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Implementation of multicriteria decision analysis in design of experiment for dispersive liquid-liquid microextraction optimization for chlorophenols determination

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ABSTRACT

A novel and efficient approach to optimization of extraction step prior the chromatographic determination of nine chlorinated phenols is described. It is based on the combination of design of experiments and multicriteria decision analysis. Such an approach is used to optimize dispersive liquid-liquid microextraction procedure for the determination of 9 chlorophenols in water samples. Three parameters are optimized – sample volume, volume of disperser solvent and extraction solvent. Combination of the technique for order of preference by similarity to ideal solution with central composite design allows to perform multi-analyte procedure optimization. It gives information about the efficiency of the system for every experimental plan point in terms of closeness to ideal solution. The optimal conditions for extraction of chlorophenols are 76 μL of extraction solvent, 0.6 mL of dispersive solvent and 6.7 mL of water sample. The presented approach has the potential to be applied in variety of optimization systems.

1. Introduction

Experimental design (or design of experiments, DoE) allows to simultaneously change variables (usually 3–5) during optimization studies. As a result savings in time and material inputs are obtained in comparison to "change one factor at a time" approach. In analytical chemistry it is usually applied at the stage of analytical technique operational conditions optimization [1] and selecting optimal extraction conditions [2]. DoE can be applied at the stage of procedure validation to determine robustness [3] or accuracy [4].

The Technique for order of preference by similarity to ideal solution (TOPSIS) is one of a number of multicriteria decision analysis (MCDA) tools [5]. It is used to support decision making process by ranking of available alternatives. The result of TOPSIS analysis is full ranking of alternatives according to relevant criteria. Ranking is expressed in 0–1 scale, where 0 is ideal negative solution (set of the least optimal values for all criteria) and 1 is ideal solution (all criteria are characterized by optimal values). It is used for problem solving in such areas as operation research, environment and sustainability, supply chains management, material sciences, quality assessment and many others [6]. TOPSIS is widely applied in environmental sciences, including management of ecosystem, waste, water quality, energy production and selecting other sustainable solutions [7]. TOPSIS is selected from several MCDA techniques, as it is simple to use, gives full ranking (not only selects the optimal alternative) and performs well, even with many alternatives included during assessment. TOPSIS analysis generates a numerical value, so it can be combined with other techniques. TOPSIS has been combined with DoE in an automotive industry, to calculate a similarity to ideal solution value for a single alternative [8].

Chlorophenols (CPs) are a group of pollutants that are formed during chlorination of humic acids but they originate also from other anthropogenic sources, such as industrial processes or formation during water disinfection processes [9]. Their determination involves chromatographic analysis with isolation and preconcentration with solid phase extraction, purge and trap analysis or microextraction techniques [10]. Among them frequent choice is dispersive liquid-liquid microextraction [11]. It is used because of its relative simplicity, short extraction time and low consumption of solvents.

Dispersive liquid-liquid microextraction (DLLME) involves the application of a three phase system, consisting of liquid sample, extraction solvent and dispersive solvent [12–14]. The extraction solvent must be immiscible with sample and analytes should be highly soluble in it. Dispersive solvent has to be miscible with

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extraction solvent and at the same time it has to be soluble in the sample. Microlitres of extraction solvent are mixed with half to one millilitre of dispersive solvent and such mixture is injected into sample. Dispersive solvent is rapidly dissolved in sample and "cloudy solution" is formed. Due to large surface organic phase – sample contact area the extraction process is rapid. After collection the extract is analysed.

Experimental design is very often applied to optimize procedure parameters for a single analyte. It is applied for optimization of DLLME determination of palladium with five factors central composite design [15]. Similarly, a four factor plan was applied to optimize microwave assisted DLLME followed by spectrophotometric determination of uranium in water samples [16].

Optimization of the procedure dedicated for determination of two compounds can be tricky as optimum parameters for one compound can be sub-optimal for the second one. For the simultaneous optimization of rhodamine B and rhodamine 6G multiplication of extraction recoveries for both compounds is applied [17]. In such a case, the application of multianalyte optimization approach is more desired.

The common approach to optimize multianalyte procedure is to sum the responses for all analytes. Such approach is presented for optimization of DLLME procedure for determination of 6 endocrine disrupting compounds [18]. As it was discussed before summing the responses for analytes is also not reccomended approach as no information is obtained if the optimum parameters are reached for all of analytes or for some of them only. In this approach analytes with higher responses carry higher weight and as a result also importance. In this way, optimization is in fact performed for the analytes of the largest peak areas and the analytes of small peak areas carry residual importance to optimization significance.

Another interesting approach for simultaneous optimization of multiple responses of the system is introduction of desirability function. It allows to find the values of the parameters, where all responses are in desirable range [19]. By the application of weights, similarly as it is performed in TOPSIS, it is possible to assign the importance to response in relation to others. The methodology was successfully applied to optimize electrophoretic separation of four compounds with five separation parameters [20]. It can be applied to optimize parameters when more analytes are determined and different optimum parameters are obtained for respective analytes, like in case of determination of 15 organochlorine compounds in biological samples [21].

To perform multi-objective optimization usually a desirability function is applied [18]. Very briefly, for every optimization criterion desirability function equation is assumed, as well as completely desirable response (d = 1) and completely undesirable response (d = 0). After defining desirability functions, they are combined into a single score called global desirability (D) as presented with Eq. (1). If any of criteria is undesirable, then D = 0. Application of desirability function allows for setting the relative importance of criteria ($r_1, r_2 \ldots r_n$).

$$D = \left(d_1^{r_1} \times d_2^{r_2} \times \ldots \times d_n^{r_n}\right)^{\frac{1}{\sum ri}} \quad (1)$$

The aim of the paper is to present the possibility of TOPSIS application in combination with DoE at the stage of multianalyte optimization of amounts of solvents used in DLLME. TOPSIS can offer an interesting alternative to the application of desirability function. Discussion of advantages of such combination over other approaches is provided.

2. Materials and methods

2.1. Reagents and solvents

The following substances are purchased from Sigma Aldrich (Germany): 2,4-dichlorophenol (2,4-DCP), 2,6-dichlorophenol (2,6-DCP), 2,4,6-trichlorophenol (2,4,6- TCP), 2,3,4-trichlorophenol (2,3,4-TCP), 2,4,5-trichlorophenol (2,4,5-TCP), 2,3,4,5-tetrachlorophenol (2,3,4,5-TeCP), 2,3,5,6- tetrachlorophenol (2,3,5,6-TeCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), pentachlorophenol (PCP) as well heptane (anhydrous, 99%). Acetone (chromasolv for liquid chromatography, 99.8%) is supplied by Sigma-Aldrich (Germany) and potassium carbonate (anhydrous, ACS reagent, 99%) are obtained from Sigma-Aldrich (USA). Acetic anhydride, required for the derivatization of chlorophenols, is purchased from Sigma-Aldrich (Switzerland). Acetonitrile (HPLC purity, 99.9%) is purchased from Merck (Germany). A stock standard solution of CPs is prepared in methanol (5 mL), with concentration levels of approximately 5000 $\mu g\,L^{-1}$ for dichlorophenols (DCPs), 2000 $\mu g\,L^{-1}$ for trichlorophenols (TCPs), 1000 $\mu g\,L^{-1}$ for tetrachlorophenols (TeCPs) and pentachlorophenol and stored in a refrigerator with no light. All aqueous solutions are prepared by diluting stock solutions in an appropriate amount of ultrapure water obtained from a Mili-Q® apparatus (Merck KGaA, Germany). Centrifugation is carried out by using a centrifuge supplied from Eppendorf SG (Germany). To remove any organic compounds left in the centrifugation step, the glassware is rinsed with tap water and cleaned with soap. Then, it is soaked for at least twelve hours in a 5% HNO_3 solution, rinsed very thoroughly with deionized water and placed into an ultrasonic bath (Bandelin Sonorex, Germany) for 15 min. Cleaned glassware is oven dried at 120 °C in a furnace.

2.2. Instrumentation

Chromatographic determination of CPs was performed with GC-ECD system, precisely a GC8000 Top (USA), electron capture detector ECD850 (TermoQuest, Italy) and equipped with an on-column injector. Separation and identification of chlorophenols is obtained with a DB-5 column (60 m × 0.32 mm × 0.25 m) (Agilent Technologies, USA) and Guard Column (10 m × 0.32 mm) (Zebron Phenomenex, USA). Chromatographic software used is Chroma software (version 1.12). The initial temperature is 100 °C (held for 1 min) and is followed by heating to 180 °C at a rate of 15 °C min^{-1}, then it is raised to 240 °C at a rate of 50 °C min^{-1} and held for 3 min. Hydrogen, as a carrier gas, is generated with a hydrogen generator (HG2600, Claind Italy) at a pressure of 130 kPa. Nitrogen (purity 99.999%), as make-up gas for ECD, is before passed through a molecular sieve trap and an oxygen trap. The detector is operated at 330 °C.

2.3. DLLME-GC-ECD procedure

In order to perform DLLME and derivatization at the same time, appropriate volume of aqueous solution (5.31; 6; 7; 8; 8.68 mL) is transferred into a 10-mL glass test tube (OMNILAB, Germany) with a screw cap and PTFE/silicone membrane (Agilent Technologies, USA) and spiked with appropriate volume of stock solution containing analytes, resulting in a concentration of 6.25 $\mu g\,L^{-1}$ for DCPs, 2.5 $\mu g\,L^{-1}$ for TCPs, 1.25 $\mu g\,L^{-1}$ for TeCPs and PCP. Subsequently, 0.4 mL K_2CO_3 (10%, w/v) is added. To investigate the effects of the disperser and extraction solvents volumes on the performance of DLLME, appropriate sample solutions were tested. Mixture of appropriate volume of the disperser solvent (acetone) and the extraction solvent (heptane) containing 50 μL of the derivatizing reagent (acetic anhydride) is rapidly injected into the aqueous sample using a 2-mL syringe (Polfa, Poland). A cloudy solution con-

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