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Ultra-Resolution Chemical Fingerprinting of Dense Non-Aqueous Phase Liquids from Former Manufactured Gas Plants Sites.

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Coal tars are the waste products in the manufacture of gas from coal or oil. From the 1810's until the explosion of the use of natural gas in the mid 20th century, tens of thousands of manufactured gas plants (MGP) all across Europe and North America produced gas for cooking, heating and lighting. Coal tars were stored and moved around on site, prior to being sold as a feedstock for the expanding chemical industry, thus minor leaks and spillages occurred frequently. Heavy coal tar contamination is therefore a common occurrence at former MGP (FMGP) sites. Coal tars are thought to be composed of between 300 and 5000 inorganic and organic compounds, many of them toxic to the environment and human health; the exact composition of a given tar being dependent on the manufacturing conditions. The need for accurate forensic chemical fingerprinting of coal tar contamination has thus grown in the past decade in Europe as legislations based on the "polluters pay principle" have been implemented.

Coal tars are heavier than water and in the subsurface form dense non-aqueous phase liquids (DNAPLs). We present a new all encompassing analytical method for the analysis of DNAPLs. The DNAPL samples are extracted in a single step using an accelerated solvent extraction (ASE) system. This produces a unique extract that is analysed by comprehensive two dimensional gas chromatography time of flight mass spectrometry (2D GCxGC-TOFMS).

Comprehensive 2D GCxGC-TOFMS is a chromatographic technique with a resolution power an order of magnitude greater than that of classic gas chromatographic techniques. Two columns with different selectivity are placed in series and permit planar resolution of the separation. The use of a time of flight mass spectrometer as a detector allows molecular identification of the eluted compounds. Comprehensive 2D GCxGC-TOFMS has previously been used for characterising complex petroleum-derived samples, such as crude oils or diesel, and the extent of their weathering, but never for the chemical fingerprinting of DNAPLs. Commonly, these analyses are conducted using a long wide bore capillary column hyphenated to a short, narrow bore polar capillary column for second dimension separation. We established, however, that reverse-phase analysis, i.e. long polar capillary column hyphenated to a short non-polar column, gave better resolution for the analysis of DNAPLs samples.

This method allows a one-step analysis avoiding conventional time-consuming chemical fractionation of the sample and presenting a unique chemical fingerprint containing up to a thousand resolved compounds that can be used for source identification and provenancing. This fingerprint, however, includes only the compounds that are readily vaporised for gas chromatography analysis. To further improve the uniqueness of the fingerprinting, we developed derivatisation methods for the DNAPL compounds containing a labile hydrogen atom (such as those present in –OH, -NH and -SH groups). The addition of polar compounds to the fingerprint provides more information about the source and the fate of the compounds since they can originate from either the manufacturing stage or the degrading processes in the subsurface.

Twelve DNAPL samples from seven different British FMGPs were analysed using this technique and statistically compared using Principal Component Analysis (PCA). Preliminary results showed that PCA could differentiate the samples relative to their manufacturing processes.

Using the reverse phase 2D GCxGC method, the chemical oxidation by potassium permanganate and aerobic degradation of a mixture of polycyclic aromatic hydrocarbons (PAHs) are studied to determine the chemical fingerprinting of these degradation processes. This should help into resolving the effect of degradation on the chemical fingerprint of field samples.