

# A rapid method for determining chlorobenzenes in dam water systems

KG Moodley<sup>1\*</sup>, DK Chetty<sup>1</sup>, SR Ramphal<sup>1</sup> and G Gericke<sup>2</sup>

<sup>1</sup>Department of Chemistry, Durban University of Technology, Private Bag 1334, Durban, 4000, South Africa

<sup>2</sup>Eskom Laboratory, Lower Germiston Road, Rosherville, Gauteng, South Africa

## Abstract

A method using direct immersion solid phase microextraction (DI-SPME) coupled to gas chromatography equipped with a flame ionisation detector (GC-FID) was developed for the analysis of 7 chlorinated benzenes in dam water. The main parameters affecting the DI-SPME process were optimised. The optimised method comprises the use of a 100 µm polydimethylsiloxane (PDMS) fibre coating; 5 ml sample size; 700 r/min rate of agitation and an extraction time of 30 min. The calibration curve was linear with correlation coefficients ranging from 0.9957–0.9995 for a concentration range of 1–100 ng/ml. The limits of detection and quantification ranged from 0.020–0.265 ng/ml and 0.204–2.65 ng/ml, respectively. Recoveries ranged from 83.6–107.2% with relative standard deviation of less than 9.2%, indicating that the method has good precision. The method is reliable and is free of matrix interferences. Water samples collected from Grootdraai Dam were analysed using the optimised conditions to assess the potential of the method for trace level screening and quantification of chlorobenzenes. The method proved to be efficient, as 1,3-dichlorobenzene, 1,4-dichlorobenzene and pentachlorobenzene were detected at concentrations of 0.429 ng/ml, 1.685 ng/ml and 1.433 ng/ml, respectively.

**Keywords:** chlorobenzenes, Grootdraai Dam, water, dam, SPME, DI-SPME, GC-FID

## Introduction

Among persistent organic pollutants (POPs), chlorobenzenes are some of the most frequently encountered compounds in aqueous systems. These compounds can enter the environment via natural and anthropogenic sources, and are ubiquitous due to their extensive use over the past several decades (Soonthorntantikul et al., 2009). Several chlorobenzene compounds, once in the environment, can be biologically accumulated, and are reputed to be carcinogens and extremely hazardous to health. Chlorobenzene compounds are listed as priority pollutants by the United States Environmental Protection Agency (USEPA) (He et al., 2000). Excessive exposure to these compounds affects the central nervous system, irritates skin and upper respiratory tract, hardens skin and leads to haematological disorders including anaemia (Kozani et al., 2007; Khajeh et al., 2006). In spite of these harmful effects, chlorobenzenes are still used widely as process solvents and raw materials in the manufacture of pesticides, chlorinated phenols, lubricants, disinfectants, pigments and dyes (Grosjean, 1991; Vidal et al., 2007). In the light of the above, it is imperative to continuously monitor the levels of chlorinated benzenes in all types of surface waters, using a low-cost but sensitive method.

Analysis of chlorobenzenes at trace and ultra-trace levels requires pre-concentration as well as sample matrix clean-up to remove any interfering components (Chisvert et al., 2009). Various pre-concentration techniques have been used for the isolation of chlorobenzenes from water. These include traditional liquid-liquid extraction (Ormad et al., 1996); solid phase extraction (Wang and Lee, 1998; Liu et al., 2004); single drop

microextraction (Tor, 2006; Khajeh et al., 2006; Vidal et al., 2005); stir bar sorptive extraction (Montero et al., 2004) and solid phase micro-extraction (SPME) (He et al., 2000; Wang et al., 2003; Huang et al., 2007). These pre-concentration steps precede analysis using gas chromatography coupled to an appropriate detector for identification. Whereas mass spectrometry (MS) and electron capture detectors (ECD) are excellent detectors for the analysis of these compounds, due to superior sensitivity, accuracy and resolution, they incur relatively high capital, operational and maintenance costs which results in decreased throughput. Although relatively low detection limits can be attained with MS and ECD as detectors, the actual limits set by environmental protection agencies are much higher and can be attained with less expensive systems. This report describes a system comprising a pre-concentration device, a standard chromatograph and a flame ionisation detector (FID). Pre-concentration was effected through direct immersion solid phase micro-extraction (DI-SPME).

Experimental parameters affecting the extraction efficiency of the selected chlorobenzenes, such as fibre type, sample size, rate of agitation, salting-out effect and extraction time, were optimised and applied to the Grootdraai Dam water samples for the quantification of chlorobenzenes.

## Experimental

### Reagents and materials

The chlorobenzenes selected for this study were: 1,2-dichlorobenzene (1,2-DCB); 1,3-dichlorobenzene (1,3-DCB); 1,4-dichlorobenzene (1,4-DCB); 1,2,4-trichlorobenzene (1,2,4-TCB); 1,2,3,4-tetrachlorobenzene (1,2,3,4-TeCB); 1,2,4,5-tetrachlorobenzene (1,2,4,5-TeCB) and pentachlorobenzene (PCB). These standards were high purity (> 98%) and were purchased together with HPLC grade methanol (99.9%) from Sigma Aldrich (Milwaukee, WI, USA). 'ACS reagent' grade sodium

\* To whom all correspondence should be addressed.

☎ +27 31 373 5133; fax: +27 31 373 5317;

e-mail: [moodlykg@dut.ac.za](mailto:moodlykg@dut.ac.za)

Received 16 April 2012; accepted in revised form 21 December 2012.