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Simultaneous determination of the full chlorophenol spectrum in human urine using gas chromatography with tandem mass spectrometry

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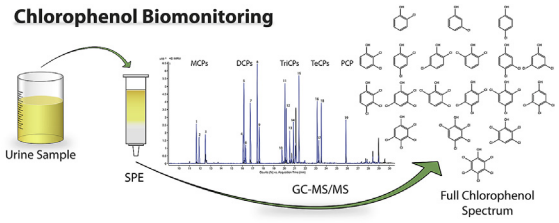
HIGHLIGHTS

- The procedure enables for the first time the simultaneous trace analysis of the full spectrum of 19 chlorophenols in urine.
- Separation using an intermediate polarity arylene polysiloxane column combined with MS/MS permits resolution of all isomers.
- The high sensitivity of the procedure with LOD of 0.01–0.03 μg/L suggests its application in population studies.

GRAPHICAL ABSTRACT



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ABSTRACT

The determination of chlorophenols in urine is an established approach for the assessment of human exposure to these ubiquitous environmental pollutants. However, an analytical procedure which enables the separate determination of all components of this substance group was still lacking. For this task we developed a method using enzymatic hydrolysis, solid phase extraction, derivatisation with bis(-trimethylsilyl)trifluoroacetamide and gas chromatography-tandem-mass spectrometry with isotope dilution. The chromatographic conditions provided baseline separation of all 19 chlorophenol derivatives. Precision within series did not exceed 15% although for urinary concentrations of 1 μg L^{-1}. The recovery was found to be well for most of the parameters. Limits of quantifications ranged between 0.04 and 0.10 μg L^{-1}. The present method is the first procedure which enables the simultaneous trace analysis of the full spectrum of chlorophenols in human urine. Thus, it may be a suitable benchmark procedure for the human biomonitoring of the exposure to these compounds in population studies.

1. Introduction

Mono- and multi-chlorinated phenols (chlorophenols) are well known ubiquitous pollutants of the environment for several decades [1,2]. The full substance group consists of three monochlorophenols (MCPs), six dichlorophenols (DCPs), six trichlorophenols (TriCPs), three tetrachlorophenols (TeCPs), and pentachlorophenol (PCP) (Fig. 1). Sources of their environmental pollution are exhausts, effluents and waste of the industry, in which these compounds are used, impact by biocidal or agricultural use of chlorophenols and pesticides, which can decompose to chlorophenols, as well as emissions from combustion processes of organic matter in the presence of chlorine [1–3]. Additionally, chlorophenols may be formed during drinking water chlorination

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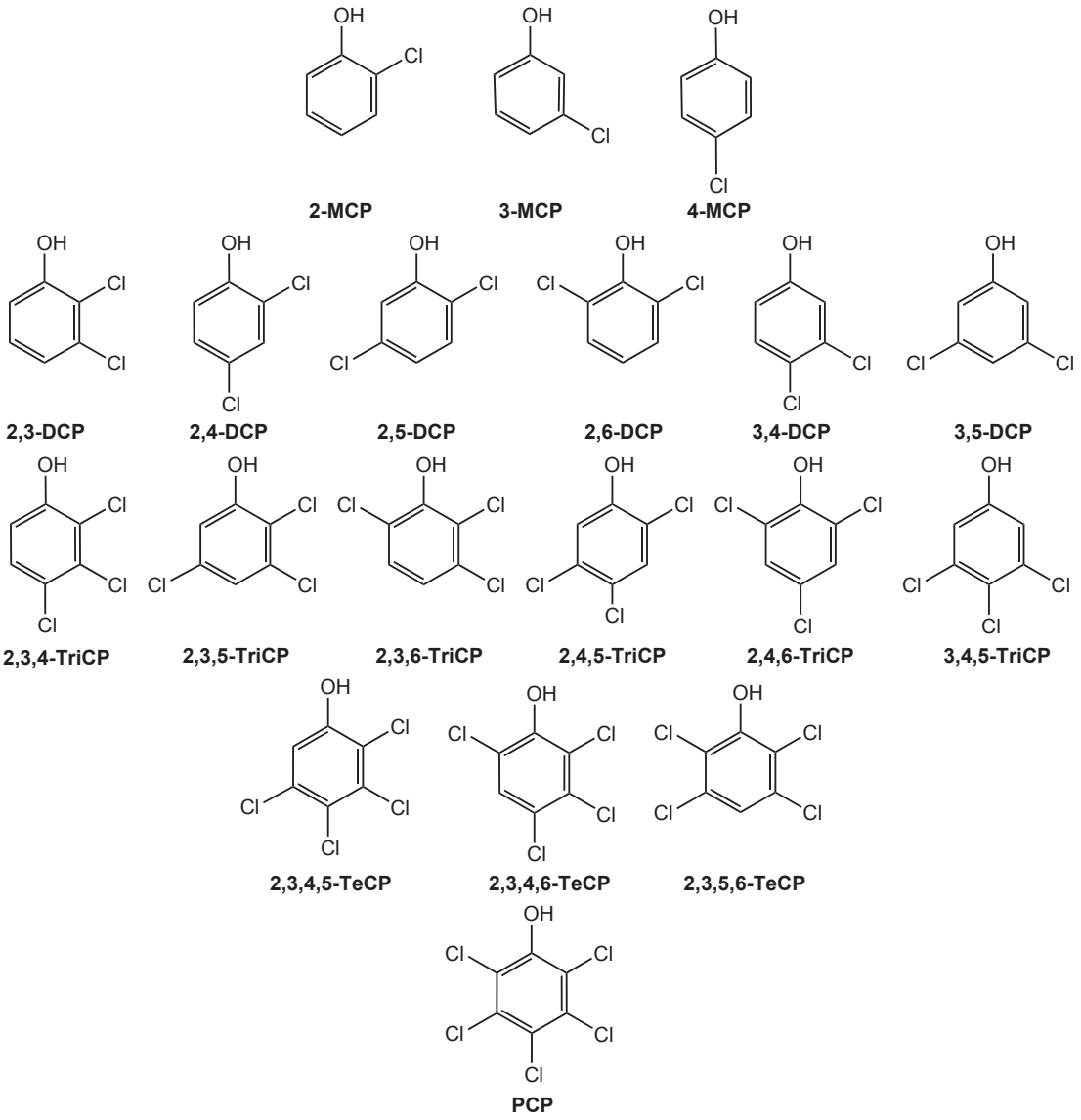

Fig. 1. Chemical structures of the nineteen chlorophenol congeners and the four groups of regioisomers.

[4]. Consequently, the exposure at such workplaces and of the environment leads to an exposure of employees and the general population to several chlorophenols in general, mainly identified by the assessment of urinary chlorophenol excretion [5–8]. Moreover, human exposure to chlorophenols cannot only occur by the intake of the compounds themselves, but also by the ingestion of chlorobenzenes, for which a human metabolism to chlorophenols has been demonstrated [9,10]. Chlorobenzenes are used in industry and agriculture as intermediates and solvents, as well as disinfectants in consumer products and can also be formed in the combustion of organic matter [11]. Furthermore, higher chlorinated phenols and benzenes can dechlorinate in the environment and produce lower chlorinated homologues [3,11]. These circumstances result in an exposure of the general population to a complex mixture of chlorophenols, which cause a relevant issue of public health. Reliable chemical trace-analysis of chlorophenols in human body-fluids is a challenging task. Ideally, all 19 chlorophenol congeners (Fig. 1) need to be determined in parallel. Since the regioisomers are isobaric compounds with similar mass spectrometrical behaviour, special attention has to be given to the chromatographic separation. However, most published analytical methods did not consider this issue comprehensively, thus showing a minimum of one co-elution or critical pair of isomers [12–15]. Undetected co-elutions may cause over-estimation of the analytical results which is critical, particularly when measuring ultra-trace concentrations. In the past, the application of less resolution procedures in occupational and populations studies, respectively, revealed a distinct exposure to a wide range of chlorophenols but also the need for high resolution techniques for the specific characterisation of the exposure [5–8]. Furthermore, in context of extensive biomonitoring studies on environmental chlorophenol exposure, measuring chlorophenols with a highly sensitive and rapid high throughput method in combination with low needs of sample volume are crucial points which cannot be achieved by the biomonitoring methods available [5,16–19]. For this reason, we developed a quick, highly sensitive, and selective biomonitoring method for the simultaneous determination of the full spectrum of all 19 chlorophenols in urine using solid-phase extraction (SPE) and gas chromatography with tandem mass spectrometry.