Chapter 1

INTRODUCTION

POLYCYCLIC AROMATIC HYDROCARBONS AND RELATED COMPOUNDS

During the last five years the spill of coal tar has become a major issue in the South African iron and steel industry, while it has been an issue in other countries for at least thirty years. Continuous spills and discards of coal tar products, refined petroleum products and lubricating oils over a few decades have degraded the quality of water, soil and sediments. These dense non-aqueous phase liquids (DNAPLs) have formed pools of "toxic blobs" in the geosphere, and due to their low solubility in water they can continue releasing small quantities of contaminants into the groundwater for centuries. Groundwater is a source of potable water for many households and farming activities nearby industrial areas and chemical releases of coal tar and petroleum products into the soils have become a serious environmental problem. The investigation into the occurrence and fate of polycyclic aromatic hydrocarbons (PAH) and related compounds in the environment is, therefore, essential. Experts see the cokemaking process as one of steel industry's areas of greatest environmental concern. Coal tar is a by-product in the iron making process and is a heterogeneous mixture of various classes of compounds, such as the poly aromatic compounds. Other products are produced from coal tar because of their stable physico-chemical properties and industrial uses. An example of such a product is creosote, which is used as a wood preservative, fuel, animal dipping agent or lubricant. The US Environmental Protection Agency (USEPA) has classed some of the compounds that occur in coal tar and its products as probable human carcinogens. In 1999, one of the PAH compounds (benzo[a]pyrene) was ranked no 8 by the Agency for Toxic Substances and Disease Registry (ATSDR). Most of the parent PAH compounds are also listed among the other 275 compounds. The environmental laboratory at Research & Development, Iscor Limited, is concerned with the study of PAHs and is responsible for the development of analytical methods. The interpretation of analytical data, using techniques such as chemical fingerprinting, is imperative. Chemical fingerprinting is an important technological tool for companies facing major liability claims for environmental damages or clean-up costs under local regulations. Every chemical mixture that leaks into water or soil leaves behind a characteristic pattern, which can be used to trace contaminants to their source. An advanced chemical fingerprinting (ACF) strategy includes a suite of sampling, chemical analysis and data interpretation methods to enable chemists to differentiate among multiple contaminant sources.

SCOPE AND PURPOSE OF THE THESIS

Several technical and research papers have been reported in the last couple of decades concerning the chemical analysis of PAHs. Various authors have developed analytical methods with the following purposes:

- Identification of sources
- Obtaining insight into the transport, fate, distribution, degradation and toxic effects of PAHs in the environment
- Risk assessments
- Effective risk management strategies to reduce environmental contamination.

Analytical methods developed require sophisticated instrumentation and skilled analysts. The work presented in this thesis has the following objectives:

- To review available information regarding analytical methods and data interpretation methods
- To investigate the physico-chemical properties of PAHs and related compounds
- To develop more sensitive, faster and more efficient analytical methodology for the extraction and determination of PAHs and related compounds in water and soil samples
- To investigate the suitability of methods for hazard identification, health risk assessments and chemical fingerprinting.
- To use stringent quality control (QC) measures to improve the quality of results
- To validate methodologies that were developed or modified during this study
- To investigate the occurrence and concentration of PAHs in water and soil samples that have been submitted to our laboratory for a PAH analysis
- To develop advanced chemical fingerprinting techniques that can be used to link contaminants to their source
- To recommend strategies for future research in the field of chemical analysis.

APPROACH AND PRESENTATION

This thesis describes the development of methodology for the determination of polycyclic aromatic hydrocarbons in water and soil samples, with emphasis on data interpretation strategies. In **Chapter 2**, a general introduction into the nature of coal tar pollution and the dense non-aqueous phase liquid problem is given. The toxicity of PAHs, drinking water standards, health advisories and exposure limits are considered. An overview is also given on currently available analytical methods that are used to determine PAHs in water and soil samples. Conventional extraction techniques, Accelerated Solvent Extraction, Solid Phase Microextraction pre-concentration steps, matrix clean-up procedures and gas chromatography/mass spectrometry are discussed. The potentials and limitations of these methods are considered. The need for analytical methods suitable for Advanced Chemical Fingerprinting is emphasised and recent advances in this field are summarised. The importance of reliable analytical results for these purposes is shown.

In **Chapter 3** the criteria are set for analytical methods investigated and developed in this study. A set of data quality objectives is discussed that can improve the quality of results and ensure reliable results.

Knowledge of physico-chemical properties is necessary to forecast partitioning of PAHs into the environment and for modelling the multiphase distributions. Properties of the selected target analytes for this study are discussed in **Chapter 4**. As data on some of the compounds are unavailable, vapor pressures were determined for a number of compounds using gas chromatography and determining the Kovats retention index of each compound.

Currently available USEPA methods for the extraction and determination of PAHs in water and soil samples were refined to be better suited for chemical characterisation. The nature of the refinements and results are discussed in **Chapter 5**. An alternative method was developed using the technique of Solid Phase Microextraction (SPME), first introduced by Pawliszyn in 1989. The results of this investigation are discussed in **Chapter 6,** focussing on efficiency, specificity, selectivity, sensitivity, matrix interference and representativeness. The suitability of this technique for health risk assessments and chemical fingerprinting is also discussed. For the purpose of health risk assessments a detection limit of 0.0092 ng/cm^3 is required for the most potent carcinogens benzo[a]pyrene and dibenz[a,h]anthracene, based on a one in a million non-cancer hazard. A detection limit of at least 0.01 ng/cm^3 for all the PAHs is required for advanced chemical fingerprinting applications. The essence of the work reported in **Chapters 4 and 6** was written up as a research paper and accepted for publication in the Journal of Analytical Environmental Chemistry. The manuscript is included in **Appendix 1**. The work covered in this publication was also presented as a paper during the 3rd Euroconference on Analytical Environmental Chemistry in, Chalkidiki, Greece. The abstract is included in **Appendix 2**. The application of the SPME-GC/MS technique for Advanced Chemical Fingerprinting was presented as a paper during the Chromatography/Mass Spectrometry Conference at Warmbaths, October 2000. The abstract is included in **Appendix 3**.

For the extraction of PAHs from soil and sludge samples, the technique of Accelerated Solvent Extraction was investigated in **Chapter 7**. The suitability of this technique for chemical fingerprinting is discussed. A fast screening technique was developed by sampling PAHs in the headspace of a soil sample using headspace SPME. The analytical performance of this method is discussed in **Chapter 8**, focussing on extraction efficiency, selectivity and suitability for chemical fingerprinting. This work was written up as a research paper and accepted for publication in the Journal of Chromatography A. The manuscript is included in **Appendix 4.**

In **Chapter 9**, the data generated by the analytical methods that were developed in the previous chapters, are used to develop diagnostic ratios. These ratios are used to trace the contamination in the environment to its source and to follow weathering processes. An improved method was developed for this purpose, based on single isomer-to-isomer ratios, instead of using the sum of the grouped isomers in an alkyl homologue. The detection limits of isomers that are used for this purpose are discussed. The use of PAH distribution patterns is illustrated to differentiate between coal tar and petroleum sources.

In the general discussion presented in **Chapter 10**, consideration is given to the reliability of the analytical methods and data interpretation techniques that were developed during this study. Future needs in the field of analytical methodology are considered and recommendations are made with respect to the scope and strategy of new developments.