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Green analytical chemistry introduction to chloropropanols determination at no economic and analytical performance costs?

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ABSTRACT

In this study we perform ranking of analytical procedures for 3-monochloropropane-1,2-diol determination in soy sauces by PROMETHEE method. Multicriteria decision analysis was performed for three different scenarios – metrological, economic and environmental, by application of different weights to decision making criteria. All three scenarios indicate capillary electrophoresis-based procedure as the most preferable. Apart from that the details of ranking results differ for these three scenarios.

The second run of rankings was done for scenarios that include metrological, economic and environmental criteria only, neglecting others. These results show that green analytical chemistry-based selection correlates with economic, while there is no correlation with metrological ones. This is an implication that green analytical chemistry can be brought into laboratories without analytical performance costs and it is even supported by economic reasons.

1. Introduction

Chloropropanols are the group of heat-induced food toxicants, formed during processing of various foodstuffs by the reaction of glycerol or acylglycerols and chloride ions in acidic environment [1]. Their occurrence in food products was first reported by Velíšek et al. in 1978 [2] in acid-hydrolyzed vegetable protein (HVP) used as a seasoning in the production of soy sauces and related products such as soups, bouillon cubes and other types of sauces [3]. The most intensively investigated chloropropanol is 3-monochloropropane-1,2-diol (3-MCPD), since its occurrence in different types of foodstuffs was reported at the highest levels [4]. Its isomer, 2-monochloropropane-1,3-diol (2-MCPD) and dichloropropanols (1,3- and 2,3-dichloropropanol; 1,3-DCP and 2,3-DCP) occur at much lower concentrations [5]. Apart from soy sauce and soy sauce-related products, the presence of 3-MCPD was reported in lower but significant levels in such foodstuffs as bakery, malt and smoked products [6].

The risk of 3-MCPD and other chloropropanols presence in food products is related to testicular and renal toxicity of its metabolites resulting in carcinogenic lesions, which was proved in studies on rodents [7]. 3-MCPD exhibits mutagenic activity *in vitro*; however, limited data based on *in vivo* studies provide rather conflicting results. Clinical studies on human beings regarding toxicological activity of 3-MCPD have not been reported so far [8].

The above-mentioned facts led to setting the regulations regarding the presence of 3-MCPD in soy sauce. The experts of the Joint FAO/WHO Expert Committee on Food Additives (JECFA) and EC Scientific Committee on Food established in 2001 a maximum tolerable daily intake (TDI) for 3-MCPD of 2 μg/kg body weight per day for HVP and soy sauce [9]. In 2001 EC set the regulatory limit of 0.02 mg/kg foodstuff regarding HVP and soy sauce [10].

In order to monitor the concentration of 3-MCPD and other chloropropanols in food products, various analytical methods have been developed. Most approaches involve initial sample clean-up, derivatization reaction (because of low volatility and high polarity of 3-MCPD) and final determination by gas-chromatography technique [5]. In 2001, the analytical procedure for 3-MCPD determination in soy sauce and related food products based on above-mentioned approach developed by Brereton et al. was validated by a collaborative trial and adopted by the Association of Official Analytical Chemists International as an official method and also as European norm EN 14573. Current trend in development of new analytical procedures for 3-MCPD and other chloropropanols determination in foodstuff samples involves the application of environmentally friendly sample preparation techniques (such as SPME, DLLME, MSPE) as well as more sophisticated separation techniques (such as GC–MS/MS) [11]. It is clear that analytical procedure for chloropropanols determination should meet green

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analytical chemistry requirements. The number of available procedures requires dedicated tools for systematic procedure selection with complex criteria.

The term of green analytical chemistry can be defined following Sandra et al. [12] as “the use of analytical chemistry techniques and methodologies that reduce or eliminate solvents, reagents, preservatives and other chemicals that are hazardous to human health or the environment and that may also enable faster and more energy efficient analyses without compromising performance criteria”. In the literature certain statements can be found that green analytical chemistry and analysis costs or analytical performance cannot go together. Some of them are *a priori* statements, not supported by any statistical evidence. Green analytical chemistry metrics is a developing branch of science, the existing metrics is summarized in the review [13].

When there are several different analytical procedures in use, Multiple Criteria Decision Analysis (MCDA) might be used to select the most preferred one. MCDA is a name for different methods used to support decision making in case of conflicts concerning some typical areas such as economy, environment, society or technology. MCDA consists of a group of several methods, whose main purpose is to construct ranking, choice or classification. It can be applied in various areas, including project planning, strategic management, environmental analysis, etc. One of the principal aims of MCDA approaches is to help decision maker to organize and synthesize information in a way that all criteria have properly been taken into account in decision making process. Among many MCDA methods Analytic Hierarchy Process (AHP), Preference Ranking Organization Method of Enrichment Evaluation (PROMETHEE) and Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) are the most popular. PROMETHEE technique has been proved to be a useful tool for ranking of analytical procedures according to their greenness [14].

The aim of the study is to present the selection of analytical procedure for 3-MCPD determination in soy sauces and related products according to different decision making assumptions. The growing concern regarding the presence of this potential carcinogen in a wide range of food products consumed by humans daily in significant amounts led to the development of several analytical methods applying various analytical techniques and characterized by different validation parameters. The wide variety of methods for 3-MCPD determination available in the literature as well as importance of this topic underlined by the European Commission (EC) made it suitable for the study described in the manuscript. The three basic scenarios, namely metrological, economic and green analytical chemistry of making decisions were investigated and discussed. The potential role of MCDA analysis as green analytical chemistry metrics and the potential trade-offs between green analytical chemistry economy and metrology is discussed.

2. Materials and methods

2.1. PROMETHEE technique

The PROMETHEE (Preference Ranking Organization Method for Enrichment Evaluations) is one of the widely applied MCDA methods. It is stated in Belton and Stewart that Brans and Vincke developed the technique [15]. PROMETHEE is a family of ranking methods that consists of six PROMETHEE techniques. This method is popular to be used in business (especially location of new investments), transportation, energy management and medicine. It becomes to be used in chemistry as well in the areas like ranking the emission factors of cars [16]. In the presented paper PROMETHEE II was applied, because the ranking of alternatives is the most beneficial analysis output from assessment perspective.

The operation of PROMETHEE II algorithm is based on comparing alternatives in pairwise manner along each criterion. To implement this algorithm it is needed to introduce two types of information: weights for criteria and the preference functions. A preference function for each criterion, expressing the difference in performance of alternative a_1 over alternative a_2 must be identified, adopting as a result the pairwise comparison approach [17]. The procedure of PROMETHEE II contains five main steps:

1. Determination of deviation based on pair-wise comparisons.
2. Application of preference functions.
3. Calculation of an overall preference index.
4. Calculation of outranking flows.
5. Calculation of PROMETHEE II complete ranking.

In details when A of n alternatives $(a_1, a_2, \ldots a_n)$ have to be ranked and G of k criteria $(g_1, g_2, \ldots, g_k)$ have to be maximized (or minimized) the decision making problem has the form as shown:

$$\max \{g_1(a), g_2(a), \ldots, g_k(a)|a \in A\}$$

Some criteria might be maximized whereas others might be minimized, the goal of the decision-maker is to identify an alternative which fits the best to all criteria. Apart from ranking itself, the result of PROMETHEE is giving numerical score for each alternative. Numerical score is known as net preference flow:

$$\varnothing(a) = \varnothing^+(a) - \varnothing^-(a)$$

where Ø denotes net outranking flow for each alternative. [15]

This parameter gives information how the alternative performs in pairwise comparisons with every other alternative from the input data matrix. In practice, these scores give information what are the differences between two following alternatives in the ranking.

The detailed mathematical description of PROMETHEE was presented in the original work by Brans and Vincke (1985). For detailed review of PROMETHEE applications in various areas, such as public administration, business, industrial location, medicine or tourism please see comprehensive review [17]. The general procedure of PROMETHEE application in this particular case is presented in Fig. 1.

2.2. Analytical procedures

One of the types of input data to PROMETHEE II algorithm is the set of alternatives. Alternative is the way to achieve the solution of the main goal stated in the decision problem. In this case the stated problem is “what is the most appropriate analytical procedure for 3-MCPD determination in soy sauce samples?”. We have found in the literature 17 fully described procedures for determination of 3-MCPD in soy sauces and related products. They are briefly described in Table 1. The procedures are based on the variety of sample preparation techniques, the great majority applies gas chromatography for separation and most of the detection systems are based on mass spectrometry. The dominating sample preparation technique is solid-phase extraction.

2.3. Criteria of assessment

Criteria describe the alternatives and they are the basis of the decision making process. The PROMETHEE algorithm requires numerical data to be an input or should be easily translatable to the numbers. The criteria (see Table 2) are often contradictory to each other, what in fact, is the basis of application of multicriteria decision analysis tools to support the decision process. For each