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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]