi-volatile mixtures.
- High resolution mass spectrometry is well-known for its increased selectivity.
- This poster presents preliminary data for a sewage treatment plant water extract collected on a research prototype GC×GC-HRTOFMS and compares the results of a selected region to those obtained by GC-HRTOFMS.

Experimental

- Sample—Extract of water sample from sewage treatment plant (STP) (provided by Peter Haglund and Ulrika Olofsson, see acknowledgement)
- Instrument—Research prototype GC×GC-HRTOFMS
  - LECO research prototype of LECO GC×GC interfaced to LECO Pegasus® GC-HRT
    - LECO Pegasus GC-HRT specifications
      - Mass Accuracy: <1 ppm
      - Mass Range: 10 –1500 m/z
      - Resolving Power: Up to 50,000
      - Detection Limit: Low pg
      - Data Acquisition Speed: Up to 200 spectra/s
  - Columns (Restek)
    - 30 m x 0.25 mm x 0.25 μm Rxi-5Sil MS/0.5m (secondary oven) x 0.18 mm x 0.18 μm Rxi-17Sil MS
  - Conditions (similar to GC×GC-TOFMS nominal mass analysis done by Peter Haglund and Ulrika Olofsson, see acknowledgement)
    - Helium carrier gas at 1.4 mL/min
    - Temperature programs
      - GC Oven: 80°C (1 min) at 4°C/min to 340°C (10 min)
      - Secondary Oven: +20°C relative to GC oven
      - Modulator: +35°C relative to GC oven
      - Modulation Period: 4 sec; hot pulse: 0.6 sec
  - Ion source 250°C, electron ionization at 70 eV
  - Acquisition range, 50 to 750 u at 12 (GC) and 120 (GC×GC) spectra/s, high resolution mode (R = 25,000)

Results and Discussion

- By GC×GC-TOFMS Haglund and Olofsson identified 2-(methylthio)-benzothiazole (MBT) in a STP water extract. This region of the chromatogram was selected for further investigation in the GC- and GC×GC-HRTOFMS data. Figure 1 shows a chromatogram (GC) and contour plot (GC×GC) of these data. The region of the MBT is marked.
- The results of data processing for peaks with S/N >50, library match >700 are shown for the selected region of MBT in Figure 2. Next to the chromatograms are tables listing the identified peaks with the mass error of the base masses and the NIST library match values. The library match value is the quality of the spectral match to the library spectrum for which a perfect match is 1000.
  - *GC-HRTOFMS found four peaks of high quality according to the metrics of the data processing, while GC×GC-HRTOFMS found six high quality peaks.*
  - *Two of the identified peaks are common to the two results—2-(methylthio)-benzothiazole (m/z 181) and dimethylbiphenyl (m/z 182). Both were confirmed by accurate mass. A third is common by class, an alkane (m/z 57).*
- Identified by GC×GC is an unsaturated hydrocarbon (m/z 69) which appears to be perfectly coeluting with the alkane and is not found in the GC-only separation.
- For the two remaining peaks found by GC×GC, the dichlorobenzamide (m/z 173) appears to be perfectly coeluting with MBT in GC-only and was not found. The tetramethylbutylphenol (m/z 135) peak found by GC×GC is also found by GC, but it has a different identification.
- Figure 3 shows accurate mass data for the peak with a base mass of 135.080 for both GC and GC×GC. The accurate mass data for both the molecular ion (206.1662) and the base peak fragment ion (135.0804), confirms the GC×GC identification with mass errors of 3.3 and 0.5 ppm, respectively. The library match for the GC data did not agree with a mass error of 269 ppm.

Conclusion

Preliminary results of a resarch prototype GC×GC-HRTOFMS demonstrate that more confident peak identifications can be made as compared to GC-HRTOFMS and GC×GC-TOFMS nominal mass. This was possible due to the high mass accuracy, high mass resolution, and high data acquisition rate of the mass spectrometer, and the high performance of the GC×GC system.

Acknowledgement

We would like to thank and acknowledge Peter Haglund and Ulrika Olofsson at the Department of Chemistry of Umeå University, Sweden for the sewage treatment plant extract and their GC×GC-TOFMS results which guided us to a good example, and Liz Humston-Fulmer of LECO for providing the GC×GC-HRTOFMS data.

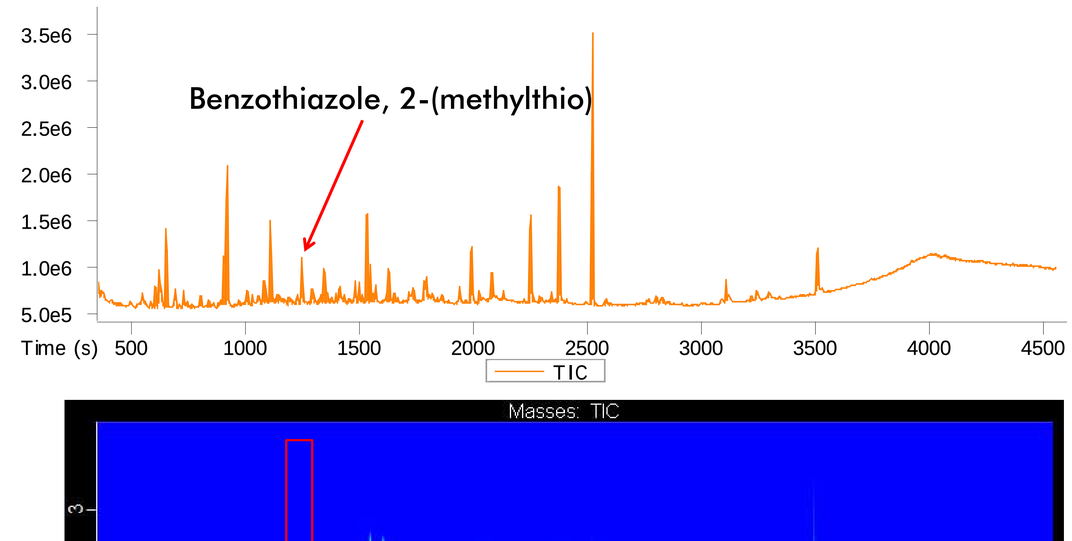
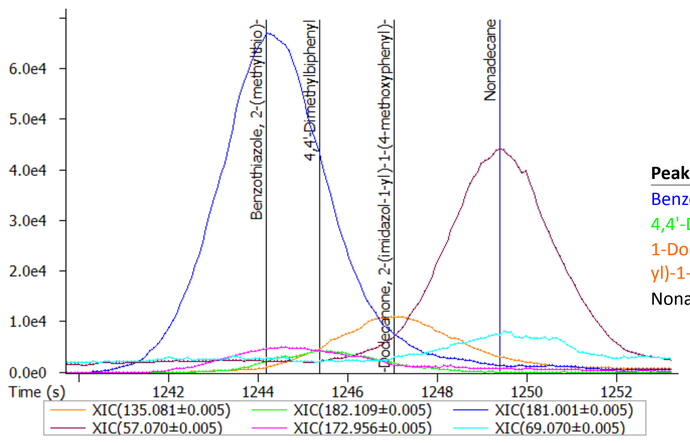
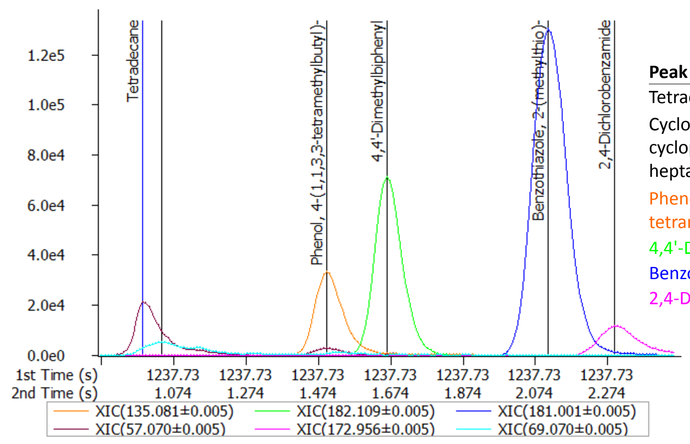


Figure 1. TIC of GC- and GC×GC-HRTOFMS separations of sewage treatment plant water extract.



Peak	Base Mass	Mass mDa	Error ppm	Library Match
Benzothiazole, 2-(methylthio)-	181.00135	-0.09	-0.5	902
4,4'-Dimethylbiphenyl	182.10900	0.00	0.0	784
1-Dodecanone, 2-(imidazol-1-yl)-1-(4-methoxyphenyl)-	135.08042	-0.02	-0.2	737
Nonadecane	57.06984	-0.04	-0.7	820



Peak	Base Mass	Mass mDa	Error ppm	Library Match
Tetradecane	57.06985	-0.03	-0.5	827
Cyclopentane, 1,1'-[4-(3-cyclopentylpropyl)-1,7-heptanediyl]bis-	69.06990	0.02	0.3	723
Phenol, 4-(1,1,3,3-tetramethylbutyl)-	135.08037	-0.07	-0.5	867
4,4'-Dimethylbiphenyl	182.10869	-0.31	-1.7	912
Benzothiazole, 2-(methylthio)-	181.00095	-0.49	-2.7	932
2,4-Dichlorobenzamide	172.95553	-0.02	-0.1	898

Figure 2. Comparison of peaks identified in GC-HRTOFMS (upper) and GC×GC-HRTOFMS (lower) for the selected region of the chromatogram in Figure 1. The GC×GC modulation shown is approximately from the center of the section of the GC chromatogram shown.

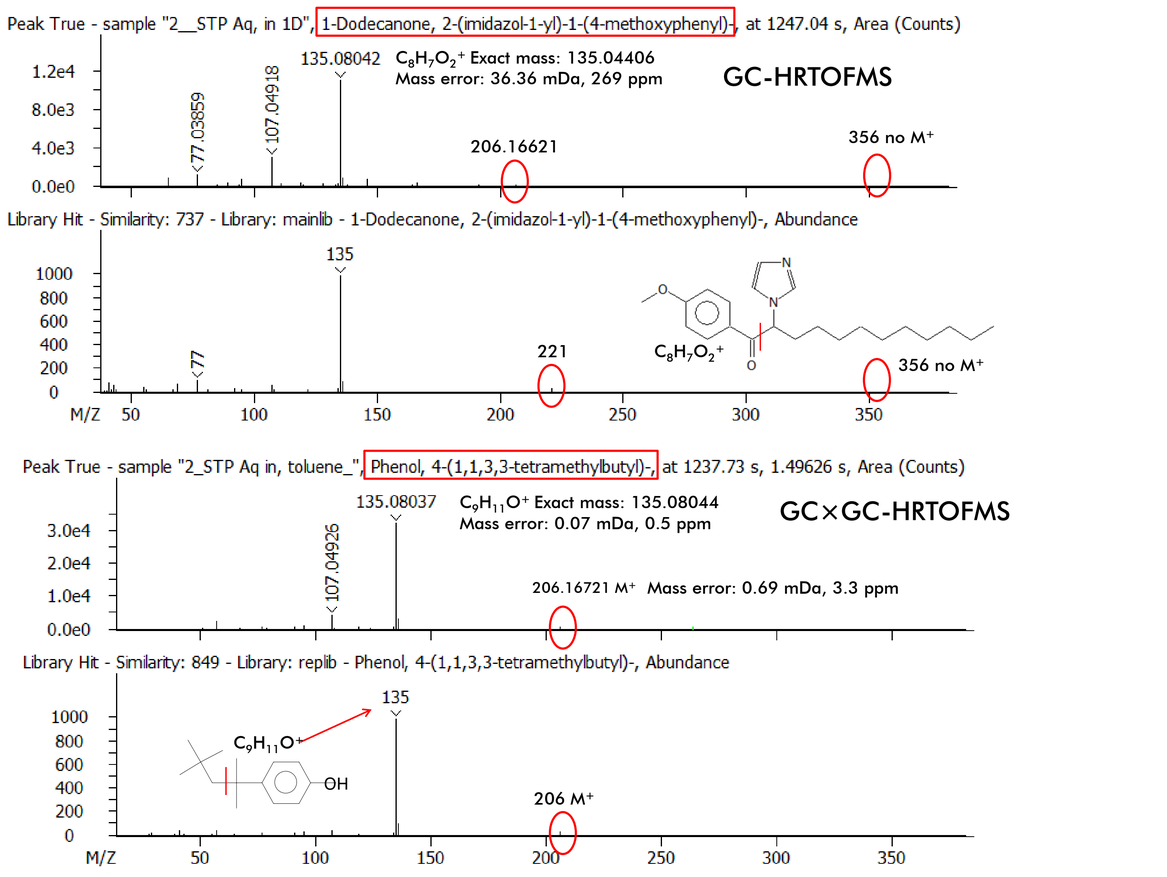


Figure 3. Peak true (deconvoluted) spectrum and library spectrum for GC-HRTOFMS (upper) and GC×GC-HRTOFMS (lower) of the same analyte.