# APPENDIX 2

Paper presented during the 3 rd Euroconference on Analytical Environmental Chemistry, Chalkikdiki, Greece, 9 – 15 October 1999.

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# 3rd Euroconference on Environmental Analytical Chemistry

*Environmetal Analytical Chemistry for*
*the 21st Century*

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***W.J. Havenga***

has participated in the **3rd Euroconference on Environmental Analytical Chemistry**

For the Organizing Committee

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# The use of SPME and GC-MS for the chemical characterisation and assessment of PAH pollution in aqueous environmental samples

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Coal tar polluted samples contain a wide variety of chemical components, such as volatile aromatic compounds (VACs) and polycyclic aromatic hydrocarbons (PAHs) with their alkyl homologues. Certain aromatic compounds have the potential to damage resources and affect the health of animals and humans in a contaminated area. Chemical analyses are needed to determine of the extent of contamination in water resources, damage assessments, the prevention of contaminated water from reaching consumers and identification of the source of contamination. In the case of source identification the method must be specific and sensitive enough to reveal special chemical characteristics that will distinguish potential sources from each other and from background levels. For example, the gas chromatograms of diesel fuel, lubricating oil, crude oil and coal tar can reveal the presence of PAHs in all cases, but they exhibit different characteristic chromatographic profiles. For more detailed analyses, the identities and proportions of the aromatic compounds in a potential source are usually determined by GC-MS to provide a fingerprint of the source, which is then compared to the aromatic profile of the sample. It has been indicated, for example, that alkylated naphthalenes and phenanthrenes, as well as $C_1$ - $C_3$ dibenzothiopenes are typical of petroleum contamination. In weathered samples, compounds most resistant to weathering, such as the alkylated PAHs and especially the heavier compounds such as phenanthrenes and chrysenes, will dominate. Thus, the proportions of marker compounds such as alkylated PAHs, as well as the proportions of other aromatic compounds, provide a fingerprint that can be used to identify the source and degree of weathering in environmental water samples

Analysis of the alkyl substituted PAHs therefore play an important role in the assessment use of results, such as hydrocarbon source identification, oil weathering processes and short- and long-term biological effects relationship. Using a non-polar phase fiber such as the 100µ polidimethylsiloxane these compounds can be extracted from an aqueous sample with the technique of Solid Phase Micro-extraction (SPME). It has , however, been reported that some alkyl substituted PAHs show much higher distribution coefficient (K) values than non-substituted PAHs. The reason for this is because PAHs with side chains are more soluble in the hydrophobic stationary phase and with increasing alkylation, the amount of analyte is more completely extracted. Using a direct SPME extraction from an aqueous matrix it is possible to use the technique of multiple extraction (ME) SPME to allow for differences between the extraction effectiveness of parent and alkylated PAHs. Chemical characterisation and the modelling of coal tar pollution in environmental samples using the technique of ME-SPME-GC/MS is discussed.

# APPENDIX 3

Paper presented during the Chromatography/Mass Spectrometry Conference, 16 – 18 October 2000, Warmbaths,

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# Advanced Chemical Fingerprinting of Polluted Water Samples Using SPME-GC/MS

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Due to its sensitivity, selectivity, specificity and discriminatory power, the potential of using GC/MS data for tracing coal tar or petrochemical pollution to suspected sources is recognised by many workers in the field of hazardous waste management. Spill identification in groundwater relies on the extraction and pre-concentration of organic compounds from the sample followed by a detailed analysis of poly aromatic hydrocarbons (PAHs) and alkyl substituted PAHs using GC/MS. SPME has been investigated in this study as a possible alternative to conventional extraction methods that are normally expensive and labor- and time consuming. The objective was to develop a simple sample preparation procedure that could be automated and coupled on-line with the final GC/MS analytical measurement. The advantages of SPME include a solvent free extraction, a high degree of selectivity, much shorter analysis time and a small sample volume. The results (analytical data for selected PAHs) obtained was used to develop interpretative methods (Advanced Chemical Fingerprinting) capable of tracing contamination in the environment to its source. The analyses of data were based on the principles that (1) each source has a unique chemical composition and (2) has a unique analyte distribution pattern. The technique of multiple extraction SPME is proposed to compensate for differences in extraction efficiencies among different PAHs when analysing characteristic analyte distribution patterns. The application was further developed to determine diagnostic (source) ratios between two PAH isomers. Using the $C_1$-D/$C_1$-P ratio of two single isomer peaks in each of these two different alkyl homologues, an alternative approach to hydrocarbon fingerprinting was developed. The results of source ratios that were determined on several ground water samples are discussed. The conclusion is made that the determination of the $C_1$-D/$C_1$-P source ratio in groundwater samples is useful, but is limited to samples containing these isomers in concentration of $> 0.07$ ng/cm$^3$. The advanced technique of MS-MS was investigated to increase the detection limits of the method and allow the determination of source ratios in samples with lower pollution levels. The results are discussed.