

# MS techniques for analyzing phenols, their metabolites and transformation products of environmental interest

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This overview covers, in particular, chlorinated phenols, alkylphenols and steroidal estrogens that have caused great concern because of their adverse effects, diffusion and resistance to (bio)degradation. We first describe strategies for combining liquid chromatography with mass spectrometry (LC-MS) to recognize metabolites, providing evidence for the advantages and the limitations of the available techniques and predicting future trends in this field. We then review the present state of the art in the analysis of the above compounds. We pay particular attention to those LC-MS methods involving the analysis of target phenolic compounds and identification of their unknown products in the various environmental compartments.

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## 1. Introduction

Phenolic compounds represent an important class of environmental contaminants [1–8] because of their adverse effects on animal and human health, widespread diffusion and persistence in several environmental compartments.

Their origin may be natural or anthropogenic. Phenols may occur naturally in water and soil as degradation products of lignin [9], one of the main components of wood and the cell walls of plants, but human activities are responsible for the introduction of many into the environment. They are produced and used as intermediates in the preparation of other chemicals (e.g., plastics [10,11], drugs [8,10,12], dyes [12], explosives [10], pesticides [12,13] and detergents [3]), and can be released as by-products or degradation products. For example, nitrophenols (NPs) and chlorophenols (CPs) may be generated as microbial metabolism products of the organophosphorus and chlorinated phenoxyalkanoic-acid pesticides [9,13]. CPs may also be formed as

by-products during the disinfection of drinking water by chlorination and as a result of the natural chlorination of organic material [13]. Alkylphenols (APs) and steroid sex hormones are compounds of special interest because of their potential effects as endocrine disruptors [8]. Nonylphenols (4-NPs) and octylphenols (OPs) are some of the primary degradation products of AP ethoxylate surfactants (APEOs) [4], while bisphenol A (BPA) monomer is released by hydrolysis of polycarbonate plastics and epoxy resins [11]. Natural estrogens and related synthetic compounds (e.g., those used in contraceptive pills) are excreted unchanged or as conjugates in the urine of mammals [7]. These conjugates, although no longer possessing significant biological activity, can be converted into more potent free forms during wastewater treatment; moreover, their inefficient removal in sewage treatment plants (STPs) [8] is responsible for their presence in surface water.

Phenols are weakly acidic compounds, with pK<sub>a</sub> values in the range 4–11. Based

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upon its low organic carbon/water partition coefficient ( $\log K_{oc} = 1.15\text{--}3.49$ ) and octanol/water partition coefficient ( $\log K_{ow} = 1.46$ ), phenol is not expected to be absorbed significantly in sediment in water [10]. However, substituted phenols and steroids tend to accumulate in solid matrices due to their lipophilicity, as indicated by their higher  $\log K_{ow}$ . As a result, some compounds [e.g., pentachlorophenol ( $\log K_{ow} = 5.15$ ), 4-NPs ( $\log K_{ow} = 4.48$ ) and  $17\beta$ -estradiol ( $\log K_{ow} = 4.01$ )] are transported little in water and are more likely to be absorbed in sediment, as absorption is also influenced by the percentage and the nature of organic matter and by the pH of ambient water [13,14].

Biodegradability and toxicity of chlorinated phenols depends on the number of halogens and on their position relative to the hydroxyl group [13,15]. Ortho-congeners and para-congeners are less toxic and biodegrade faster than meta-substituted CPs, since the chlorine atom at the position 2 or 6 shields the OH group, which is responsible for the interaction with the active site in organisms [15]. Since most ortho-congeners and para-congeners are known or suspected human carcinogens, the US Environmental Protection Agency (EPA) and the European Union (EU) have listed them as priority pollutants in the Clean Water Act [16] and in Commission Decision 2455/2001/EC [17], respectively.

As regards APs and steroidal estrogens, the main environmental concern is about the biorefractory nature of some of them and their estrogenic potential, as confirmed in numerous *in vitro* and *in vivo* studies. Recently, it was shown that estrogenicity of APs depends on the structure of the aliphatic chain: this is greatest for APs branched at the  $\alpha$ -carbon and with a chain length of 8–9 carbons [18]. Since the technical mixture of 4-NPs, used for synthesis of APEOs, comprises at least 22 4-NP isomers with a different structure of the nonyl substituent, great interest is being taken in the investigation of the different estrogenic activity of 4-NP isomers and their fate in the environment [18–20]. Among the several chemicals suspected of causing endocrine disruption, steroidal estrogens were identified as the main ones responsible for inducing estrogenic effects (e.g., feminization and hermaphroditism) in aquatic organisms [7]. *In vivo* studies have shown that exposure to a few ng/L of these compounds stimulates the formation of vitellogenin in male fish, altering their reproductive physiology [21]. The same effects were observed for AP compounds but at concentration levels of  $\mu\text{g/L}$  [7,21]. The growing concern about the environmental and health impact of endocrine disruption has induced the European Parliament to address this matter since 1997. A Community strategy [22] has been defined and a number of actions have been set out. A priority list of 553 substances [22–25] was established in order to evaluate their role in this phenomenon.

Besides conventional analytical approaches addressing target-compound monitoring, recently, many researchers have started to avail themselves of the potential of combining liquid chromatography with mass spectrometry (LC-MS) to identify polar metabolites and transformation products [26] in natural [27] as well as technical processes [28]. With respect to the subject of this review, the fate of natural estrogens in the municipal aqueous environment [21,29,30], the transformation of APEOs [4–6,31–33] in STPs and the identification of disinfection by-products in drinking water [34] are among the topics tackled and partially resolved by applying LC-MS techniques. This review comprises two main parts:

- the first part describes identification strategies based solely on using MS techniques, pointing out advantages and drawbacks of the various analyzers, the unquestionable effectiveness of the new generation of mass spectrometers and the future trends in this field; and,
- the second part reviews the state of the art in LC-MS analysis of CPs, APs and steroidal estrogens in different environmental compartments and in *de novo* identification of unknown phenols.

Most of the publications examined deal with the detection of target compounds, while there are a few that focus on studies of metabolites and transformation products.

## 2. Classical approaches to determining phenolic contaminants

Toxicity, persistence and diffusion of phenolic compounds require reliable, sensitive chromatographic detection systems for their confirmation and quantitation in complex matrices, such as environmental ones. MS coupled to a chromatographic technique is able to perform residual analysis and to provide unambiguous evidence of identification.

Gas chromatography (GC) has been used widely for the analysis of phenols in environmental samples [1,35], but the possibility of carrying out direct analyses, avoiding the problems associated with the chemical derivatization, induced several researchers to use LC-MS in this field. Since the late 1980s, thermospray (TSP) has been the most popular LC-MS interface [36]. The advent of atmospheric pressure ionization (API) techniques overcame problems related to poor sensitivity and selectivity of TSP sources that made it difficult to determine priority phenols in complex matrices [1,9,37–39]. The weakly acidic nature of phenolic compounds allows their detection in negative-ion (NI) mode both with electrospray ionization (ESI) [4–6,9,37] and atmospheric pressure chemical ionization (APCI) [5,6,9,38] sources, but steroidal estrogens have also given a good response

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