

## Direct Acetylation and Determination of Chlorophenols in Aqueous Samples by Gas Chromatography Coupled with an Electron-Capture Detector

Khalid Waleed S. Al-Janabi<sup>1\*</sup>, Fatin Nafea Alazawi<sup>1</sup>, M. Ibrahim Mohammed<sup>2</sup>, Abdul Amir H. Kadhum<sup>3</sup> and Abu Bakar Mohamad<sup>3</sup>

<sup>1</sup>Chemistry Department, College of Education, University of Baghdad, Baghdad, Iraq, <sup>2</sup>Chemical Engineering Dept., University of Technology, Baghdad, Iraq, and <sup>3</sup>Department of Chemical and Process Engineering, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia

\*Author to whom correspondence should be addressed. Email: khalid.janabi@gmail.com

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A method was developed that offers a rapid, simple and accurate technique for the determination of chlorophenols at trace levels in aqueous samples with very limited volumes of organic solvents. These compounds were acetylated, then preliminarily extracted with *n*-hexane. The enriched chlorophenols were directly analyzed using gas chromatography with an electron-capture detector. The detection limits were in the range of 0.001–0.005 mg/L, except for 2-chlorophenol, which was always above 0.013 mg/L. Relative standard deviation for the spiked water samples ranged from 2.2 to 6.1%, while relative recoveries were in the range of 67.1 to 101.3%.

### Introduction

Chlorophenols are a source of ecological anxiety because they are toxic and potentially carcinogenic at concentrations of only a few µg/L (1). Their wide distribution in industry and daily usage as wood preservative agents, pesticides, disinfectants, explosives and petrochemicals leads to pollution in the environment (2). However, purifying drinking water with chlorine may produce chlorophenols, because chlorine reacts to form chlorophenols when in contact with the dissolved phenolic compounds (3).

Liquid chromatography (LC) and gas chromatography (GC) are the best techniques to determine chlorophenols (CPs) at ultra-trace levels. Sample preparation using a selective solid-phase extractor (SPE) for the chlorinated phenols has improved the detection limits of the methods, because it enriches the ultra-trace amounts to a detectable concentration (4, 5). Analysis by GC with an electron-capture detector (ECD) is an even better choice for routine monitoring of these compounds.

In GC, pre-column derivatization is routinely employed when necessary to enhance thermal stability, increase volatility and improve separation (6). Hydrophobicity significantly increases with the increase in solute molar volume and octanol–water partition coefficient (7). Different derivatization procedures have been suggested, but alkylation and acetylation are the easiest techniques with the highest conversion yields (8). Acetylations with acetic anhydride using different catalysts have been reported in the presence of sulfamic acid (8), anhydrous nickel chloride (9), *p*-toluenesulfonamide complexes (10), tin oxide (11), melamine trisulfonic acid (12), silica sulfate (13), lithium chloride (14) and other catalysts. Nevertheless, because of what is known as the ortho-effect, CP isomers

possess considerably different octanol–water partition constants ( $K_{ow}$ ), depending on whether the chlorine atom is substituted at the ortho-, meta- or para-position (15). The ortho-effect has a major consequence on the solubility and chemical activity of a molecule. Chlorophenyl acetates (CPAs) exhibited higher retention index values on low-polarity GC capillary columns than the corresponding CPs (16).

The official method of the Environmental Protection Agency (EPA), which is based on liquid–liquid extraction (LLE), derivatization and measurement by GC–ECD has given limits of detection between 0.58 and 2.2 µg/L for the 11 priority pollutant phenols (17). CPs and other phenolics were pre-concentrated from aqueous samples using SPE cartridges and determined as trimethylsilyl derivatives by GC–mass spectrometry (MS); the detection limits were 0.01–0.25 µg/L (18).

In this work, a rapid and simple method was developed that is capable of resolving a wide range of chlorinated phenolic compounds at concentration levels of few µg/L. The efficient procedure combines simple acetylation by acetic anhydride without the use of a catalyst, followed by LLE with *n*-hexane and determination using GC–ECD. The method is convenient for the routine determination and monitoring of CPs in different water sources.

### Experimental

#### Apparatus

The analysis of CPs was performed using GC (Agilent Technologies 7890A GC-system) equipped with a nickel-63 ECD. The separating column was from J&W Scientific DB-5 (60 m i.d. × 0.32 mm × film 1 µm). The injector was from Agilent Technologies (7683B series). Injection was accomplished in a pulsed, splitless mode at 300°C. Analysis was performed with an initial column temperature of 60°C for 1 min, followed by heating to 300°C at 20°C/min and held for 8 min. ECD was held at 320°C. Nitrogen gas was used as the makeup gas for the ECD, the purge flow was 60 mL/min for 45 s, and gas saver flow was 20 mL/min for 2 min. Helium gas was employed as carrier gas at a constant flow rate of 1 mL/min.

#### Materials

The standard materials for chlorinated phenols [2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), 2,3,4,5-