Trends in Analytical Chemistry 118 (2019) 538–547

Contents lists available at ScienceDirect

Trends in Analytical Chemistry

journal homepage: www.elsevier.com/locate/trac

A new tool for evaluating and/or selecting analytical methods: Summarizing the information in a hexagon

Ana Ballester-Caudet [a], Pilar Campíns-Falcó [a, *], Bibiana Pérez [b], Raquel Sancho [b], Mónica Lorente [b], Guadalupe Sastre [b], Carina González [b]

[a] *MINTOTA Research Group, Departament de Química Analítica, Facultat de Química, Universitat de València, Dr. Moliner 50, 46100, Burjassot, Valencia, Spain*
[b] *GAMASER S.L. (Global Omnium), Isaac Peral, 4, 46980, Paterna, Valencia, Spain*

ARTICLE INFO

Article history:
Available online 22 June 2019

Keywords:
Metric tool
Analytical methods
Selection
Characterization
Analytical performance
Sustainability
Environmental impact
Cost-effectiveness
Penalty points
Hexagon pictogram

ABSTRACT

A quantitative evaluation tool is proposed, which aims to assess optimal selection or/and testing of analytical methods. Objective criteria related to analytical performance, sustainability, environmental impact and economic cost are evaluated through the definition of penalty points divided into five different blocks, namely, figures of merit, toxicity and safety, residues, carbon footprint and economic cost. For each block, the overall qualification is scaled from 0 to 4 and it is depicted on a regular hexagonal pictogram that allows a user friendly comparison of analytical procedures. The present evaluation tool aims to be a guideline for evaluating and/or selecting analytical procedures that are in line with Green Chemistry philosophy, but also balancing the figures of merit needed for solving a given problem, safety and cost-effectiveness. Real examples have been tested.

1. Introduction

Green Analytical Chemistry (GAC) principles [1] serve as a guide to define the framework of green analytical procedures. Current working directions are focused on scaling down the sample amount or, what is more, applying direct methodologies [2]. Moreover, it is encouraged the application of solvent-less extraction techniques [3–5] and/or the introduction of less toxic solvents [6–8]. Regarding the measurement process, the miniaturization is of outstanding interest, being real-time field measurements the most valuable option [9]. All these novel ideas share a common main challenge of sustainable development, which is to achieve a good compromise between the quality of analytical results and greening analytical operations.

Initially, the implementation of GAC principles to the every-day tasks has been carried out qualitatively through the use of the NEMI pictogram [10]. Nowadays, the establishment of the basis for a quantitative assessment by means of the use of metrology is of growing interest. However, it is worth mentioning that the development of an evaluation tool is a complex task, given the diversity of sample matrices and figures of merit that must be considered, such as LOD, precision, accuracy and linear range, among others. In the literature, there are some propositions for the quantitative assessment of the greenness of analytical procedures. Traditional green chemistry metrics such as atom economy, E-factor and Reaction Mass Efficiency can be found mainly addressed to organic synthesis [11,12]. Atom economy and E-factor sustainability is based on measuring the mass of the reagents used and the mass of generated waste per mass of obtained product, respectively. Furthermore, a semi-quantitative tool that defines penalty points according to how the parameters analyzed differ from an ideal Eco-Scale has been also suggested [13]. The aim of a quantitative evaluation is to detect the weak aspects of the analytical procedure that could be improved and adapted to the requirements of the GAC.

Starting from the considerations outlined and partial metrics stablished previously by MINTOTA [14–16], a new quantitative tool is proposed here. In order to compare different analytical methods in terms of environmental impact when facing a specific problem (i.e., to control a physicochemical parameter), several aspects must be considered and contrasted prior to an ultimate selection. To do

---

* Corresponding author.
E-mail address: pilar.campins@uv.es (P. Campíns-Falcó).

https://doi.org/10.1016/j.trac.2019.06.015
0165-9936/

so, MINTOTA proposed a tool, namely CALIFICAMET [16], for evaluating a method performance with respect to its sustainability, associated risks, analytical features, and related costs. In this regard and after several efforts by this group [14,15], the developed tool comprises the rating of five variables: related to the method sustainability, the estimation of the carbon footprint as a metric parameter to evaluate the environmental negative impact of a methodology and the study of the generated residues in terms of their quantity, type, and potential recycling; as for associated chemical and health risks, they are assessed according to the toxicity, hazard, and safety considerations (all referred as "toxicity" hereafter) of the involved reagents/materials; the analytical performance is qualified through the adequacy of the figures of merit to solve the problem faced; finally, the related cost of the methodology is estimated from the consumption of reagents and energy, as well as the staff hours and instrumentation required for a given number of samples (500), which is then normalized to one (i.e., cost per sample) for a proper comparison. Except for the carbon footprint and the cost of the method which are quantified in absolute terms, the rest of the variables is rated using a 1–5 scale in a qualitative manner. As illustrative cases, four scenarios were assessed by using the CALIFICAMET tool in Ref. [16].

However, a complete tool should take into account all the features of the techniques employed as well as the key aspects that define chemical analytical methods including greenness and a higher degree in absolute terms. In this sense, the present paper includes penalty points in CALIFICAMET in order to increase the degree of quantitation of the tool and also a new pictogram is developed. Assuming an ideal hypothetic sustainable analytical method, no penalty points are assigned. It means the analytical protocol is associated with nontoxic reagents or solvents, low generation of wastes (or subject to appropriate treatment), low energy consumption and an optimum cost-benefit relation. In addition to this, safety for both the analyst and the environment should be guaranteed. Taking into account these sustainable aspects, for each of the variables that differ from the abovementioned hypothetic case, penalty points (PPs) are assessed. As the total score of penalty points increases, the analytical procedure is worse. The processed information is summarized in a hexagon as pictogram that serves for rapid evaluation. Most companies want to clearly communicate their efforts and results to reduce environmental impact and to work properly, particularly GAMASER. As a result, there is a need for a reliable and easy to use tool that does not exist today and the hexagon-CALIFICAMET can be an option.

2. Definition of the evaluation tool

The evaluation tool proposed comprises five different blocks, as indicated in Table 1. Firstly, analytical procedures are evaluated taking into consideration figures of merit, which are divided into two different groups. On the one hand, Figures of merit 1 (FM-1) that involves: the sample treatment, method characteristics and calibration procedure. On the other hand, Figures of merit 2 (FM-2) apply for the quality control and accuracy. Additionally, toxicity and safety blocks state how toxic and hazardous the chemical products employed are and the exposition of the analyst to risks. Moreover, the amount of residues generated and their treatment are evaluated in the residues block. Regarding the environmental impact, the calculation of the carbon footprint [15] is addressed. Finally, the annual economic cost associated with the analytical procedure under study is calculated. An evaluation template describing the items considered in each of the aforementioned blocks is shown in subsequent sections. Each item has penalty points assigned, which are indicated on the right side of the template.

2.1. Figures of merit evaluation

The quality parameters or figures of merit are divided into two different groups as mentioned above, namely figures of merit 1 (FM-1) and figures of merit 2 (FM-2). The lower the penalty points associated, the better the adaptation of the figures of merit for solving the analytical problem. In figures of merit (FM-1), parameters related to the sample treatment (Table 2), several characteristics of the method (Table 3) and calibration (Table 4) are evaluated. These tables include the aspects considered for each parameter and the penalty points assigned in function of the several possibilities of the topic, stablishing the best option too. For each parameter a maximum penalty points have been assigned based on its incidence in the global position. In reference to parameters related to sample treatment, Table 2 indicates that the best option, without penalty points corresponds to a methodology, which does not use preservation and storage conditions for the sample, requiring a micro amount of it and does not employ reagents or solvents, dilution or concentration for achieving the required concentrations for the chosen technique and pretreatment and the number of samples for weekly analyzing is higher than 50. Table 2 gives the penalty points for the other considered aspects different to the best option described previously. In general, no more than four situations have been considered in order to facilitate the application of the metric tool. In reference to characteristics of the method, no penalty points are assigned to a method: in-line, automatic, portable, nondestructive, multicomponent, rapid (analysis time less than ten minutes) and robust (see Table 3). The best method in reference to calibration is considered when this step requires minimal requirements as it is shown in Table 4.

Specifically, the precision (see Table 4) of the method is evaluated by the Horwitz equation (ISO/IEC 17025 Testing Laboratory) according to the Equation (1).

$$\mathrm{RSDR}\ (\%) = 2(1 - 0,5 \cdot \log C) \quad (1)$$

where C is the concentration of the analyte in the sample and RSDR is the relative standard deviation calculated from results

Table 1
Variables of the evaluation tool considered in order to characterize and/or select the most convenient analytical procedure.

Parameter	Implication	Interpretation
Figures of merit	Adequacy of the analytical parameter relative to the sample/method and quality control	The lower the value, the better the adaptation of the figures of merit for providing a reliable analytical result
Toxicity and Safety	Health, hazard and safety	The higher the value, the worst the contribution to health, environment and safety
Residues	Environmental and sustainability	The higher the value, the worst the environmental impact and sustainability
Carbon footprint (kg CO_2)	Environmental and sustainability	The lower the value, the better the contribution to environment and sustainability (expressed as kg CO_2 equivalent)
Annual cost (€)	Cost-effectiveness	The higher the value, the worst the cost-benefit relation

Table 2
Figures of merit related to the sample treatment of the evaluation tool. Penalty points (PPs) associated are indicated on the right side.

			PPs
Sample treatment and preparation	Preservation	No	0
		Physical	1
		Chemical	2
	Storage	No	0
		Under normal conditions	1
		Under special conditions	2
	Amount	Micro	0
		Macro	1
	Reagents/solvents used	No	0
		≤3	1
		>3	2
	Amount of reagents, solvents	<1 g	1
		1–10 g	2
		10–50 g	3
		>50 g	4
	Instrumental vs Adequacy to the method	No need to dilute/concentrate	0
		Dilute/Concentrate 5 times	1
		Dilute/Concentrate more than 5 times	2
	Number of weekly samples	≥50	0
		50–1	1
		<1	2
	Pretreatment	None	0
		Filtration	1
		Stirring/Drying on stove	2
		Acid digestion	3
			18

generated under reproducibility conditions. The Horrat value refers to the repeatability of the results (RSDr) and establishes the assumption RSDr = 0.66 • RSDR. Values of the precision evaluation for several analyte concentrations are listed in the supporting information, SI.

Table 3
Figures of merit regarding the method characteristics of the evaluation tool. Penalty points (PPs) associated are indicated on the right side.

			PPs
Method characteristics	Method categories	in-line	0
		on-line	1
		off-line	2
	Operational mode	Automatic	0
		Semiautomatic	1
		Manual	2
	Portability	Yes	0
		No	1
	Method/Sample	No destructive	0
		Destructive	1
	Analytes/sample	Multicomponent	0
		Unicomponent	1
	Time of analysis/sample	<10 min	0
		10–100 min	1
		>100 min	2
	Robustness	Yes	0
		No	1
			10

Table 4
Figures of merit related to the calibration process evaluated by the proposed tool. Penalty points (PPs) associated are indicated on the right side.

			PPs
Calibration	Frequency	Annual	1
		Monthly	2
		Weekly	3
		Daily	4
	Required time	≤30 min	1
		30 min - 2 h	2
		2 h–8 h	3
		>8 h	4
	Number of standards	5	1
		5–7	2
		>7	3
	Lineal adjustment R^2	$R^2 \geq 0,990$	0
		$R^2 < 0,990$	1
	LOD, LOQ limits	LOD <1/10 Legislation value	0
		1/10 ≤ LOD ≤1/3 Legislation value	1
		LOD >1/3 Legislation value	2
	Working range and linearity	Suitable	0
		Partially suitable	1
		Inadequate	2
	Precision	Horrat value (r/R) ≤ Horwitz	0
		Horrat value (r/R) > Horwitz	1
			17

Figures of merit 2 (FM-2) concerns to the parameters related to quality control/verification (Table 5) and the accuracy (Table 6) of the analytical method under study. Uncertainty approach is employed to assess the suitability of the method of analysis to be used by the laboratory. An uncertainty function (Uf) defines a maximum uncertainty value by using the detection limit of the method (LOD) and the concentration of analyte (C) in the sample according to the following Equation (2) (ISO/IEC 17025 Testing Laboratory):

$$Uf = \sqrt{\left(\frac{LOD}{2}\right)^2 + (0,1 \cdot C)^2} \tag{2}$$

A suitable method must provide results with a maximum standard uncertainty given by the previous formula.

2.2. *Toxicity and safety evaluation*

Classification and labelling of the chemicals of the globally harmonized system (SGA) [17], as shown in Fig. 1, was considered. The assignment of the penalty points is based on data found in the literature [18] for these parameters. The evaluation procedure consists of collecting the pictograms present in the reagents used in the analytical method studied. Health and environmental hazards are considered in the toxicity evaluation section, as indicated in Table 7. Regarding the evaluation of safety, penalty criteria are listed in Table 8. The higher the penalization reached, the worst the contribution to health, environment and safety.

It is worth mentioning that the “Amount of reagent” item present in the evaluation template for toxicity and safety accounts for a

Table 5
Figures of merit FM-2 related to the quality control of the evaluation tool. Penalty points (PPs) associated are indicated on the right side.

			PPs
Quality control	Frecuency	Working day	1
		1/2 Working day	2
		Serie of 5 samples	3
		Each sample	4
	Time required	0–30 min	1
		30 min–1 h	2
		>1 h	3
	Number of standards	≤2	1
		3	2
		>3	3
			10

Table 6
Figures of merit FM-2 regarding the accuracy of the evaluation tool. Penalty points (PPs) associated are indicated on the right side.

			PPs
Accuracy	Frequency	Working day	1
		1/2 working day	2
		Series of 5 samples	3
		Each sample	4
	Time required	0–30 min	1
		30 min - 1 h	2
		>2 h	3
	Concentration levels	≤2	1
		3	2
		>3	3
	Magnitude/Size	RSD_{method} (%) ≤ RSD (Uf, %)	0
		RSD_{method} (%) > RSD (Uf, %)	1
	Selectivity	Yes	0
		No	1
			12

Table 7
Toxicity penalty criteria regarding the chemical products employed in the analysis. Penalty points (PPs) associated are indicated on the right side.

		PPs
Toxicity: health and environmental hazards	Severe toxicity	3
	Corrosive	2
	Irritating	1
	Irritating to eyes	2
	Irritating to respiratory system and skin	3
	Mutant	3
	Carcinogen	3
	Toxic/Poisonous	3
	Systemic toxicity for target organ	3
	Toxicity to the aquatic environment	1
	Amount of reagent*	1–3
		27

Table 8
Safety penalty criteria during the analytical procedure. Penalty points (PPs) associated are indicated on the right side.

		PPs
Safety: Physical hazards	Explosives	4
	Flammables	1
	Causes burns	2
	Low pressure gases	1
	Self-reactive substances	1
	Pyrophorics	1
	Substances experience spontaneous heating	4
	Water-activated flammable gases	2
	Organic peroxides	4
	Corrosive for metals	2
	Amount of reagent*	1–3
		25

quantitative assessment of the chemicals employed in the analysis. Penalization ranges from 1 to 3 points according to the following formula:

$$\frac{\frac{\sum\left(A_{reagents}+B_{calibration}+C_{Quality\ control}+D_{accuracy}\right)}{3}}{Maximum\ PPs} \tag{3}$$

In the previous formula, the term $A_{reagents}$ refers to the amount of reagents or solvents employed from sample treatment (see Table 2). B term stands for the sum of the penalty points assigned to the number of standards used and frequency of the calibration (see Table 4) while C term accounts for the standards and frequency during the quality control procedure (see Table 5). The last term D accounts for the penalty points associated with the needed frequency of accuracy validation (see Table 6). Eventually, the maximum penalty points in the denominator are computed by the sum of the penalties from all the items listed in Tables 7 and 8, respectively, except the item related to the amount of reagent. This means toxicity and safety evaluations run up to 24 and 22 penalty points, respectively.

2.3. Residues evaluation

The definition of green chemistry metrics to evaluate waste generation of analytical methods has been defined in Table 9 in accordance with values found in the bibliography [13,19]. Penalty points are assigned depending on the amount of wastes produced by the analysis, the possibility of waste processing such as recycling and the type of disposable material generated once the analysis is completed.

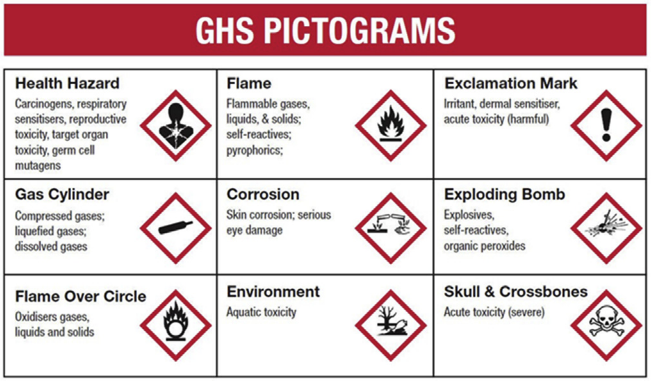

Fig. 1. Pictograms of the globally harmonized system of classification and labelling of chemicals (GHS).

2.4. Environmental impact evaluation

The parameter used to quantify the environmental impact of the analytical procedure is expressed by kilograms of CO_2 equivalent or the so called carbon footprint [15], whose estimation is computed by means of the following expression:

$$kg\ CO_2\ eq = \sum Instrument\ Power\ (kW) \cdot Analysis\ time\ (h) \cdot Emission\ factor\ for\ electricity\ \left(kg\,\frac{CO_2}{kWh}\right) \tag{4}$$

in which the electricity consumed by the instrumental equipment is multiplied by the analysis time per sample (in hours) and by a reference constant value emission factor equal to 0.247 kg CO_2/kWh [20]. The power consumption taken as reference for several analytical procedures is listed in the supporting information, SI.

2.5. Economic cost evaluation

An estimation of the annual economic cost (in €) is calculated taking into consideration the sum of the criteria listed in Table 10.

3. Final representation of the method evaluation

Once the penalty points computation for the variables of the method has been performed, a scale of five levels with an overall

Table 9
Definition of penalty points (PPs) to assess waste generation of an analytical procedure.

		PPs
Amount	None/Negligible	0
	<1 g	1
	1–10 g	2
	10–100 g	3
	100–500 g	4
	500–1000 g	5
	>1 kg	10
Waste treatment	Recycling/Unnecessary	0
	Degradation	1
	No treatment	3
Disposable material	No	0
	Yes (glass)	2
	Yes (plastic)	5
		18

Table 10
Parameters considered for the evaluation of the annual economic cost.

Parameters	Reference values
Number of samples	Annual average
Time of analysis (in hours)	Per sample
Equipment cost	To be defined for each analysis
Amortization period	10 years
Salary skilled personnel	15 €/hour
Electricity consumption	0,15 €/kWh
Reagents	To be defined for each analysis
Consumable material	To be defined for each analysis

qualification ranging from 0 to 4 is established. In Table 11 the score assignment for each variable of the evaluated method is related to the definition of intervals of the penalty points. It is worth mentioning that the notation [a, b] implies that $a \leq x \leq b$ while [a, b] covers the interval $a \leq x < b$. The higher the score, the following implications are assumed:

- The worse the adaptation to the control of the analytical parameters
- The higher the environmental and health impact
- The less cost-effective analytical procedure

The final qualification mark is represented by means of a regular hexagon with six equilateral triangles. Each triangle corresponds to a variable of the evaluated method, except for the case of the toxicity and safety variables that are included in the same triangle (see Fig. 2).

4. Evaluation examples

The proposed evaluation tool has been employed to characterize several analytical procedures involved in water industry analysis. Specifically, the evaluation process consists of assigning the penalty points for the studied method for all the variables from Fig. 2. In addition to this assessment, two simulated procedures are tested taking as reference the studied method: one applies green chemical principles whereas the least green alternative is also analyzed. In reference to carbon footprint, the greenest method considers the shortest analysis time less than 10 min (i.e. 1 min) whereas the worst environmentally friendly analysis is supposed to be performed in 101 min (see Table 3). In order to define the most sustainable method in reference to the cost parameter, the analysis time is evaluated following the same criteria as for the carbon footprint calculation. Additionally, the number of samples per week is also taken into account. The greenest alternative considers at least 50 weekly samples while only one sample is considered in the worst sustainable analysis method (see Table 2).

To assess waste generation, the greenest analytical procedure is defined by the lowest number of penalty points as listed in Table 9, that is, negligible amount of waste produced, unnecessary waste treatment and non-disposable material generated. The worst environmental analytical procedure accounts for the opposite evaluation with the highest penalty points assigned. The greenest option for figures of merit 1 and 2 assigns the lowest number of penalty points from Tables 2–6 except for the intrinsic characteristics of the analysis method such as uni/multicomponent analysis and (non)destructive analysis. The opposite holds for the worst environmentally friendly analysis procedure. In addition to this, method categories, portability, robustness, linear adjustment, LOD/LOQ limits, selectivity and accuracy magnitude/size are fixed to the original analysis method evaluated. Regarding the toxicity and safety evaluation criteria, the most sustainable analysis is defined by the lowest penalty points assigned to the $A_{reagents}$, $B_{calibration}$, $C_{quality\ control}$ and $D_{accuracy}$ terms (see Amount of reagent section in

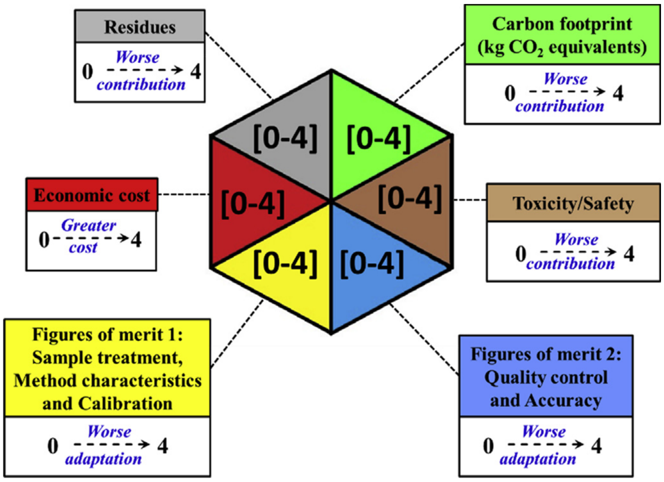

Fig. 2. Regular hexagon with six equilateral triangles em-ployed to evaluate and quantify the sustainability of an analytical procedure.

Table 11
Overall qualification (OQ) of the variables of the method according to penalty points ranges.

OQ	Penalty points scale for all the variables						
	FM-1	FM-2	Toxicity	Safety	Residues	Carbon footprint	Economic cost
0	[0, 5]	[0, 4]	[0, 5]	[0, 2]	[0, 5]	[0, 0,1)	[0, 5000)
1	[6, 15]	[5, 8]	[6, 12]	[3, 5]	[6, 10]	[0,1, 0,5)	[5000, 15000)
2	[16, 25]	[9, 12]	[13, 18]	[6, 9]	[11, 15]	[0,5, 1)	[15000, 30000)
3	[26, 35]	[13, 16]	[19, 25]	[10, 14]	[16, 20]	[1, 2)	[30000, 50000)
4	[36, 45]	[17, 23]	[26, 33]	[15, 22]	[21, 24]	[2, >30[a]]	[50000, >50000[a]]

[a] All the above-indicated values are included.

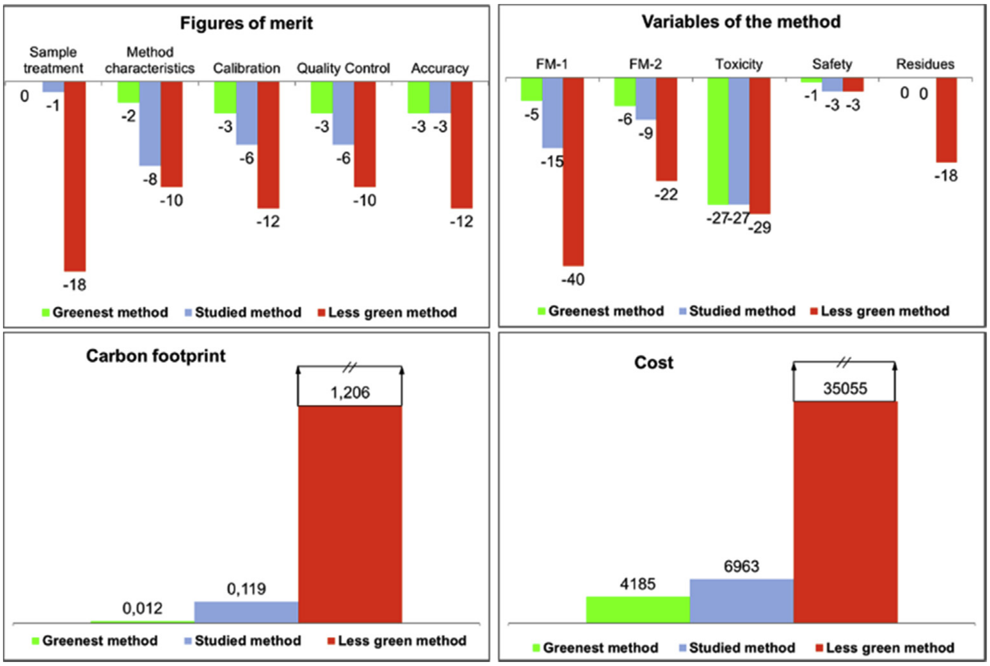

Fig. 3. Representation of the variables of the studied method (blue) for the determination of Hg by AAS, a predicted greenest method (green) and a predicted less green method (red).

Tables 7 and 8) in contrast to the worst sustainable analysis that accounts for the highest number of penalty points.

Once the evaluation tool has applied for the before mentioned three analytical procedures, results are represented in histogram graphs. For the sake of comparison, the studied method and the simulated greenest and less green alternatives are depicted jointly in order to evaluate the variability of PPs and hexagons.

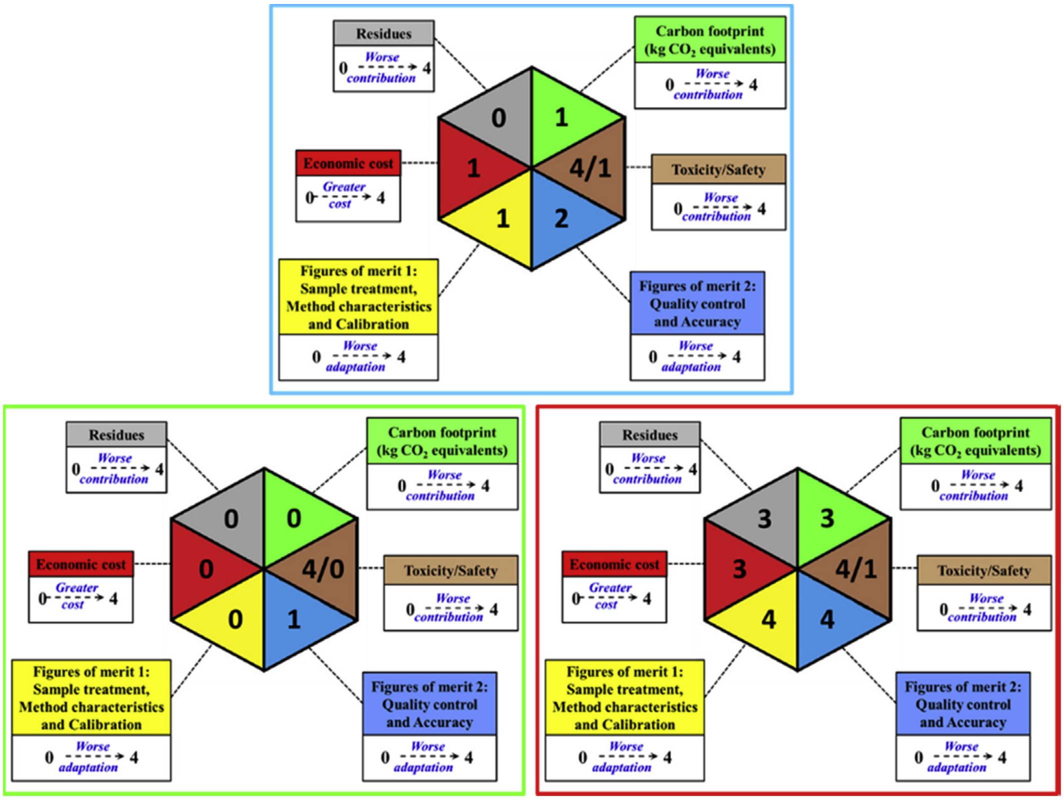

Fig. 4. Regular hexagonal pictogram for the evaluation of Hg determination by AAS for the studied method (blue), a greenest method (green) and the less green method (red).

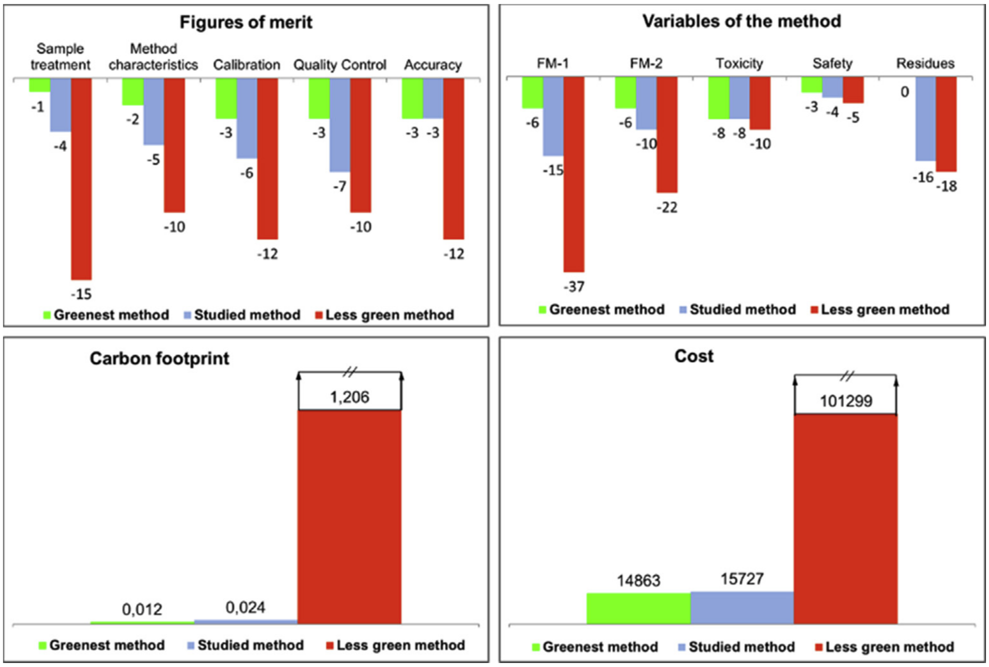

Fig. 5. Representation of the variables of the studied method (blue) for the Hg determination by ICP-MS and simulated green-est method (green) and less green method (red).

Routine physicochemical procedures in water industry have been chosen to show the evaluation tool performance. Firstly, the analytical determination of mercury is characterized when employing atomic absorption spectroscopy (AAS) (see Fig. 3 and Fig. 4) and inductively coupled plasma in tandem with mass spectrometry (ICP-MS) (see Fig. 5 and Fig. 6). Figs. 3 and 5 give the penalty points for each determination and Figs. 4 and 6 show the hexagon pictograms obtained according Table 11. The mercury

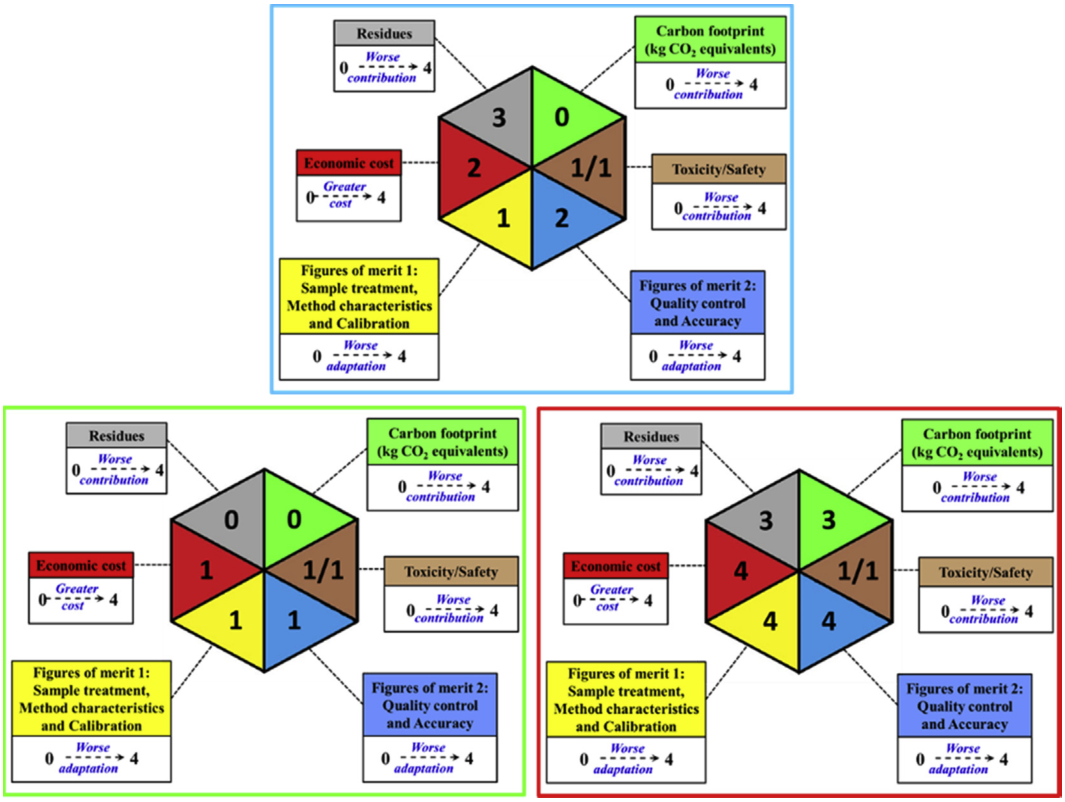

Fig. 6. Regular hexagonal pictogram for the evaluation of the studied method (blue) for the Hg determination by ICP-MS and simulated greenest method (green) and less green method (red).

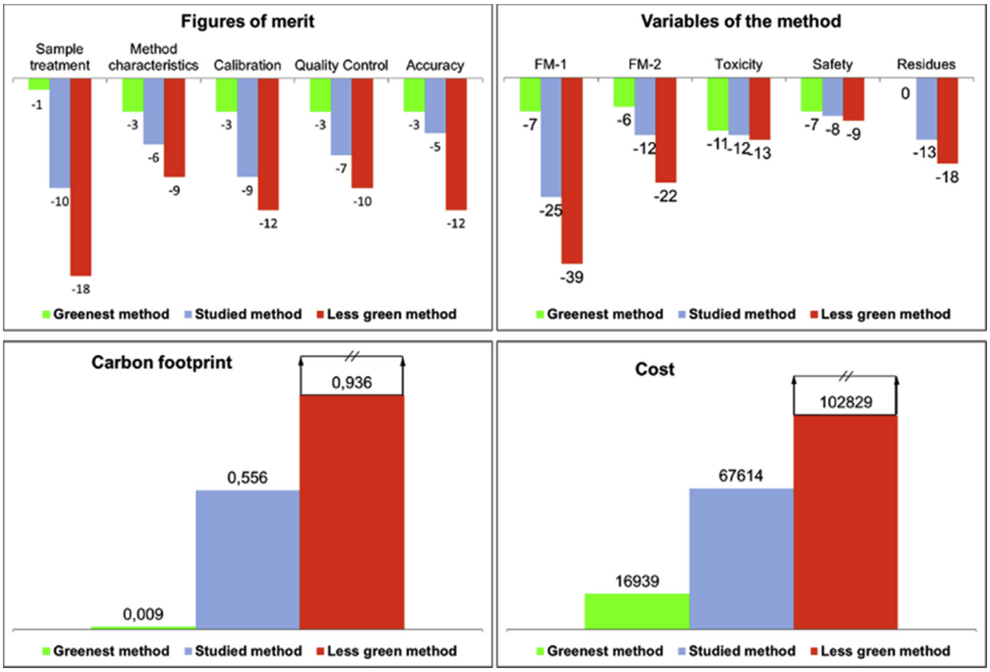

Fig. 7. Representation of the variables of the studied method (blue) for the determination of pesticides by GC-MS with thermic desorption module, a predicted greenest method (green) and a predicted less green method (red).

determination by AAS technique offers advantages in terms of sustainability because it involves a method without sample treatment and the generation of residues is minimum. However, the use of significate amounts of mercury standards increases the penalty points associated to the toxicity, as it can be seen in Fig. 3 showing the PPs and Fig. 4, which gives the hexagon. On the other hand, the

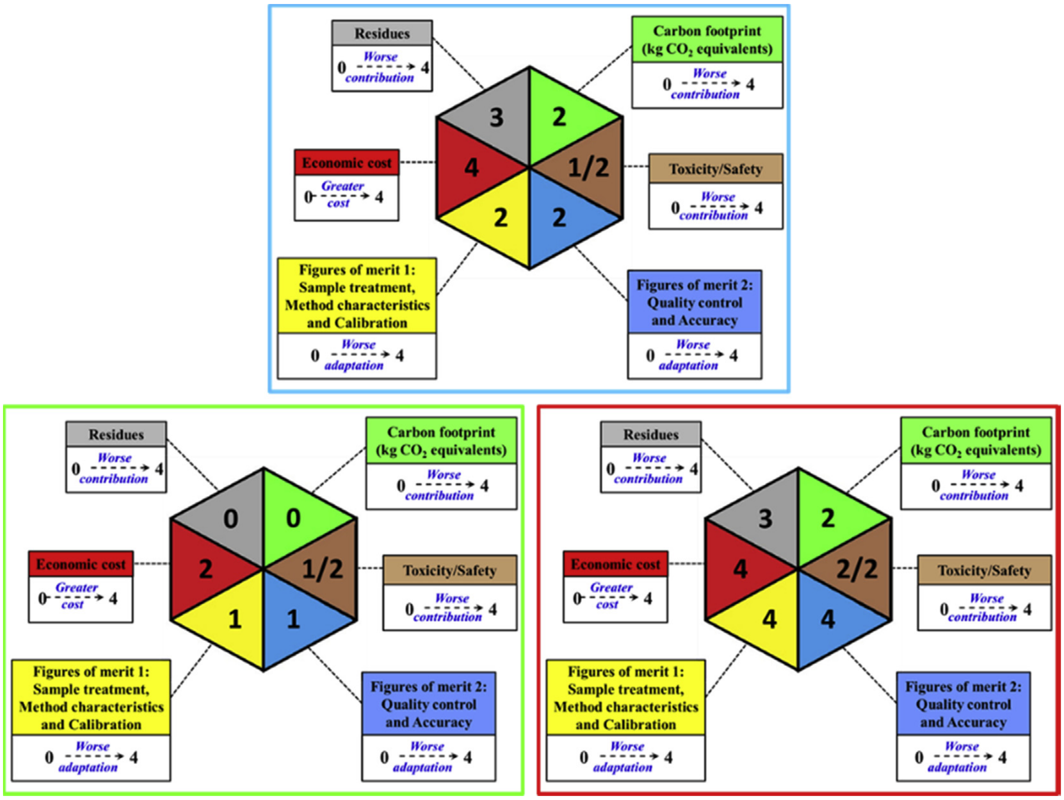

Fig. 8. Regular hexagonal pictogram for the evaluation of pesticides determination by GC-MS with thermic desorption module for the studied method (blue), a greenest simulated method (green) and the less green method (red).

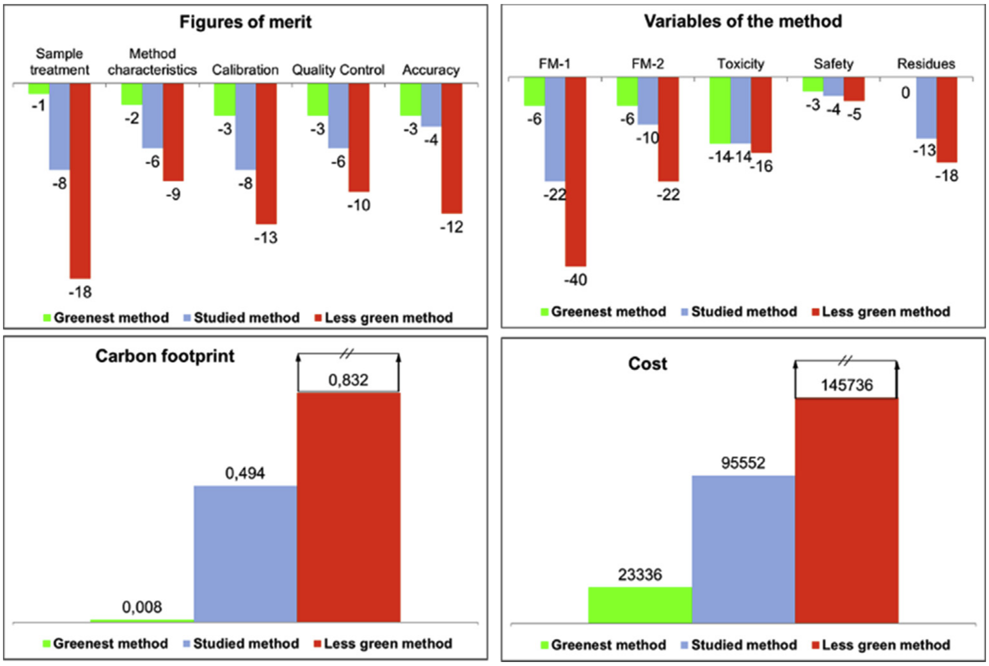

Fig. 9. Representation of the variables of the studied method (blue) for the determination of pesticides by LC-MS, a predicted greenest method (green) and a predicted less green method (red).

ICP-MS technique is considered as a highly sensitive method of analysis that requires sample treatment. Moreover, the ICP-MS technique offers no possibility to perform a direct determination due to the heavy instrumentation, giving rise to a higher penalization score. Additionally, it generates a considerable amount of residues (see Figs. 5 and 6 for PPs and hexagon, respectively). The simulated procedures for both methodologies, AAS and ICP-MS indicated an adequate variation in PPs and hexagon pictograms.

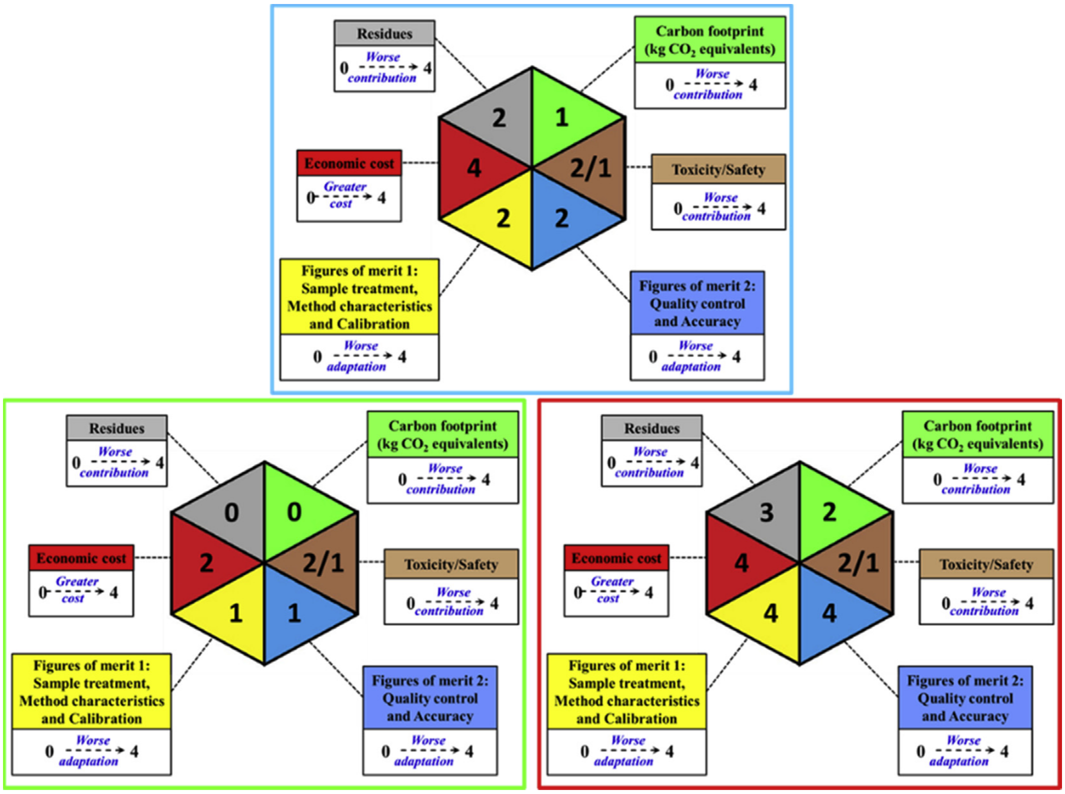

Fig. 10. Regular hexagonal pictogram for the evaluation of pesticides determination by LC-MS for the studied method (blue), a greenest simulated method (green) and the less green method (red).

Regarding chromatographic techniques, the determination of pesticides is investigated. It is observed that the gas chromatography coupled to mass spectrometry (GC-MS) with thermal desorption module (see Fig. 7 and Fig. 8) has disadvantages compared to the liquid chromatography technique (LC-MS) as it can be seen in Fig. 9 and Fig. 10. It involves a longer and more complex sample treatment and it implies the manipulation of gases under pressure that increases the penalization in the evaluation process.

Additional evaluation results for other methods are shown in the supporting information, SI.

5. Concluding remarks

The establishment of a complete evaluation tool has been proposed to characterize and/or to select analytical procedures. The suggested quantitative tool allows a user friendly visual inspection of the characteristics of an analytical procedure by means of the regular hexagonal pictogram. This pictogram, composed of six equilateral triangles, accounts for the variables of the analytical method that are assessed and quantified, such as the figures of merit, toxicity and safety, residues, environmental impact and economic cost. This is a powerful tool that aims to guide the selection of the analytical procedure that possesses the best compromise between sustainability and cost-effective aspects. The existence of green chemistry metrics is widely encouraged not only in research laboratories but also in industries since greenness is a contemporary driving force that promotes the development of more environmentally-friendly analytical scenarios.

Acknowledgements

The authors would like to thank to the EU-FEDER and MCIU-AEI of Spain (Project CTQ-2017-90082-P) and to the Generalitat Valenciana (PROMETEO Program 2016/109) for financial support. A. B.-C. is grateful to Generalitat Valenciana (PROMETEO Pro-gram) for her post-doc grant. P.C.-F. and GAMASER express their gratitude to GV- AEST/2018/034 funding.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.trac.2019.06.015.

References

[1] A. Gałuszka, Z. Migaszewski, J. Namieśnik, The 12 principles of green analytical chemistry and the significance of green analytical practices, TrAC Trends Anal. Chem. (Reference Ed.) 50 (2013) 78–84. https://doi.org/10.1016/j.trac.2013.04.010.

[2] M. Tobiszewski, A. Mechlińska, B. Zygmunt, J. Namieśnik, Green analytical chemistry in sample preparation for determination of trace organic pollutants, TrAC Trends Anal. Chem. (Reference Ed.) 28 (2009) 943–951. https://doi.org/10.1016/j.trac.2009.06.001.

[3] F. Pena-Pereira, I. Lavilla, C. Bendicho, Liquid-phase microextraction techniques within the framework of green chemistry, TrAC Trends Anal. Chem. (Reference Ed.) 29 (2010) 617–628. https://doi.org/10.1016/j.trac.2010.02.016.

[4] A. Spietelun, L. Marcinkowski, M. de la Guardia, J. Namieśnik, Green aspects, developments and perspectives of liquid phase microextraction techniques, Talanta 119 (2014) 34–45. https://doi.org/10.1016/j.talanta.2013.10.050.

[5] A. Spietelun, L. Marcinkowski, M. de la Guardia, J. Namieśnik, Recent developments and future trends in solid phase microextraction techniques towards green analytical chemistry, J. Chromatogr., A 1321 (2013) 1–13. https://doi.org/10.1016/j.chroma.2013.10.030.

[6] H.M. Mohamed, Green, environment-friendly, analytical tools give insights in pharmaceuticals and cosmetics analysis, TrAC Trends Anal. Chem. (Reference Ed.) 66 (2015) 176–192. https://doi.org/10.1016/j.trac.2014.11.010.

[7] C. Capello, U. Fischer, K. Hungerbühler, What is a green solvent? A comprehensive framework for the environmental assessment of solvents, Green Chem. 9 (2007) 927–934. https://doi.org/10.1039/b617536h.

[8] N. Roy, A. Gaur, A. Jain, S. Bhattacharya, V. Rani, Green synthesis of silver nanoparticles: an approach to overcome toxicity, Environ. Toxicol. Pharmacol. 36 (2013) 807–812. https://doi.org/10.1016/j.etap.2013.07.005.

[9] N. Jornet-Martínez, Y. Moliner-Martínez, C. Molins-Legua, P. Campíns-Falcó, Trends for the development of in situ analysis devices, in: R.A. Meyers, M. Valcarcel (Editors), Encycl. Anal. Chem., John Wiley & Sons Ltd., Sussex, 2017, pp. 1–23. https://doi.org/10.1002/9780470027318.a9593.

[10] L.H. Keith, L.U. Gron, J.L. Young, Green analytical methodologies, Chem. Rev. 107 (2007) 2695–2708. https://doi.org/10.1021/cr068359e.

[11] P. Anastas, N. Eghbali, Green chemistry: principles and practice, Chem. Soc. Rev. 39 (2010) 301–312. https://doi.org/10.1039/b918763b.

[12] K. Van Aken, L. Strekowski, L. Patiny, EcoScale, a semi-quantitative tool to select an organic preparation based on economical and ecological parameters, Beilstein J. Org. Chem. 2 (2006) 1–7. https://doi.org/10.1186/1860-5397-2-3.

[13] A. Gałuszka, Z.M. Migaszewski, P. Konieczka, J. Namieśnik, Analytical Eco-Scale for assessing the greenness of analytical procedures, TrAC Trends Anal. Chem. (Reference Ed.) 37 (2012) 61–72. https://doi.org/10.1016/j.trac.2012.03.013.

[14] C. Molins-Legua, S. Meseguer-Lloret, Y. Moliner-Martinez, P. Campíns-Falcó, A guide for selecting the most appropriate method for ammonium determination in water analysis, TrAC Trends Anal. Chem. (Reference Ed.) 25 (2006) 282–290. https://doi.org/10.1016/j.trac.2005.12.002.

[15] J. Pla-Tolós, P. Serra-Mora, L. Hakobyan, C. Molins-Legua, Y. Moliner-Martinez, P. Campins-Falcó, A sustainable on-line CapLC method for quantifying antifouling agents like irgarol-1051 and diuron in water samples: estimation of the carbon footprint, Sci. Total Environ. 569–570 (2016) 611–618. https://doi.org/10.1016/j.scitotenv.2016.06.18.

[16] N. Jornet-Martínez, S. Bocanegra-Rodríguez, R.A. González-Fuenzalida, C. Molins-Legua, P. Campíns-Falcó, In situ analysis devices for estimating the environmental footprint in beverages industry, in: A.M. Grumezescu, A.M. Holban (Editors), Processing and Sustainability of Beverages, vol. 2, Elsevier, Amsterdam, 2019, pp. 275–317 (Chapter 9), https://doi.org/10.1016/B978-0-12-815259-1.00009-4.

[17] S. Tarín, A. Huici, M.X. Guardino, NTP 726: Clasificación y etiquetado de productos químicos: sistema mundialmente armonizado (GHS), Instituto nacional de higiene y seguridad en el trabajo, Spain, 2004. www.insht.es/InshtWeb/Contenidos/Documentacion/.

[18] T.V.T. Phan, C. Gallardo, J. Mane, GREEN MOTION: a new and easy to use green chemistry metric from laboratories to industry, Green Chem. 17 (2015) 2846–2852. https://doi.org/10.1039/c4gc02169j.

[19] J. Płotka-Wasylka, A new tool for the evaluation of the analytical procedure: green Analytical Procedure Index, Talanta 181 (2018) 204–209. https://doi.org/10.1016/j.talanta.2018.01.013.

[20] J. Jiménez, L. De la Cruz, J. Carballo, A. Domenech, Enfoques metodológicos para el cálculo de la Huella de Carbono, OSE Estudios Gráficos Europeos S.A., Spain, 2011.