

# Multi-criteria decision analysis for selection of the best procedure for PAHs determination in smoked food

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## Keywords

green analytical  
chemistry  
Multi-Criteria Decision  
Analysis  
PROMETHEE  
smoked meat

## Abstract

Making a proper decision in multifacitated situation is very challenging task. Especially, if there are many alternatives and criteria, even contradictory ones. The support tools may be application of Multi-Criteria Decision Analysis methods. In this study the application of PROMETHEE (Preference Ranking Organization Method for Enrichment Evaluations) as one of Multi-Criteria Decision Analysis method in selection of the most preferable analytical procedure for polycyclic aromatic hydrocarbons determination in smoked products is presented.

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## 1. Introduction

The most common analysts' considerations involve the selection of appropriate methods of sample preparation, reagents, analytical techniques, and conditions for analytical determination. Unfortunately, there is a huge number of alternatives, thus making a proper decision is not an easy task. It is necessary to know the decision problem, the need and purpose of the analysis, as well as the criteria of the decision and the available alternatives. It is a difficult task to judge clearly, which of the analytical procedures is the best in a given case. In this situation the application of Multi-Criteria Decision Analysis methods may be a useful and desirable solution. These tools allow describing a given problem using numerical values, and enable to obtain final results also as numerical values. The scores are presented in a form of a full ranking of available options, which allows selecting objectively the best alternative. Moreover, the decision is made in a systematic way. Detailed information about Multi-Criteria Decision Analysis usage in area of chemical sciences, especially analytical chemistry may be found in [1].

One of the most popular tools is PROMETHEE (Preference Ranking Organization Method for Enrichment Evaluations). In this work selection of the most preferable analytical procedure for polycyclic aromatic hydrocarbons (PAHs) determination in smoked products using PROMETHEE is presented and discussed.

## 2. Experimental

### 2.1 Polycyclic aromatic hydrocarbons in smoked products

Polycyclic aromatic hydrocarbons are a large class of organic compounds that are composed of two or more fused aromatic rings [2]. Mainly they are formed through incomplete combustion or pyrolysis of organic matter and during various industrial processes. Additionally PAHs are also formed during food preparation methods such as grilling, roasting and smoking. In Europe about 15% of fish products for consumption are prepared using smoking process [3]. In food industry mostly benzo[*a*]pyrene is controlled as a marker of the carcinogenic PAHs in food with maximum limits in certain foods in the EU [4]. Analytical procedures may involve variety of sample preparation techniques, for instance Soxhlet extraction, solid-phase extraction, and liquid-liquid extraction, pressurized liquid extraction and QuEChERS, etc. [5]. Therefore, which of the analytical procedures is the best for this given purpose?

### 2.2 Components of Multi-Criteria Decision Analysis

#### 2.2.1 Main goal of analysis

Main aim of the analysis is finding the greenest analytical procedure for PAHs determination in smoked products such as meat and fish. Analysis includes assessment only for benzo[*a*]pyrene, as a marker of carcinogenic PAHs in food. In case of analytical procedure consideration, also metrological factors have to be satisfactory but mainly environmental factors are considered.

#### 2.2.2 Criteria of assessment

In Multi-Criteria Decision Analysis methods criteria are factors that are allow to make an evaluation of a given problem, and describe alternatives. Technical evaluation of analytical procedure involve limit of detection (*LOD*) and precision, expressed as relative standard deviation (*RSD*). Criteria as amount of sample, total time needed to perform analysis and number of procedural steps are involved. The information on reagents are designate in a reference to Analytical Eco-Scale approach [6]. On the other hand, solvents evaluation is based on calculations proposed by Tobiszewski and Namieśnik [7]. Criteria with preferences functions are *LOD*, *RSD*, Amount of sample, Time of analysis, Score for solvents, Score for other reagents, Number of procedural steps, all with preference function “the lower the better”. It is possible to differentiate the importance of criteria by assessing appropriate weight values to all criteria. In this particular case study we assumed that all criteria influence similarly on the main goal.



**Table 1**Analytical procedures of benzo[*a*]pyrene determination in smoked meat and fish.

Number	Matrix	Abbreviation	Ref.
1	Smoked fish	ASE-GC-MS	[8]
2	Cold-smoked fish (mackerel)	LLE-GC-MS	[9]
3	Cold-smoked fish (salmon)	LLE-HPLC-FLD	[10]
4	Smoked meat	SPE-GC-FID	[11]
5	Smoked meat	MAE-RP-HPLC-FLD	[12]
6	Smoked fish	MAE-DLLME-GC-MS	[13]
7	Smoke-cured fish products	Sox.-GC-MS	[14]

### 2.2.3 Alternatives

Alternatives are the subject of considerations. They represent possible analytical procedures that may reach the stated goal. Proposed analytical procedures for PAHs determination in smoked products are summarized in Table 1.

#### 2.3 PROMETHEE analysis

All the data values are taken directly or indirectly from indicated above scientific papers (Table 1.). Indirectly means, that some of them are calculated into numerical values. The set of data prepared for PROMETHEE analysis consists of alternatives described by criteria. In this work PROMETHEE algorithm is used as commercial computer software - VisualPROMETHEE software.

## 3. Results and discussion

For PAHs determination in smoked fish and meat, all introduced criteria are define as being equally important. With such assumptions, it is possible to obtain result as a complete ranking of alternatives, what is presented in Table 2. Phi presented in Table 2 is a balance between the positive and negative preference flows and it includes both of them and presents as a single score. As it is presented, the best

**Table 2**

Final results of PROMETHEE analysis.

Rank	Alternatives	Number (cf. Table 1)	Phi
1	MAE-RP-HPLC-FLD	5	0.6190
2	ASE-GC-MS	1	0.1905
3	MAE-DLLME-GC-MS	6	0.0714
4	LLE-HPLC-FLD	3	0.0000
5	LLE-GC-MS	2	-0.0714
6	SPE-GC-FID	4	-0.3571
7	Soxhlet-GC-MS	7	-0.4524



analytical procedure for PAHs determination in smoked meat and fish is technique based on high performance liquid chromatography with spectrofluorometric detection, preceded by microwave-assisted extraction. MAE-RP-HPLC-FLD procedure is characterized by the most desired criteria's values in response to other alternatives. On the other hand, the worst analytical procedures are Soxhlet-GC-MS and SPE-GC-FID. Their low positions in the ranking are due to high score for solvents. Thus, highly toxic and hazardous solvents are used, involving their huge amounts. In procedure with Soxhlet extraction as a pre-treatment over 300 mL of dichloromethane is used. Moreover, Soxhlet-GC-MS is characterized by the highest value for limit of detection, what is not desired.

#### 4. Conclusions

Many chemical decision problems are complex and are characterized by interdisciplinary nature. Thus there is a need of comprehensive assessment that includes environmental, economic and metrological point of view. Multi-Criteria Decision Analysis methods combine multioutput information into single value, that is easy to be compared other possibilities. They allow solving complex problems (with many criteria and alternatives) in a technically valid and practically useful way. It was found that the best procedure for PAHs determination in smoked meat and fish is MAE-RP-HPLC-FLD.

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