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Introduction

Alkyl substituted naphthalenes are often found in the marine environment following spillages of crude oils, such as that occurring presently (May 2010) in the Gulf of Mexico. Alkyl naphthalenes (Figure 1.) also dominate oil industry produced waters and are common contaminants within the tissues of marine organisms (Booth *et al.*, 2007).

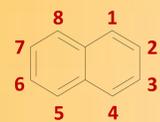


Figure 1. Numbering of alkyl position on naphthalene

Alkyl naphthalenes with alkyl substituents >C₄ are only rarely reported, possibly due to the large numbers of isomers possible (e.g. >7000 C₈ isomers are possible), with the consequence that no one isomer dominates. However, given the additive nature of narcotic toxicants, the total burden of these isomers may still be appreciable but overlooked.

Our recent research has demonstrated that alkylated naphthalene isomers can differ in their toxicity therefore it is imperative to develop methods to improve chromatographic separation of isomers.

In the present study we used GC x GC-ToF-MS to optimise chromatographic conditions for the separation of a range of C₂-C₈ alkylated naphthalene standards.

Methodology

GC x GC-ToF-MS analyses were conducted using an Agilent 7890A GC fitted with a Zoex GC x GC modulator coupled to an Almsco BenchTOF time-of-flight mass spectrometer (Almsco International, Llantrisant, Wales, UK). Data processing conducted using GC Image™ v2.0.

The system used the following parameters: ion source 300°C, transfer line 280°C, 1 µl sample injection at 280°C. The first-dimension column was a 100% dimethyl polysiloxane 50 m x 0.25 mm x 0.40 µm VF1-MS (Varian, Palo Alto, USA), and the second-dimension column was a 50% phenyl polysilphenylene siloxane 1.5 m x 0.1 mm x 0.1 µm BPX50 (SGE, Melbourne, Australia). Helium was used as carrier gas and the flow was kept constant at 0.7 ml/min.

The temperature program, adapted from Bouvier *et al.* (2009) was identical for both the first and second dimension column ovens. The ovens were held at 70°C for 1 minute, then raised from 70 to 300°C at 2°C/min and held a 300°C for 20 min. The second dimension time was 2 sec and the hot pulse 0.2 sec.

Results

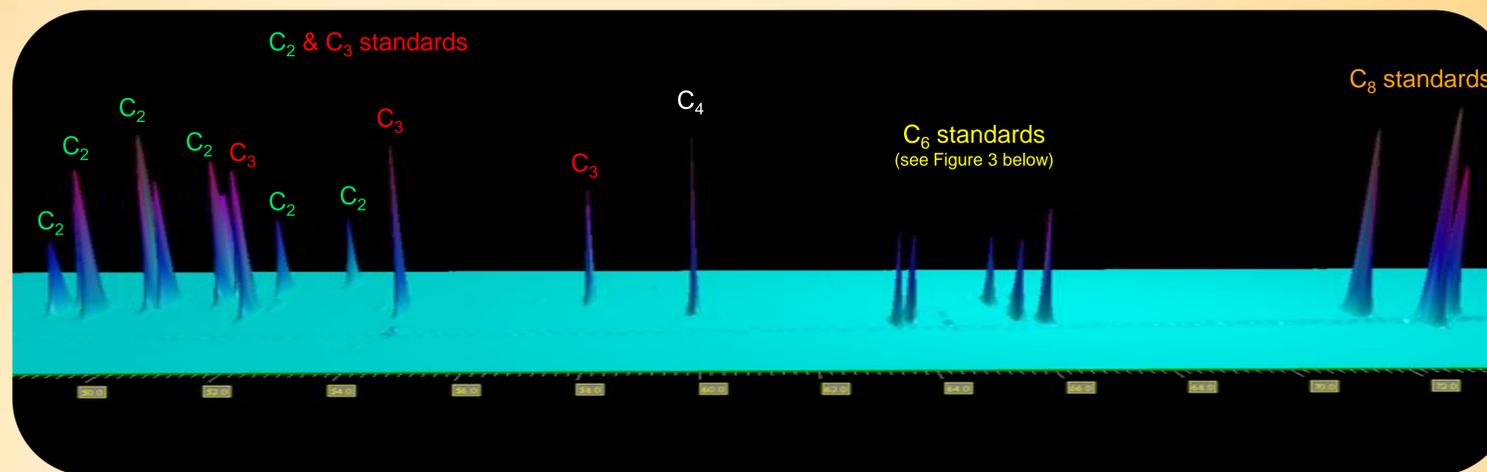


Figure 2. 3D GC x GC Plot of a range of C₂₋₈ alkyl substituted naphthalene standards

Identification of individual alkyl naphthalenes was achieved by interpretation of mass spectra and can be further supported by co-injection of individual standards.

Alkyl Chain length	Important ions (m/z)
C ₂	156, 141
C ₃	170, 155
C ₄	184, 169
C ₆	212, 197
C ₈	240, 225, 155

Figure 3 (A-C) below, demonstrates the chromatographic separation achieved using the C₆ di-*iso*-propyl naphthalene isomers as an example (NB. 1,8-DiPN standard not available).

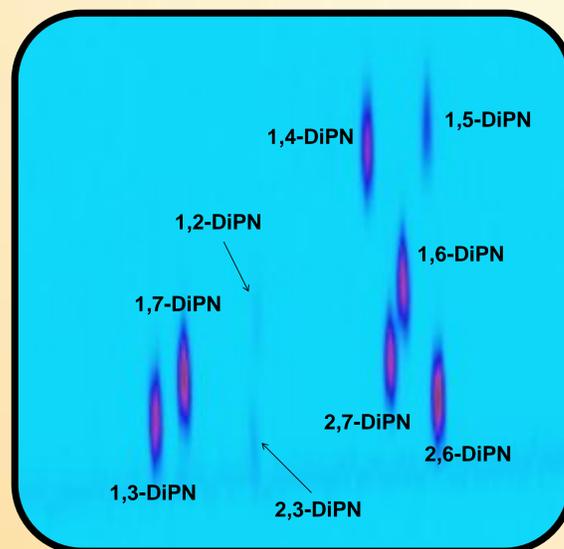


Figure 3. (A) Contour plot of C₆ di-*iso*-propyl naphthalenes

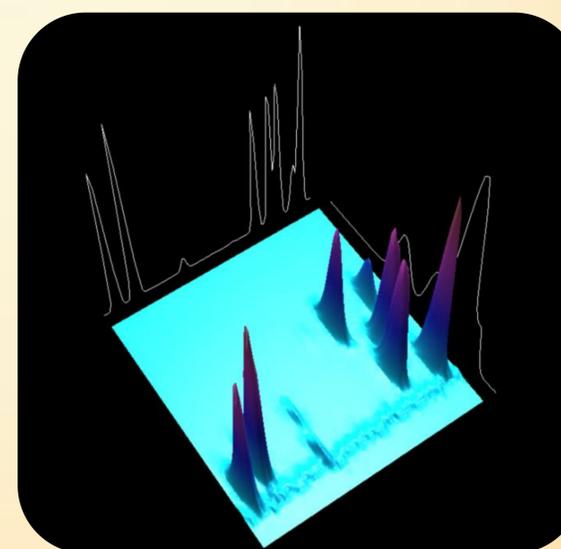


Figure 3. (B) 3D Plot of C₆ di-*iso*-propyl naphthalenes

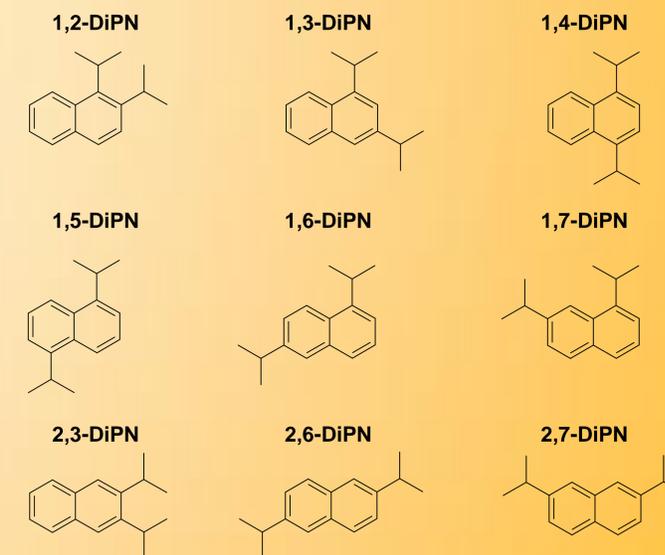


Figure 3. (C) Structures of C₆ di-*iso*-propyl naphthalene (DiPN) isomers

Conclusions

- GC x GC-ToF-MS was able to resolve and generate interpretable mass spectra of all C₂₋₈ alkyl naphthalene standards.
- Methodology applicable to tissue extracts since alkyl naphthalenes have been shown to bioaccumulate in mussels (see Poster K.08.)

References

- Booth, A.M., Sutton, P.A., Lewis, C.A., Lewis, A.C., Scarlett, A.G., Chau, W., Widdows, J., Rowland, S.J. *Environ. Sci. Technol.* **42**(2) 457-464.
- Bouvier, C., Reumkens, N., Buijs, W. *J. Chromatography. A* **1216** (2009) 6410-6416.

Acknowledgments

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