



Exploratory analysis and ranking of analytical procedures for short-chain chlorinated paraffins determination in environmental solid samples [☆]



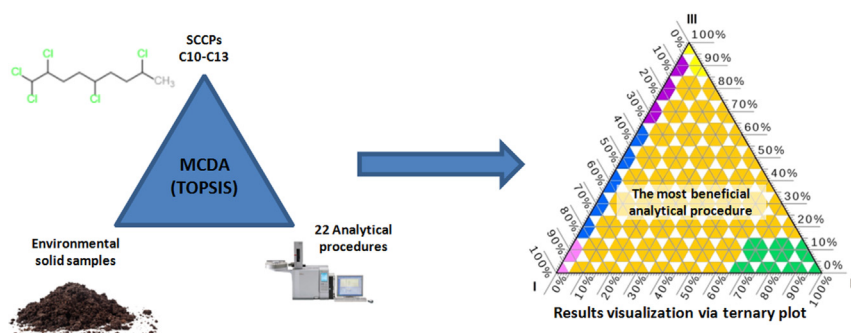
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HIGHLIGHTS

- MCDA with chemometrics allows to select analytical method for SCCP determination.
- Ternary plots are useful in modeling different weights of criteria.
- The presented approach is useful in assessing analytical procedures greenness.
- The presented methodology can be used in various decision making processes and as a sensitivity analysis.

GRAPHICAL ABSTRACT



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ABSTRACT

Short-chain chlorinated paraffins are ones of the most recent chemical compounds that have been classified as persistent organic pollutants. They have various applications and are emitted to the environment. Despite the fact, that the content levels of these compounds in the environmental compartments should be monitored, there is still a lack of well-defined and validated analytical procedures, proposed or suggested by the national or international environmental protection agencies. Finding an appropriate analytical procedure (sensitive and green at the same time) from many available ones is very often a difficult task. Therefore it can be supported with multicriteria decision analysis. The dataset consisting of 22 procedures was described by 7 criteria, mainly referring to procedures greenness. The data treatment with cluster analysis and principal component analysis revealed the internal structure of the dataset. Moreover, both statistical tools allowed for reduction of dataset criteria to three. This was used for applying ternary plot to show the multicriteria decision analysis results within all possible weights. With the aid of chemometric and multicriteria decision analysis tools it was easy to assess the set of analytical procedure. Depending on the applied weights to assessment criteria different analytical procedures are the most appropriate (winners).

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[☆] *Capsule:* Multicriteria decision analysis combined with multivariate statistics allows to select sustainable procedure for SCCPs determination in environmental solid samples.

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1. Introduction

The short-chain chlorinated paraffins (SCCPs) are one of the main group of chemical compounds classified as a chlorinated n-alkanes (also commonly referred to as a chlorinated paraffins) in which the carbon chain length ranged from C10 to C13 and the degrees of chlorination varies from 40% to 50% (by weight) (Fiedler, 2010; Sun et al., 2017). Considering the SCCPs

physicochemical properties (high chemical stability, high viscosity, low vapor pressure) they have been widely used as flame retardants (FR) and plasticizers in wide spectrum of commercial and consumer products or as the parts of indoor equipment, such as rubbers, paints, inks, textiles, varnishes and adhesives. As a consequence of their high production volumes and toxicity, SCCPs are considered as a serious environmental threat (Zhang et al., 2017). It is caused by the fact that they are released directly to the environment during their production and indirectly during the use of commercial and consumer products made of synthetic materials. The SCCPs were classified by International Agency for Research on Cancer (IARC, 1990) as possible carcinogens (listed in group 2B) (Cao et al., 2017). As a result, in 2017 the SCCPs were classified by the experts of Stockholm Convention as one of the new categories of Persistent Organic Pollutants (POPs) (Liu et al., 2017; Li et al., 2014). This statement warrants to perform the research aimed at monitoring of the presence of these compounds in various compartments of the environment. Despite the fact, that the SCCPs compounds have been significantly limited or banned in the United States, Japan, Canada and European Union, they are still produced and consumed in a significant amounts in other parts of the World (Xia et al., 2019). Because of this, the SCCPs might be found in urban air, indoor air, house dust, aquatic environment, sediments, soils, animal feed materials, food products and biota (Dong et al., 2019).

The analytical procedures generally employed for SCCPs determination in environmental samples are a complex processes, which have two main drawbacks (Bayen et al., 2006). First one is associated with the use of a significant amount of organic solvents during the sample preparation process, especially in a case of ordinary solvent extraction (SE). This phenomenon might be limited by application of assisted extraction techniques such as accelerated solvent/pressurized liquid extraction technique (ASE/PLE) or ultrasound solvent extraction technique (USE) (Eljarrat and Barceló, 2006). The application of this alternatives gives a possibility to significantly reduce the wastes generation without the loss of extraction efficiency (van

Mourik et al., 2015). The second drawback is the quantification of SCCPs in environmental samples. Mainly it is caused by the lack or very limited accessibility of appropriate reference standard solutions or reference standard materials, their highly complex nature and low response to the most commonly used detection systems (Chen et al., 2013). To obtain the reliable analytical information about SCCPs congeners in environmental samples it is required to use one of the proposed solutions (Yuan et al., 2017; Schinkel et al., 2018): (i) complex SCCP solutions that contain characteristic carbon chain length deliveries and are characterized by different degrees of chlorination; (ii) single-chain SCCP solutions that consist of homologues of a single carbon chain length and are characterized by not the same degrees of chlorination; (iii) well-defined SCCP compounds that are clearly characterized by carbon chain length, chlorine number as well as chlorine position; (iv) isotopically labeled SCCP compounds with the appropriate characterized specific composition. The SCCPs determination in environmental, food or biological samples requires advanced analytical techniques, mainly at the separation and final determination stages (Schinkel et al., 2018; Pellizzato et al., 2009). As a result, there is an urgent need to gather the most important data about the various types of analytical procedures for SCCPs determination and to select the most optimal solution (Figs. 1 and 2).

Ternary plot as a graphical data presentation method allows to depict the ratios of the three variables as positions in an equilateral triangle. The advantage of using ternary plot is that three variables can be conveniently plotted in a two-dimensional graph. This manner of visualization is mostly used to describe a composition of three component system (Dhoot et al., 2018). The rules for reading and plotting compositions are well known. In brief, a ternary system consists of three components, where each apex of the triangle indicates one of the pure components A, B, or C. In a ternary system every point represents a different composition of the three components. The space inside the triangle is divided into a set of small equilateral triangles which can be further subdivided to make it easier to read coordinates by more precise location of

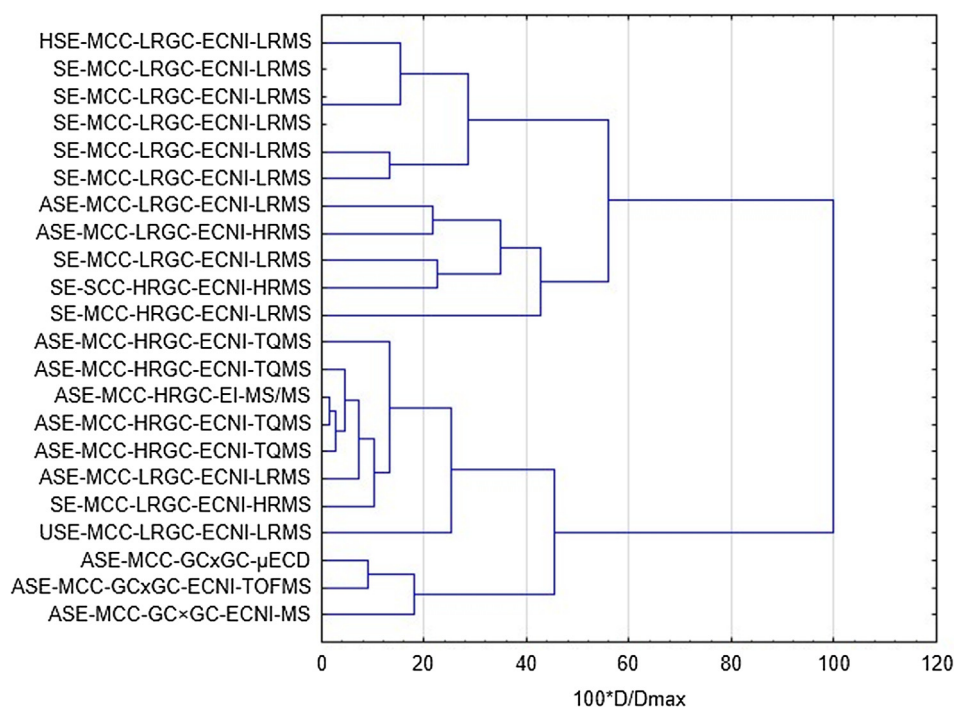


Fig. 1. Clustering of variables in case of SCCPs determination in solid samples using Cluster (Explanation of figure caption acronyms: GCTIME – time of chromatographic analysis, CLUPSOLV – amount of solvent during cleanup, CLUP – number of cleanup steps, MDL – method detection limit, EXSOLV – amount of extraction solvent, EXTIME – extraction time, SAMPL – sample mass).

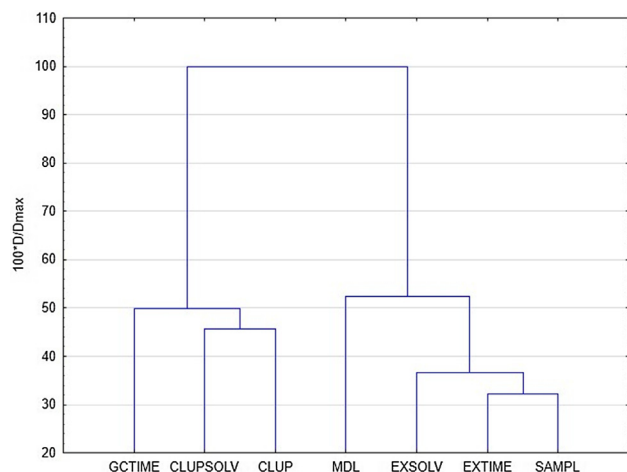


Fig. 2. Grouping of analytical procedures for SCCPs determination with Cluster Analysis.

the composition. The sum of three components A, B and C represents 100%.

Triangle projection is commonly used method in chemical sciences. The most well-known Gibbs triangle is used for visualization three-component mixtures in chemistry or material sciences (Basso et al., 2013). Additionally, ternary may be used to perform sensitivity analysis (SA). In more mathematical sense, SA provide studies of how the uncertainty in the output of a model (numerical or otherwise) can be apportioned to different sources of uncertainty in the model input (Saltelli et al., 2004).

The aim of the study is finding internal patterns in the dataset describing analytical procedures for SCCPs determination in environmental solid samples (soil and sediment) and selection of the most appropriate one from among 22. The application of Principal Component Analysis (PCA) and Cluster Analysis (CA) allow to select the groups of variables or reduce the number of variables to multicriteria decision analysis. Here, to overcome the problem of subjectivity of weights assignment the ternary graph is used to present the ranking results for entire range of weights assigned to criteria.

Table 1
Analytical procedures taking into consideration during the described studies.

No.	Analytical protocol acronym	Sample type	Ref.
1	HSE-MCC-LRGC-ECNI-LRMS	bottom sediment from the Czech Republic	(Štejnarová et al., 2005)
2	ASE-MCC-LRGC-ECNI-LRMS	bottom sediment from Pearl River and the Pearl River Estuary (China)	(Geiß et al., 2015)
3	ASE-MCC-HRGC-ECNI-TQMS	bottom sediment of the Bohai Sea (China)	(Ma et al., 2014)
4	SE-MCC-LRGC-ECNI-LRMS	urban soil of Shanghai	(Wang et al., 2014)
5	SE-MCC-LRGC-ECNI-LRMS	marine sediment from coastal area of Barcelona (Spain)	(Castells et al., 2008)
6	SE-MCC-LRGC-ECNI-LRMS	river sediment from the Yellow River (China)	(Li et al., 2018)
7	ASE-MCC-HRGC-ECNI-TQMS	soil from e-waste dismantling area (China)	(Yuan et al., 2017)
8	ASE-MCC-GCxGC-μECD	soil and bottom sediment	(Muscalu et al., 2017)
9	ASE-MCC-GCxGC-ECNI-TOFMS	river sediment from the Yellow River (China)	(Qiao et al., 2016)
10	SE-SCC-HRGC-ECNI-HRMS	river sediment from the Detroit River (USA)	(Tomy et al., 1997)
11	ASE-MCC-HRGC-EI-MS/MS	soil from Taizhou (China)	(Bo et al., 2010) (Yuan et al., 2010)
12	ASE-MCC-GC × GC-ECNI-MS	soils and sediments from an e-waste dismantling area (China)	(Xu et al., 2019)
13	USE-MCC-LRGC-ECNI-LRMS	agricultural surface soil (China)	(Aamir et al., 2019)
14	ASE-MCC-HRGC-ECNI-TQMS	soil and sediment from Shandong Peninsula (China)	(Zhao et al., 2019)
15	SE-MCC-LRGC-ECNI-HRMS	soil from Switzerland	(Bogdal et al., 2017)
16	SE-MCC-LRGC-ECNI-LRMS	suburban soils of Shanghai	(Wang et al., 2017)
17	SE-MCC-LRGC-ECNI-LRMS	sediments from Huangpu River (Shanghai)	(Wang et al., 2019)
18	ASE-MCC-LRGC-ECNI-HRMS	background soils from Western Europe	(Halse et al., 2015)
19	SE-MCC-HRGC-ECNI-LRMS	sediments from the Laizhou Bay (China)	(Pan et al., 2018)
20	ASE-MCC-LRGC-ECNI-LRMS	sediment of the urbanized coastal (Pearl River Delta, Shenzhen, Hong Kong, Tokyo Bay)	(Zeng et al., 2017)
21	ASE-MCC-HRGC-ECNI-TQMS	soil from Fildes Peninsula at King George Island and Ardley Island, Antarctica	(Li et al., 2016)
22	SE-MCC-LRGC-ECNI-LRMS	surface soil from Guangzhou suburban area (China)	(Chen et al., 2013)

Acronyms listed in the table: ASE – accelerated solvent extraction; ECNI – electron capture negative ionization; HRGC – high-resolution gas chromatography; HSE – hot solvent extraction; LRGC – low resolution gas chromatography; LRMS – low resolution mass spectrometry; MCC – multilayer clean-up column; SCC – single layer clean-up column; SE – Soxhlet extraction; TQMS – triple quadrupole mass spectrometer; USE – ultrasonic extraction; μECD – micro-electron capture detector;

2. Materials and methods

2.1. Dataset collection, alternatives and criteria

Statistical analysis in terms of economic and environmental aspects has been subjected to the analytical procedures employed in the process of the determination of the content level of SCCPs in environmental solid samples, such as the soil and bottom sediment. This type of samples has been selected, due to the fact that it is a common research subject, mainly it is caused by the ability to determine the impact of local industrial centers manufacturing the various types of synthetic materials (in some regions the SCCPs are still added as the components of the synthetic materials) on the environment, characteristic samples composition and the fact that bottom sediment and soil in many cases are one of the endpoints transport paths of SCCPs in the environment (the deposition and enrichment of SCCPs on the solid samples surface). The assessment would be more comprehensive if precision and recovery were also included, apart from LOD. Unfortunately, precision data were not stated in the most of papers, if included they were very similar and therefore did not carry any variability. Recovery, if stated, was presented as range of values for the group of analytes and therefore, not applicable as input data.

The basic input data for further statistical analysis were parameters characterizing different analytical methods developed to SCCPs determination in environmental solid samples, especially soil and bottom sediment. In the following studies, 22 analytical protocols (see Table 1) described in detail in the scientific literature and employed to SCCPs determination in soil and bottom sediment samples were the subject of evaluation. The analytical procedures that were not fully characterized in terms of applied criteria could not be taken to analysis. The vast majority of them is associated with the solvent extraction assisted with appropriate analytical extraction equipment, application of multilayer clean-up column at the stage of sample preparation and the gas chromatography combined with the mass spectrometer working in electron capture negative ionization mode.

Analytical methods (Table 2) assessment criteria consider the analytes extraction process, extracts clean-up associated with the use of organic solvents and inorganic acids, time consumption

Table 2

The criteria that were employed to describe dataset of analytical protocols for SCCPs determination in environmental solid samples.

Variable	Explanation	Acronym
Extract clean-up process	The application of inorganic acids such as H ₂ SO ₄ and HCl during the extracts clean-up process	CLUP
Amount of organic solvents in clean-up process	Total amount of organic solvents utilized in the extracts clean-up procedure [mL]	CLUPSOLV
Extraction solvent	Total amount of extraction solvents utilized in the defined procedure [mL]	EXSOLV
Extraction time	Total time needed to perform the extraction process with applied extraction technique [h]	EXTIME
GC working time	Total time of GC analysis of a single sample (single injection) [min]	GCTIME
MDL	Method Detection Limit of the SCCPs [ng·g ⁻¹]	MDL
Amount of sample	The amount of solid dry sample needed to perform the analysis [g]	SAMPL

during the chromatographic separation and basic validation parameter. Almost every analytical procedure described in the literature, after the analytes extraction it was necessary to clean up the obtained extracts to remove the potential sulfur organic compounds (copper application activated by HCl solution) and other organic compound (by the application of acid silica gel – with H₂SO₄), which might interrupt the final determination process and influence on the final results. The type of solvent was considered on the basis of total analytical hazard value presented in other study (Tobiszewski and Namieśnik, 2015). To consider the amount and hazards related to different types of solvents total analytical hazard values were multiplied by the volumes required in each analysis.

2.2. Cluster analysis

The high number of criteria and alternatives may sometimes negatively influence the results of analysis, especially consistency of the judgments in a reference to large amount of data. Therefore, the number of these factors, being the input data, should be reduced (summarized in Table 2). This can be obtained with well established chemometrics method called Cluster Analysis (CA) (Trebuña and Halčinová, 2012). It belongs to multivariate statistical tools, which may be useful in an analysis to split the variables or objects into reasonably homogeneous groups. This division is performed according to the similarity or dissimilarity of elements. Variables and objects in chemometrics are represented by different equivalents in Multicriteria Decision Analysis (MCDA), criteria and alternatives, respectively.

In brief, in case of clustering without supervision, the unsupervised algorithm finds internal patterns in the dataset with no *a priori* information or assumptions about the dataset. More details about the algorithm may be found elsewhere (Massart and Kaufman, 1983). In CA the way, on which similarity (dissimilarity) of elements will be determined could be define be the degree of correlation, association or distance (Trebuña and Halčinová, 2012). In this case the last one is applied. The grouping of variables and objects is performed with Euclidean distance measure and Ward cluster formation method. Firstly, parameters describing analytical procedures are divided into three clusters (the clustering interpretation is set to 51% of the distance to maximum distance ratio as we require three clusters for further analysis), then analytical procedures are grouped into clusters and subclusters. Clusters, means group of elements, which are characterized by some similarities between them. After standardization of initial dataset, calculations for CA are performed with Statistica 12 software (StatSoft Polska Sp. z o.o.).

2.3. Principal component analysis

One of the most widely used techniques for dimensionality reduction is Principal Component Analysis (PCA) (Abdi and Williams, 2010). The main goal of this multivariate statistical technique is to extract the important information from the large dataset. In other words, its aims at increasing the interpretability with

the least possible loss of information. It is possible by creating new uncorrelated variables that successively maximize variance. The new orthogonal variables, that express some information are called principal components (PCs). The pattern of similarity among the elements may be displayed as coordinates in the system or points in maps (Jolliffe, 2002). In brief, mathematical treatment of the input data matrix with PCA, where objects are described by many variables, is based on limitation of many variables to small number of factors. Therefore, the original dimension of the input data matrix is reduced to two parts – factor loadings and factor scores. The first one includes the weights of each variable in each factor (new latent variable). Therefore, if this weight is high, it means that the contribution of the original variable is also high. Accordingly, it is possible to identify which variables influence the objects. Thus, it allows to designate factors that are significantly important for the main aim of an issue. PCA calculations were done with Statistica 12 software (StatSoft Polska Sp. z o.o.).

2.4. Technique for order of preference by similarity to ideal solution

One of MCDA algorithms is TOPSIS (*Technique for Order of Preference by Similarity to Ideal Solution*). This expert system for decision making was developed by Hwang and Yoon in 1981 (Hwang and Yoon, 1981). The analysis leads to final ranking of considered alternatives, therefore selection of the best option among all available ones is possible. Finding a winner in case of TOPSIS is based on choosing the alternative that simultaneously has the shortest distance to the positive ideal solution and at the same time the farthest distance to the negative ideal solution.

The assessment procedure for MCDA can be performed in few steps (Bystrzanowska and Tobiszewski, 2018). At the beginning, the main aim of the analysis should be indicated. Thus, in this particular case study, analysis is connected with selection of the best analytical procedure for SCCPs determination in environmental solid samples. The inherent elements of MCDA methodology are criteria and alternatives, which then should be specified. In general, criteria are groups of parameters that describe each available option (alternative) and hence make the evaluation possible. Bearing in mind some issues connected with SCCPs determination, seven criteria are taken into account (Table 2). Hence, these parameters are related to different parts of analytical procedure – from sample preparation to final determination. Alternatives are available options taken into considerations. For SCCPs determination in environmental solid samples, there are analytical procedures, involving different analytical techniques, as it is described in Table 1. In case of MCDA methods application, all the factors must be in a form of numerical values or they must be easily transformable into them.

Next step of MCDA assessment is assigning a proper weight value to each criterion. It means, that it is possible to indicate which criteria are more or less important from the point of view of the main analysis aim.

The last step is application of TOPSIS. The basis of its algorithm involve the input data as a matrix consisting of *n* alternatives and

described by m criteria. TOPSIS mechanisms can be described in several steps as described in other papers (Bystrzanowska et al., 2019a; Bystrzanowska et al., 2019b). All TOPSIS calculations are performed in Excel program (Microsoft Office 2016).

3. Results and discussion

3.1. Exploratory analysis

The first stage of analysis is grouping of variables with cluster analysis. Two well-formed groups of variables are formed. The first group is associated with the first stages of analysis – extraction solvent, extraction time and sample size. This can be explained by the high solvents requirements and long extraction time to extract SCCPs from sample of larger size. Another variable that is more loosely connected to this cluster is method detection limit. This is in contrary with the intuition as it would be expected to achieve lower MDLs when higher sample mass, extraction solvent volume and extraction time are applied.

The second cluster is formed by the variables that are related to latter parts of analysis. It seems to be obvious that higher number of clean-up operations is related to larger consumption of organic solvents. More loosely related variable is the time of chromatographic separation.

The next part of the study was clustering of the objects with CA. Two very well formed clusters are observed and within each cluster two subclusters are formed. The lower group is mainly formed by procedures based on accelerated solvent extraction – based sample preparation. The upper group of objects is formed mainly by procedures that are based on Soxhlet extraction. Both of groups can be further divided into subgroups. The separation into subgroups in the first case can be explained by differences in final determination technique – procedures 8, 9 and 12 are based on GC × GC, while second subgroup is formed by procedures based on other final determination technique. The reason for formation of two subgroups in the second cluster remains unexplained.

The second part of explanatory analysis is the application of PCA for further exploration and limitation of the number of variables to MCDA. The slope analysis indicates that PC1 explains 41.2%, PC2 15.8% and PC3 15.3% of initial total variability. As a result three first principal components explain 72.4% of initial total variability. Although PC4 explains 12.9% of total variability and normally would be included in further considerations, the aim of PCA in this particular case is to limit the number of variables to three principal components. For this reason PC4 is not included in next parts of the study. The factor loadings to the first three principal components are presented in Table 3.

The factor loading to three PCs to large extend confirm the clustering obtained with CA. Sample mass, extraction time and extraction solvents have strong factor loadings on PC1 as it was observed in case of CA results. Similarly to previous results, MDL is loosely related to this group of variables. What was not observed in case of CA results is negative loading of “solvents used during clean-

up” variable. PC2 is positively loaded with three variables – sample mass, number of clean-up steps and GC separation time. This result deviates from those obtained with CA. PC3 is positively loaded with MDL and chromatographic separation time.

The application of statistical tools as CA and PCA allow to select and reduce the number of variables for further utilization for multicriteria decision analysis. The application of different algorithms applied in this area may lead to slightly different results of grouping analysis.

3.2. Ranking analysis

MCDA methods, including the TOPSIS algorithm allow to obtain results of analysis in a form of a ranking of available options. Positions in a ranking strongly depend on the preferences of the decision maker that are expressed as the weight values assigned to the criteria. In the simplest case, there are no dominant criteria, so weights for all criteria are equal. Usually, it is more desirable to apply the weights of individual factors to differentiate the importance of criteria. It is obvious, that with changing the weights values, the ranking results will also change. This dependence can be shown graphically using ternary plot, commonly known in chemistry as a Gibbs triangle.

In this study, ternary plot is used to present the winning analytical procedures, within variety of weights for individual components. To our best knowledge, it is the first case study in chemistry field, where TOPSIS and its SA are combined and their results visualized using ternary plot projection. Components are groups of criteria taken into evaluation in TOPSIS algorithm. The step value on each axis is set every 10%, so this value can be treated as weight resolution. In Figs. 3 and 4 the results of TOPSIS analysis for finding the most appropriate analytical procedure for SCCPs determination in environmental solid samples are shown. The winning analytical procedures with certain weight proportions of the components have been marked with different colors. It is worth to mention that obtaining the three components has been reached by two methods – CA and PCA.

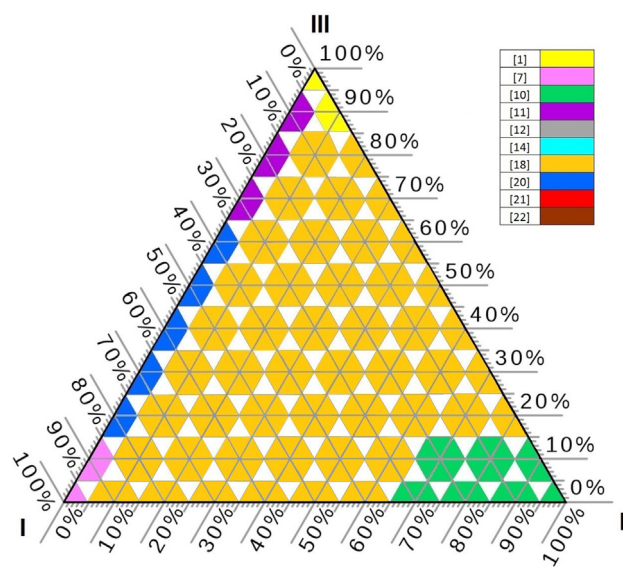


Fig. 3. Visualization of TOPSIS analysis combined with CA for selection of the most preferable analytical procedure in case of SCCPs determination in environmental solid samples as form of Gibbs Triangle (I – sample mass, amount of extraction solvent and extraction time, II – time of chromatographic analysis, amount of solvent during cleanup and number of cleanup steps, III – procedure detection limit).

Table 3
Factor loadings to the first three principal components. Loadings $>|0.5|$ are bolded.

Variable	PC1	PC2	PC3
SAMPL	0.726	0.569	-0.213
EXTIME	0.810	0.192	-0.255
EXSOLV	0.812	0.179	0.321
CLUP	-0.460	0.589	-0.319
CLUPSOLV	- 0.692	0.315	0.185
GCTIME	-0.290	0.492	0.665
MDL	0.518	-0.160	0.530

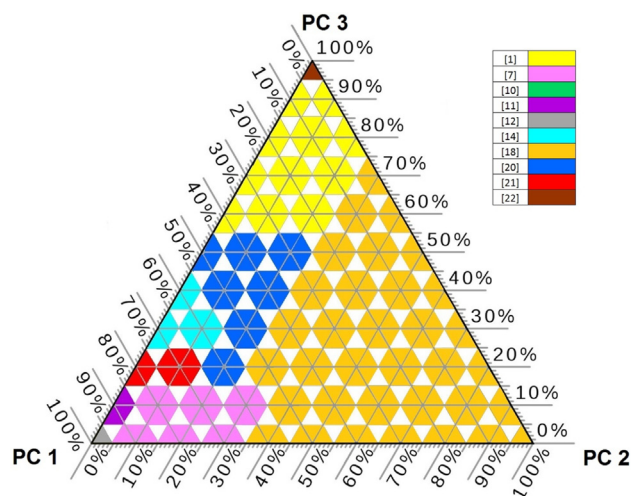


Fig. 4. Visualization of TOPSIS analysis combined with PCA for selection of the most preferable analytical procedure in case of SCCPs determination in environmental solid samples as form of Gibbs Triangle.

In Fig. 3 the winning procedure is presented within the varying weights. In each corner of ternary plot groups of criteria selected with CA are pure components – I is sample mass, amount of extraction solvent and extraction time, II is time of chromatographic analysis, amount of solvent during cleanup and number of cleanup steps, III is method detection limit. From the ternary plot it can be easily read that for the best MDL procedure 1 should be selected (yellow triangle in top of the figure), for the best greenest procedure at sample preparation step procedure 7 is the winner (bottom left pink triangle) and for green procedure at cleanup stage with short chromatographic time procedure 10 is the first choice (bottom right green triangle). The selection according to single criterion is not desirable, it is beneficial to select procedure according to all criteria at the same time. The inner part of ternary plot shows how the first rank procedure changes with varying weights. For most of combination of weights procedure 18 is the most beneficial and it should be clearly stated that it was not the first rank for any of pure components. Procedure 18 ASE-MCC-LRGC-ECNI-HRMS is based on extraction with hexane (not dichloromethane) with acetone and due to low initial sample mass (2.5 g) comparatively only 102 mL of such solvents mixture is applied. The procedure is characterized by short chromatographic run time of less than 18 min.

The second way of limitation of criteria number to fit the ternary plot is the application of PCA. As in the case of grouping of variables with CA there is no information loss, during transformation of initial variables to principal components, some of information is lost. In this case study three principal components explain 72.36% of initial variance. In case of PCA application in the corners of ternary plot pure principal components are located. In the remaining parts of ternary plot weights for different combinations of principal components are graphically presented (Fig. 4). As it was in case of dimensionality reduction with CA, the ranking results show that procedure 18 is the first rank for considerable range of weights combinations. Because some of the information is lost during calculation of principal components, the ranking results differ and procedures such as 14, 21 and 22 appear as winners and they were absent in CA rankings. We think that both CA and PCA can be applied for reduction of data dimensionality. In some specific cases the one should be selected, which allows for more clear distinction of three groups of criteria.

TOPSIS algorithm allows to obtain the ranking of alternatives and find the best option due to allocation of the positive ideal and negative ideal solutions. The most desired alternative must

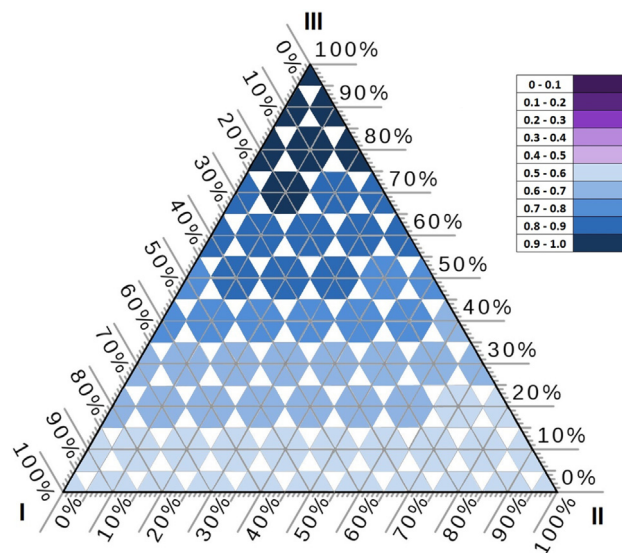


Fig. 5. Similarity to ideal solution of analytical procedure number 16 as a result of TOPSIS analysis combined with CA (I – sample mass, amount of extraction solvent and extraction time, II – time of chromatographic analysis, amount of solvent during cleanup and number of cleanup steps, III – procedure detection limit).

have the shortest distance from the ideal positive solution and furthest from the negative ideal solution of the geometric point by using the Euclidean distance. The final score of the analysis is a value that determines similarity to ideal solution. Thus, the closer value to 1, the more it reflects the perfect solution.

Application of TOPSIS method together with the ternary plot projection, allows for presentation how an alternative is close to the ideal solution, while weights are changing. An idea is presented in Figs. 5 and 6, depending on the method used for data dimensionality reduction (CA or PCA). Procedure number 16, based on GC-ECNI-MS techniques was selected as the example for further discussion. It is selected as its value of similarity to ideal solution varies strongly across applied weights. The degree of procedure's similarity to ideal solution is shown in a triangular diagram using a blue-violet color gradient – different colors for specific range of closeness. Fig. 5 shows the similarity to ideal solution score for procedure 16. It has score above 0.9 for weights close to III corner with MDL as single criterion group. With high weights for I and II groups the similarity to ideal solution falls to the range 0.5–0.6.

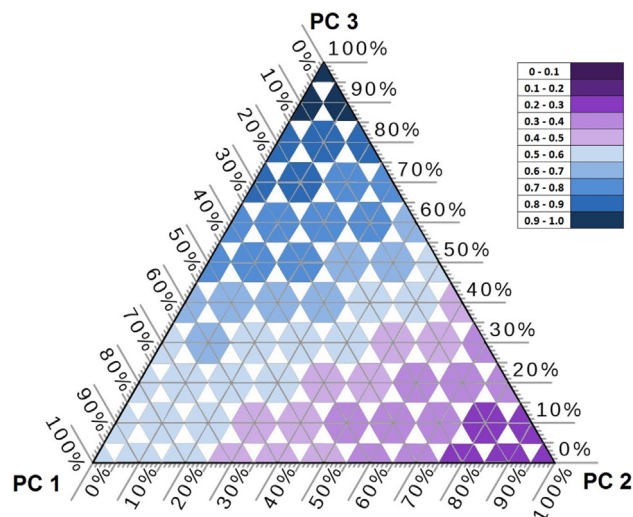


Fig. 6. Similarity to ideal solution of analytical procedure number 16 as a result of TOPSIS analysis combined with PCA.

The results of similarity to ideal solution mapping of procedure 16, for reduction of data dimensionality with PCA are presented in Fig. 6. Similar pattern is obtained as this procedure's best performance is within region of high weights assigned to III principal component. The difference here is much worse performance in region with high weights for principal component II, with the values of similarity to ideal solution in the range 0.3–0.4.

4. Conclusions

The application of TOPSIS together with PCA or CA allows to select the most beneficial analytical procedure for SCCPs determination in environmental solid samples. The application of ternary plot allows to present the best alternative and similarity to ideal solution in the function of changing weights for three groups of criteria. To reduce the number of criteria to three CA or PCA can be used, giving similar results. The presented methodology can be applied in various decision making processes and as a sensitivity analysis. In addition, the performed studies give a reason to develop new or to appropriate modify the current analytical procedure which might be considered as the reference analytical procedure for the SCCPs determination in the environmental solid samples. Taking into account obtained results, appropriately developed analytical procedure might be considered as a green solution and be the significant tool to obtain the reliable analytical information about the content level of SCCPs in studied environmental samples.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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