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Determination of phenolic compounds in air by using cyclodextrin-silica hybrid microporous composite samplers

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ABSTRACT

An analytical method for the determination of phenolic compounds in air samples based on the use of cyclodextrin-silica hybrid microporous composite samplers is proposed. The method allows the determination of phenol, guaiacol, cresol isomers, eugenol, 4-ethylphenol and 4-ethylguaiacol in workplaces according to the Norm UNE-EN 1076:2009 for active sampling. Therefore, the proposed method offers an alternative for the assessment of the occupational exposure to phenol and cresol isomers. The detection limits of the proposed method are lower than those for the NIOSH Method 2546. Storage time of samples almost reaches 44 days. Recovery values for phenol, guaiacol, o-cresol, m-cresol, p-cresol, 4-ethylguaiacol, eugenol and 4-ethylphenol are 109%, 99%, 102%, 94%, 94%, 91%, 95% and 102%, respectively with a coefficient of variation below 6%. The method has been applied to the assessment of exposure in different areas of a farm and regarding the quantification of these compounds in the vapors generated by burning incense sticks and an essential oil marketed as air fresheners. The acquired results are comparable with those provided from a reference method for a 95% of confidence level. The possible use of these samplers for the sampling of other toxic compounds such as phthalates is evaluated by qualitative analysis of extracts from incense sticks and essential oil samples.

1. Introduction

Most of the generally accepted classifications of VOCs are based on their physicochemical properties. The World Health Organization (WHO) suggested that the term "volatile organic compounds" should cover only compounds adsorbed on a solid sorbent and whose boiling points lie between 50 °C and 260 °C. By contrast, the US Environmental Protection Agency (EPA) definition of VOCs includes polar and non-polar C2–C10 compounds, whose vapor pressure at 25 °C exceeds 13.33 Pa. Moreover, VOCs can be classified in accordance with a number of their properties as degree of volatility, ozone-forming potential, polarity or their effects on particular ecosystems [1].

The evaluation of VOCs in ambient and workplace air requires the use of a sampling technique to take a representative sample and avoid any variation in their composition. Since the concentration of contaminants varies over time, small sample volumes are not considered representative samples and accordingly short sampling times are not recommended [2]. Moreover, the low levels of pollutants in air samples make enrichment to be necessary. This enrichment is determined by detector sensitivity and quantification requirements [3]. The principal techniques for sampling analytes from atmospheric air that combine the isolation of analytes and their enrichment are: dynamic techniques, passive techniques and denuder techniques [4].

The principal disadvantages of passive techniques are that the enrichment factor is dependent on ambient conditions and also that it is less effective than other sampling techniques. Denuder techniques require laminar flow through the tube and denuder preparation is time-consuming and laborious [4]. The collection of samples using dynamic techniques has a high cost but, on the other side, it encloses a very effective enrichment. Then, the use of solid adsorbents and active sampling is usually recommended to evaluate workplace exposure. [3,5,6].

The use of solid adsorbents requires the optimization of retention and desorption conditions as well as the determination of the recovery percentage. Norm UNE-EN 1076:2009 describes the requirements and test methods for measuring gases and vapors using pumped [7]. This norm indicates that the recovery can be obtained by using standard gaseous mixtures or from spiked sampling tubes.

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Several techniques to prepare standard gaseous mixtures have been proposed, which can be classified in static techniques, dynamic techniques and mixed techniques [8,9].

VOCs include aliphatic and aromatic hydrocarbons, aldehydes, ketones, ethers, acids, alcohols or phenolic compounds as phenol and alkylphenols. Specifically focusing on the phenols, their emission in the atmosphere is due to emissions of some plant species, animal, snuff smoke and even the use of air fresheners and cleaning products, in addition to industrial activities [10–15].

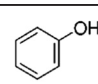
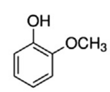
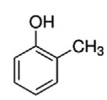
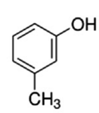
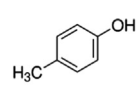
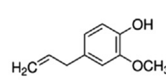
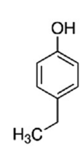
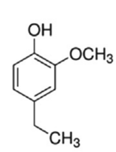
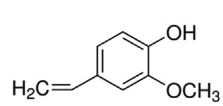
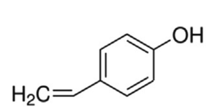
Intensive agricultural activities can be a major source of pollution and bad odors for the environment, so these facilities should be located in areas away from the population. For example, the literature describes the presence of high levels of mercaptans, phenol, xylene, 2-methyl-1-propanol, toluene, 4-ethylphenol, … in the indoor and outdoor air of cattle and pig fattening farms [11,12].

Volatile phenols and other VOCs are found in indoor air and they are originated from various sources such as the use of air fresheners (incense or essential oils) or cigarette smoke. In this regard, high levels of phenol, cresol, toluene or xylene have been found in rooms perfumed with incense [14,15], as well as in places where tobacco smoke tends to accumulate [13].

A traditional method for sampling phenols is related to their retention as phenolates by using impingers containing an aqueous solution of sodium hydroxide. However, it usually requires the preconcentration of the analytes prior to their quantification [16–18]. Alternatively, solid adsorbents can be used, being silica gel followed by solvent desorption the most common. The polarity of the adsorbed compound determines the binding strength of the silica gel; high-polarity compounds will displace low-polarity compounds. The tendency of silica gel to adsorb water vapor and displace collected components is its chief disadvantage [2]. The use of thermal desorption and other sorbents as porous polymeric sorbents is also described [19,20].

On the other hand, the use of solid phase microextraction (SPME) has been proposed for the sampling of phenols in air samples. The SPME has proven to be a very useful tool for situations in which the analyte concentration could be considered as nearly constant in time. The use of SPME has been proposed for

Table 1
Boiling point and structure of some volatile phenols [29].

Compound		CAS	$T_{boil.}$
Phenol		108-95-2	181.8 °C
2-Methoxyphenol (Guaiacol)		90-05-1	205.0 °C
2-Methylphenol (o-Cresol)		95-48-7	191.0 °C
3-Methylphenol (m-Cresol)		108-39-4	202.3 °C
4-Methylphenol (p-Cresol)		106-44-5	202 °C
2-Methoxy-4-(2-propenyl)phenol (Eugenol)		97-53-0	255 °C
4-Ethylphenol		123-07-9	219 °C
4-Ethyl-2-methoxyphenol(4-Ethylguaiacol)		2785-89-9	246.5 °C
2-Methoxy-4-vinylphenol		7786-61-0	245 °C
4-Vinylphenol		2628-17-3	206.2 °C