Analytical Eco-Scale for assessing the greenness of analytical procedures

Article *in* TrAC Trends in Analytical Chemistry · July 2012

DOI: 10.1016/j.trac.2012.03.013

4 authors:

Agnieszka Gałuszka
Jan Kochanowski University
103 PUBLICATIONS **6,273** CITATIONS
SEE PROFILE

Zdzisław M Migaszewski
Jan Kochanowski University
125 PUBLICATIONS **3,506** CITATIONS
SEE PROFILE

Piotr Konieczka
Gdansk University of Technology
123 PUBLICATIONS **3,745** CITATIONS
SEE PROFILE

Jacek Namieśnik
Gdansk University of Technology
998 PUBLICATIONS **31,190** CITATIONS
SEE PROFILE

Analytical Eco-Scale for assessing the greenness of analytical procedures

Agnieszka Gałuszka, Piotr Konieczka, Zdzisław M. Migaszewski,
Jacek Namieśnik

We propose the analytical Eco-Scale as a novel comprehensive approach to evaluating the greenness of analytical methodology. It is based on assigning penalty points to parameters of an analytical process that are not in agreement with the ideal green analysis. This approach compares different parameters and different steps of the analytical process.

Traditional green chemistry metrics (e.g., Atom Economy, E-factor and Reaction Mass Efficiency), which were introduced for organic preparations, do not usually fit the purposes of green analytical chemistry. Existing databases for evaluation of green analytical methods refer to known procedures and instruments, and do not encourage new, more environmentally-friendly equivalents.

As an alternative to traditional green chemistry metrics, the analytical Eco-Scale can be a good, semi-quantitative tool.

Keywords: Analytical Eco-Scale; Analytical procedure; Eco-Scale; Environment friendly; Green analytical chemistry; Green chemistry metrics; Greenness; Method selection; Penalty point; Twelve principles of green chemistry

Agnieszka Gałuszka, Zdzisław M. Migaszewski
Geochemistry and the Environment Div., Institute of Chemistry, Jan Kochanowski University, 15G Świętokrzyska St., 25-406 Kielce, Poland

Piotr Konieczka, Jacek Namieśnik*
Department of Analytical Chemistry, Chemical Faculty, Gdańsk University of Technology (GUT), 11/12G Narutowicz St., 80-233 Gdańsk, Poland

*Corresponding author.
Tel.: +48 58 347 10 10;
Fax: +48 58 347 26 94;
E-mail: chemanal@pg.gda.pl

1. Introduction

The concept of green chemistry emerged at the beginning of the 1990s and can be perceived as a contribution of chemists to the idea of sustainable development [1,2]. As stated in the most popular definition of green chemistry proposed by Anastas [1], the principal objectives of green chemistry are reduction and elimination of the use and the generation of hazardous substances. The branch of chemistry that contributes most to the use and the generation of hazardous substances is organic synthesis. For this reason, green organic synthesis has dominated green chemistry for almost a decade.

In 1999, the term "green analytical chemistry" was proposed [3] and, in the same year, the father of green chemistry, Anastas, drew attention to the need to develop green analytical methodology [1]. Since that time, interest in implementing green chemistry principles in analytical chemistry has grown dramatically. This interest has resulted in recent publication of three books on this subject [4–6] and numerous scientific articles [7–9], but some of the important issues still require detailed explanation. One such problem is green analytical metrics.

The canons of green chemistry are the 12 principles proposed by Anastas and Warner [10]. The analytical consequences of these principles, related directly to six of them (principle number 1, 5, 6, 8, 11 and 12), have been discussed elsewhere [5,11].

Generally, the conformity of different analytical issues with the 12 principles of green chemistry refers to reagents, energy, waste and methods (Fig. 1). Method selection is crucial and controls other issues. In modern analytical laboratories, different methods and techniques can be used for determination of a single analyte. Metrological quality of the results [i.e. accuracy, precision, selectivity, limits of detection (LODs)], cost of analysis, and specific standard procedures that are recommended for environmental, medical or other purposes are usually taken into account when selecting analytical methodologies. However, this approach does not consider the green chemistry principles.

0165-9936/$ - see front matter © 2012 Elsevier Ltd. All rights reserved. doi:http://dx.doi.org/10.1016/j.trac.2012.03.013

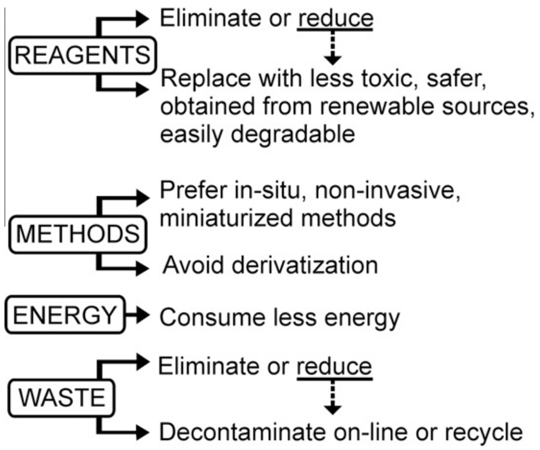


Figure 1. Analytical consequences of the 12 principles of green chemistry.

In this article, we propose a new, comprehensive tool for semi-quantitative evaluation of analytical methodologies that will make possible comparison and selection of the greenest alternative, and will enable the greenness of new or modified methods to be tested.

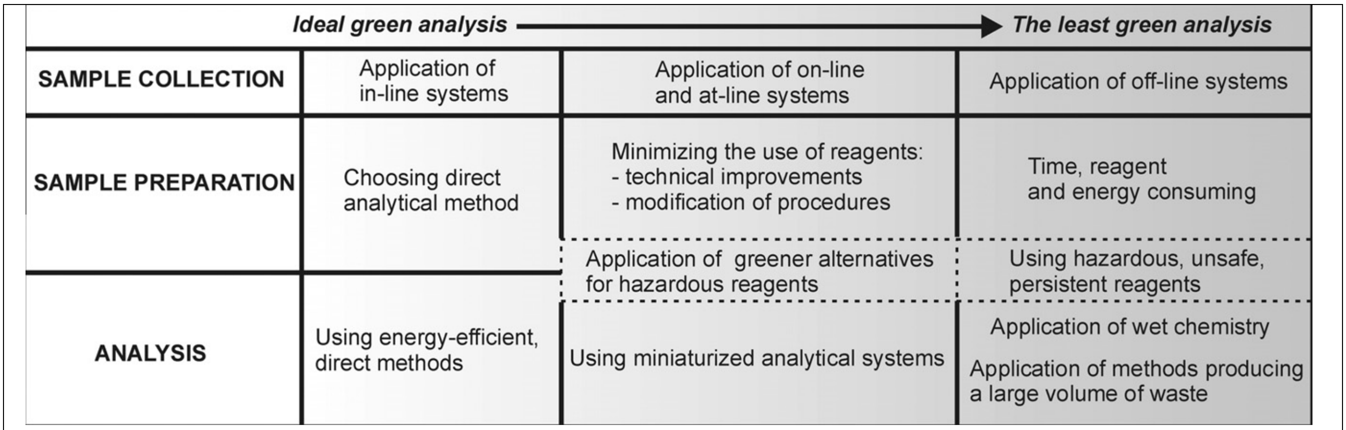
2. Green chemistry metrics

The evaluation of analytical methodologies in the context of green chemistry is very difficult because of the large number and the diversity of analytes and analytical methods, the complexity of sample matrices and the special analytical criteria that need to be considered (e.g., precision, accuracy and LODs). We should stress that, in some cases, it is impossible to meet certain green chemistry criteria in analytical methodology. In this situation, efforts are needed to improve the method. A good example of this approach is minimization of the use of reagents that cannot be eliminated or substituted by using flow-injection systems [12] or miniaturizing analytical systems [13].

Another difficulty of green analytical methodology is the multi-step character of the analytical process. Each of the steps should be considered in relation to development of greener analytical procedures (Fig. 2). Tobiszewski et al. [7] pointed out that the least green step in the analytical process is sample preparation. The best approach is to eliminate this stage by applying a direct analytical method. In general, four aspects can be distinguished when developing new, greener analytical procedures, which are also called ''Sustainable Analytical Procedures'' [14]:

(1) method-oriented [12,15,16];
(2) analyte-oriented [17];
(3) process-oriented [18]; and,
(4) a combination of two or three of the approaches mentioned above [19].

The principal question that can be asked when searching for a green analytical method is: ''How to evaluate different procedures in order to choose the greenest one?'' There are general guidelines for green procedures, which usually consider only one aspect of a given method, {e.g., selection of a greener solvent



	Ideal green analysis →		→ *The least green analysis*
SAMPLE COLLECTION	Application of in-line systems	Application of on-line and at-line systems	Application of off-line systems
SAMPLE PREPARATION	Choosing direct analytical method	Minimizing the use of reagents: - technical improvements - modification of procedures	Time, reagent and energy consuming
		Application of greener alternatives for hazardous reagents	Using hazardous, unsafe, persistent reagents
ANALYSIS	Using energy-efficient, direct methods	Using miniaturized analytical systems	Application of wet chemistry Application of methods producing a large volume of waste

Figure 2. Comparison of the green chemistry criteria for three key steps in an analytical process.

[20,21]}. Recently, an application of green analytical chemistry in a chromatography laboratory was discussed [16]. However, most of current approaches to evaluating green methodology are based on *a priori* judgment (i.e. not based on a scientific approach, but on instinctive selection of an analytical method). However, it may sometimes lead to bias [e.g., the use of high-performance liquid chromatography (HPLC) and supercritical fluid chromatography (SFC) in pharmaceutical industry]. Unexpectedly, the first method was found greener on the basis of life-cycle assessment [16]. We need a more quantitative approach to selecting a green analytical method.

The application of traditional green chemistry metrics in green analytical chemistry is limited. The most popular parameters {e.g., E-factor [22], Atom Economy [23], Reaction Mass Efficiency [24] and the Eco-Scale [25]} were introduced for the purposes of organic synthesis.

Koel and Kaljurand [6] tried to adopt the Atom Economy to analytical procedures. However, this approach requires knowledge of the number of molecules of the analyte that gives a measurable analytical signal, which it is not always possible to obtain.

One of the most comprehensive ways to assess the greenness of analytical methods used for environmental purposes is a free Internet-searchable database – National Environmental Methods Index (NEMI) – which can be found at the website http://www.nemi.gov. The rating of the existing methods is done on the basis of four criteria that refer to properties of reagents or wastes used in this method [26]:

(1) persistent, bioaccumulative, toxic;
(2) hazardous;
(3) corrosive (pH <2 or >12); and,
(4) volume (mass) of waste is >50 mL(g).

Another example of an Internet database that can be helpful in selecting a green analytical method is the Green Chemical Alternatives Wizard (http://ehs.mit.edu/greenchem/) developed by Massachusetts Institute of Technology. This database is oriented towards chemicals and processes that can be changed to reduce the volume of hazardous wastes in laboratories.

A very interesting approach to green organic synthesis evaluation, named Eco-Scale, was proposed by Van-Aken et al. [25], who assumed that an ''ideal'' reaction, which has a score of 100 in the Eco-Scale, uses inexpensive compounds, and is conducted at a room temperature with a 100% yield, and is safe for both the operator and the environment. For each of the parameters that differs from ''the ideal value'', penalty points are assigned, lowering the total score. The higher the score, the greener and more economical organic preparation is. This concept can be adapted to evaluate green analytical methods.

3. Green chemistry in analytical procedures

In many analytical procedures, it is impossible to reduce the use of reagents. There are some practices that can make such analyses greener. Toxic reagents should be replaced by their safer equivalents, alternative solvents should be preferred and the hazard of analytical wastes should be ameliorated. This last task can be achieved by on-line decontamination of wastes (recycling, degradation and passivation) [18].

Every analytical procedure comprises several steps, the number of which strongly depends on the sample properties and the analytical method. Generally, the greater the number of steps involved, the less green the analytical procedure is (due to increased energy use and larger volume of waste). Thus, an ideal approach to green analytical methodology would be to reduce the number of stages in a given analytical procedure. However, some of the steps are inevitable. The role of green analytical chemistry is to search for more environmentally benign analytical methodology. In this section, we discuss the most important issues in the green chemistry approach to multi-stage analytical procedures.

3.1. Sample collection, preservation, transport and storage

The first step of every analytical procedure is sample collection. In some specific cases, analysis can be performed directly on-site, without transport of sampled material to the instrument (e.g., using a portable XRF device). This type of sample collection is called in-line sampling [7] and can be considered the greenest approach to this step of the analytical procedure.

The time delay between sampling and obtaining analytical results is crucial for the greenness of analytical procedure. In this respect, on-line and at-line sampling represent a medium-green approach, and, according to Tobiszewski et al. [7], off-line sample collection should be avoided. The greenness of sample collection can also be discussed in terms of the energy use (some sampling instruments need a power supply) and resources used (e.g., sample packaging and filters). In general, the more items used in this step, the less green is the procedure.

Many samples (e.g., environmental, biological and food) need preservation because of physical and chemical changes that may occur during sample collection, transport, storage and preparation. Preservation is very important for the overall quality of analysis, because it assures the representativeness of the sample. There are different techniques used for sample preservation and their application depends on analyte and sample types. Detailed description of sample-preservation techniques is beyond the scope of this article and is given elsewhere [27]. In general, these techniques can be divided

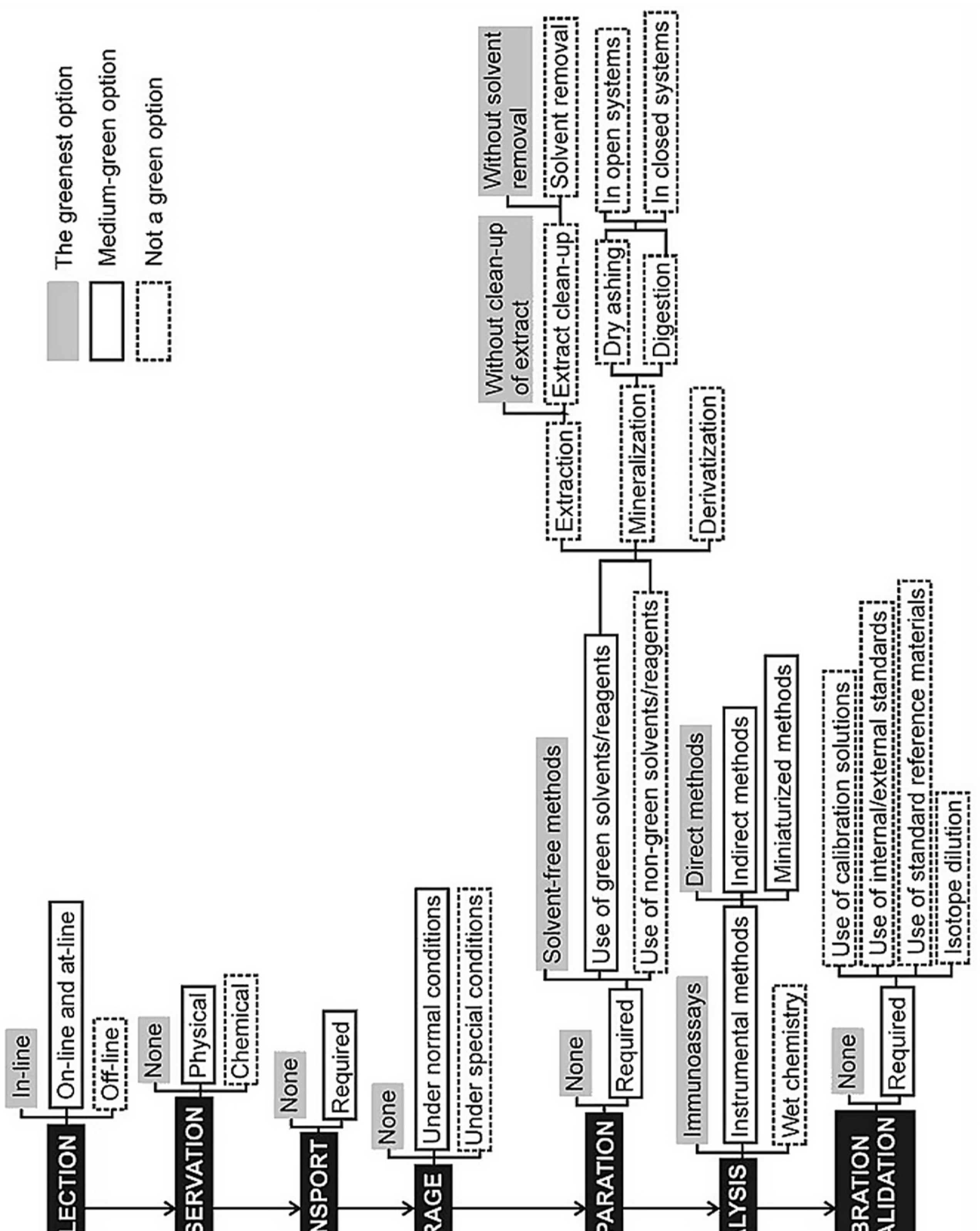


Figure 3. Green alternatives for different steps of analytical procedure.

into: physical (chilling, freezing, and filtration) and chemical (acidification, alkalization, addition of preservation agents). Sample preservation is not a green step in an analytical procedure, because it requires energy and/or the use of chemicals. The best option for green analytical methodology is to avoid sample preservation, if possible.

The next important issue regarding preliminary steps of an analytical procedure is sample transport. Its incompatibility with green chemistry principles results from energy use [i.e. vehicle fuel and specific conditions for sample storage (e.g., chilling)]. This step could be avoided by applying field analysis (field screening), which has a few advantages, as it:

(1) allows real-time analysis;
(2) requires no, or little, sample preparation;
(3) uses portable instruments [28];
(4) uses minimal energy and reagents; and,
(5) is cost effective [6].

If transport is unavoidable, the distance between sampling site and analytical laboratory should preferably be as short as possible.

Sample storage is an optional step in an analytical procedure, and usually depends on laboratory capacity for performing analysis. Samples can be stored under ambient conditions (room temperature, dark, well-aerated room) or under special conditions (frozen or cooled). Sample storage for an extended period of time (weeks or months) usually needs chemical preservation. From the point of view of green analytical chemistry, this option is the least favorable.

3.2. Sample preparation

As mentioned above, sample preparation is a critical step for the greenness of analytical procedure. It usually comprises several operations in which non-green reagents (e.g., organic solvents and strong acids) are often required. There are analytical procedures in which sample preparation is unnecessary or is minimized to routine activities (e.g., weighing, grinding, and sieving). The most important operations in a sample-preparation step are dry ashing, digestion, extraction, post-extraction clean-up and derivatization.

Determination of trace elements in solid samples by the majority of instrumental methods requires the sample to be decomposed. The most common techniques of solid-sample decomposition are dry ashing and wet digestion. Dry ashing and subsequent dissolution of ash in acids is often referred to as mineralization. In dry ashing, a sample is heated in a crucible placed in a muffle furnace at a temperature in the range 400–800°C. After ashing, the residues are dissolved in acids. Digestion is another type of solid-sample decomposition for trace-element determinations, which also uses reagents (usually mineral and oxidizing acids) and large amounts of energy. Hydrochloric, sulfuric, nitric,

Table 1. The penalty points (PPs) to calculate analytical Eco-Scale

	Reagents		
		Sub-total PP	**Total PP**
Amount	<10 mL (g)	1	Amount PP × Hazard PP
	10–100 mL (g)	2	
	>100 mL (g)	3	
Hazard (physical, environmental, health) [45]*	None	0	
	Less severe hazard	1	
	More severe hazard	2	
	Instruments		
Energy [39]	⩽0.1 kWh per sample		0
	⩽1.5 kWh per sample		1
	>1.5 kWh per sample		2
Occupational hazard	Analytical process hermetization		0
	Emission of vapors and gases to the air		3
Waste	None		0
	<1 mL (g)		1
	1–10 mL (g)		3
	>10 mL (g)		5
	Recycling		0
	Degradation		1
	Passivation		2
	No treatment		3

* PPs are assigned to each of hazard category posed by a reagent. Each reagent can have more than one hazard category, thus the sub-total PP value for a single reagent may be greater than 2.

perchloric and hydrofluoric (HF) acids are the acids most commonly used to decompose samples [29]. They can be applied individually or in mixtures. Acid digestion can be performed in open vessels using hot-plate or commercial sample-digestion devices, but, in many laboratories, microwave-digestion systems are used for accelerating and making the preparation step safer. Unfortunately, it is impossible to make dry ashing and digestion greener, and, for many samples (e.g., soil and geological samples), the use of HF is recommended.

The only green way to avoid decomposition of solid samples for trace-element determinations is to use direct analytical methods, but they may not always be applicable due to higher LODs (XRF) or a lack of matrix-matched standards and reference materials [laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)].

The most problematic aspect in determination of organic compounds is use of organic solvents that leads to generation of hazardous waste. The source of large quantities of wastes in organic analysis particularly includes: derivatization, extraction and clean-up of the extracts. According to the eighth principle of green chemistry [10], derivatization should be avoided. However, in some cases, derivatization may be an alternative to sample preservation [30]. Preparation of samples of organic compounds for determination is time consuming (it takes about 61% of the time of analysis) [31] and reagent consuming. This step of analytical procedure offers many options [32], which certainly should aim to make the analysis greener.

The greatest progress in making analytical procedures greener has been achieved in the field of extraction. The greenest option for preparing samples for determinations of organic compounds comprises solventless techniques [33–36]. If it is impossible to apply a solvent-free technique, the green alternative is reduction using a solvent or replacing organic solvents with ‘‘green solvents’’. The first goal can be achieved by applying shorter, smaller diameter chromatographic columns [16,37] or using selected types of extraction {e.g., solid-phase extraction (SPE), pressurized fluid extraction (PFE), microwave-assisted extraction (MAE), liquid-phase microextraction (LPME), or single-drop microextraction (SDME)

Table 2. The examples of penalty points (PPs) for hazards and energy of selected reagents and analytical techniques

Reagent	Number of pictograms	Signal word	Penalty points
Acetic acid (glacial)	2	Danger	4
Acetic acid (30%)	1	Danger	2
Acetylene	2	Danger, Warning	3
Ammonia solution (25%)	3	Danger	6
Benzoic acid	1	Warning	1
Dichloromethane	1	Warning	1
Hydrochloric acid (30%)	2	Danger	4
Hydrogen peroxide (30%)	2	Danger	4
n-Hexane	4	Danger	8
Nitric acid (65%)	2	Danger	4
Potassium dichromate	5	Danger	10
Sodium hydroxide (30%)	1	Danger	2
Sulfuric acid (25%)	1	Danger	2
Technique		**Energy used**	
FTIR Immunoassay Spectrofluorometry Titration UPLC UV-Vis Spectrometry		<0.1 kWh per sample	0
AAS GC ICP-MS LC		⩽1.5 kWh per sample	1
NMR GC-MS LC-MS X-ray diffractometry		1.5 kWh per sample	2

FTIR, Fourier transform infrared spectroscopy; UPLC, Ultra-performance liquid chromatography; AAS, Atomic absorption spectrometry; GC, Gas chromatography; ICP-MS, Inductively coupled plasma mass spectrometry; LC, Liquid chromatography; NMR, Nuclear magnetic resonance spectroscopy; GC-MS, Gas chromatography-mass spectrometry; LC-MS, Liquid chromatography-mass spectrometry.

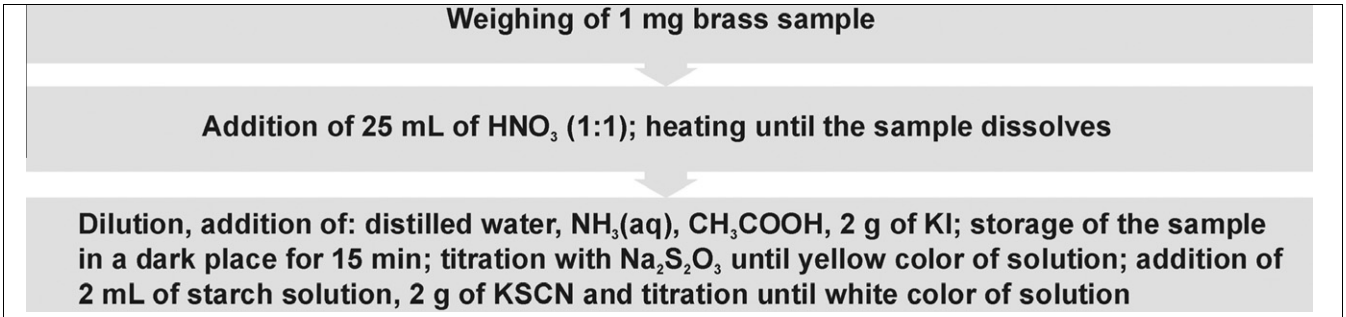


Figure 4. Analytical procedure for a determination of copper in a brass sample by titration.

Table 3. The penalty points (PPs) for Cu determination by titration in a brass sample

Reagents	Penalty points
HNO_3: 10 mL	8
NH_3(aq.): 2 mL	6
CH_3COOH: 10 mL	2
KI: 2 g	0
$Na_2S_2O_3$	0
Starch	0
KSCN: 2 g	1
	∑17
Instruments	**Penalty points**
Heater	2
Occupational hazard	3
Waste	8
	∑13
Total penalty points: 30	
Analytical Eco-Scale total score: 70	

Table 4. The penalty points (PPs) for electrogravimetric Cu determination in a brass sample

Reagents	Penalty points
HNO_3: 10 mL	8
NH_3(aq.)	6
H_2SO_4: 2 mL	2
NH_4NO_3: 2 g	1
	∑17
Instruments	**Penalty points**
Heater	2
Occupational hazard	3
Waste	5
	∑10
Total penalty points: 27	
Analytical Eco-Scale total score: 73	

[34,36]}. Supercritical fluids, subcritical water, ionic liquids are examples of ''green solvents'' [7].

Post-extraction clean-up of organic compounds aims to minimize the influence of interfering compounds on the detection of the analyte. Several methods are available (e.g., alumina column, Florisil column, or silica-gel column), and they are based on different mechanisms (e.g., adsorption, size-separation, partitioning, or oxidation-reduction) [38].

In the context of green analytical chemistry, clean-up of the extracts is an additional step in an analytical procedure, which uses extra reagents and resources,

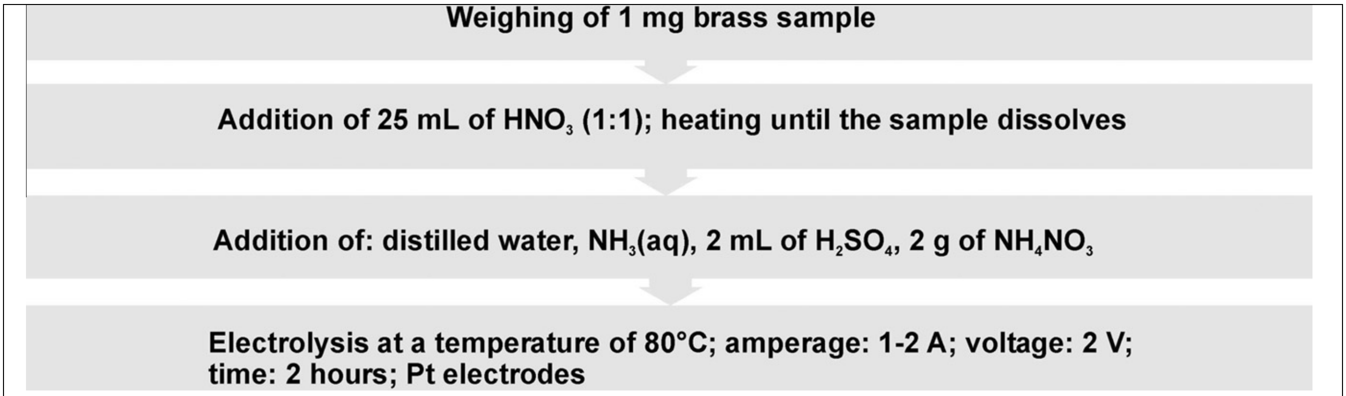


Figure 5. Analytical procedure for an electrogravimetric determination of copper in a brass sample.

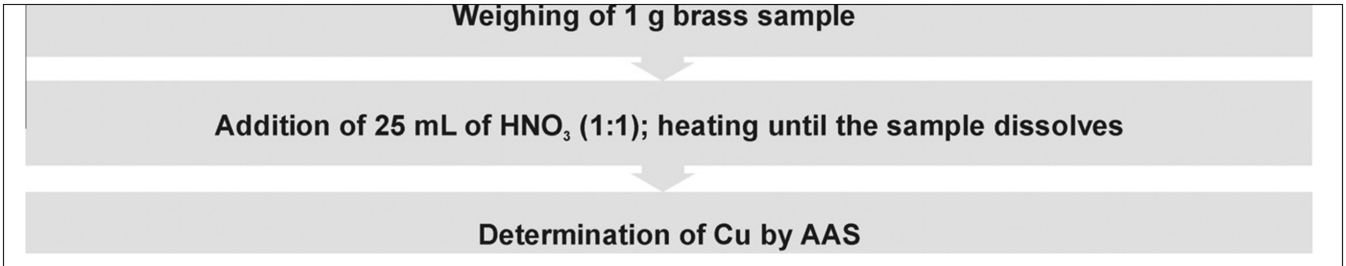


Figure 6. Analytical procedure for a determination of copper in a brass sample by atomic absorption spectrometry.

generates extra waste, and, if possible, it should be avoided.

3.3. Analysis

Sample analysis requires using various analytical methods and usually more than one technique is capable of determining a single analyte. The selection of analytical method is commonly made on the basis of its accuracy, precision, selectivity and LODs. According to green analytical chemistry, it should also consider the environmental and health impact [39]. There are several classifications of analytical techniques. One of them, based on the need for sample preparation, is especially important for green analytical chemistry. In this classification, two types of analytical technique are distinguished:

(1) direct, requiring no sample preparation; and,
(2) indirect, needing sample preparation.

Garrigues and de la Guardia [40] provided a comprehensive review of the direct methods. They divided direct methods into remote sensing, and methods without and with sample damage. The non-destructive measurement techniques for solid-sample analysis include NIR spectroscopy, Raman spectroscopy, X-ray fluorescence and nuclear magnetic resonance. Direct analysis with sample damage is possible using electrothermal atomic absorption spectrometry (ETAAS), arc and spark optical emission spectrometry, laser ablation (with ICP-OES or ICP-MS), glow discharge (with ICP-OES or ICP-MS), laser-induced breakdown spectroscopy (LIBS) and desorption electrospray ionization mass spectrometry (DESI-MS). Other analytical methods that allow direct analysis encompass neutron activation, thermogravimetric and

Table 5. The penalty points (PPs) for Cu determination by AAS in a brass sample

Reagents	Penalty points
HNO_3: 10 mL	8
Cu standard solutions	3
Acetylene	3
	$\sum$14
Instruments	**Penalty points**
Heater	2
Spectrometer	2
Occupational hazard	3
Waste	8
	$\sum$15
Total penalty points: 29	
Analytical Eco-Scale total score: 71	

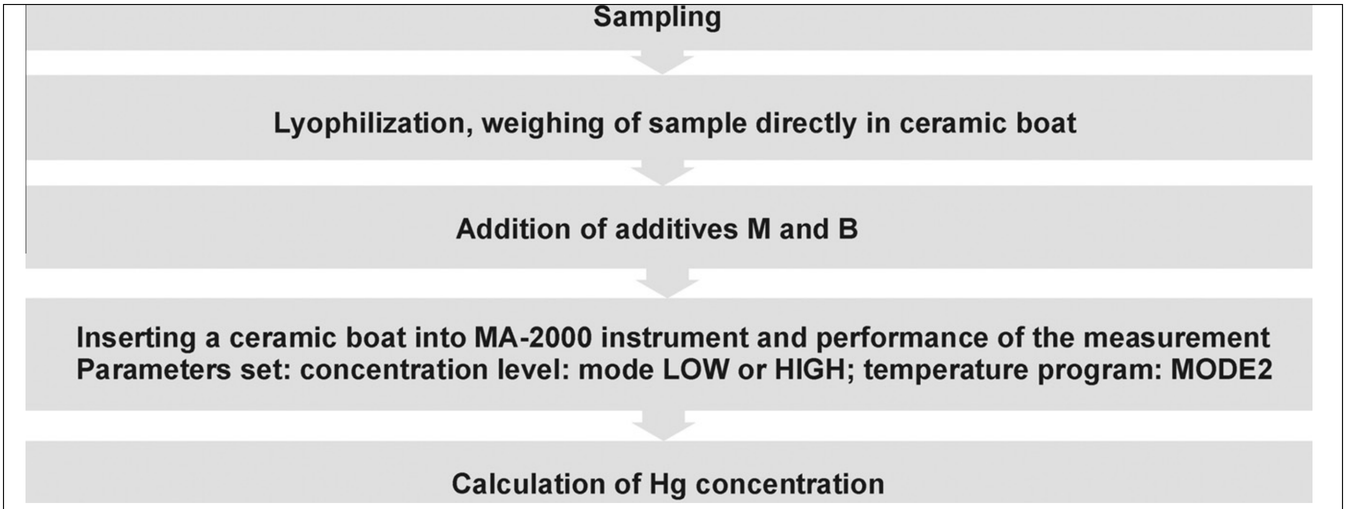


Figure 7. Analytical procedure for a determination of mercury in an animal tissue by cold-vapor atomic absorption spectrometry.

Table 6. The penalty points (PPs) for Hg determination by CVAAS in an animal tissue

Reagents	**Penalty points**
Additives M and B	0
Hg standard solutions	2
	∑2
Instruments	**Penalty points**
Freeze-drying instrument	2
Hot-plate	2
Spectrometer	2
Occupational hazard	0
Waste	2
	∑8
Total penalty points: 10	
Analytical Eco-Scale total score: 90	

electrochemical methods, and immunoassays [30]. Of the direct methods, real-time electrochemical monitoring [41] and vibrational spectroscopy (FTIR, NIR, and Raman) [42] are considered promising green analytical tools.

A modern trend in instrumental analysis, which meets the needs of green analytical chemistry, is miniaturization of analytical methods [43]. The most important advantages of analytical instrument miniaturization for the greenness of analytical procedures include reducing the use of toxic reagents and a resulting decrease in waste generation [44].

3.4. Calibration and validation

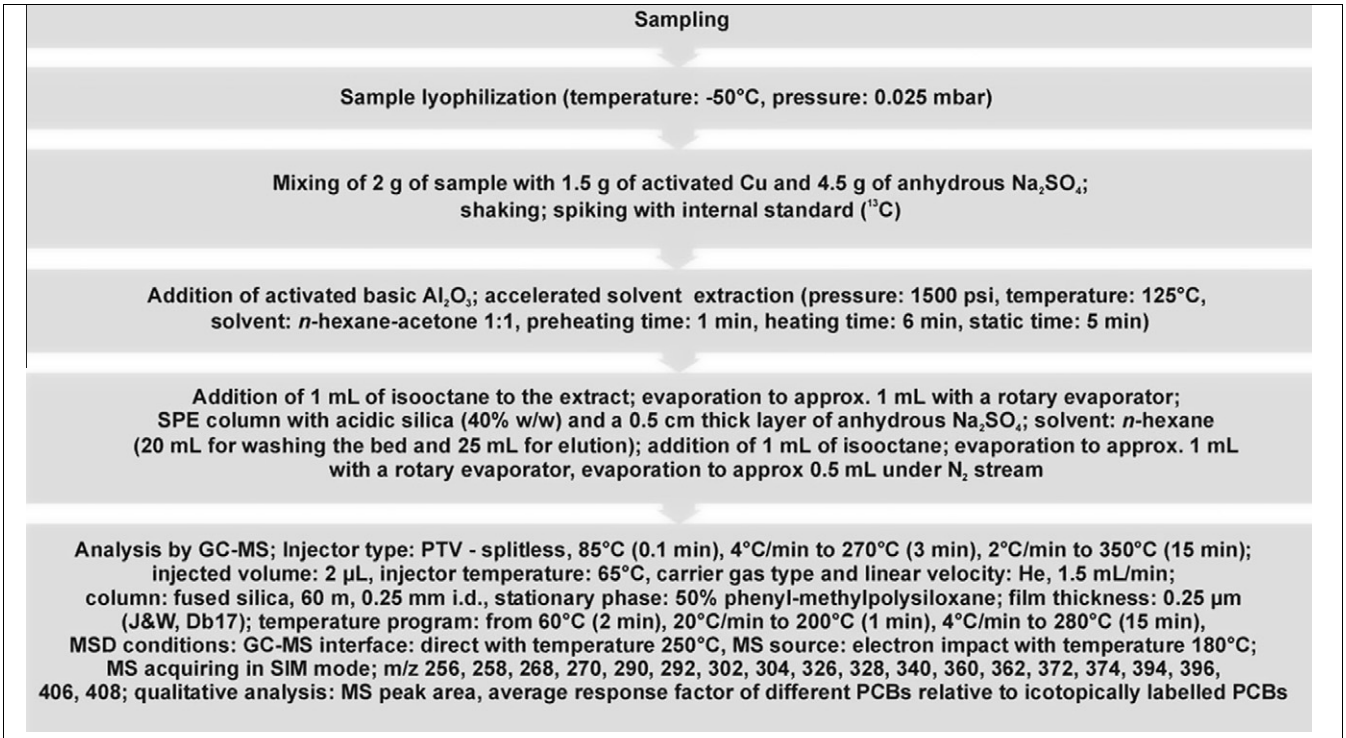
Calibration and validation of analytical methods are very important for quality assurance. They are prerequisites for quantitative analysis. However, the use of calibration solutions, internal/external standards, standard reference materials or isotope dilution contribute to enhanced reagent consumption and waste generation. This step of analytical procedure is not always considered in evaluation of the greenness of analytical methodologies, but its contribution to waste generation should not be underestimated.

4. The concept of the analytical Eco-Scale

The short discussion of analytical procedures in the context of green chemistry presented in the previous section shows that there are more or less green alternatives for each step of the procedure (Fig. 3). On the basis of the data presented in Fig. 3, features of the ideal green analysis can be deduced. This ideal green analysis will be a key parameter in our analytical Eco-Scale concept.

4.1. The ideal green analysis

The ideal green analysis can be characterized by elimination or minimal use of reagents, minimal energy use, and no waste generation. These criteria are met only by



Sampling

Sample lyophilization (temperature: -50°C, pressure: 0.025 mbar)

Mixing of 2 g of sample with 1.5 g of activated Cu and 4.5 g of anhydrous Na_2SO_4; shaking; spiking with internal standard (^{13}C)

Addition of activated basic Al_2O_3; accelerated solvent extraction (pressure: 1500 psi, temperature: 125°C, solvent: *n*-hexane-acetone 1:1, preheating time: 1 min, heating time: 6 min, static time: 5 min)

Addition of 1 mL of isooctane to the extract; evaporation to approx. 1 mL with a rotary evaporator; SPE column with acidic silica (40% w/w) and a 0.5 cm thick layer of anhydrous Na_2SO_4; solvent: *n*-hexane (20 mL for washing the bed and 25 mL for elution); addition of 1 mL of isooctane; evaporation to approx. 1 mL with a rotary evaporator, evaporation to approx 0.5 mL under N_2 stream

Analysis by GC-MS; Injector type: PTV - splitless, 85°C (0.1 min), 4°C/min to 270°C (3 min), 2°C/min to 350°C (15 min); injected volume: 2 µL, injector temperature: 65°C, carrier gas type and linear velocity: He, 1.5 mL/min; column: fused silica, 60 m, 0.25 mm i.d., stationary phase: 50% phenyl-methylpolysiloxane; film thickness: 0.25 µm (J&W, Db17); temperature program: from 60°C (2 min), 20°C/min to 200°C (1 min), 4°C/min to 280°C (15 min), MSD conditions: GC-MS interface: direct with temperature 250°C, MS source: electron impact with temperature 180°C; MS acquiring in SIM mode; m/z 256, 258, 268, 270, 290, 292, 302, 304, 326, 328, 340, 360, 362, 372, 374, 394, 396, 406, 408; qualitative analysis: MS peak area, average response factor of different PCBs relative to icotopically labelled PCBs

Figure 8. Analytical procedure for determination polychlorinated biphenyls in sewage sludge by gas chromatography coupled to mass spectrometry.

Table 7. The penalty points (PPs) for PCB determination in sewage sludge by GC-MS

Reagents	Penalty points
Cu powder: 1.5 g	1
HCl: 2 mL	3
Na_2SO_4 (drying agent): 4.5 g + 1 g	0
Isotopically labeled PCBs standard mixture	4
Activated Al_2O_3: 1 g	0
n-Hexane: 15 mL + 45 mL	16
Acetone: 15 mL	8
Isooctane: 2 mL	8
Acidic silica (98% of H_2SO_4: 20 mL)	4
PCBs standard solution	4
	$\sum 48$
Instruments	**Penalty points**
Sampler	1
Transport	1
Freeze-drying instrument (−50°C, 0.025 mbar)	2
ASE extractor (1500 hPa, 125°C)	2
Rotary evaporator	2
Oven (for acidic silica preparation)	2
GC-MS	3
Occupational hazard	0
Waste	4
Total penalty points: 65	$\sum 17$
Analytical Eco-Scale total score: 35	

a few methods, which do not need sampling, sample transport, preservation, and preparation (i.e. based on direct measurements). There are examples of these analytical methods in sub-section 3.3. In determination of many analytes, there is no direct method available, so we propose that the ideal analysis should have the following characteristics:

(1) reagents do not pose hazards (physical, environmental, health);
(2) less than 0.1 kWh of energy per sample is consumed; and,
(3) no waste is produced.

4.2. *Components of the Eco-Scale*

The basis for our concept of an analytical Eco-Scale is that the ideal green analysis has a value of 100. This approach is analogous to the Eco-Scale proposed by Van Aken et al. for evaluating the greenness of organic synthesis [25]. For each of analytical procedure parameters (amount of reagents, hazards, energy and waste), penalty points are assigned if it departs from ideal green analysis (Table 1). Because the influence of hazardous substances depends on their amount, we propose that the total penalty points should be calculated by multiplying the sub-total penalty points for a given amount and hazard.

The sum of penalty points for the whole procedure should be included in the Eco-Scale calculation, according to the following formula:

$$\text{Analytical Eco-Scale} = 100 - \text{total penalty points}$$

The result of calculation is ranked on a scale, where the score:
>75 represents excellent green analysis,
>50 represents acceptable green analysis,
<50 represents inadequate green analysis.

Assignment of penalty points to categories of hazard and energy needs a detailed explanation. For assessing the hazard of reagents used in analytical procedures, different classifications of hazardous substances can be applied. For example, the NEMI database uses EPA (Environmental Protection Agency) Toxic Release Inventory, Clean Water Act and Clean Air Act for environmental hazard assessment, and NFPA (National Fire Protection Association) classification for health and safety hazard assessment, respectively [26]. We propose to evaluate physical, environmental and health hazards on the basis of the Globally Harmonized System of Classification and Labeling of Chemicals (GHS), which is the most comprehensive, up-to-date classification of chemicals [45]. For convenience and simplicity, we propose that pictograms and signal words should be included in evaluation of the hazards posed by reagents used in an analytical procedure. Each reagent can be characterized by one or more of the nine pictograms (flame, flame over circle, corrosion, gas cylinder, skull and crossbones, exclamation mark, environment and health hazard). For each pictogram, penalty points are assigned. Two signal words are used in GHS: ''danger'' (more severe hazard, category 1 and/or 2) and ''warning'' (less hazard, other categories). We propose the following system of penalty point assignment to hazards:
none (no pictogram) = 0 penalty points
less severe hazard = 1 penalty points
more severe hazard = 2 penalty points.

Penalty points for energy use will be assigned according to the values proposed by Raynie and Driver [39]. The least energy-consuming laboratory practices and instruments (<0.1 kWh per sample) are, e.g., immunoassays, titration, hot-plate solvent evaporation (<10 min), needle evaporator, sonicator, and UV-Vis spectrophotometer [39]. The most energy-consuming techniques are NMR, GC-MS, LC-MS, X-ray diffraction, hot-plate solvent evaporation (>2.5 h).

Examples of penalty points assigned to reagents for hazards and to analytical techniques for energy use are given in Table 2.

4.3. *Examples of analytical Eco-Scale calculation*

In this sub-section, we evaluate several examples of analytical procedures for their greenness using the analytical Eco-Scale. These examples present both instrumental and wet-chemistry methods applied for determination of organic (PCBs) and inorganic (Cu, Hg) analytes in different matrices (sewage sludge, brass, and biological material).

The procedures are covered as follows:

(1) Cu determination in a brass sample by titration is presented in Fig. 4, and the details about assigning penalty points are given in Table 3,
(2) Cu determination in a brass sample by an electrogravimetric method is presented in Fig. 5, and the details about assigning penalty points are given in Table 4,
(3) Cu determination in a brass sample by an AAS method is presented in Fig. 6, and the details about assigning penalty points are given in Table 5,
(4) Hg determination by CV-AAS in an animal-tissue sample is presented in Fig. 7, and the details about assigning penalty points are given in Table 6,
(5) PCB determination in sewage sludge by GC-MS is presented in Fig. 8, and the details about the penalty points are given in Table 7.

All the three methods of Cu determination in a brass sample have similar Eco-Scale values. Of these methods, electrogravimetry has the highest rank (73 in Eco-Scale) and is followed by AAS (71 in Eco-Scale). Surprisingly enough, titration has quite a high rank in the analytical Eco-Scale (70 in Eco-Scale). This example shows that wet-chemistry methods may be considered green in some individual cases, depending on the reagents used. In our example, three of seven chemicals used are not hazardous.

Determination of Hg in an animal tissue by CV-AAS represents the greenest methodology of all the examples presented. Its high rank in the Eco-Scale (90) results from the minimal reagent use. By contrast, determination of PCBs in sewage sludge by GC-MS has the highest value of total penalty points (65) resulting in the lowest rank in the analytical Eco-Scale (35). This poor score for GC-MS arises due to the use of hazardous solvents, and it could be improved by replacing these chemicals with their green alternatives. According to their analytical Eco-Scale rank, a determination of Hg by CV-AAS represents excellent green analysis, determinations of Cu by titration, electrogravimetry and AAS are examples of acceptable green analysis, and a determination of PCBs by GC-MS is inadequate green analysis.

5. Summary

After more than 10 years of activities in the field of green analytical chemistry, establishment of a convenient, comprehensive method for evaluating the greenness of different analytical methodologies is a priority. Such green analytical metrics should give an opportunity to compare different parameters and different steps of analytical processes to enable the search for the weakest points, which could be improved in order to meet green chemistry requirements. Existing green analytical evaluation tools (e.g., NEMI database) allow selection of one of the known procedures. This approach does not encourage the adoption of new methodologies.

The proposed analytical Eco-Scale can be a good semi-quantitative tool for laboratory practice and educational purposes. It is simple and fast to use, has well-defined criteria of evaluation and can be applied to any known and new methodologies. We believe that all these features will influence wide application of the analytical Eco-Scale in analytical laboratories.

We are aware that the proposed concept has its limitations. Some of analytical methods and techniques may not achieve the best ranking on the analytical Eco-Scale, despite their certain benefits for determination of a given analyte group. For example, determination of organic compounds is usually much more complicated and multi-stage than determination of trace elements, which results in much higher number of penalty points and lower rank in the Eco-Scale. Thus, application of the analytical Eco-Scale will be especially important for the search for new, greener methodologies, because it clearly and evidently indicates the weakest points in analytical procedures.

References

[1] P.T. Anastas, Crit. Rev. Anal. Chem. 29 (1999) 167.
[2] M.M. Kirchhoff, Resour. Conserv. Recycl. 44 (2005) 237.
[3] J. Namieśnik, Environ. Sci. Pollut. Res. 6 (1999) 243.
[4] M. de la Guardia, S. Armenta, Green Analytical Chemistry: Theory and Practice, Elsevier, Amsterdam, The Netherlands, 2010.
[5] M. de la Guardia, S. Garrigues (Editors), Challenges in Green Analytical Chemistry, Royal Society of Chemistry, Cambridge, UK, 2011.
[6] M. Koel, M. Kaljurand, Green Analytical Chemistry, Royal Society of Chemistry, London, UK, 2010.
[7] M. Tobiszewski, A. Mechlińska, B. Zygmunt, J. Namieśnik, Trends Anal. Chem. 28 (2009) 943.
[8] W. Wardencki, J. Curyło, J. Namieśnik, Polish J. Environ. Stud. 14 (2005) 389.
[9] M. Tobiszewski, A. Mechlińska, J. Namieśnik, Chem. Soc. Rev. 39 (2010) 2869.
[10] P.T. Anastas, J.C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, USA, 1998.
[11] M. Koel, M. Kaljurand, Pure Appl. Chem. 78 (2006) 1993.
[12] A. Molina-Díaz, J.F. García-Reyes, B. Gilbert-López, Trends Anal. Chem. 29 (2010) 654.
[13] L. Ramos, J.J. Ramos, U.A.Th. Brinkman, Anal. Bioanal. Chem. 381 (2005) 119.
[14] S. Armenta, S. Garrigues, M. de la Guardia, Trends Anal. Chem. 27 (2008) 497.
[15] Y. Gaber, U. Törnvall, M.A. Kumar, M.A. Amin, R. Hatti-Kaul, Green Chem. 13 (2011) 2021.
[16] R.E. Majors, D. Raynie, LC-GC N. Am. 29 (2011) 118.
[17] M. Farré, S. Pérez, C. Gonçalves, M.F. Alpendurada, D. Barceló, Trends Anal. Chem. 29 (2010) 1347.
[18] S. Garrigues, S. Armenta, M. de la Guardia, Trends Anal. Chem. 29 (2010) 592.

[19] S.B. Savvin, V.V. Kuznetsov, Y.V. Ermolenko, I.Y. Chernikova, A.V. Mikhailova, Pure Appl. Chem. 81 (2009) 2123.
[20] R.K. Henderson, C. Jiménez-González, D.J.C. Constable, S.R. Alston, G.G.A. Inglis, G. Fisher, J. Sherwood, S.P. Binks, A.D. Curzons, Green Chem. 13 (2011) 854.
[21] K. Alfonsi, J. Colberg, P.J. Dunn, T. Fevig, S. Jennings, T.A. Johnson, H.P. Kleine, C. Knight, M.A. Nagy, D.A. Perry, M. Stefaniak, Green Chem. 10 (2008) 31.
[22] R.A. Sheldon, Chem. Ind. 23 (1992) 903.
[23] B.M. Trost, Angew. Chem., Int. Ed. Engl. 34 (1995) 259.
[24] A.D. Curzons, D.J.C. Constable, D.N. Mortimer, V.L. Cunningham, Green Chem. 3 (2001) 1.
[25] K. Van Aken, L. Strekowski, L. Patiny, Beilstein J. Org. Chem. 2 (2006) 3.
[26] L.H. Keith, L.U. Gron, J.L. Young, Chem. Rev. 107 (2007) 2695.
[27] S. Mitra, R. Brukh, in: S. Mitra (Editor), Sample Preparation Techniques in Analytical Chemistry, John Wiley and Sons, Holboken, New Jersey, USA, 2003, p. 1.
[28] W. Wardencki, R. Katulski, J. Stefański, J. Namieśnik, Crit. Rev. Anal. Chem. 38 (2008) 259.
[29] J.R. Dean, Methods for Environmental Trace Analysis, John Wiley and Sons, Chichester, West Sussex, UK, 2003.
[30] J. Namieśnik, P. Szefer, Ecol. Chem. Eng. S 15 (2008) 167.
[31] R.E. Majors, LC-GC Int. 9 (1991) 16.
[32] T. Hyötyläinen, Anal. Bioanal. Chem. 394 (2009) 743.
[33] C. Nerín, J. Salafranca, M. Aznar, R. Batlle, Anal. Bioanal. Chem. 393 (2009) 809.
[34] M. Urbanowicz, B. Zabiegała, J. Namieśnik, Anal. Bioanal. Chem. 399 (2011) 277.
[35] J. Curyło, W. Wardencki, J. Namieśnik, Polish J. Environ. Stud. 16 (2007) 5.
[36] W. Wardencki, J. Namieśnik, J. High Resolut. Chromatogr. 23 (2000) 297.
[37] W. Wardencki, J. Namieśnik, Polish J. Environ. Stud. 11 (2002) 185.
[38] C. Zhang, Fundamentals of Environmental Sampling and Analysis, John Wiley and Sons, Hoboken, New Jersey, USA, 2007.
[39] D. Raynie, J.L. Driver, Green assessment of chemical methods, 13th Green Chem. Eng. Conf., Washington, DC, USA, 2009.
[40] S. Garrigues, M. de la Guardia, in: M. de la Guardia, S. Garrigues (Editors), Challenges in Green Analytical Chemistry, Royal Society of Chemistry, Cambridge, UK, 2011, p. 13.
[41] J. Wang, Acc. Chem. Res. 35 (2002) 811.
[42] J. Moros, S. Garrigues, M. de la Guardia, Trends Anal. Chem. 29 (2010) 578.
[43] L.J. Kricka, Clin. Chim. Acta 307 (2001) 219.
[44] M. Pena-Abaurrea, L. Ramos, in: M. de la Guardia, S. Garrigues (Editors), Challenges in Green Analytical Chemistry, Royal Society of Chemistry, Cambridge, UK, 2011, p. 107.
[45] United Nations, Globally Harmonized System of Classification and Labeling of Chemicals (GHS, Rev. 4), United Nations, New York, USA, 2011.