

## COMPOSITIONAL CHARACTERISATION OF AQUATIC NOM BY MICRO-SCALE SEALED VESSEL (MSSV) PYROLYSIS

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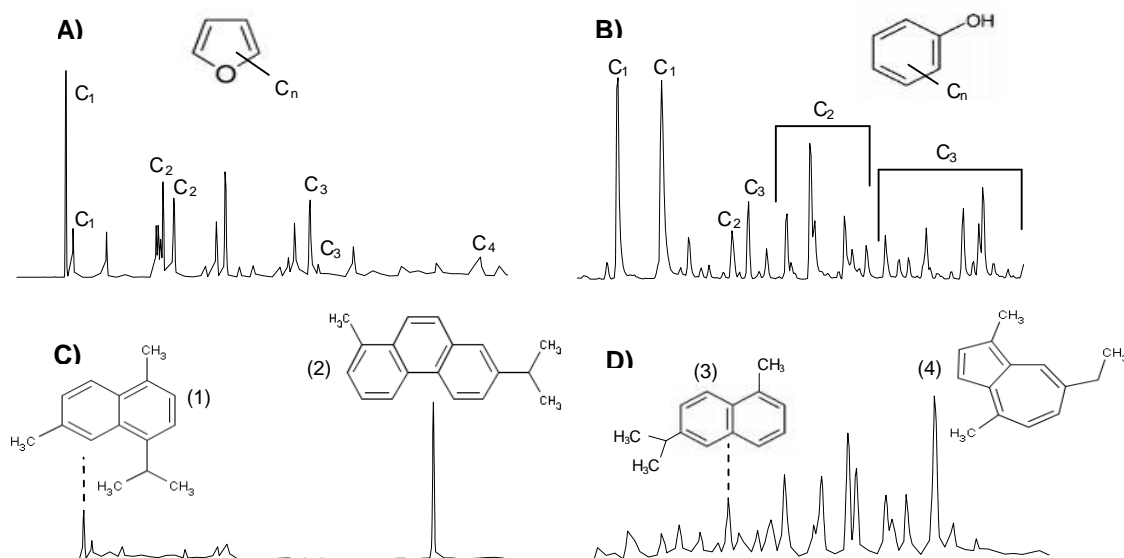
Analytical pyrolysis (e.g. flash or Curie-point) has proved useful for characterisation studies of naturally occurring OM, however, excessive degradation or high, biologically-inherited, structural polarity may limit GC (MS) detection of pyrolysis products. Closed-system micro-scale sealed vessel (MSSV) pyrolysis can overcome some of these issues. Although predominantly applied to kinetic studies of petroleum formation from sedimentary hydrocarbons (Horsfield *et al.*, 1989), the relatively mild thermal conditions of the MSSV experiment (i.e. 250-350°C/days Cf. >500°C and ballistic heating of flash pyrolysis) can facilitate both fragmentation and de-functionalisation of a wide variety of biochemicals. The recent MSSV detection of bacterial biomarkers in natural organic matter (NOM) of groundwater (Greenwood *et al.*, 2006) demonstrated the utility of this approach for yielding source diagnostic biomarkers from macro-molecularly bound precursors. Another recent study (Berwick *et al.*, 2006) similarly demonstrated the effectiveness of this approach for characterizing the nitrogen-containing pyrolysates of a number of aquatic NOM fractions.

This paper reports more holistically on the broad range of MSSV pyrolysates detected from a suite of NOM fractions isolated from various source and treated waters. An improved understanding of the structure and origins of NOM in potable sources will help understand practical NOM related issues such as disinfection by-product formation, fouling of membrane filters and microbial re-growth during distribution.

The hydrophobic (HPO), transphilic (TPI) and colloid NOM fractions yielded a broad range of pyrolysates, including many hetero-atomic products (i.e. oxygen- and sulphur- as well as the nitrogen-organics) of varied source diagnostic potential. The HPO fraction, for example, comprised alkylated furans indicative of polysaccharide precursors and higher plant derived products such as cadalene (1), retene (2), eudalene (3) and chamazulene (4). The colloid fraction yielded steranes indicative of eukaryotic input and many carbazole and indole products likely derived from alkaloid or bacterial structures.

Many more abundant MSSV products (e.g. alkylated phenols, benzenes and naphthalenes) are not diagnostic of specific structural precursors. A better understanding of

the biological origins and thermal generation of such products is sought by analysis of selected standards (e.g. polysaccharides, proteins, amino sugars and lignin) representing likely NOM structural precursors. Furthermore, the MSSV thermal profiles of pyrolysates from several samples have been investigated over the temperature range of 250°C - 350°C (at a constant 72hr). The product distributions are particularly scrutinised for evidence of additional molecular information to that provided by conventional pyrolysis and other characterisation methods (e.g.  $^{13}\text{C}$ -NMR, thermochemolysis) useful for establishing the structures and source inputs of recent organic materials like NOM.



**Figure 1.** Selected ion chromatograms from the MSSV pyrolysis GCMS of the HPO fraction of NOM from a Uruguay water source showing A) 81+82+95+96 Da - alkyl furans; B) 108+121+122+136 Da - alkyl phenols; C) 183+198+219 Da - miscellaneous aromatics; and D) 169+184 Da - miscellaneous aromatics.

## REFERENCES

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