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Optimization of headspace experimental factors to determine chlorophenols in water by means of headspace solid-phase microextraction and gas chromatography coupled with mass spectrometry and parallel factor analysis☆

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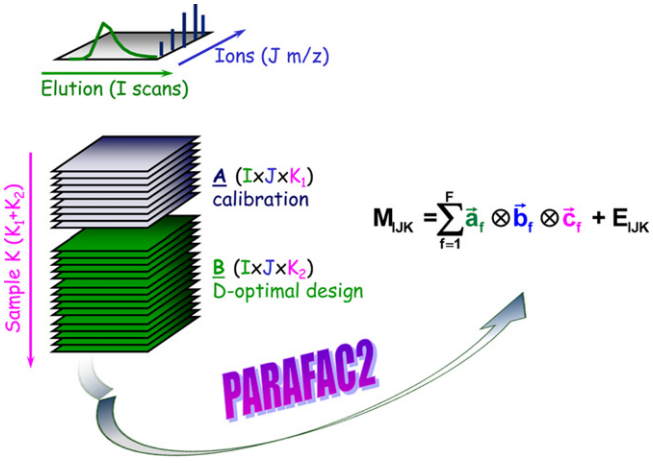
HIGHLIGHTS

- D-optimal design allows the reduction of experiments from 48 to 18 maintaining the precision.
- A procedure based on HS-SPME–GC/MS to determine chlorophenols, below ppt units, has been used.
- HS-SPME–GC/MS has been used to analyze four chlorophenols in river water samples.
- Decision limits, from 39 to 208 ng L^{-1}, has been obtained with a false positive probability fixed at 5%.
- Unequivocally identification of chlorophenols was verified after taking place the PARAFAC decomposition.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work an analytical procedure based on headspace solid-phase microextraction and gas chromatography coupled with mass spectrometry (HS-SPME–GC/MS) is proposed to determine chlorophenols with prior derivatization step to improve analyte volatility and therefore the decision limit (CCα). After optimization, the analytical procedure was applied to analyze river water samples. The following analytes are studied: 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (2,4,6-TrCP), 2,3,4,6-tetrachlorophenol (2,4,6-TeCP) and pentachlorophenol (PCP). A D-optimal design is used to study the parameters affecting the HS-SPME process and the derivatization step. Four experimental factors at two levels and one factor at three levels were considered: (i) equilibrium/extraction temperature, (ii) extraction time, (iii) sample volume, (iv) agitation time and (v) equilibrium time. In addition two interactions between four of them were considered. The D-optimal design enables the reduction of the number of experiments from 48 to 18 while maintaining enough precision in the estimation of the effects. As every analysis took 1 h, the design is blocked in 2 days.

The second-order property of the PARAFAC (parallel factor analysis) decomposition avoids the need of fitting a new calibration model each time that the experimental conditions change. In consequence,

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the standardized loadings in the sample mode estimated by a PARAFAC decomposition are the response used in the design because they are proportional to the amount of analyte extracted.

It has been found that block effect is significant and that 60 °C equilibrium temperature together with 25 min extraction time are necessary to achieve the best extraction for the chlorophenols analyzed. The other factors and interactions were not significant. After that, a calibration based in a PARAFAC2 decomposition provided the following values of CCα: 120, 208, 86, 39 ng L^{-1} for 2,4-DCP, 2,4,6-TrCP, 2,3,4,5-TeCP and PCP respectively for a probability of false positive set at 5%. Also, the accuracy (trueness and precision) of the procedure is assessed. Finally, river water samples have been analyzed with the proposed method showing the absence of the chlorophenols studied.

1. Introduction

Chlorophenols are very toxic chemicals that are produced by adding chlorine to the phenol. It has been found that their toxicity is higher when increases the number of atoms of chlorine in the molecule, being pentachlorophenol (PCP) the most toxic of them [1]. For this reason, they have been classified as possibly carcinogenic to humans (group 2B) by the International Agency for the Research on Cancer (IARC).

The use of these substances in very diverse activities such as wood treatment, pesticides, has led to a widespread distribution in the environment. Directive 2008/105/EC [2], that establishes environmental quality standards in the field of water policy, has fixed a maximum allowable concentration (MAC) for PCP of 1 μg L^{-1} in river and lakes.

However, chlorophenols in drinking water have been found. Its appearance is due to reaction of chlorine used for disinfection with phenolic groups present in the water. For this reason, the Environmental Protection Agency [3] has established to PCP the same maximum limit in drinking water (1 μg L^{-1}), since it is considered to be suspicious of causing cancer [3,4].

Consequently, because of the toxicity of these substances and the fact that legislation is establishing smaller maximum concentrations for these substances the development and optimization of methods with low detection limits are necessary. The bibliography frequently refers to the use of the gas chromatography with mass spectrometry (GC/MS) for the analysis of these compounds together with a previous step of preconcentration of the sample like solid-phase microextraction (SPME). Because there are numerous factors that can influence in the SPME and, therefore, in the detection limit of the technique, the optimization step is an important stage previous to the validation of the method. Among the factors related to SPME, the most common are the sample volume, extraction time and temperature, salt addition, speed and time of agitation of the sample [5,6]. Likewise, it is frequent to compare the result obtained using fibers with different coatings and by direct immersion in the sample or by headspace (HS) [7,8]. The advantage of making the extraction of analytes by means of HS is that the deterioration of the fiber is avoided, especially when complex samples as wastewater are analyzed. Nevertheless, the low volatile of these compounds makes it necessary for the use of derivatization reactions to improve the extraction, increasing the time necessary for the analysis. Ribeiro et al. [9] obtain detection limits (LOD) from 0.005 to 1 μg L^{-1} for the analysis of chlorophenols in aqueous samples without derivatization by direct immersion of the fiber. Also, Guerra Simões et al. [7] get LOD between 0.053 and 4.1 μg L^{-1}. On the other hand, Reguerio et al. [8] achieve LOD from 0.013 to 0.021 μg L^{-1} when the derivatization reaction is carried out with acetic anhydride and the analysis is made by means of HS-SPME–GC–MS/MS. In Ref. [10] the use of a programmed temperature vaporizer inlet (PTV) combined with HS–GC/MS for the detection of chlorophenols derivatizated with acetic anhydride was proposed with LOD from 0.005 to 0.008 μg L^{-1}. Also, Ho et al. [6] optimize a method based on purge-assisted headspace solid-phase microextraction (PA/HS-SPME) combined with GC/MS for which values of detection limits between 0.0001 and 0.0004 μg L^{-1} in aqueous samples without derivatization are obtained. These values are lower than those obtained with derivatization methods. A recent review on extraction and preconcentration techniques for the analysis of chlorophenols in environmental and food samples can be found in [11].

Nevertheless in few cases the probabilities of false positive and false negative in the evaluation of the limit of decision were calculated. In [12] the determination of chlorophenols by means of SPME–GC/MS without the previous step of derivatization has been made by direct immersion of the fiber, obtaining values of decision limit (CCα) and detection capability (CCβ) from 0.29 to 0.67 μg L^{-1} and from 0.56 to 1.31 μg L^{-1} respectively, with a probability of false positive, α, and false negative, β, of 5%. The advantage of using CCα and CCβ against the LOD is that the two probabilities of error are evaluated.

This work develops a new procedure in the field of the experimental optimization joins D-optimal design with PARAFAC decomposition. As the aim is to optimize the headspace experimental factors, the concentration of each analyte is fixed and several experimental factors are changed. In this procedure the response values used in the experimental design are the loadings of samples of a PARAFAC decomposition standardized by the loadings of the internal standard to eliminate the effect of changes between chromatographic runs; this is the multiway version of usual internal standardization in chromatography. The standardized loadings are proportional to the quantity recovered in the headspace step. Consequently, the largest standardized loading is the best one. If the data are trilinear, the second order advantage of PARAFAC allows the use of just one calibration model with independence of the experimental conditions.

The strategy developed has been applied with headspace solid-phase microextraction and gas chromatography coupled with mass spectrometry (HS-SPME–GC/MS) technique in river water samples to determine four chlorophenols namely 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol. As pentachlorophenol has a maximum allowable concentration, the procedure has been validated according to Document SANCO 12495/2011 [13]. The unequivocal identification of each chlorophenol and trueness and precision have been assessed. The new way of using the two methodologies together led to reduce the use and quantity of solvents and also provides greater versatility in the analysis.

2. Theoretical background

2.1. PARAFAC and PARAFAC2 models

In this section, the parallelism that exists between the PARAFAC decomposition and a physical model of GC/MS data, under