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An analytical hierarchy process for selection of the optimal procedure for resveratrol determination in wine samples

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Abstract

The study shows the application of analytical hierarchy process (AHP) in ranking the analytical procedures, that are applied for resveratrol determination in wine samples. 19 different analytical methodologies are described by metrological, economic and environmental criteria, that are further divided into 10 subcriteria. Before AHP application , the amount of input data is decreased with cluster analysis. The first run of AHP is aimed to rank the clustered analytical procedures, while the second analysis is performed to select the best procedure from the cluster with the highest rank obtained in the first AHP run. The procedure based on a direct sample injection to high performance liquid chromatography with UV detection is the most beneficial one. AHP is excellent tool for the assessment and the selection of the most appropriate analytical procedure from several available. The choice of MCDA method is dictated by the fact, that so far, no examples of the usage of a given method for the selection of the optimal analytical procedure have been found in the literature.

Keywords: wine samples analysis; multi-criteriadecision analysis; AHP; sample preparation

1. Introduction

Without a doubt, the relationship between diet and health has developed an intense research in bioactive compounds in foods. Among food and beverages products, wine seems to be an essential component and may be partially responsible for health-promoting properties. Wine, especially the red variety, has been studied extensively over many years. It is well known, that moderate consumption of red wine, is associated with several potential health benefits, such as lower risk of cardiovascular or neurological diseases and anti-cancer properties [1].

The most significant and beneficial health properties of wine consumption are related to compounds with high antioxidant capacity like polyphenols, including trans-resveratrol [1].

Resveratrol is a phenolic compound, occurring naturally in over-ground part of plants, mainly in seeds, skin and leaves. It is synthesized from phenylalanine through the shikimic pathway and three key enzymes are involved in this pathway: coenzyme A ligase, phenylalanine ammonium lyase, and stilbene synthase The biosynthesis of these enzymes can be induced by stress, thus resveratrol is a phytoalexin synthesized by grapes after exposure to biotic or abiotic stress [1]. Therefore, it can be stated, that resveratrol is produced in grapes as self-protection against toxins and it can be found within the skins [2]. The persistence of the grape skins during the fermentation process impacts on the resveratrol content in final products, meaning wines. The concentration of this compound is lower in white wine than in red wine, due to the fact, that skins are removed earlier during production of the white wines [3].

Resveratrol has recently been the subject of intensive investigation. This is mainly due to being reported as a potent antioxidant, anticancer, anti-inflammatory and chemoprotective agent. Moreover, this compound is associated with increased longevity, and cardiovascular protective effects, due to its ability to reduce platelet aggregation, modulate lipid metabolism, and inhibit oxidation of low density lipoprotein, [4, 5]. The increased awareness of the trans-resveratrol beneficial impact on human health and the challenges associated with its low and variable abundance in samples characterized by complex matrix composition, have driven the need to develop rapid and reliable methods for resveratrol analysis in wine and related samples. Many analytical procedures have been developed for determination of resveratrol in wine, which are based on the application of gas chromatography (GC), high performance liquid chromatography (HPLC) and capillary electrophoresis (CE) [6, 7, 8, 9]. Pre-concentration step is often required, because resveratrol occurs at low concentration level as well as, because wine is characterized by complex matrix composition. However, several direct methods are also reported. Taking into consideration separation and determination technique, derivatization process is often required to:

- increase volatility and thermal stability of analytes, improve resolution as well as detection parameters when the gas chromatography is applied;

- improve sensitivity and separation properties when the liquid chromatography is utilized;
- give charge to a specific components, while using electrophoresis [10].

Some articles report application of combination of analyte pre-concentration, extraction and derivatization, what is in accordance with green analytical chemistry, which arise from the principles of sustainable development [3].

Although, there is a large number of reports in the literature, which show the results of the determination of resveratrol compound in the wine industry, there is a lack of critical comparisons of developed methodologies, not only in terms of the parameters of the analytical merits achieved, but also in terms of their green character. It is clear, that analytical procedure for resveratrol determination should meet green analytical chemistry requirements. The large number of available procedures requires the application of dedicated tools for systematic procedure selection within complex criteria and many alternatives [3].

The approach, that gives the possibility to assess the analytical procedures taking into account their environmental impact is Multicriteria Decision Analysis (MCDA). The group of MCDA tools may be applied to select the most preferred procedure and/or rank the remaining ones [11, 12]. MCDA is used to select the most appropriate procedure to determine aldrin in water samples, with green analytical chemistry principles taken into consideration in another study [11]. The ranking of analytical procedures is obtained with Preference Ranking Organization METHod for Enrichment of Evaluations (PROMETHEE). In different study, with this MCDA technique completely different weighting criteria are applied to investigate the influence of metrological, economic and environmental factors on the final ranking results [12]. Another MCDA tool - Technique for Order of Preference by Similarity to Ideal Solution (TOPSIS) is used for the assessment of analytical procedures, that are applied for the determination of ibuprofen in wastewater samples [13].It should be emphasized that MCDA and chemometrics/multivariate statistics have different jargons. The equivalents of variables and objects known in chemometrics, in MCDA are criteria and alternatives.

This study aims to present the selection of analytical procedure for resveratrol determination in wine samples, from 19 available procedures, according to different decision making criteria. *Analytical Hierarchy Process(AHP)* as MCDA algorithm is applied for data analysis and its applicability is discussed. The choice of method is dictated by the fact, that so far, no examples of the usage of given method for the selection of the optimal analytical procedure have been found in the literature.

2. Materials and methods

2.1. AHP technique

The AHP is a multicriteria decision analysis technique that was developed by Saaty [14]. It is mainly used to aid solving complex decision making problems. In this methodology, the problem is structured in a hierarchy of different levels constituting of the main goal, criteria, sub-criteria and alternatives. This structure organizes the components of the problem from the most general, placed in the upper part of the hierarchy, to the more detailed, located in the lower part. Elements from different levels are compared in pairs. It allows to assess relative preference with respect to each of the elements at the next and higher level. The intensity of preference between two elements is established on the basis of Saaty's Fundamental Scale [15]. A linear and bipolar scale consists of nine possible numeric values. Description of each degrees of a scale are presented in Table 1.

Table 1 Pair-wise comparison scale [16, 17]

Intensity of importance on an absolute scale	Definition	Explanation
1	Equal importance	Two activities contribute equally to the objective
3	Moderate importance of one over another	Experience and judgment slightly favor one activity over another
5	Essential or strong importance	Experience and judgment strongly favor one activity over another
7	Very strong importance	An activity is strongly favored and its dominance demonstrated in practice
9	Extreme importance	The evidence favoring one activity over another is of tile highest possible order of affirmation
2, 4, 6, 8	Intermediate values between the two adjacent judgments	When compromise is needed

According to the given data, the degree of advantage of one element over another is determined. Value 1 means, that element A is of the same importance as B. On the other hand, 9 means total advantage A over B or vice versa. Odd steps are usually used. However, if it is not possible to make such an assessment by the decision maker, then even degrees (intermediate values) as 2, 4, 6, 8 are used. The determination of the advantage of one ofthe elements is based on the so-called axiom of reciprocity, that is a reverse system. If the responder considers, that object A has a very strong advantage over object B (A = 7B), then B will be 7 times weaker than A (1/7A = B).

As it was mentioned previously, AHP considers a set of evaluation criteria, and a set of alternative options among, which the best resolution is chosen. The best option is not that one, that optimizes each single criterion, but rather that one, which achieves the most suitable trade-off among the different criteria. It is important to note, that AHP allows to make a good decision, even if some of the criteria are contrasting. Generally obtaining each scale`s value is possible due to results from a questionnaire, that is designed to obtain Saaty's Scale values.

In this step experts experience and knowledge may be required to be used, as well as stakeholders` opinions.

More detailed description of AHP theory is available in references [18, 19]. The procedure is also described by Lin and Yang [20]. According to them, AHP algorithm can be briefly described in several simple steps as follows [18, 19, 20]:

1. Defining the problem, determining the goal of analysis and building the hierarchical structure model

First of all, the main aim of the analysis should be defined. Criteria or sub-criteria as well as alternatives should be also determined. Later, all the information should be put in hierarchy structural skeleton of AHP model. The number of hierarchies (levels) depends on the complexity of the problem that is analyzed. However, they are structured from the top with a goal, by criteria and sub-criteria on an intermediate levels, till the alternatives, which are putted on the lowest level of hierarchy. In other words, they are presenting a range of information from general to more detailed one. Hierarchy system allows to determine the influence possessed by the function among elements, as well as their impact on the entire system. It is the first step, and the most important at the same time. The quality of performance affects the correctness of results, especially the consistency between pair-wise comparisons of elements.

2. Establishing a pair-wise comparison matrix of the criteria

In this step, the elements of a particular level are compared pair-wise, with respect to a specific element in the upper level. The purpose of such analysis is to derive the degree of relative importance amongst elements. In this way, it can be judged, which element is preferred and how much more it is preferred over another. First, criteria are compared pair-wise with respect to the goal, then sub-criteria (if they are defined) are compared pair-wise with respect to the criteria, and finally alternatives are compared with respect to the each sub-criteria or criteria. The priorities of the corresponding elements are possible to compute, thanks to an assessment, which uses 9-point scale proposed by Saaty [16]. It allows to transform the verbal judgments into numerical quantities representing the values. Given results may be presented in the form of judgmental matrix. It is worth to notice, that it is mostly applicable when each hierarchy does not contain more than seven elements.

Otherwise, these elements should be clustered and divided into an additional hierarchy (for example by inclusion of sub-criteria). Comparison of two elements may be mathematically presented as:

$$A_{i,j} = \frac{W_i}{W_j} i, j = 1, 2, 3, \dots, n \tag{1}$$

where $A_{i,\,j}$ denotes the weight exchange value of the pair-wise comparison of element e_i and e_j, and W_i and W_j denote the relative weights amongst elements.

3. Derivation of the eigenvector and maximum eigenvalue (normalization of the pair-wise comparison matrix)

Based on the comparison matrix, the eigenvector is derived. It describes the degree of relative importance amongst the elements. In addition, at the same time, the maximum eigenvalue can be derived. This value may be used to determine the strength of consistency amongst comparisons, and further may be used as a reference index. The method of derivation is performed according to the equilibrium:

$$AW = nW \tag{2}$$

Priorities of criteria can be estimated by finding the principal eigenvector W (normalized vector) of the matrix A [19, 21]. The maximum eigenvalue λ_{max} equals the number of order. It may be presented as follows:

$$AW = \lambda_{max} W \tag{3}$$

By normalized solution, the relative weight W_i, $W_i = 1, 2, 3, \dots, n$, can be derived. By the Perron-Forbenius rule, the following relative weight can be derived:

$$\lambda_{max} = \left(\frac{1}{n}\right)\left(\frac{W_1^{`}}{W_1} + \frac{W_2^{`}}{W_2} + \cdots + \frac{W_n^{`}}{W_n}\right) \tag{4}$$

$$W^{`} = AW \tag{5}$$

4. Determination of the consistency of the pair-wise (consistency index and consistency ratio)

If matrix A is a consistent matrix, then the maximum eigenvalue of A should equal to its number of order. However, in practice the pair-wise comparison matrix cannot achieve complete consistency. This difference of value between λ_{max} and n can be used to judge the degree of consistency.

Consistency index (CI) may be calculated as follows:

$$CI = \frac{\lambda_{max}}{(n-1)} \quad (6)$$

If the consistency index ≤ 0.1, it means, that the consistency level is satisfactory.

To check the correctness of comparisons, consistency ratio (CR) is also designated. It is calculated to determine inconsistencies in the evaluation. It measures how consistent the judgments have been relative to large samples of purely random judgments. It is determined in accordance with equation:

$$CR = \frac{CI}{RI} \quad (7)$$

If the consistency ratio ≤ 0.1, it means, that the evaluation within the matrix is acceptable. Instead if *CR* is more than 0.1 the judgments are untrustworthy, because they are too close for comfort to randomness and the assessment is valueless or must be repeated.

For each comparison matrix, a corresponding random index (RI) is used. It is an index of randomly generated reciprocal matrix from the 9-point scale, with reciprocals forced. Its value for computation is presented in Table 2.

Table 2 The average consistencies of random matrices [22]

Size	1	2	3	4	5	6	7	8	9	10
RI	0.00	0.00	0.58	0.90	1.12	1.24	1.32	1.41	1.45	1.49

5. Evaluation of alternatives according to the priorities identified

According to identified priorities (criteria, sub-criteria, and their weights), the most suitable alternative is chosen. The optimum solution is an answer for decision problem.

2.2. AHP analysis using Super Decision Software

Actually, most of study cases are complex, so there are lots of different criteria and alternatives. Thus, calculations without software support may be time-consuming and labor-intensive, in addition it is easy to make a mistake. That is why, MCDA algorithms are very often used as a commercial computer software. Furthermore, some of the parameters may be calculated automatically, so the number of actions is minimized. Performing the analyses with the software creates more clear form of presentation. In this case, Super Decisions software was selected to be applied. It was developed by Thomas Saaty [23], who is also the developer of AHP tool. It implements the Analytical Hierarchy Process for decision making with dependence and feedback. It allows to perform hierarchy structure, including several levels. In the Super Decisions software a decision model is made up of clusters, nodes and links. Clusters are groups of nodes, which are logically related factors of the decision [24]. Connections are made among nodes to define comparison groups. If nodes are connected then links automatically appear between their clusters.

It is also possible to put values of elements` weighting in it. The decision-making process automatically involves the calculation of inconsistency. It is useful for identifying possible errors in judgments as well as actual inconsistencies. In case of a negative outcome, the software marks the problematic elements and recommends required changes.

2.3. Criteria

To structure the hierarchy model properly, the criteria and alternatives are required to be determined. The criteria such as parameters, indicators, etc. should be determined in relation, to which the decision-making variants will be assessed with the main goal in mind. The selection of the best analytical procedure for resveratrol determination is a complicated decision making process. This evaluation should be compatible with sustainable development concept [25]. In other words, in this case, there should be a balance between the environment, the economy and the technical aspect. According to this assumptions, 3 main groups of criteria are established: environmental, metrological and economic. To each set of criteria, some sub-criteria are assigned. The division of measured parameters is presented in Table 3.

Table 3 Criteria and sub-criteria for evaluation in case study of resveratrol determination

Criterion	Sub-criterion	The description
Environmental	Amount of wastes	Amount of waste generated during sample analysis expressed in grams.
	Procedure steps	Number of steps performed in each procedure.
	Reagent toxicity	Toxicity – weighted amount of solvents.
Metrological	LOQ	Limit of Quantitation
	RSD	Relative Standard Deviation

Economic	Amount of sample	The amount of sample needed to perform analysis, expressed in mL
	Energy consumption	Energy consumed by the equipment used during analysis.
	Number of other analytes	The amount of other analytes than trans-resveratrol determined with the analytical procedure.
	Reagents price	The price of solvents, derivatization agents and other reagents expressed in Euro.
	Sample throughput	The amount of samples that can be analysed with analytical instrument in one hour.

It is worth to notice, that in AHP algorithm each sub-criteria may be used only once. Thus, it is possible to put chosen sub-criteria in one of the groups: environmental or metrological or economic. In addition, such amount of evaluation parameters is a significant problem. As it was mentioned before, each hierarchy should not contain more than seven elements. Hence,it influenced further division of all the parameters into groups.

2.4.The alternatives: analytical procedures

One of the types of input data to AHP algorithm is the set of alternatives - proposed solutions for analyte determination. Alternative is a way to achieve the solution of the main goal stated in the decision problem. In the presented case, they are alternatives, which constitute to the possible options – analytical procedures for resveratrol determination. The data is collected by searching the scientific databases (ACS, RSC, ScienceDirect, Springerlink, Wiley). The required information qualified later as the sub-criteria (Table 3) is extracted from articles or standard procedures. Most of the criteria are assessed with the values, that are directly taken from the literature data. The 19 fully described procedures are taken into consideration. The analytical procedures include analysis that are based on various sample preparation, separation and detection techniques. Information on the alternatives for reaching the main goal of MCDA assessment are presented in Table 4. If full data on analytical procedure is not available in a reference paper, such analytical procedure is not included in the assessment. However, there are methods to deal with such a problem, like application of simple linear models, maximum likelihood or multiple imputation models [26].

Table 4 Analytical procedures for resveratrol determination as alternatives in decision-making process

Alternative No.	**Analytical methodology**	**Abbreviation**	**Ref.**
1	Solid Phase Extraction- High Performance Liquid Chromatography- Ultraviolet Absorption Spectrophotometry	SPE-HPLC-UV	[31]
2	Direct Injection-High Performance Liquid Chromatography- Diode Array Detector-Ultraviolet–Visible Spectroscopy	DI-HPLC-DAD-UV-VIS	[32]
3	Solid Phase Micro Extraction - MultidimensionalGas Chromatography- Mass Spectrometry-Olfactometry	SPME-MDGC-MS-O	[33]
4	Reverse Phase- High Performance Liquid	RP-HPLC-UV-ED	[34]

	Chromatography- Ultraviolet Absorption-Electrochemical detection		
5	Stir Bar Sorptive Extraction-Thermal Desorption-Gas Chromatography- Mass Spectrometry	SBSE-TD-GC-MS	[35]
6	Solid Phase Extraction-Chemiluminescence detection	SPE - chemiluminescence	[36]
7	Solid Phase Extraction-Dispersive Liquid Liquid Micro Extraction- Gas Chromatography- Time Of Flight- Mass Spectrometry	SPE-DLLME-GC-TOF-MS	[37]
8	Solid Phase Extraction-Gas Chromatography-Mass Spectrometry	SPE-GC-MS	[38]
9	Direct Injection-High Performance Liquid Chromatography-Ultraviolet Absorption Spectrophotometry	DI-HPLC-UV	[39]
10	Direct Injection-High Performance Liquid Chromatography-Electrospray Ionization-Mass Spectrometry	DI-HPLC-ESI-MS	[40]
11	Differential Pulse Voltammetry-Electrodeposition Of Reduced Graphene Oxide Modified Glassy Carbon-Scanning Electron Microscopy	DPV(ERGO/GC- Electrode)-SEM	[8]
12	High Performance Liquid Chromatography-Fluorescence Detection	HPLC-FED	[41]
13	Liquid Liquid Extratcion- High Performance Liquid Chromatography-Photodiode Array Detector	LLE-HPLC-PDE	[42]
14	High Performance Liquid Chromatography-Ultraviolet Absorption	HPLC-UV	[9]
15	Liquid Chromatography-Mass Spectrometry	LC-MS	[43]
16	Microextraction by Packed Sorbent-Ultra-performance Liquid Chromatography- Photodiode Array Detector	MEPS-UPLC-PDA	[9]
17	Turbulent-Flow Chromatography- Liquid Chromatography-Mass Spectrometry	TFC-LC-MS	[44]
18	Liquid Chromatography- Ultraviolet–Visible Spectroscopy-Mass Spectrometry	LC-UV-VIS/MS	[45]
19	Capillary Electrophoresis- Electrochemical Detection	CE-ED	[6]

2.4. Cluster analysis

The high number of possible alternatives may negatively influence the analysis results, especially on CI and CR indexes. Thus, Cluster Analysis is used to reduce the number of alternatives being an input data. It is well established chemometric method [27]. Very briefly, it is aimed for grouping the objects (in MCDA called alternatives) according to their similarity. It is clustering without supervision, so unsupervised algorithm is finding internal patterns in the dataset with no *a priori* information or assumptions about data. For more details on the algoritmh please refer to [28]. The grouping of variables is performed with Euclidean distance measure and Ward cluster formation method. All Cluster Analysis calculations are performed with Statistica software. Before application of cluster analysis algorithm, the initial dataset is standardized.

3. Results and discussion

3.1. Clustering of analytical procedures

Analysis starts from hierarchy model construction, where the main aim is to find the best methodology for resveratrol determination. First task is to define a set of criteria, sub-criteria and alternatives. Large amount of parameters is a significant problem. It is solved by dividing criteria into 3 groups and establishing sub-criteria, what is described in a previous subsection. As it is also mentioned earlier, AHP is applicable if the number of the available alternatives is low. As the initial number of alternatives is 19 it is needed to apply a method of data dimensionality reduction. Cluster analysis is a good choice as it is very simple to use and widely accepted data clustering method. The clustering interpretation is set to 60 % of the distance to maximum distance ratio. Therefore, for initial AHP analysis, instead of 19 alternatives 5 clusters of alternatives are ranked to select the most beneficial cluster, that is considered in further calculations. Fig. 1 shows clustering outcome.

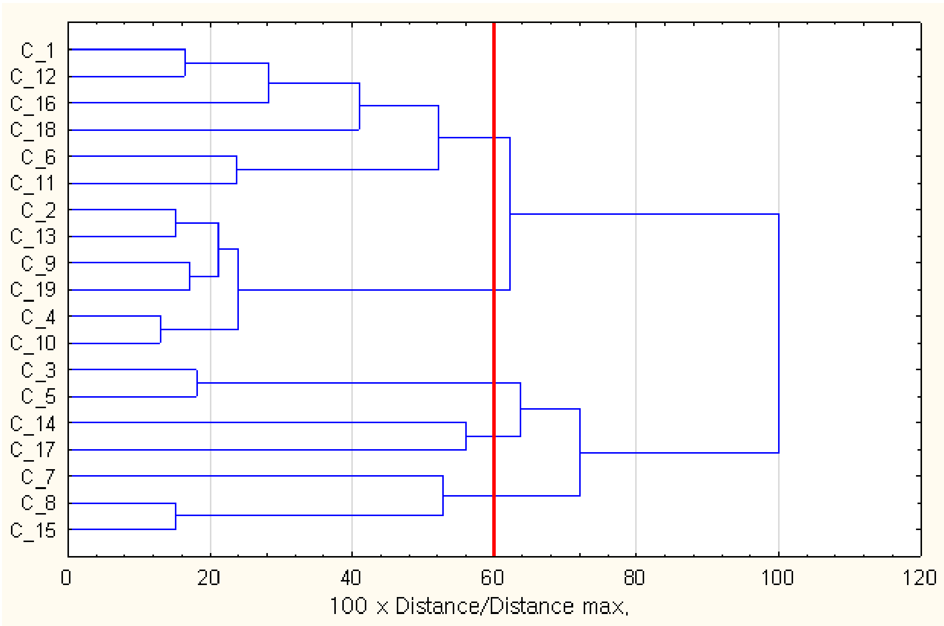


Figure. 1. The results of clustering of analytical procedures with CA

Selection of the best analytical procedure for resveratrol determination is presented in 2 stages. In the first one, assessment of 5 groups (5 Clusters) as the alternatives is conducted. In the second one, the selection of the optimal procedure from the winning cluster is performed. Standardized mean values of criteria for groups of alternatives obtained from the first step, are input data to AHP model.

The first cluster contains four analytical procedures based on liquid chromatography, one electrochemistry and one chemiluminescence based procedure. Very high sample throughput is the discriminator for this group. The second cluster consists of five liquid chromatographic procedures with or without sample preparation and one electrophoresis based procedure. They are characterized by good precision and low number of procedural steps (these two variables can be connected as precision depends on the number of operations). Third cluster contains two gas chromatography based procedures. The discriminators for this cluster are; poor precision, very high reagents price, but low toxicity and numerous procedural steps. Fourth cluster gathers two liquid chromatographic procedures that are characterized by high limits of detections, poor precision and high requirement of sample volume. Fifth cluster contains two gas chromatographic and one liquid chromatographic procedures. The discriminators for this cluster are high reagents toxicity and high waste generation. However, they allow to determine other analytes than resveratrol.

3.2. AHP model creation

According to the scheme of hierarchy model on Fig. 2, main goal, criteria, sub-criteria and alternatives are defined and particularly divided into specified groups. All of them are put in right hierarchical order. Then connection between them is proposed. The goal is connected to each of the criteria, each criterion is linked with sub-criteria and each sub-criterion is connected to each of the alternatives.

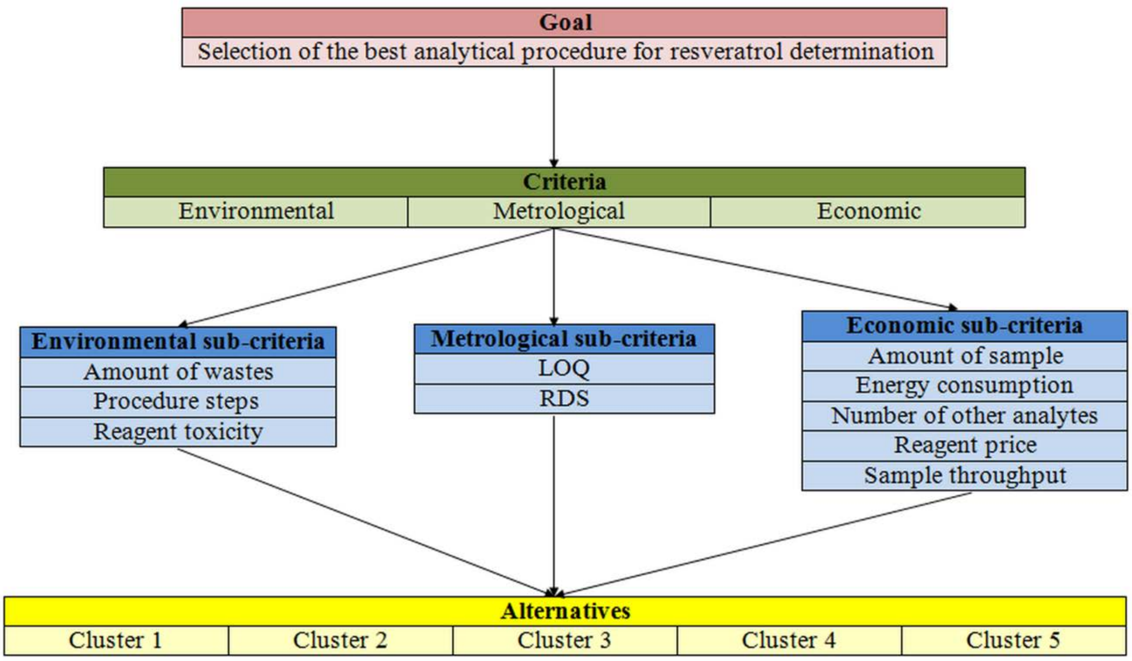
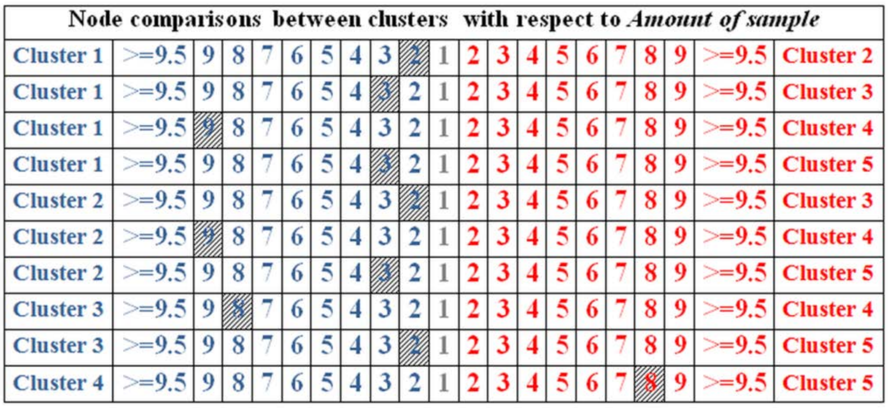


Figure. 2. Hierarchical structure of AHP model for selection of best analytical procedure for resveratrol determination – first stage clusters ranking

After building a proper model, questionnaire is given to an expert, to set the relative importance of criteria. Their preferences in pair-wise comparisons are defined by using the Saaty`s 9-degree scale. This evaluation is made for criteria with a respect to main goal, then for sub-criteria with a respect to the each group of criteria, and finally for alternatives with a respect to each sub-criteria. Making pair-wise comparisons of each two alternatives, is based on determining, which is smaller/bigger and estimate how many times (multiples). For this purpose, calculations are made using Microsoft Excel. Here also Saaty`s Fundamental Scale is used. Then given results are introduced into matrix. With reference to rules and mathematical equations presented in section *2.1. AHP technique*, pair-wise comparison between elements in model are conducted. In Fig. 3 the sheet for pair-wise comparison among clusters with respect to *Amount of sample* using Super Decision software ispresented. As it is showed in the first line, basing on parameters` values, analytical procedures classified in Cluster 1 are equally to moderately more important than those placed in Cluster 2.



Node comparisons between clusters with respect to *Amount of sample*																				
Cluster 1	>=9.5	9	8	7	6	5	4	3	**2**	1	2	3	4	5	6	7	8	9	>=9.5	Cluster 2
Cluster 1	>=9.5	9	8	7	6	5	4	**3**	2	1	2	3	4	5	6	7	8	9	>=9.5	Cluster 3
Cluster 1	>=9.5	**9**	8	7	6	5	4	3	2	1	2	3	4	5	6	7	8	9	>=9.5	Cluster 4
Cluster 1	>=9.5	9	8	7	6	5	4	**3**	2	1	2	3	4	5	6	7	8	9	>=9.5	Cluster 5
Cluster 2	>=9.5	9	8	7	6	5	4	3	**2**	1	2	3	4	5	6	7	8	9	>=9.5	Cluster 3
Cluster 2	>=9.5	**9**	8	7	6	5	4	3	2	1	2	3	4	5	6	7	8	9	>=9.5	Cluster 4
Cluster 2	>=9.5	9	8	7	6	5	4	**3**	2	1	2	3	4	5	6	7	8	9	>=9.5	Cluster 5
Cluster 3	>=9.5	9	**8**	7	6	5	4	3	2	1	2	3	4	5	6	7	8	9	>=9.5	Cluster 4
Cluster 3	>=9.5	9	8	7	6	5	4	3	**2**	1	2	3	4	5	6	7	8	9	>=9.5	Cluster 5
Cluster 4	>=9.5	9	8	7	6	5	4	3	2	1	2	3	4	5	6	7	**8**	9	>=9.5	Cluster 5

Figure. 3. Sample comparison results on 9-point scale

According to the given weight values from the questionnaire, which represent decision maker preferences, it is found, that the environmental aspect has 20% impact on the main assessment goal, while the metrological and economic aspect, 60% and 20%, respectively. It is understandable, that expert values the metrological performance of analytical procedure are very high in comparison to environmental and economic performance. The results from weighting sub-criteria with a respect to each criterion as the percentage importance are presented in Table 5.

Table 5 Weighting of sub-criteria with a respect to each criterion - percentage influence on each group of criteria

Economic		Environmental		Metrological	
Sub-criteria	Influence [%]	Sub-criteria	Influence [%]	Sub-criteria	Influence [%]
Amount of sample	6.364	Amount of wastes	20	LOQ	50

Energy consumption	9.994	Procedure steps	20	RDS	50
Number of other analytes	45.32	Reagent toxicity	60		
Reagent Price	9.463				
Sample throughput	28.858				

Due to the expert`s opinion, taking into account economic aspect, the most important is the number of other analytes, which may be determined by using one method, followed by sample throughput. On the other hand, from the environmental point of view, the influence of reagent toxicity influences on environmental criteria in around 60%, so it is the major parameter in this group. When it comes to the metrological point of view, both parameters: LOQ and RSD, are also characterized by the same importance. The results of expert's opinion, on the importance of criteria on the final ranking show, that RSD and LOD have the highest weight.

After the weighting process, CI and CR indexes are checked. In all comparisons, the inconsistency value is smaller than 0.1, so the consistency level is satisfactory and evaluation within the matrix is acceptable. It gives an information, that the judgments are trustworthy, thus the results obtained can be considered reliable. What is the most important, the AHP allows to indicate sequentially, which judgments are the most inconsistent. In this way the value, that best improves consistency is suggested [29]. However, this is not always leading to a more accurate set of priorities, which corresponds to decision-makers` preferences. Greater consistency does not imply greater accuracy. Nevertheless, one should strive to achieve an acceptable level of consistency.

3.3. Ranking of alternatives

The AHP ranking results show, that the best group of alternatives is Cluster 2, what is presented on Fig. 4. The Raw column is read directly from the Limit Supermatrix. The Normalized values are obtained from them by summing and dividing each by the sum. Thus the Normals column presents the results in the form of priorities, what is usual way to report the results. While the Ideals are obtained by dividing the Raw values by the largest raw value.

Name	Graphic	Ideals	Normals	Raw
Cluster 1		0.615809	0.201743	0.067248
Cluster 2		1.0000000	0.327606	0.109202
Cluster 3		0.663172	0.217259	0.072420
Cluster 4		0.238161	0.078023	0.026008
Cluster 5		0.535304	0.175369	0.058456

Figure. 4. Final result for the first stage of analysis

Second rank is taken by Cluster 3, follow by Cluster 1 and Cluster 5. The difference between these 3 groups is insignificant. Cluster 4 is last in ranking. Analytical methodologies included in this group are the least preferred by decision-makers.There are two procedures in this cluster, viz high performance liquid chromatography coupled to ultraviolet absorption and turbulent-flow chromatography coupled liquid chromatography with mass spectrometry as detection technique. Both of these procedures are characterized by high value of LOQ and RDS, what is not favorable (LOQ and RDS influences on metrological criteria in 50 %). In addition, high toxicity of reagents used in these procedures is noted, what is not desirable from the idea of green analytical chemistry (the influence of reagent toxicity influences on environmental criteria group in around 60%).

The last step of the research aims to find out, which analytical procedure from Cluster 2 is the most suitable decision-maker's requirements. In this case, new hierarchy process was constructed, as described in Figure 5.

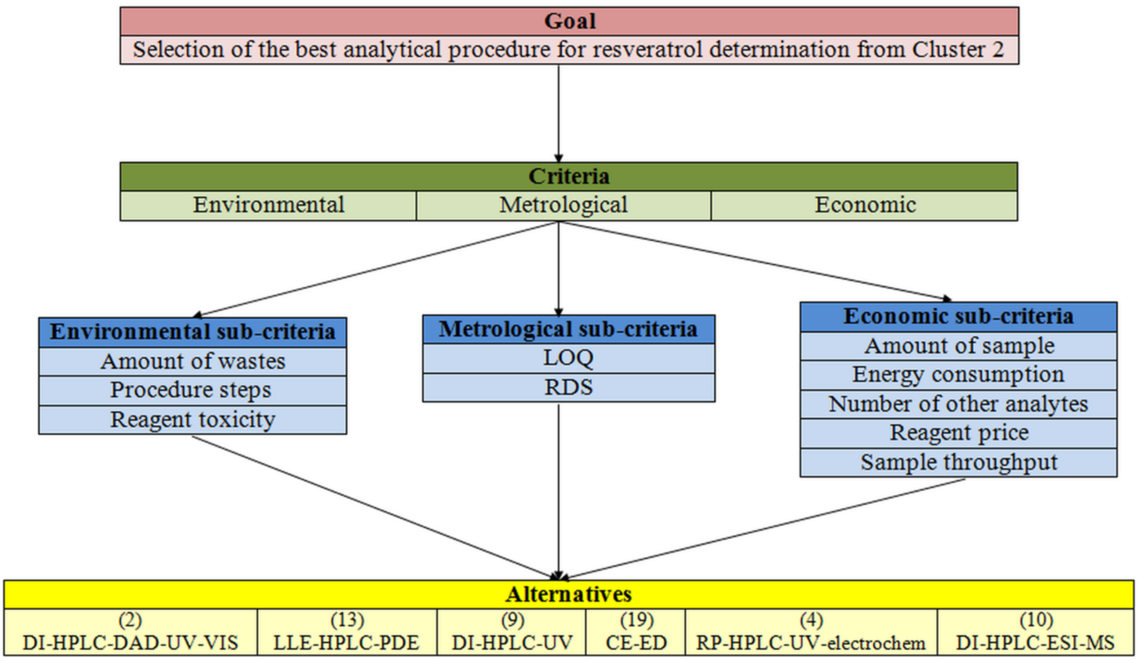


Figure. 5. Hierarchical structure of AHP model for selection of best analytical procedure for resveratrol determination – second stage, ranking within winning cluster

Goal, criteria and sub-criteria are the same, as in the first assessment step. Also the same weight values for each level with a respect to the higher level are put. Instead, alternatives are different. In this case, only Cluster 2 is taken into account. Within the group there are: DI-HPLC-DAD-UV-VIS, LLE-HPLC-PDE, DI-HPLC-UV, CE-ED, RP-HPLC-UV-electrochemical detection, DI-HPLC-ESI-MS. As it can be seen, most of the procedures are based on high performance liquid chromatography, except one, which is based on capillary electrophoresis. Most of these procedures are performed in direct way, without sample preparation step. These procedures are different in the case of final detection technique.

The inconsistency values for all comparisons does not exceed 0.1 as before in the first stage, so analysis may be continued without apprehension, that the results obtained can be unreliable. The final results show, that DI-HPLC-UV is the best analytical methodology in terms of assumed criteria and their weights, what is presented in Figure 6. This procedure is characterized by a low reagent toxicity as well as a low waste generation. Moreover, metrological parameters are satisfactory. This procedure involves only two steps, filtration and final determination. From the other site, no other analytes can be determined by application of this methodology.

Name	Graphic	Ideals	Normals	Raw
(2) DI-HPLC-DAD-UV-VIS		0.796915	0.179057	0.059686
(4) RP-HPLC-UV-electrochem		0.996484	0.223897	0.074632
(9) DI-HPLC-UV		1.000000	0.224687	0.074896
(10) DI-HPLC-ESI-MS		0.813540	0.182792	0.060913
(13) LLE-HPLC-PDE		0.245560	0.055174	0.018391
(19) CE-ED		0.598130	0.134392	0.044797

Figure. 6. Final results for the second stage of analysis

Second rank is taken by RP-HPLC-UV-electrochemical detection. The difference between these 2 analytical methodologies is insignificant. Similarly, to the above described procedure, the methodology parameters (LOQ, RSD) are very satisfying and the number of the procedure steps is low (3).However, this procedure involves reagents, which are more toxic than those utilized in procedure based on DI-HPLC-UV. In addition, higher amount of wastes is generated. Against, other analytes can be detected by the application of this methodology. Third DI-HPLC-ESI-MS is ranked, however DI-HPLC-DAD-UV-VIS is ranked just behind it. Both methodologies involve two steps, though, the latest generates more wastes. Reagents required in both procedures are characterized by the same degree of toxicity and the reagent price. However, procedure based on DI-HPLC-ESI-MS is characterized by better metrological parameters.

It is worth to notice, that generally the highest ranks are taken by method, which are based on direct injection. The results are not surprising, because the possibility of direct injection is characterized by many advantages. First of all in this case sample preparation stage is avoided and so number of analytical steps – one of assessment criteria. This operation is related to production of lots of waste, consumption of lot of time and it is also a source of most errors during the analysis. It is also connected with environmental aspect. While indirect injection, no solvents are required. That is why, these methodologies may be called as green ones. Moreover, all of these procedures are characterized by good analytical parameters.

The last one in the ranking from the Cluster 2 is LLE-HPLC-PDE. This is consistent with the results obtained above, due to fact, that this methodology includes liquid-liquid extraction. This one is characterized by inverse properties than those taking into account direct dosing.

It's worth pointing out, that the results obtained relate only to this specific case, where weight values for each criteria - environmental, metrological, economic are established on 20%, 60% and 20%. If we modify the weights, for instance on 25%, 50%, 25% respectively, then the results will be essentially the same. Changes of criteria`s or sub-criteria`s weights while maintaining similar values` relations, will not influence outcomes significantly. The tool, that may predict how much changes of parameters` values will affect final score is Sensitivity Analysis [30]. Super Decisions software also makes possible to perform a complex sensitivity analysis. However, it is not applied in this case study, due to fact, that it is not the main aim of the study and values are based on questionnaire`s results indicating stakeholders` preferences.

4. Summary

AHP algorithm applied in the selection of the most appropriate analytical procedure is a useful tool. Application of the methodology, presented in this study, allows to select the best solution in proper way concerning various criteria. The large dataset, inappropriate for AHP assessment is reduced with CA. Such procedure leads to rank analytical procedures considering metrological parameters as well as environmental and economic aspects. The application of presented methodology for the selection of proper analytical methodology for determination of selected analytes can be considered green, since low environmental impact is noticed.

For the first time AHP is used for selection of optimal analytical procedure due to decision makers` preferences. Nowadays, conducting chemical analysis in accordance with sustainable development is challenging. AHP algorithm is an valuable aid to find a compromise between metrological, environmental and economic aspects.

In this study, the AHP is applied for data analysis obtained for procedures used for determination of trans-resveratrol in wine samples. The procedure ranked as the best is based on direct injection-high performance chromatography coupled to ultraviolet absorption spectrophotometer. This proves the competitiveness of direct analytical procedures. Moreover, the procedure DI-HPLC-UV is also characterized by good metrological parameters. The application of Super Decisions software is easy to be applied and can be used as routine tool for analytical procedures comparison.

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Compliance with Ethical Standards

Conflict of Interest: Magdalena Fabjanowicz declares. that she has no conflict of interest. Marta Bystrzanowska declares, that she has no conflict of interest. Jacek Namieśnik declares, that he has no conflict of interest. Marek Tobiszewski declares, that he has no conflict of interest. JustynaPłotka-Wasylka declares, that she has no conflict of interest.

Ethical approval: This article does not contain any studies with human participants or animals performed by any of the authors.

Informedconsent: Not applicable.

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