

**QUANTIFICATION OF UNRESOLVED COMPLEX MIXTURE (UCM)  
HYDROCARBONS USING MULTI-DIMENSIONAL GAS CHROMATOGRAPHY  
TIME-OF-FLIGHT MASS SPECTROMETRY (GCXGC-TOF-MS)**

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Weathered petroleum hydrocarbon residues are characterised by ‘humps’ or unresolved complex mixtures (UCMs) of hydrocarbons when analysed using traditional gas chromatography. We have previously shown that comprehensive two-dimensional gas chromatography - time of flight-mass spectrometry (GCxGC-ToF-MS) can be used to resolve and identify hydrocarbons in UCMs accumulated by mussels (Booth *et al.*, 2006). Tissue extracts from mussels (*Mytilus edulis*) collected around the UK, which exhibited impaired health, contained large amounts of aromatic hydrocarbon UCM (Widdows *et al.*, 1995). GCxGC-ToF-MS analysis of the bioaccumulated aromatic UCM extracts (up to 125 ug g dry tissue<sup>-1</sup>) permitted unprecedented resolution and characterisation of thousands of previously unidentified aromatic hydrocarbons with branched alkyl substituents. The major UCM components were monoaromatic hydrocarbons comprising highly branched alkylbenzenes (BABs), alkyltetralins (BATs) and alkylindans and indenenes (BINs). A smaller, but still significant contribution to the UCM came from alkylated diaromatics and PAHs. The compounds are proposed to arise during petroleum generation by similar mechanisms to their abundant and well-characterised un-branched homologues. However, branching leads to extensive isomerism (chromatographic ‘humps’) and resistance to biodegradation (environmental persistence).

Here we describe the use of GCxGC-ToF-MS as a tool for the quantitative and semi-quantitative analysis of both individual hydrocarbons and entire compound classes (*e.g.* alkylbenzenes) in UCMs. The aromatic UCM hydrocarbon fraction was isolated from both crude oil (Tia Juana Pesado and Alaskan North Slope) and mussel tissue extracts (North Sea, UK) using open column chromatography. The extracts were analysed at a known concentration, together with a complex standard of known aromatic hydrocarbons using GCxGC-ToF-MS. The hydrocarbon standard was used to produce a calibration curve which was analysed at concentrations approximating those of individual compounds present in the

UCM of the oil samples and mussel tissue extracts. These analyses permitted the direct quantitation of a few UCM components and the semi-quantitation of the major compounds classes (*e.g.* benzenes, indans, tetralins, indenenes, naphthalenes etc). This approach also offers the semi-quantitation of any UCM component provided they can be ascribed to a particular compound class from their mass spectrum. If this is possible, then the individual compound (*e.g.* alkylbenzene) can be semi-quantified using one or more alkylbenzenes present within the hydrocarbon standard calibration mixture.

As a result we have been able to determine the compound class distribution within the selected crude oils with more confidence and accuracy than has been previously possible. Furthermore, the studies using the mussel tissue samples have permitted the compound class contribution and the concentration of individual hydrocarbons bioaccumulated by mussels and inducing toxic responses to be determined.

## REFERENCES

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