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Application of multicriteria decision analysis in solvent type optimization for chlorophenols determination with a dispersive liquid–liquid microextraction

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ABSTRACT

This study presents a novel support tool for the optimization and development of analytical methods. The tool is based on multi-criteria decision analysis (MCDA), namely the Technique for Order of Preference by Similarity to the Ideal Solution (TOPSIS), that allows users to rank possible solutions according to their requirements. In this study, we performed rankings of pairs of eight extraction and three dispersive solvents used in DLLME for chlorophenols extraction from water samples. The first ranking involved sensitivity and precision of the method for each of the nine chlorophenols. The tool is a quantitative solution to the common analytical problem that the change of analytical performance results in better performance for some analytes and worse for others. The second ranking included the assessment of the greenness of each pair of solvents, based on toxicological, ecotoxicological and environmental persistence criteria. The third ranking was based on a combination of sensitivity, precision and greenness criteria. Heptane as an extraction solvent and acetone as a dispersive solvent were selected as the most appropriate ones. The TOPSIS tool is a successful, easy to implement, incorporation of green analytical chemistry values to analytical method optimization.

1. Introduction

Green analytical chemistry is a concept that incorporates environmental awareness of chemists' activities into analytical laboratories [1]. As the sample preparation step is often regarded as one of the most polluting ones from the whole analytical procedure [2], much emphasis is put on the development of microextraction techniques [3], including dispersive liquid–liquid microextraction (DLLME) [4,5].

The principle of the DLLME technique is the application of a two-solvent system [6]. The first solvent, called an extraction solvent, has to be insoluble in water and has to be able to extract target compounds. The second solvent is called "dispersive" and it has to be miscible with the extraction solvent and the sample matrix (usually water). The mixture of both solvents is injected to the sample, the rapid dissolution of the dispersive solvent in water results in dispersion of the extraction solvent in the whole sample volume—it is called the formation of a "cloudy solution". The solvent is recovered after centrifugation. If the extraction solvent is lighter than water, it is required to apply specially designed probes that allow recovering a solvent lighter than water [7]. Many applications of the DLLME include the determination of organic compounds in liquid matrices, but this technique is also used in the determination inorganic analytes and is helpful in solid samples analysis [8].

Application of solventless extraction techniques [9] is one way of complying with green analytical chemistry principles. It is not always convenient or even possible so techniques that involve solvents are still intensively developed. It is important to apply solvents that are green but the environmental impact of solvents is seldom considered during method development. Greener solvents were applied as more environmentally benign mobile phases in HPLC [10,11] or less toxic extraction solvents. Recently, bio-based solvents have attracted interest to be applied in analytical chemistry [12,13]. Also, the parameters that make the solvent green are not yet well defined and diverse approaches are reported in papers. Environmental, health and safety (EHS) parameters can be used for the assessment of analytical solvents [14]. Another approach includes scoring of solvents based on toxicological hazards and exposure potentials of the solvents [15]. The first attempts to apply life-cycle analysis were also made [16].

The Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) is one of the multi-criteria decision analysis

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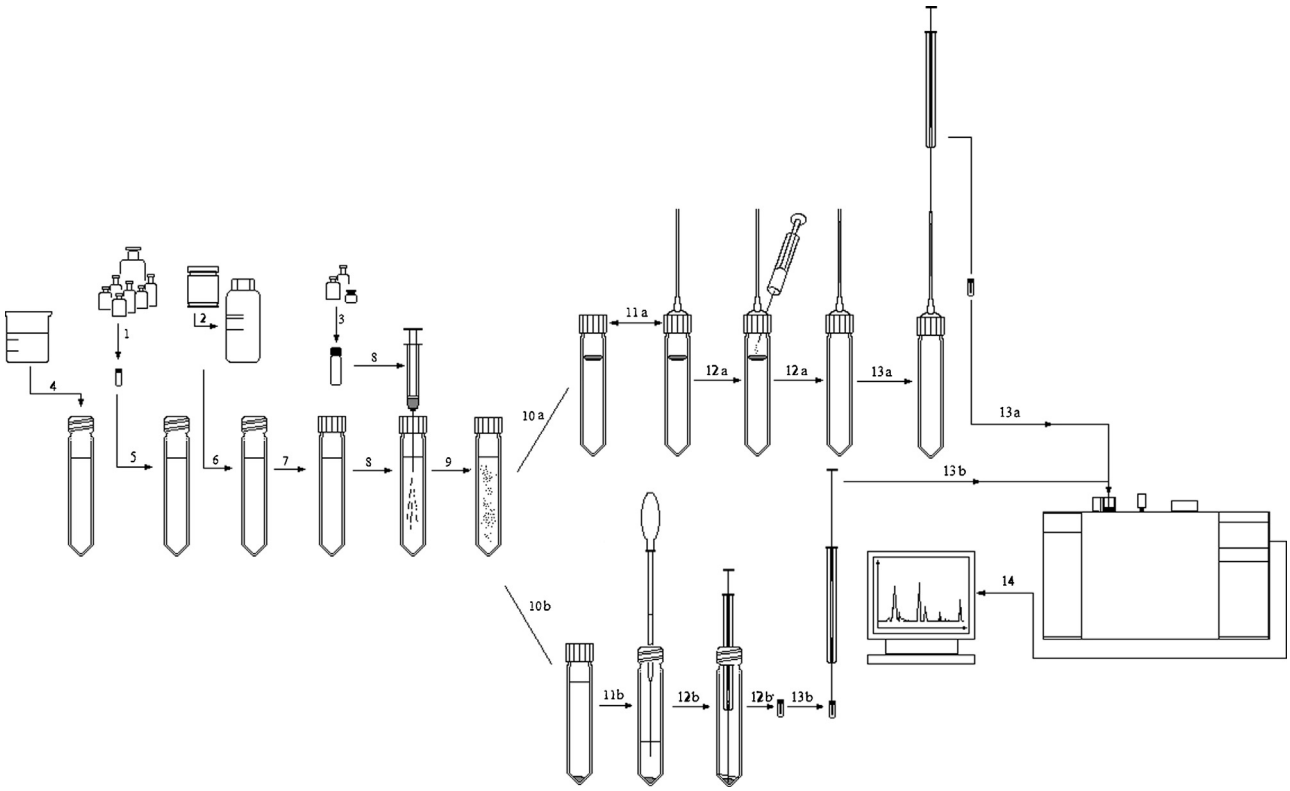

Fig. 1. Scheme of the DLLME-GC-ECD procedure used for the determination of chlorophenols in water samples, depending on the extraction solvent used.
Description: (1–3) Preparation of a stock solution, 5% (w/v) K_2CO_3 solution, mixture of disperser and extractive solvents containing the reagent derivatization (acetic acid), respectively; (4) Filling the test tube with deionized water; (5 and 6) Addition of the proper amount of stock solution and 5% (w/v) K_2CO_3 solution to the aqueous sample; (7) Closing the centrifuge tube with a screw cap; (8) Rapid injection of mixture solvents into an aqueous sample with a 2-mL syringe; (9) Formation of cloudy solution; (10) Centrifugation: the aqueous sample containing a lower-density extraction solvent (a) or higher-density extraction solvent (b); (11a) A replacement of the screw cap with another one considering a narrow part of Pasteur's Pipette; (12a) Injection of deionized water with a 5-mL glass syringe into an aqueous sample in order to raise the level of water; (13a) Removing an extract with a 10-μL microsyringe and analyse it. (11b) Removing the water phase with a Pasteur Pipette; (12b) Removing an extract and transferring to a GC vial. (13b) Injection of the sample extract into the GC for analysis; (14) Data analysis.

(MCDA) techniques [17]. It is applied to solve problems or choose the optimal solution in multivariate systems. TOPSIS has been applied in environmental sciences to optimize municipal solid waste management systems [18], the selection of flood management strategies [19] or the assessment of environment value [20]. It has been used as a support tool in green analytical chemistry, to choose the most favourable, in terms of performance and environmental impact, analytical procedure for pharmaceuticals determination in wastewater samples [21]. The MCDA approach is often applied if criteria describing the stated problem come from completely different areas—i.e. when environmental, social and economic aspects are combined. The application of MCDA in analytical procedure optimization can be beneficial as it is used to select the best solution, if contradictory goals are to be achieved. As an example taken from analytical chemistry, the change of a parameter can improve the procedure performance for some analytes, at the same time decreasing the performance of others.

The aim of the study is:

- to incorporate the quantitative assessment of solvent hazards into the selection of the type of solvent(s) used in analytical extraction;
- to present the applicability and benefits of the application of MCDA in the optimization of the solvent type for extraction.

To the best of our knowledge, it is the first attempt to apply MCDA as a support tool in analytical method optimization.

2. Materials and methods

2.1. Reagents and solvents

The following substances: 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 pentane (reagent grade, 98%), chlorobenzene (ACS reagent, 99,5% for gas chromatography), dichloromethane (anhydrous, 99.8%), hexane (anhydrous, 95%), toluene (anhydrous, 99.8%) isooctane (anhydrous, 99.8%), and heptane (anhydrous, 99%) were purchased from Sigma Aldrich (Germany). Acetone (chromasolv for liquid chromatography, 99.8%) was supplied by Sigma-Aldrich (Israel), terachloroethylene (chromasolv for liquid chromatography, 99.9%) and potassium carbonate (anhydrous, ACS reagent, 99%) were obtained from Sigma-Aldrich (USA). Acetic anhydride required for the derivatization of chlorophenols, was purchased from Sigma-Aldrich (Switzerland). The containers with sorbents for moisture were stored under inert gas to prevent leakage or degradation of the derivatizing reagent. For further purification, molecular sieves (Merck, Germany) were added to extraction solvents. Nitric acid (≥65%) used for cleaning glassware and acetonitrile (HPLC purity, 99.9%) was purchased from Merck (Germany).

A stock standard solution of CPs was prepared in methanol (5.00 mL), with concentration levels of approximately 5000 $\mu g\,L^{-1}$ for dichlorophenols (DCPs), 2000 $\mu g\,L^{-1}$ for trichlorophenols