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Multivariate statistical comparison of analytical procedures for benzene and phenol determination with respect to their environmental impact

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ABSTRACT

The study describes the possibility of application of self-organizing maps technique to assess the greenness of analytical methodologies. The metrological and "environmental impact" parameters of procedures for benzene and phenol determination in water samples were sets of input data for chemometric analysis. Totally 47 objects and 8 variables formed the data used for analysis. The major factors responsible for non-green character of the methodology are the amount of organic solvent and amount of solid wastes formed. The results of the assessment methods with NEMI symbols and Eco-scale are in good agreement. Greener procedures for benzene and phenol determination are those based on SPME. In case of phenol the methodologies based on GC separation are much greener than those based on LC. The results also show that it is easier to apply green methodologies for benzene, as a compound with lower polarity and hence with less affinity to, than for phenol. The SOM assessment methodology can be useful in choosing the proper analytical procedures.

1. Introduction

Phenol and benzene are well-known environmental pollutants [1]. Because they are toxic and mutagenic, benzene is carcinogenic [2], there are maximum allowable concentrations set for these compounds in water. This gives obligation to monitor water quality with a certain frequency [3]. Therefore large number of water samples are analysed for the concentrations of benzene and phenol, in the laboratories worldwide. There are many analytical techniques that can be applied to determine both phenol and benzene. They are based on gas chromatographic, liquid chromatographic and other separation techniques. The sample preparation techniques involve not only liquid phase extractions and solid phase extractions but also direct analysis and others. It is without doubt that the proper selection of the analytical protocol from their great variety should be based on considering also the environmental impact of the procedure.

Green analytical chemistry is the philosophy of analysts, originating from green chemistry, based on the activities leading to minimizing the environmental impact of analytical operations [4]. There are several ways to make analytical procedures greener, including the application of microwaves [5], ultrasounds [6] or high pressure [7] to enhance the extraction efficiency, reduce extraction time and consumption of solvents. The other approaches to reduce environmental impact are application of procedures without sample preparation step [8], application of microextraction techniques, like solid-phase microextraction [9], liquid phase microextraction [10], single drop microextraction [11] and similar techniques. All these techniques are characterized by low organic solvent consumption.

The tools of reducing procedural environmental impact are relatively well established and still widely developed. The situation is different in case of tools to assess procedural impact on the environment, as there are only a few of them and they are scarcely developed. The first of the assessment methods is NEMI (National Environmental Methods Index) labelling [12]. This assessment procedure is relatively simple as only four procedural parameters are considered in a binary manner. The symbol circle has four equal parts, each representing one aspect of procedural possible environmental impact. If the procedure does not meet one of the requirements the corresponding part of the circle is not filled with colour. The procedure does not meet the greenness requirements when any of the chemicals used in the procedure are listed as Persistent, Bioaccumulative and Toxic, any of the chemical used in

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the procedure is listed on TRI (Toxic Release Inventory) or on any of RCRA's (Resource Conservation and Recovery Act) lists as hazardous, the pH during any stage of procedure is below 2 or above 12 and the amount of generated wastes is above 50 g. The procedure that meets the standards of green analytical chemistry has all four fields filled green. The disadvantage of NEMI symbols is the need to search some substances lists for all the compounds used in the procedure.

The second assessment method is Eco-scale [13], which is a more quantitative assessment tool. The procedure involves calculation of Eco-scale score, where penalty points are given for any non-green aspect, including waste generation and its management, consumption of solvents and reagents with respect to their amount and toxicity and energy consumption. The penalty points for each reagent are connected to its amount in the ranges <10 g (mL), 10–100 g (mL) and >100 g (mL). The number of penalty points is also related to the number of pictograms, which are accompanied by “danger” word multiplied by 2. In case of potential occupational exposure to hazards related to the procedure, extra penalty points are given resulting in lower Eco-scale score. The result of assessment with Eco-scale is the number, which gives good information about protocol greenness, however there is no information given about the structure of the non-green methodological aspects. The Eco-scale score above 75 suggests that the procedure is “green”, the score between 50 and 75 indicates that the procedure is at “acceptably green” level and the score below 50 corresponds to “non-green” analysis. Recently, self-organizing maps (SOMs) technique was applied to compare the greenness of group of analytical procedures [14]. With this technique it is possible to compare the group of analytical techniques with respect to their greenness and metrological parameters simultaneously.

The aim of the study is to assess the analytical methodologies used for benzene and phenol determination in terms of greenness with multivariate statistical techniques. The factors responsible for deteriorating effects on environment will be identified and investigated. Then NEMI and Eco-scale will be assessed with the SOM technique. The new approach is to compare procedures for two different analytes, simultaneously.

Table 1
The analytical procedures as input objects for the analyses.

No.	Procedure abbreviation	Analytical procedure	Reference
Benzene			
1	HS-GC–FID–PID	Headspace gas chromatography–photoionization detection and flame ionization detection	[15]
2	HS-GC–MS	Headspace – gas chromatography–mass spectrometry	[16]
3	HS-PTV–GC–MS	Headspace programmed temperature vaporization–gas chromatography–mass spectrometry	[17]
4	HS-SPME–GC–FID	Headspace solid phase microextraction–gas chromatography–flame ionization detection	[18]
5	HS-SPME–GC–FID	Headspace solid phase microextraction– gas chromatography–flame ionization detection	[19]
6	HS-SPME–GC–MS	Headspace solid-phase microextraction–cryo-trap gas chromatography–mass spectrometry	[20]
7	DI-SPME–GC–MS	Direct immersion solid-phase microextraction–gas chromatography–mass spectrometry	[21]
8	HS-SPME–GC–MS	Headspace solid-phase microextraction–gas chromatography–mass spectrometry	[22]
9	SPME–GC–FID	Solid phase microextraction–gas chromatography–flame ionization detection	[23]
10	needle trap–GC–FID	Needle trap device–gas chromatography–flame ionization detection	[24]
11	HS-SPDE–GC–MS	Headspace solid-phase dynamic extraction–gas chromatography–mass spectrometry	[25]
12	DAI–GC–FID	Direct aqueous injection–gas chromatography–flame ionization detection	[26]
13	PT-GC–PID	Purge and trap – gas chromatography–photoionization detection	[27]
14	PT-GC–MS	Purge and trap – gas chromatography – mass spectrometry	[28]
15	HSM–GC–FID	Headspace solvent microextraction–gas chromatography–flame ionization detection	[29]
16	DSDME–GC–FID	Directly suspended droplet microextraction–gas chromatography–flame ionization detection	[30]
17	DLLME–GC–FID	Dispersive liquid–liquid microextraction–gas chromatography–flame ionization detection	[31]
18	DLLME–GC–FID	Dispersive liquid–liquid microextraction–gas chromatography–flame ionization detection	[32]
19	DLLME–GC–FID	Dispersive liquid–liquid microextraction–gas chromatography–flame ionization detection	[33]
20	SDME–GC–MS	Ionic liquid single drop microextraction–gas chromatography–mass spectrometry	[34]
21	HS-SPDE–GC–MS	Headspace-single drop microextraction–gas chromatography–mass spectrometry	[35]
22	HF-LPME–GC–FID	Hollow fibre – liquid phase microextraction–gas chromatography–flame ionization detection	[36]
23	HF-SPME–GC–FID	Hollow fiber solid phase microextraction–gas chromatography–flame ionization detection	[37]
24	USAE-ME–GC–FID	Ultrasound-assisted emulsification microextraction–gas chromatography–flame ionization detection	[38]
25	UA-DLLME–GC–FID	Ultrasound-assisted dispersive liquid–liquid microextraction–gas chromatography–flame ionization detection	[39]
26	USA-DDSME–GC–FID	Ultrasonic-assisted drop-to-drop solvent microextraction–gas chromatography–flame ionization detection	[40]
Phenol			
27	LPME–HPLC–UV	Liquid-phase microextraction–high performance liquid chromatography–ultraviolet detection	[41]
28	SM-LLLME–HPLC–UV	Stir-membrane liquid–liquid–liquid microextraction–high performance liquid chromatography–ultraviolet detection	[42]
29	SPE–LC–MS	Solid phase extraction–liquid chromatography–mass spectrometry	[43]
30	SPE–HPLC–UV	Solid phase extraction–high performance liquid chromatography–ultraviolet detection	[44]
31	SPE–LC–ED	Solid phase extraction–liquid chromatography–electrochemical detection	[45]
32	on-line-SPE–LC–ED	On-line – solid phase extraction–liquid chromatography–electrochemical detection	[46]
33	IC–FD–ED	Ion chromatography–online electrochemical derivatization based on porous electrode–fluorescence detection	[47]
34	CLC–ED	Capillary liquid chromatography–electrochemical detection	[48]
35	SPE–GC–FID	Solid phase extraction–gas chromatography–flame ionization detection	[49]
36	SBSE–TD–GC–MS	Stir bar sorptive extraction–thermal desorption–gas chromatography–mass spectrometry	[50]
37	SPME–GC–MS	Headspace solid phase microextraction–gas chromatography–mass spectrometry	[51]
38	DLLME–HPLC–DAD	Dispersive liquid–liquid microextraction–high performance liquid chromatography–diode-array detection	[52]
39	SPE–GC–ITDMS	Solid phase disk extraction–gas chromatography–mass spectrometry	[53]
40	CFME–GC–FID	Continuous flow microextraction–gas chromatography–flame ionization detection	[54]
41	SPE–GC–MS	Solid phase extraction–gas chromatography–mass spectrometry	[55]
42	ITSPME–GC–FID	In-tube solid phase microextraction–solvent desorption–gas chromatography–flame ionization detection	[56]
43	SDE–GC–FID	Steam distillation extraction–gas chromatography–flame ionization detection	[57]
44	LGLME–CE	Liquid–gas–liquid microextraction capillary electrophoresis	[58]
45	FI–CL	Flow injection–chemiluminescence detection	[59]
46	DLLME–spectrophotometry	Dispersive liquid–liquid microextraction–microvolume spectrophotometry	[60]
47	PVPervaporationFIA	Pervaporation–flow injection analysis	[61]

2. Materials and methods

The all input data originate mostly from scientific articles. The searches were performed in ScienceDirect, SpringerLink, ACS, RSC, Wiley and Taylor & Francis databases. Three of the methodologies were taken from standard procedures database. The search was performed for procedures based on every analytical technique. The only criterion for the procedure to be included in SOM analysis is completeness of input data. A detailed description of procedure was needed allowing extraction of required information, such as the amounts of organic solvents and reagents used. Furthermore, the information on limit of detection, precision and recovery was required. If any of these information was missing the analytical procedure was not included in the SOM analysis. Most articles taken into consideration were published within last 10 years but three of them were published in 1990s.

Most of the procedures are based on gas chromatographic or liquid chromatographic separation with various sample preparation techniques, involving microextraction, solid phase extractions and some other more rarely applied techniques. The analytical procedures taken for chemometric analyses are summarized in Table 1.

The variables and their abbreviations taking into consideration during the analyses are summarized in Table 2. The variables are related to the greenness assessment scores – Eco-scale and NEMI, or directly to the environmental impact of the analytical procedure – mass of solid waste generated and amount of organic solvent used. The next group of variables are related to the technical details of the procedure – injection volume, initial sample volume or the number of analytes that can be determined during analysis. The last variable is LOD. The other metrological parameters – coefficient of variance and recovery – were excluded from the analysis, because of little variance carried by these parameters.

Self-organizing maps (SOMs) approach introduced by T. Kohonen [62] allows representing multivariate data in lower dimensional variable space. An additional advantage is the opportunity to visualize in one and the same map the similarity patterns between the objects studied and the variables describing them. Moreover, being a powerful data exploration technique, SOM is able to reveal relationships between objects and variables without any external supervision.

SOM is an unsupervised technique known in the networks, which learn to detect their own relationships without external help. It is assumed that class membership is broadly defined by the input patterns sharing common features, and that the network will be able to identify those features across the range of input patterns.

One particularly interesting class of unsupervised system is based on competitive learning, in which the output neurons compete amongst themselves to be activated, with the result that only one is activated at any one time. This activated neuron is called a winner-takes-all neuron or simply the winning neuron. Such competition can be implemented by having lateral inhibition connections (negative feedback paths) between the neurons. The result is that the neurons are forced to organize themselves. Such a network is called a self-organizing map (SOM).

This map, known also as a topographic map, has the advantages of keeping the input information in its proper neighborhood at each stage of processing and the neurons representing information of related type to be kept together by specific connections. In principle, the spatial location of an output neuron on the map corresponds to a specificity already existing in the input data set.

SOM algorithm is a non-linear projection of the dataset from multi-dimensional space into two-dimensional array of cells or nodes. Each node in the map is initialized as a random unit vector in the space of variables. Each object from the data set is considered as an n-dimensional input vector. The classification procedure follows the rule “winner-takes-all” meaning that the object in consideration chooses to populate the node with unit vector that most closely matches the input data described by the input vectors. The winning vector changes its weights in order to correspond to the input data. Vectors of the neighborhood that match the nodes around the winning node are also respectively modified. Thus, the self-organizing maps algorithm recognizes similar vectors and locates them in one and the same node. The final result of the analysis is a two dimensional map which preserves the distribution of initial data set in non-parametric way without any external information or training.

The map is presented on two-dimensional planes for each variable, indicating variable distribution pattern on the different parts of the map with various colours. The SOM classification helps identify cluster structure of the map. Additionally, the SOMs obtained could be grouped according to the similarity between the variables (variable planes).

Matlab 6.5 software was used for calculations. All calculations aiming SOM classification were performed by a free toolbox (SOM Toolbox 2.0), which can be downloaded from http://www.cis.hut.fi/projects/somtoolbox/.

3. Results and discussion

3.1. Procedures for benzene determination

The results of SOM analysis of procedures for benzene determination are presented in Fig. 1. The red colour on the plane corresponds to the high values of given variable, and in contrast blue colours to low variable values. If the planes corresponding to two variables are characterized by similar colours distribution it means that these variables are correlated. In Fig. 1 the maps are

Table 2
Input variables for statistical data analysis.

Variable	Abbreviation	Units	Remarks
Limit of detection	LOD	$\mu g\ L^{-1}$	–
Volume of sample	SV	mL	–
Injection volume	IV	μL	The volume of liquid injected to injector. In case of thermal desorption the value was close to zero
Number of other analytes determined	OAPA	Unitless	Number of analytes other than benzene or phenol determined in a single analytical run
Amount of organic solvent	AOS	mL	The total amount of all organic solvents used in the analytical protocol
Solid waste	SW	g	The total mass of all wastes generated during analysis with the analytical protocol
NEMI score	NEMI	Unitless (range 0–4)	NEMI score was calculated for each analytical methodology, unless it was accessible
Eco-scale score	ECOS	Unitless (range 0–100)	Eco-scale score was calculated for each analytical methodology

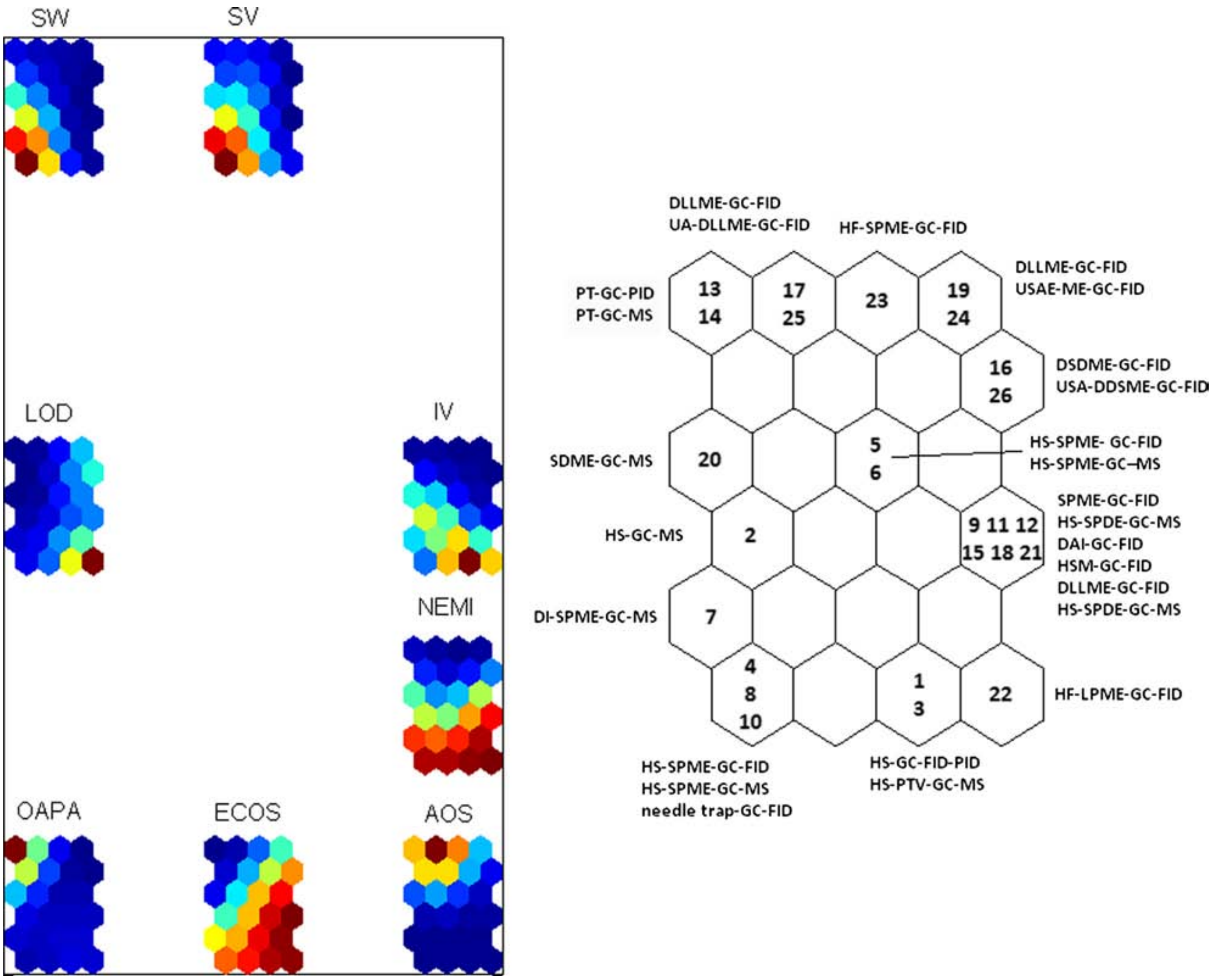

Fig. 1. Grouping of variables for classification of benzene determination procedures (left) and hit diagram with the procedures (right). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

located according to their similarity. The hit diagram gives information where a given object is located and gives easy possibility to read, if the values for each variable are high or low. For example, object 22, means HF-LPME–GC–FID procedure is located in the right–down corner of the plane. It means that the methodology in comparison to others is characterized by low sample volume needed, low solid waste amount generated and high LOD, NEMI and Eco-scale scores.

The analysis of grouping of variables can give some information about the nature of analytical procedures for benzene determination. The technique-related parameters are similar – sample volume and generation of solid wastes are grouped together and injection volume variable is also similar to the remaining two. The procedures involving large sample volume and extensive wastes generation (e.g. 4, 8, 10 being located in the lower–left part of the hit diagram) are based on headspace analysis, where large amount salts are used to enhance transfer of analytes from water to gaseous phase. These procedures are still categorized as green ones by NEMI and Eco-scale. Application of salts in the procedure does not alter the greenness assessment, because inorganic salts commonly used in analytical laboratories are neither harmful nor toxic. Sample injection volume and LOD are positively correlated, which seems to be contradictory to the common knowledge. The procedures with high injection volume and high LOD are based on headspace analysis with large volume gaseous sample introduction. The volume of gaseous sample introduced is large but the amount of analyte introduced is not extraordinary. The volume of solvent is negatively correlated with NEMI and Eco-scale scores. This means that the organic solvents used are the main contributors to the hazard caused by analytical methodologies. The methodologies that are designed for multianalyte determination require more organic solvents. These methodologies are assessed by NEMI and Eco-scale as less green. Finally, NEMI and Eco-scale assessment methods are in good agreement. There is a small discrepancy between these two assessments methods. The procedures that are located in the upper right part of the hit diagram are categorized by Eco-scale as green, whereas by NEMI as less green. These procedures are solvent microextraction techniques. NEMI assessment protocol does not involve considering the amount of solvent used, while Eco-scale assessment to a greater extent considers amount and the danger related to given solvent application. That is why solvent microextraction techniques are responsible for differences in assessment with NEMI and Eco-scale methods.

The SOM analysis can deliver information on which methodologies are the most favourable in terms of green analytical chemistry. The procedures located in lower part of the hit diagram are categorized as the least environmentally harmful. The great majority of the procedures are based on sample preparation techniques commonly considered as green. In fact, the generalization of which techniques are greener is hard and the individual procedural solutions should be tested for being green or not.

3.2. Procedures for phenol determination

The dataset of procedures for phenol determination are characterized with greater diversity of techniques involved. The grouping of variables is similar to the case of benzene. The main difference is that the amount of solid wastes generated is not so much correlated to the initial sample volume. Again the amount of organic solvent is the main factor responsible for making the analytical procedure more environmentally problematic.

A clear distinction of analytical procedures based on LC and GC can be observed (Fig. 2). Procedures based on LC and on SPE sample preparation are located in the upper part of the hit diagram, while methodologies based on GC and other techniques (flow injection analysis, spectrophotometry, ionic chromatography) are located in the lower part of this diagram. The procedures based on LC and SPE are characterized by large initial sample volume, high solid waste generation and organic solvent consumption. The main differences between GC and LC methodologies lie in the “environmental parameters”, not the metrological ones. The values of LOD are not different between these two groups. Also the values of recoveries and RSDs, the parameters excluded from the SOM analysis, were significantly indifferent between these two groups.

3.3. Procedures for benzene or phenol determination

The idea of simultaneous SOM classification for benzene and phenol is applied to compare the potential environmental impact of methodologies when analytes are characterized with different physicochemical properties. Fig. 3 shows the SOM analysis results for procedures devoted to determination of phenol and benzene. For easier interpretation neurons with hits corresponding to phenol methodologies are coloured grey. Most of the methodologies for benzene and phenol determination are well separated with SOM algorithm, which means that these methodologies differ. The methodologies for phenol determination are generally located in the upper part of the hit diagram. These methodologies are characterized by higher LOD values, larger solid waste generation, organic solvent consumption and larger sample volume.

NEMI and Eco-scale scores are considerably lower for the methodologies for phenol (NEMI – 2.72, Eco-scale – 75.5) determination than for benzene determination (NEMI – 3.54, Eco-scale – 90.3). To obtain some information about the cause of such results it is good to consider the physicochemical parameters of both analytes. Water solubility is 1750 and 80,000 mg L^{-1}, Henry's constant 550 and 0.05 Pa m^3 mol^{-1}, octanol/water partitioning coefficient (log K_{OW}) 2.2 and 1.4 for benzene and phenol,

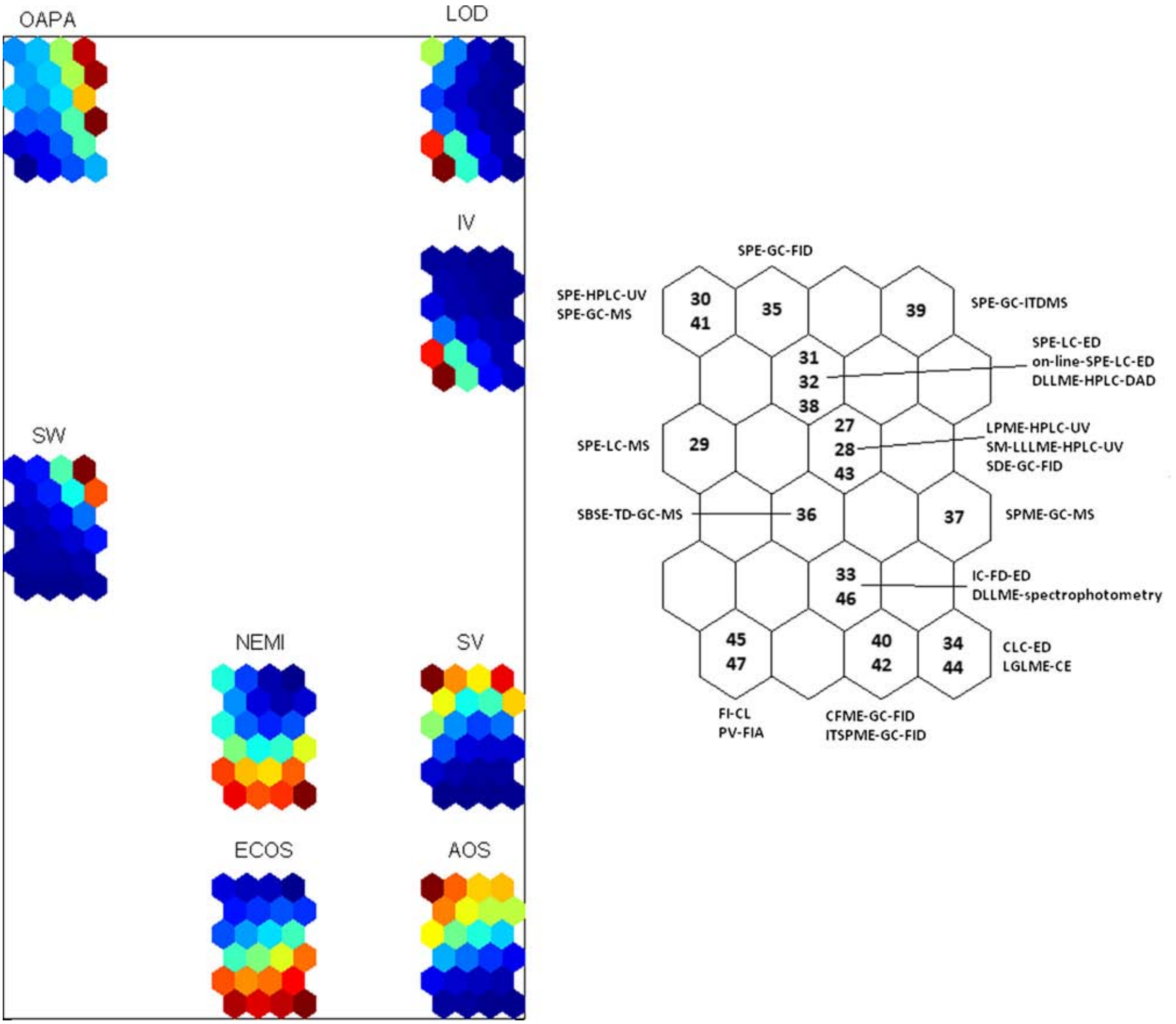

Fig. 2. Grouping of variables for classification of phenol determination procedures (left) and hit diagram with the procedures (right).

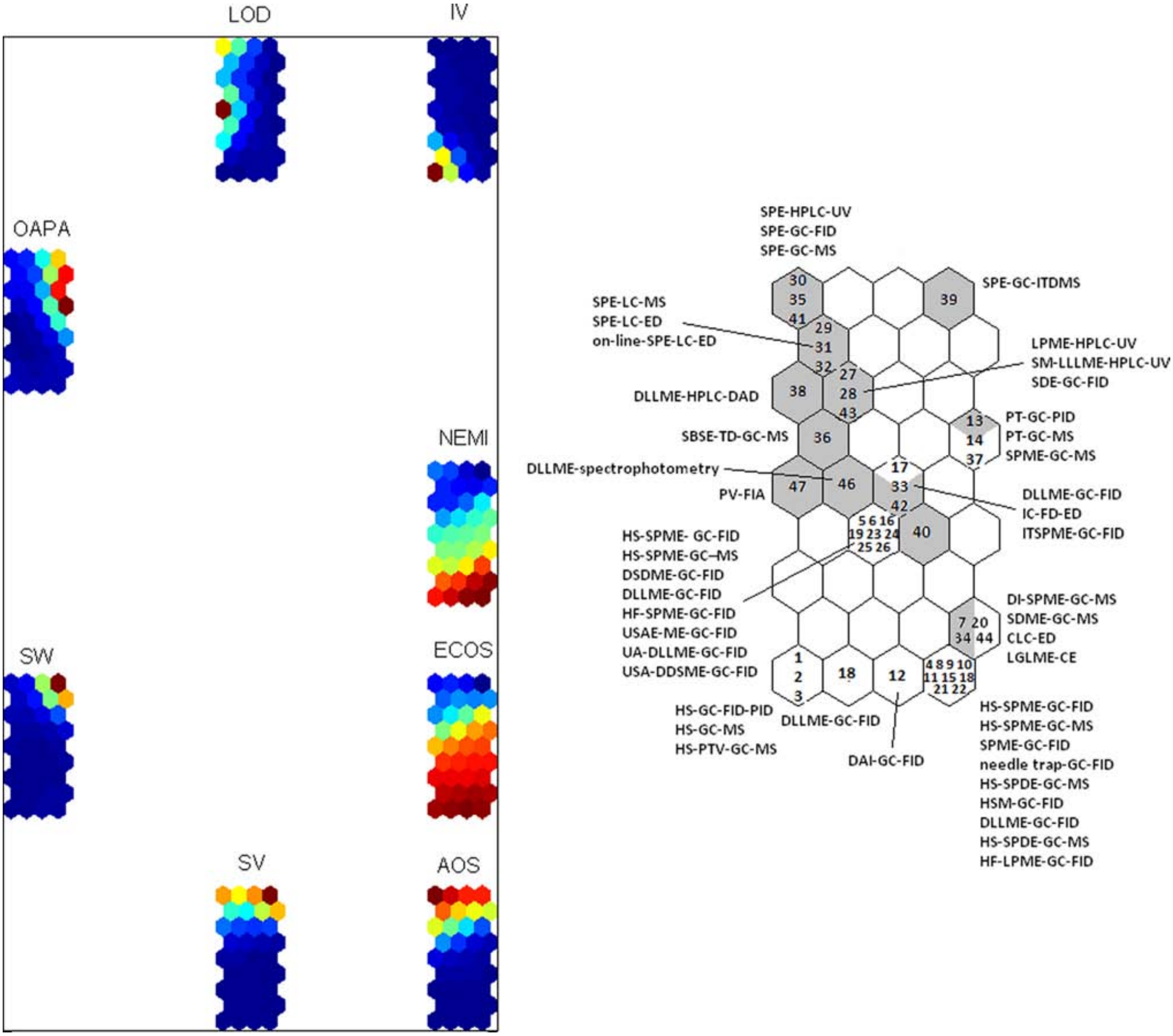

Fig. 3. Grouping of variables for classification of benzene and phenol determination procedures (left) and hit diagram with the procedures (right). Grey colour of the neurons in the hit diagram corresponds to phenol determination procedures.

respectively. All the physicochemical constants favour benzene to be more easily extracted to gaseous phase, organic solvent or solid phase sorbent. More effort, in terms of materials and energy, is needed to effectively extract more polar analyte, such as phenol.

4. Conclusion

The SOM analysis allowed determining factors responsible for the negative environmental impact of methodologies for benzene and phenol determination in water samples. The results also show that NEMI and Eco-scale results are in good agreement in cases of both analytes. The main factor responsible for causing environmental impact is consumption of organic solvents. The methodologies involving excessive solvent consumption at sample preparation step, like SPE sample preparation, should be avoided. Similarly, gas chromatographic separation should be chosen over liquid chromatographic one whenever possible. The main discriminators among analytical procedures are those related to environmental impact, while the metrological parameters are characterized by relatively little variance.

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