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Green Analytical Chemistry: Social dimension and teaching

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Abstract

Green Analytical Chemistry (GAC) is the idea which every analytical chemist should be familiar of. Due to continuous improvement in the subject both from the apects of theory and experimentation, the dynamic way analytical chemistry studies are evoloving in the frame of chemistry degrees should not be surprising. Recently, many efforts have been made in order to include Green Chemistry principles to Education, also in the field of analytical chemistry, where twelve GAC principles play a main role. The understanding and awareness of these principles and other evolving related concepts requires special teaching of GAC as a part of curriculum at undergraduate and graduate levels. This article is focused on the main concepts and challenges of teaching GAC and also presents the current accomplishment in this field. In addition, teaching social responsibility in GAC is discussed. Several case studies are also presented as an example for the learners.

Keywords

Green Analytical Chemistry; teaching methods; social responsibility; educational materials; GAC metrix

1. Green Analytical Chemistry: history, principles and recent trends

The interest and concern for the sustainable environment is constantly increasing, thus, it becomes important to examine the activities of those chemists and chemical engineers which may meaningly impact on the environment, both at the laboratory and the industrial scale [1]. Introduction of the green chemistry idea is associated to the dissemination of the principles of the sustainable development and the highly visible tendency to implementation of these principles in laboratories and chemical plants. In fact, the principles of green chemistry have been adopted in the specific fields of chemistry and thereafter, several other sets of principles have been issued such as Principles of Green Chemical Technology, 12 principles of Green Enginnering and 12 principles of Green Analytical Chemistry [2].

The adverse effects of the application of analytical procedures may cause damage to the environment and serious risks for operators. Therefore, for these reasons, it is essential to think about the effects as well as consequences of actions taken by the researchers/users of analytical methods. Respecting the viewpoint of people who take care of the environment also considering economic aspects of analytical methodologies, the special attention should be paid to the inherent risk of some samples type, aliquot of reagents and solvents used, the consumption of energy related with advanced instrumentation and, without a doubt, resulting laboratory wastes and emissions coming from the numerous steps of analytical methodologies [3]. Such a responsibility among the analytical chemists' society appeared long before the introduction of the term Green Analytical Chemistry. Several innovative advances in the sample preparation as well as measurement and data handling were introduced in the middle of the 1970s. It needs to be mentioned that the methodological milestones (Figure 1) which were conceived to increase the green character of the analytical procedures were mainly achieved before formulation of GAC concepts [4]. One of the most important idea was to apply the term “clean waste” instead of word “waste”, suggesting an alternative method which includes an additional chemical effort to minimize the environmental impact of FIA determinations. That was the beginning of the clean analytical chemistry concept. In 1995, the opportunities proposed by the degradation processes contribution and flow injection analysis to enhance analytical methods were confirmed. In the same year, the manuscript entitled: “Towards environmentally conscientious Analytical Chemistry through miniaturization containment and reagent replacement” was published and it is said that this was the first declaration of the principles of what is today called Green Analytical Chemistry [5]. In another work [6], a term “waste minimization” was introduced and recommended to the analytical practice. Although a term Green Analytical Chemistry was not applied in this work, it is recognized as the pioneer works of GAC because the green idea was inherently present. Since that time, the development of green analytical practices has accelerated and improved as for the introduction of methodologies and instrumentations as it can be seen in Figure 1.

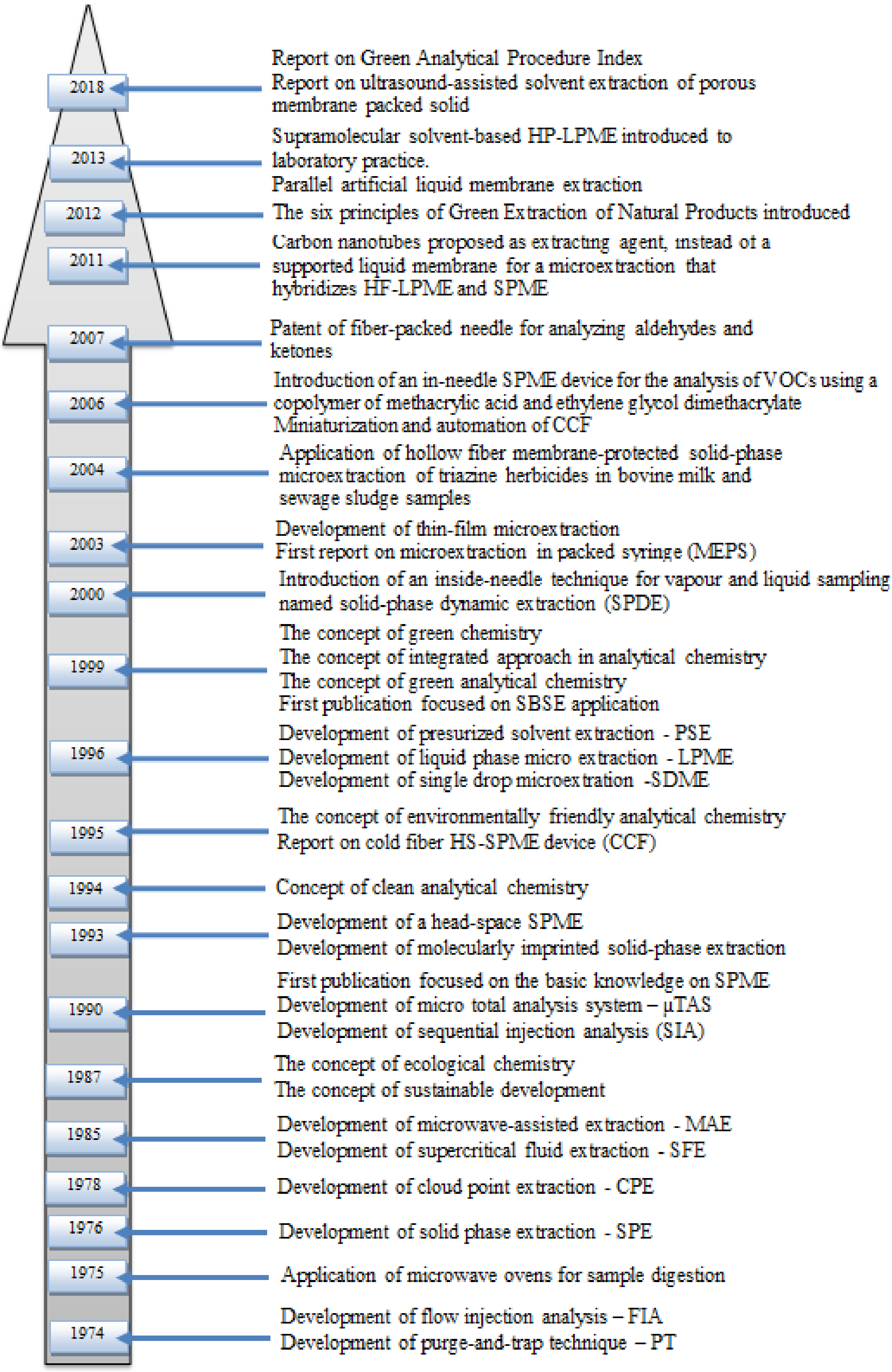


Figure 1. Milestones of Green Analytical Chemistry [7-12]

Nowadays, Green Analytical Chemistry is the idea which every analytical chemist should know. Thus, it is not surprising that analytical chemistry studies in the frame of chemistry degrees around the world have evolved in different ways [13]. This is mainly due to the development in analytical chemistry field but also due to the on-going trend to be more and more eco-friendly which is many often pointed out during the chemical study. However, teaching analytical chemistry today is, in general opinion, maintaining the past advances in order to improve the main analytical figures of merit of the available and common approaches and also to improve them [13]. From the other side, it is required to adequately response to the questions and problems associated with our social compromise with the safety of operators and the environment. Hence, teaching analytical chemistry should include the way of thinking about the analytical problems as well as their solutions in terms of sustainability, considering and paying attention to both, the well known past knowledge of analytical figures of merit related to different approaches, and ways to reduce the use of persistent, bioaccumulative, toxic, hazardous or corrosive solvents and the resulting waste generation [13].

Recently, many efforts have been made in order to include Green Chemistry principles to Education, also in the field of analytical chemistry, where twelve Green Analytical Chemistry principles play a main role. Education in GAC would balance both ethical and chemical aspects. Hence, the concept is to convince the students on the fact that chemistry is not only a risk for the planet, indeed it has great promises for human health care as well as sustainable environment. Now it is teachers' obligation to transmit this kind of knowledge.

2. Teaching Social Responsibility in Green Analytical Chemistry

Social responsibility is undoubtedly one of the pillars of modern chemistry [14], and in particular of analytical chemistry [15]. This is because, in principle, every area of life today depends on data obtained and transmitted via (bio)chemical research. These areas include health, culture, transport, industry, energy, new technologies and building, which are of strategic importance to our ever-expanding globalized states and societies [16]. Analytical chemistry should be socially responsible, because the data and knowledge that it provides affects every element of the reality that surrounds us.

The 20th century was undoubtedly the age of chemistry, which contributed enormously to raising living standards, the industrialization of societies, and the economic development of states. However, this did not come without a cost. The degradation of the natural environment as well as biological, physical pollution and aesthetic damage, these all called for an alternative development policy [17]. The concept of sustainable development, initiated at the turn of the 1980s and 1990s, was a proposal aimed at striking a balance between the continuous improvement of the quality of life and the exploitation of finite natural resources. At the beginning of the 21st century, sustainable development became one of the leading paradigms of contemporary chemical education [18].

The corporate and scientific social responsibility and the idea of sustainable development is a topic which has been present in the public discourse for a long time. However, until now both have been treated either as a way of justifying application for funds for research and development, or as a fig leaf of social involvement of public institutions or enterprises [19]. The situation is similar in the chemical industry, which increasingly treats both issues strategically — as the foundation of its operations and the basis of research and commercial projects [20]. There are two basic benefits arising from the application of social responsibility and sustainable development in the chemical industry: socialization and rationalization. Grounding analytical chemistry in both concepts can increase the efficiency of the industry itself, and at the same time have a positive impact on society, which is the most important beneficiary for the chemical branch.

2.1. *The humanistic coefficient: the rationalization and socialization of analytical chemistry*

The socialization of the chemical industry means enabling and facilitating the participation of internal and external stakeholders in the creation, implementation and evaluation of chemical policy, both on a macro (e.g. state or union of states) and micro (e.g. companies or regions) scale. The internal stakeholders in the chemical industry are primarily the managers, employees, customers, suppliers, regulators and partners of chemical companies. The external stakeholders are institutions within the broad environment of the chemical industry, including in particular public administration, universities, think tanks or non-governmental organizations (NGOs). Rationalization, in turn, means using the potential of knowledge management, both in the form of interdisciplinary analytical teams and the use of operational databases. This is important especially in the area of analytical chemistry, for which the metrological quality of data and information is of premium value.

The socialization of analytical chemistry provides an insight into the activities of chemists from the viewpoint of their key beneficiary (society) and main stakeholders, while rationalization facilitates the solving of social problems, both in the area of costs generated by chemical production and problems related to the distribution of information. The implementation of the principle of rationalization and socialization of analytical chemistry is important primarily because the data, information and knowledge contained in analytical reports form the basis for political decisions that make a profound impact on our lives [21].

Rationalization and socialization can be referred to two types of associations (connotations) of the social responsibility of analytical chemistry: internal and external [22]. Rationalization refers in particular to the internal connotations (and stakeholders) associated with the generation and acquisition of the highest quality of (bio)chemical data, while socialization is mainly concerning the process of packaging and transferring information and knowledge to external stakeholders, both commercial customers and public policy makers. However, it is worth emphasizing that rationalization and socialization should characterize all entities and processes involved in chemical activities. Their differentiation and connection with a different type of stakeholder is purely analytical (*nomen omen*).

2.2. Green analytical chemistry as a tool for teaching and promoting social responsibility

The concept of green chemistry is the synthesis of socialization, rationality, responsibility and sustainability in the chemical industry [23]. It is a response to the unprecedented development of the chemical industry, generating high social and ecological costs. The enormous number of chemicals that cause damage to the natural environment on an exceptional scale requires thought and specific repair programs. However, as widely known, it is easier, faster and cheaper to prevent rather than to repair. The paradox of chemistry, which undoubtedly contributed to raising living standards, is that it is not well-viewed today — instead, it stands for contamination, artificiality and the very opposition of nature [13]. Green chemistry can contribute to not only reducing or preventing environmental risks and disasters, but also to improving the social (including media) image of the chemical industry.

Green chemistry is an appropriate platform for teaching and promoting social responsibility because it is a social movement itself [24]. It can be treated initially as a bottom-up and later an institutionalized way for the representatives of the chemical industry to organize themselves in order to implement socio-technological change expressed in an innovative approach to chemistry as a forefront of sustainable development. Green chemists have treated themselves as advocates of a healthier, safer and more sustainable society, without any political inclinations, but with a clear desire to convince the intellectual elites and technocrats to their ideas. They also realized how important role education could play in the dissemination of this new idea.

Social responsibility should form one of the strategic currents that run through chemistry teaching, especially analytical chemistry. Nothing is better suited to achieve this goal than the concept of green chemistry [25]. If we want the responsible and socially sensitive analytical chemists who would take care of the metrological quality of data and information, we have to educate them from the very beginning — from pre-school, through school and ending at university. This should be done not by creating separate chapters in chemistry textbooks or by arranging guest lectures by humanists, but by integrating chemical instrumentation and nomenclature with social and ethical themes [26]. Green chemistry offers the most effective tools for linking chemistry with topics such as health, development and social justice at every level of school and academic education.

The need to take social responsibility into account in chemistry education is confirmed by a study conducted on a sample of 6,100 students, in which it turned out that Science, Technology, Engineering and Mathematics (STEM) students treat the development of their own career as a goal more important than social development [27]. It is possible that no one ever opened their laboratories to the world; no one made them aware that they are agents of change. Chemists will become socially sensitive if they are consequently encouraged to be conscious and responsible. They can be inspired by engagement in solving specific problems — e.g. during group activities, and in particular by linking chemistry education with everyday life, with interesting human stories, with real-life examples, with something that involves them [28].

Social responsibility, sustainable development, justice, honesty and transparency should not be enclosed in the conceptual ghetto of incomprehensible theories, but become the very foundation of education preparing for chemistry in practice — a compass that will not only help navigate in an increasingly complex world, but also indicate a direction worth taking.

3. Teaching Green Analytical Chemistry: challenges

Without a doubt the teaching and practice of analytical chemistry reflects the measurement science development over the time. Both, qualitative as well as quantitative measurements can be track down to "old" prebiblical times, and have been significant throughout the human history, while nowadays, they are the key to the modern society functioning [22]. This is mainly because the environment is more and more polluted and its monitoring is undoubtedly indispensable. From the other side, analytical chemistry involves highly toxic reagent consumption and waste generation introducing a "brick" to pollute the environment. Thus, in recent years, many efforts have been made in order to incorporate GAC principles to analytical practice, but this brings new challenges, including the Education and teaching of Green Analytical Chemistry.

It needs to be stated that teaching GAC cannot mean that some lessons concerning the side effects of old, existed methods will be added, but all the matter must be changed and modified by adding the environmental ethical compromise, from the beginning to the end of the analytical process [13]. Thus, greening teaching practices must engage a powerful theoretical effort together with a modification in analytical practices. This should be started from the seminars as well as practical work recommended to students. In addition, incorporating decontamination steps in the analytical laboratory experiments should be carried out [29]. All of these mean that the challenge today is to establish new objectives without devoting the existed ones and it must convert all teaching practices from the subject and content of the theoretical lessons to the laboratory practices [13]. In addition to this issue, a huge challenge is to create such a team of teachers able to make a huge pedagogical effort which must be made in all different aspects. Some of them are the integration of GAC theoretical principles in the university textbooks as well as the generalized application of material safety data sheets (MSDS) on both the laboratory notebook documents and as complementary data from protocols of analytical method [13]. Moreover, the introduction of green parameters and pictograms used for evaluation of alternative methodologies to solve the same analytical problem could be helpful in forming a new mentality in young students. Aspects worth considering for greening Analytical Chemistry teaching practices are presented in Figure 2.

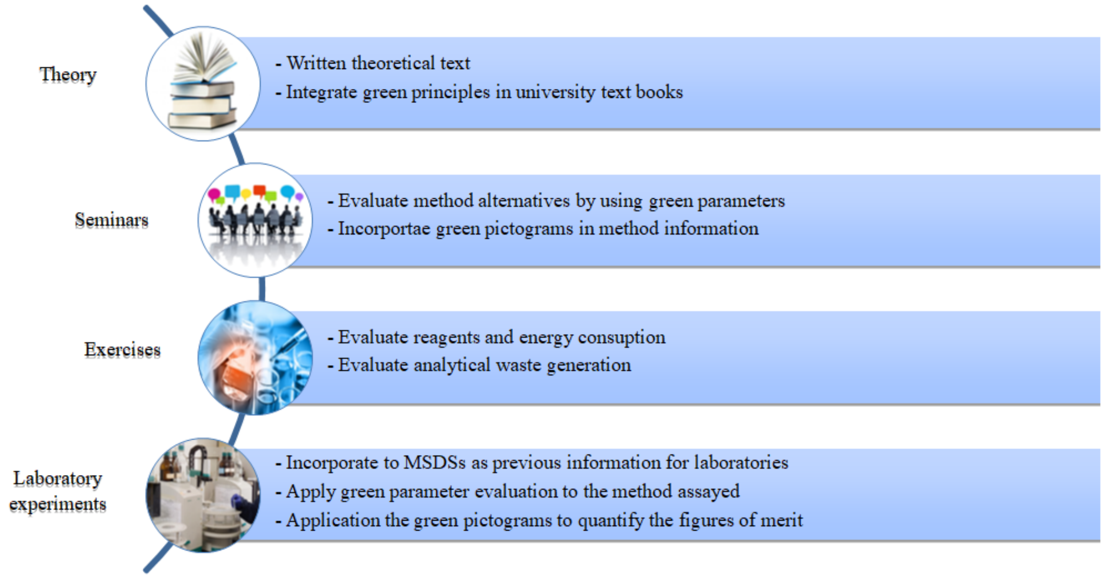


Figure 2. Aspects to be considered for greening Analytical Chemistry teaching practices

3.1. Awareness in the field of green analytical chemistry

Presently, personal health and environment protection are given more consideration in the field of chemistry, especially in more economically developed countries. The needed awareness in the field of green analytical chemistry should be perceived multidimensional. There is the need to turn laboratory practices into more environmentally friendly. In addition, it is an urgent international necessity to reduce pollution problems and become more eco-friendly not only in the laboratory but also in everyday life. The need to increase the environmental awareness especially in low-income societies emerges from the current public idea of responsible and respectful citizenship concerning environmental issues. The education towards sustainable development and in-depth understanding of Principles of Green Chemistry becomes a primary and central goal [2].
Moreover, one should realize the deficiencies not only in the educational sphere, but also in the research and literary fields. If the analytical procedure is called "green" basing only on one of the Twelve Principles of Green Analytical Chemistry, it is a meaningful gap in the research area. Such a narrow vision of a green analytical chemistry may cause confusion. Proper understanding of chemical principles and methodologies are fundamental for human and environmental health. Future chemists must become aware of the importance of sustainable strategies in chemical research and industry [30].

The design of chemical product such as new analytical methodology defines the level of the impact on the ecological environment. Therefore, future analytical chemists first need to learn how to take a full account of the methodology optimization development, waste recycling, including other required chemical product aspects. Secondly, after methodology products have been developed and the application has been scrapped, consider the proper methods to deal with the final waste [2].

The challenge students need to face is the compromise between the base of 12 principles of GAC (operator, sample, reagent, instrument, method waste) and the performance parameters (accuracy, precision, sensitivity). Decreasing in performance parameters may consequently lead to miniaturizing instruments or declining in sample numbers, reagents, energy and waste. In practice, representativeness, accuracy, selectivity, sensitivity and precision will drop if the sample size in the sampling process is being reduced. However, there are different solutions noteworthy for students facing the need of compromise between improving green aspects of analytical methods and increasing value of the analysis [31]:

- "Modifying *in situ* measurements to improve calibration by running standards between sample
- Using chemometrics and statistics for the reduction of the amount of sample
- Using integrated analytical systems for the improvement of the analytical efficiency
- Using chemometric data treatment to allow the development of solvent-free methods based on direct measurements without any sample pretreatment (i.e; near-infrared/mid-infrared/Raman spectrometry, UV-Vis spectroscopy, fluorescence, nuclear magnetic resonance techniques" .

The application of the above-mentioned methods may reduce the time of analysis as well as the use of reagents and solvents in the same time avoiding the pretreatment of samples.
Following two principles of GAC; automation and real-time analysis for pollution prevention, students should be aware of multiply advantages in miniaturization of analytical instruments; portability of instruments in on-site analysis. Moreover, miniaturization ensures improvement of sensitivity and the speed of separation as well as reduced waste production and energy consumption, lower costs allowing at-line, quick analysis or less consumables and space. In addition, the number of samples in miniaturized system (a lab on a chip) is smaller than when traditional analysis takes place, which is important in such areas as biomedical science or forensic. The miniaturized separation system usage is greener than conventional methods [31].

3.2. Educational materials for teaching

The challenge in education in the analytical chemistry discipline would be to reach a compromise between the growing environmental friendliness of analytical methods and improving quality of the results as well as to assess whether applied methods are green. Another encounter considers education aids such as reliable and well-written material. In contrast to green chemistry, in green analytical chemistry there are not many literature items, especially when it comes to typical student materials, i.e. scripts. However, there are more and more books [32-40]. In addition to the books published, several publishers published special editions related to green analytical chemistry in their journals. For example, Elsevier in Trends in Analytical Chemistry had a special issue entitled: Green Extraction Techniques [32].
Primarily, students should be taught the principles of green analytical chemistry. Noteworthy is the fact that it is impossible to formulate universals for all potential applications, however clear guidelines would provide students with GAC framework essential for better understanding [41]. Gałuszka et al. [41] using four of the principles provided in 1998 by Anastas and Warner revise and supplement the 12 principles of green chemistry to achieve full possible application in analytical chemistry.

As stressed previously, the necessity of effective green analytical chemistry teaching requires not only relevant students' materials but also the use of modern memorizing methods, which aid information retention or retrieval memory. Thus, below presented mnemonic SIGNIFICANCE (Figure 3) which includes the 12 Principles of GAC seems useful for students. Furthermore, an important element that will help in understanding and assessing whether the methods evaluated are green, would be green analytical metrics, which are discussed in more detail in the next section.

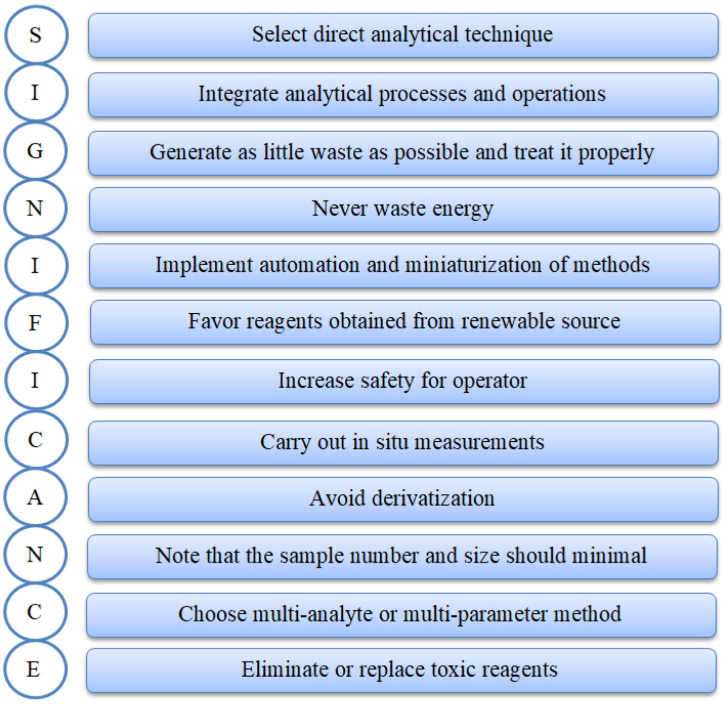


Figure 3. The principles of green analytical chemistry expressed as the mnemonic SIGNIFICANCE based on the idea published in [41].

In addition, the six principles of green extraction of natural products has been introduced in 2012 as a new idea to meet the challenges of the 21st century, to protect the environment and consumers, and in the meantime enhance competition of industries to be more innovative, ecologic and economic. Within this green extraction concept, an extract should be obtained in such a way to have the lowest possible impact on the environment (less energy and solvent consumption, *etc*.), and whose eventual recycling would have been planned for (co-products, biodegradability, *etc*.) [12].

3.3. Metrics for assessing green analytical procedures

Nowadays, many analytical chemists who publish work focused on the newly developed methodology, claim in their work that this new procedure is green, however, very often no evaluation of the greenest (e.g. in the form of applied metrics of greenness, and comparisons with previously developed analytical or standard procedures) is performed. This is also educational challenge, how to prove students that the communiques of methodology greenness are many often based on the authors' impressions or uncertain assumptions and such proceeding is wrong [42]. There are several literature examples where this kind of thinking is wrong. Thus, calculations that give an answer for question whether an analytical procedure can be considered green, should be carried out by utilizing the tools that serve such assessment [7] and such proceedings should be learned from the earliest steps of the analytical chemists. However, it may provoke to ask another question: how to measure the greenness of analytical methods? Without a doubt, it can be stated that one of the main problems of GAC is that there are no well-established methods of “greenness” assessment [42], while in general, green chemistry has several existed metrics systems [43]. The most popular metrics in green chemistry are environmental impact factor, atom economy, and reaction mass efficiency. These are mainly used to evaluate the green character of chemical reactions, applicable in organic synthesis. But also other tools were introduce for the fragrance or pharmaceutical industries [44, 45]. Because these tools are associated to the mass of the reaction product, it is not possible to use them in the field of green analytical chemistry.

Only few published and universal methods for assessment of the green character of analytical procedures exist and these should be presented to students as an option to choose during these researches. One of the oldest tool that can be applied to evaluate the greenness of analytical methodologies is National Environmental Methods Index (NEMI) [36]. In this tool, analytical methodologies are assessed by applying the pictogram - greenness profile symbol - divided into four fields (Figure 4A), however, each part mirrors different aspect of the described analytical methodology and the field is filled green if certain requirements are met.

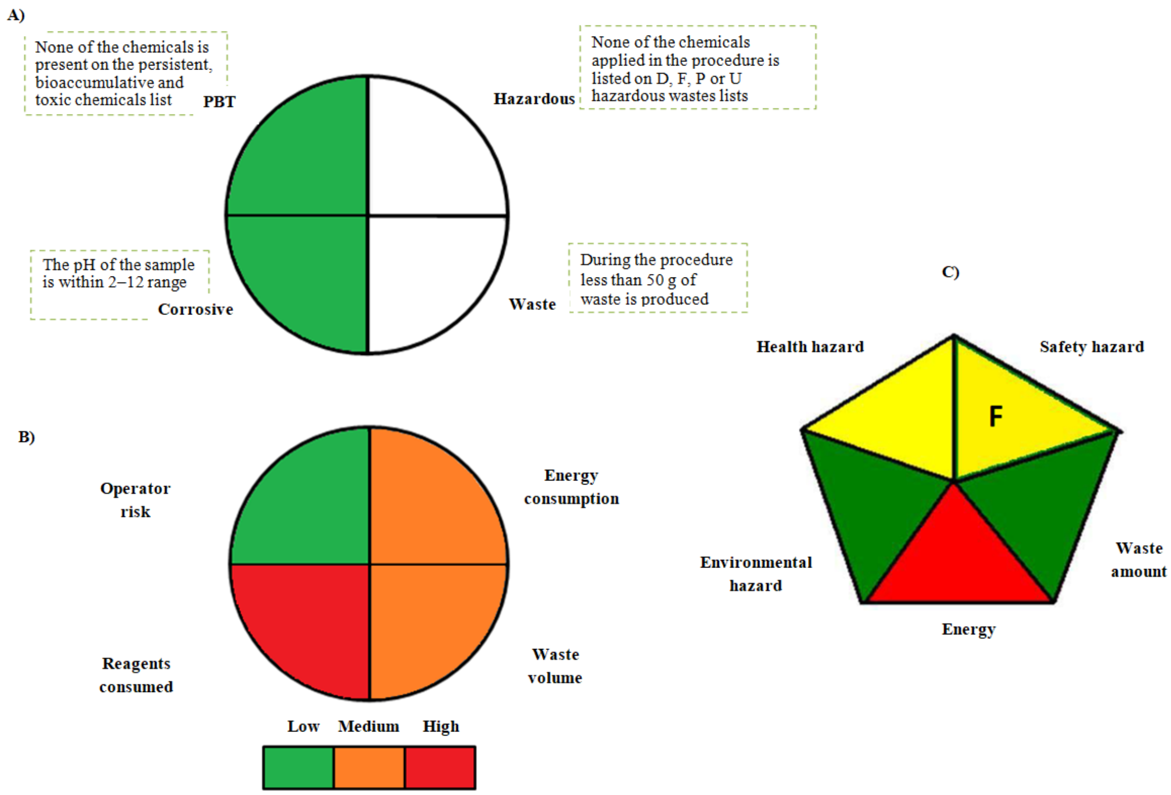


Figure 4. Assessment of analytical procedure by A) NEMI tool and B) additional pictogram proposed by Guardia et al. [36], pictogram proposed by Raynie et al. [46]

The NEMI as a greenness assessment tool is easy to read by potential procedure users, however, it presents only general information about an environmental impact of the evaluated methodologies. Moreover, the NEMI pictogram cannot be considered as being semi-quantitative because this symbol presents each threat either below or above a certain value. In addition, preparation of a pictogram is time consuming because each compound has to be checked, especially if many, non-typical chemicals are used in the procedure. Each compound has to be checked if it is inherent on at least one of the lists as EPA's TRI list [47] and Resource Conservation and Recovery Acts lists [48]. However, all of the proposed pictograms are time consuming, thus, this drawback is common to all. Therefore, in order to ameliorate the NEMI tool, Guardia et al. [36] suggested a supplementary pictogram (Figure 4B) to classify, applying a color scale, three levels of assessment of procedures for how green they are. Based on the same principle of the green symbols, a circle with four fields could be applied to quantify-from red to orange and green-the high, medium, or low risk engaged for operators and the levels of solvents as well as reagent and energy consumption and wastes. This alteration makes the NEMI procedure evaluation more quantitative.

Another tool for evaluating chemical methods including analytical methodologies relative to features of green chemistry has been introduced by Raynie et al. [46]. In this tool, the evaluation classify the risk potential into five categories as follows: health, safety, environmental, energy, and waste, based on toxicity, bioaccumulation, reactivity, waste generation, corrosivity, safety, energy consumption, and related factors (Figure 4C). Assessed procedures obtain a 1-3 score for each attribute applying available chemical data. All of the criteria are presented on pentagram and marked green, yellow or red depending on the impact on the environment [46]. The visual presentation of this tool permits individual researchers to make their own value verdicts about conflicting green criteria, thus, this tool is most precious in comparing procedures.

Another comprehensive tool for semi-quantitative evaluation of analytical procedures that can be used by the students as well as researchers is Analytical Eco-Scale introduced by Namieśnik et al. [49]. This tool can be used for comparison and assortment of the greenest alternative, but also it provides possibility to assess the green character of the new or modified methods to be evaluated. The idea of Analytical Eco-Scale is based on the definition of the ideal green analysis, which can be characterized, by reduction or elimination of reagents as well as energy consumption, and no generation of waste. The basis for the Analytical Eco-Scale concept is that the ideal green analysis has a value of 100 points. Each of the analytical methodology parameters including reagents and solvents amount, hazards, waste and energy, penalty points (PPs) are assigned if it departs from ideal green analysis. Due to the fact that the impact of hazardous substances depends also on their amount, it was proposed that the total PPs should be calculated by multiplying the sub-total PPs for a given hazard and amount [49]. The sum of PPs for the whole methodology should be included in the Eco-Scale calculation, in accordance with to the formula presented in Figure 5.

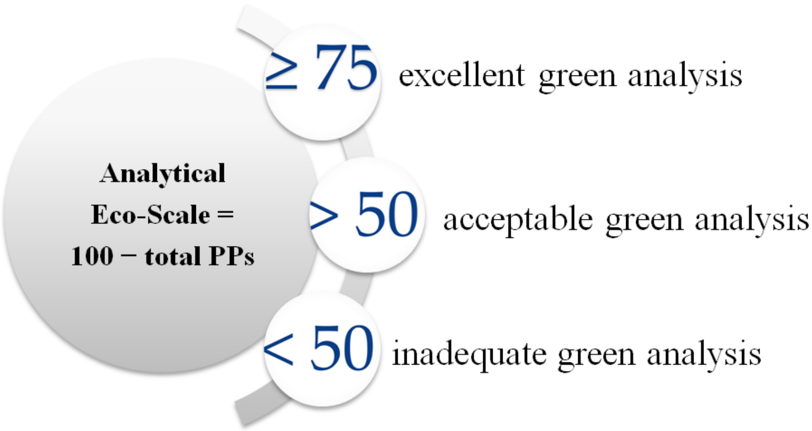
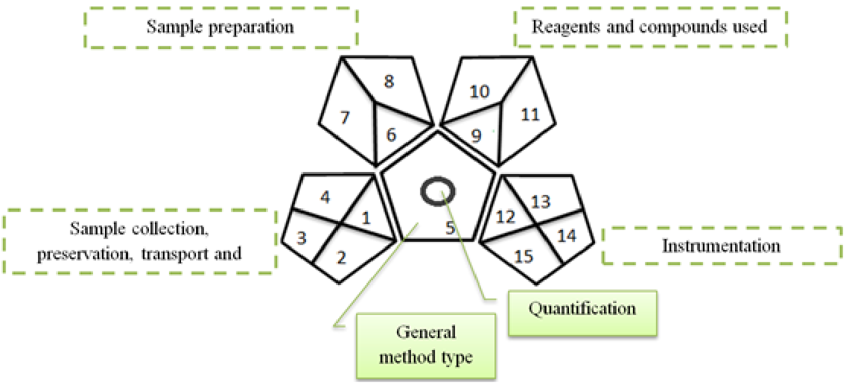


Figure 5. Equation for the calculation of Analytical Eco-Scale and its description

In 2018, Płotka-Wasylka introduced to analytical practice a new tool called Green Analytical procedure Index (GAPI) [7]. The GAPI tool uses a pictogram to classify the greenness of each analytical procedure stage, applying a color scale, with three levels of evaluation for each stage. A GAPI symbol consists of five pentagrams and can be used to assess and quantify-from green through yellow to red-the low, medium and high environmental impact engaged for each stage of the analytical procedure. Similar as in NEMI, each part of GAPI pictogram reflects a different aspect of the described analytical methodology and the field is filled green if certain requirements are met. Description of Green Analytical Procedure Index parameters used for the assessment of procedure as well as GAPI symbol are presented in Figure 6.



Category	Green	Yellow	Red
Sample preparation			
Collection (1)	In-line	On-line or at-line	Off-line
Preservation (2)	None	Chemical or physical	Physico-chemical
Transport (3)	None	Required	-
Storage (4)	None	Under normal conditions	Under special conditions
Type of method: direct or indirect (5)	None sample preparation	Simple procedures, eg. filtration, decantation	Extraction required
Scale of extraction (6)	Nanoextraction	Microextraction	Macro-scale
Solvents/reagents used (7)	Solvent free methods	Green solvents/reagents used	Non green solvents/reagents used
Additional treatments (8)	None	Simple treatments (extact clean up, solvent removal, etc.)	Advances treatments (derivatization, mineralization, etc.)
Reagent and solvents			
Amount (9)	<10 mL (<10 g)	10-100 mL (10-100 g)	>100 mL (>100 g)
Health hazard (10)	Slightly toxic, slight irritant; NFPA health hazard score is 0 or 1.	Moderately toxic; could cause temporary incapacitation; NFPA = 2 or 3.	Serious injury on short term exposure; known or suspected small animal carcinogen; NFPA = 4.
Safety hazard (11)	Highest NFPA flammability, instability score of 0 or 1. No special hazards.	Highest NFPA flammability or instability score is 2 or 3, or a special hazard is used.	Highest NFPA flammability or instability score is 4.
Instrumentation			
Energy (12)	≤0.1 kWh per sample	≤1.5 kWh per sample	>1.5 kWh per sample
Occupational hazard (13)	Hermetization of analytical proces	-	Emission of vapours to the atmosphere
Waste (14)	<1 mL (<1 g)	1-10 mL (1-10 g)	>10 mL (<10 g)
Waste treatment (15)	Recycling	Degradation, pasivation	No treatment
ADITIONAL MARK: QUANTIFICATION			
Circle in the middle of GAPI: *Procedure for qualification and quantification*		No circle in the middle of GAPI: *Procedure only for qualification*	
NFPA, *National Fire Protection Association*			

Figure 6. Green Analytical Procedure Index symbol and parameters description

The GAPI tool is a good semi-quantitative tool for educational purposes and laboratory practice. It is characterized by several advantages: has well-defined evaluation criteria, is very simple and fast to apply, and can be used to any known and new methodologies. The GAPI symbol not only supplies an immediately noticeable perspective to the user and reader but also provides exhaustive information on assessed methodologies [7].

4. Main concepts for teaching GAC

Making analytical chemistry more benign is the basic approach that combines old and new concepts of analytical chemistry and as such, it should be transmitted into the teaching of green analytical chemistry.

Being benign implies the consideration of the key words concerning the sustainable development context: safety, reduced energy consumption and decontamination of waste. Considering this, it seems quite clear: The environmental mentality in analytical chemistry is a recent compromise of chemistry but it should be carefully considered in order to assure the sustainable development of our discipline [50]. Changing chemistry according to the principles of green chemistry through introductory chemistry courses, we can change the mentality of those who practice chemistry, students and citizens.

An important goal in teaching analytical chemistry is to change the attitude of chemistry student, also change the attitude of future generations about chemistry and its impact on the environment, and eventually leads to the sustainable development through green chemistry. The basic concepts for teaching green analytical chemistry are related to the well-known principles of green analytical chemistry [41, 51].

For a long time, some of the principles of green chemistry have been included in teaching analytical chemistry since they are essential for safety and lab costs: natural reagents, non or less-toxic solvents, drop reactions or work with a small amount of sample mass and reagents. This will enhance the safety of students, but also reduce waste and costs of purchasing new chemicals. Also, these efforts were not mandatory and they only depended on ethic preferences of teachers and lab staff.

In achieving this goal, additional efforts should be made to educate teachers about transmitting sustainability messages in analytical chemistry teaching. To chemistry students or related professions it should be quite clear that the principles of green analytical chemistry should be a daily thinking styles of solving analytical problems, some kind of obligations and in no case a matter of choice.

As pointed out in recent paper [2], the main concepts for teaching green analytical chemistry should be:

i) application of less toxic solvents and reagents; As an alternative to the process of greening the analytical methods, the consumption of reagents and solvents, as well as the sample mass can be reduced. This will finally contribute to the environmentally acceptable approach and result in laboratory costs and waste amount reduction. Initially it is good to reduce the consumption of toxic reagents and solvents or replace them with less toxic, but the ultimate goal could be the use of completely benign ones as the reagents from nature.

ii) reduction and on-line decontamination of waste; It is very important to seek for new online decontamination options that involve recovery or detoxification of wastes. The benefits of such a procedure are numerous but most evident improvements are in the economical and environmental aspects.

iii) lower power consumption; Modern analytical methods imply the use of the new instrument techniques, often in-field measurement or the use of portable instruments which reduce the time of analysis, lowers both lab costs and power consumption.

iv) integration of analytical procedure; According to a modern approach of analytical chemistry, all of the analytical steps become one analytical problem that needs to be solved integrally.

v) automation, miniaturization; The last but, apparently, the most important concepts, atomization and miniaturization are directly related to all other concepts, permitting dramatic reduction in the consumption of reagents and waste generation [41].

Obviously, the new concepts in teaching green analytical chemistry include the greening of analytical methods and also the development of new green methodologies. Depending on the analytical procedure, sampling, sample processing and the use of reagents, it implies the use of hazardous and harmful chemicals, and eventually the generation of hazardous waste, rarely in large quantities. Safety concerns regarding to the lab and waste have become the reason for developing new ideas of improving the safety in a laboratory and reducing successfully the amount of waste or decontaminating it. Hazard and waste become recognized as design flaws or, more positively, as opportunities for innovation. Experiments can be performed in laboratories that are more comfortable and alluring as well as more economical to maintain [25].

Analytical chemistry gives the opportunity for innovations in both teachings and science, in the context of waste treatment or by using new reagents, for example, natural reagents that increase students` understanding and sensitivity to the environmental consequences of their scientific choices [25, 52].

The possibility of automation in the process of developing the method is always an added value and implies the possibility of integration of the entire analytical procedure, beginning from the sampling, then reagent delivery, detection and direct decontamination of waste.

Very often, flow injection analysis (FIA), sequential injection analysis (SIA), or other techniques based on similar principles are a very powerful tool in the efforts of automation or minimization of the methods, to green the existing method significantly [53].

It is very important to emphasize the advantages of using these systems: wide potential of application, reduction of solvent and reagents consumption and sample size, increase of sample throughput, the ability to use different detectors, improved sensitivity and other basic analytical features of the method. Considering that the most of these devices can be found in laboratories or obtained at an acceptable price, this analytical tool becomes a very interesting and inventive tool in teaching green analytical chemistry.

In all these efforts to include a new approach in the teaching of green analytical chemistry, the importance of analytical features of the methods should not be neglected. Green analytical chemistry concepts are not introduced in order to replace the existing ones. New concepts, rather, can be considered complementary to the existing concepts and can be studied through the curriculum by giving them the same attention. Green analytical chemistry is also a tool for obtaining information of analytes of different origin, taking into account the safety in the laboratory and with minimal environmental impact, but without scarifying the analytical requirements: sensitivity, selectivity, robustness, accuracy and precision.

However, at the end we will ask:

i) What do new concepts in teaching green analytical chemistry bring to the teachers? Much effort in mastering new teaching skills.

ii) What do students get? - Interesting and innovative approach to chemistry with the ability of critical thinking about experimental design. They will learn the development of new environmental friendly analytical methods. Students will become better chemists and more responsible citizens because they will learn to solve the problem not always in an easier way, but in a more socially responsible way. They will learn to manage the risks and find a compromise between the demands of the profession, the economy and the environment.

iii) What about chemistry? Chemistry will become more acceptable to students. They will understand the content of the course in depth and consequently, the public perception of all the benefits that analytical chemistry brings will change on positive. Much more students will find a science discipline - chemistry - as enjoyable and worth selecting for their future profession.

A Table 4 summarizes relevant information in terms of green analytical chemistry of works discussed in this section.

Table 1. Basic concepts and improvements in the teaching of green analytical chemistry

Concepts in teachig GAC	Recommendation	Improvements	The main goal
Less toxic or innocuous solvents and reagents	Application of reagents from nature and benign solvents	Save costs; More comfortable and safer lab	
Reduction of waste	On-line decontamination or less reagents and solvents	Better economical and environmental aspects	
Lower power consumption	New instrument techniques; In-field measurements portable instruments	Reduce the time of analysis, Lower lab costs; Lower power consumption	
Integration of analytical procedure	All analytical steps become one analytical problem	Integral approach to learning and problem-solving models	Safety lab and more socially responsible analytical chemist
Automation, miniaturization	Application of methods based on flow injections and similar techniques	Less reagents and waste, enhanced analytical features	
Analytical figure of merit	Should not be neglected	New green analytical method with enhanced analytical features	

5. Case studies

Changing the mentality of future chemists and chemical engineers is already beginning through the introductory courses of green chemistry. The most important responsibility is for the instructors who need to make additional effort and apply the proposed concepts in teaching analytical chemistry to the classroom and, even more importantly, in the lab.

There are texts that help teachers to understand the basic principles of green chemistry and how to introduce them into the teaching process. However, lab manuals for green analytical chemistry are seldom available. There are also a few scientific papers problematizing the teaching green analytical chemistry in specialized Educational journals.

There is a growing need to expand the range of pedagogical materials from the same chemical subdisciplines most notably to the analytical/environmental and physical chemistry [54].

Numerous studies are available that provide direct green analytical methods. Special authors were referring to the NEMI bases that make green methods easier to identify by giving analytical teachers and chemists the opportunity and responsibility to select low environmental impact processes.

S. Dutta and A. K. Das [55] have suggested fifteen Green Analytical Chemistry experiments, which can be practiced by the graduate students of chemistry. In this work the conventional method was described and a green laboratory proposal was offered with additional comments. These experiments cover some of the most significant achievements in the application of green analytical chemistry: solvent free, pressurized-solvent extractions, microwave-assisted treatments, ultrasound-assisted leaching, solid phase extractions, green spectrometry and so on. Thus, students become familiar with basic principles of analytical, environmental and green chemistry through real world application [55].

In the early days of green analytical chemistry education, at Hendrix College a laboratory was developed for teaching green analytical chemistry as an introductory course to students by using simple, outcome-based assessment tools, guiding three basic criteria: experiments should both apply and teach the principles of green chemistry, train students in analytical techniques, and use environmental samples. In the lab they use modified standard UV-Vis molecular and flame atomic absorption spectroscopy protocols to analyze the iron. These experiments allow them to maintain a green laboratory while engaging student interest through parallels to more toxic materials. Although the introductory program cannot create experts, students will be "green" educated to continue and choose their professional and personal lives that in accordance with their green ethics, will have a significant and positive impact on the environment [56, 57].

There are many examples of using simple herbal extracts for chemical analysis. These processes are safe for undergraduate and high school students. Using available materials in conducting research, as well as taking into account personal experiences of students, may maximize student participation and increase interest in initiating research. The use of low quality herbal extracts in chemical analysis is a green chemistry approach and does not have to sacrifice the quality of chemical education. There are three good examples of green analytical methods in teaching through the categorization of problem based learning, and method development-based learning. Students study green chemistry through these categorizations using herbal extracts as natural reagents, with careful guidance and design of research projects. Students' experience; participation in the conferences and publications was achieved with a minimum budget [52].

There are also educational papers that describe the application of green extraction methods in the analysis of environmental samples. For example, there was a designed experiment to introduce students into the philosophy of green analytical chemistry by using solvent microextraction techniques (SME) in determination of phosphorus in water, an environmentally friendly alternative to solvent extraction. Students are involved in the development of a miniaturized methodology with the assessment of the main experimental parameters that affect the extraction process using univariate optimization, preparation of the phosphorus calibration curve, and determination of the corresponding figures of merit [58].

Buckley et al. [59] have shown that a classic example of green chemistry can be introduced in the undergraduate analytical chemistry laboratory. This experiment is divided into two major parts: liquid CO_2 extraction of D-limonene from orange rind and quantitative analysis of extract by gas chromatography (GC-FID). The procedure established natural product extraction, calibration curves, and internal standards while simultaneously demonstrating alternative solvent selection for pollution prevention and increased chemical safety. Undergraduate students have applied some of the important principles of green chemistry including pollution prevention, energy efficiency, renewable raw materials, safer solvents, design for degradation, and safer chemistry for accident prevention [59].

The extraction of heavy metals from environmental samples using micelle-mediated extraction has been used as a pilot lab in an advanced undergraduate analytical chemistry laboratory. The aim of this study was to introduce students with basic principles of green analytical chemistry and environmental through a "real world" application. Extraction of heavy metals from surface waters and wastewater was carried out using an environmentally benign preconcentrating technique. Atomic absorption spectrometry (AAS) was used for metal identification. The analytical procedure consisted of; preparation of calibration curve, analysis of water samples, evaluation of the matrix effect, analysis of several spiked samples and analysis of reference sample. This study has provided students with hands-on experience in environmental analysis that uses an alternative technique instead of hazardous and volume-consuming organic solvent methods. New method demonstrates minimization of laboratory wastes and the replacement of the remaining small volume of wastes with less hazardous surfactants, which is beneficial for both laboratory personnel and the environment [60].

The experiment of extraction and antibacterial properties of thyme leaf (*Tymus vulgaris*) extracts was carried out in teaching undergraduate analytical chemistry. Approximately 600 students in advanced general chemistry and quantitative analysis classes at UC Berkeley have successfully conducted this experiment. Students developed critical reasoning, analytical skills (solid−liquid extraction, chromatography basics, TLC and HPLC of thyme extract) and met microbiology techniques (Kirby−Bauer disk diffusion). The main goal of the experiment was to incorporate green analytical chemistry into the curriculum. Several important principles of green chemistry have been applied such as use of renewable feedstocks, design for degradation, use safe solvents and auxiliaries and prevention [61].

Microwave extraction is a research topic that has affected several areas, especially in green analytical chemistry. Chemat et al. [62] have developed a new green procedure in teaching green analytical chemistry, using microwave energy as energy source, to teach the fundamental concepts of extraction of essential oils from orange peel. Qualitative and quantitative analysis has been performed by using gas chromatography (GC-FID and GC-MS). Green extraction method has been conducted by using Dean-Stark glassware and a Vigreux column inside a microwave oven without adding water and solvents. The advantages of using microwave energy for extraction of essential oils would be: reduced equipment size, energy efficiency, elimination of process steps and organic solvents, faster process and increase production. This experiment gives students fundamental and sustainable principles of green analytical chemistry [62].

The analysis of whiskey by dispersive liquid−liquid microextraction coupled with gas chromatography-mass spectrometry (GC-MS) helped the students to developed hands-on skills of green chemistry extraction on “real-world” samples [63]. The pedagogical importance of this procedure was in the exploration of the power of MS and the post processing software to determine compounds in the whiskey samples. In this experiment, students have determined the content of individual components in whiskey based on literature data. In addition, students have critically analysed the results obtained, acquired MS database skills as well as searching scientific literature for the given problem. This has reduced the longevity of the process and the consumption of energy and chemicals [63].

One can note that in the some above reported experiments, as analytic technique used for quantification, is spectrometry. Nevertheless, the main role in “greening” this experiment has some other aspects of procedure.

Based on reports from some authors [64] it may be the easiest way to develop and apply a green analytical method based on spectrometry. Spectroscopy methods require, in general, low amounts of reagents, a reduced treatment of samples, and are suitable to be easily mechanized, thus reducing the operator and environment risks and scaling down the consuming of hazardous products [65]. According to this, it has been expected that we have more educational green analytical chemistry papers that discuss the appliance of the green spectrometry in teaching.

However, the experiment that can be employed to introduce green analytical chemistry principles to undergraduate students is proposed by Hg determination in milk by AFS and the online passivisation of analytical wastes. The method was designed to feature two key requisites of a green analytical method: use of less toxic reagents and waste management [29].

In addition, electrochemical devices offer unique opportunities for addressing the challenges of green analytical chemistry, namely providing effective process monitoring while minimizing its environmental impact [66]. There is a research showing that using ion-selective electrode as an alternative way of the greening process of in-line electrochemical procedure, like the Just-Dip-It approach that almost fulfills the 12 principles of GAC [67]. It was reported on the application of microcell for electrochemistry in the undergraduate analytical laboratory with the aim of reducing hazardous waste [68]. Based on this, it seems interesting to use a construction of glucose biosensor in undergraduate analytical chemistry laboratory that allows analysis in a drop. These experiments offer high educational content related to biosensor principles and new contemporary trends in analytical chemistry [69].

Quantitative analysis by voltammetry is proposed for undergraduate chemistry students for understanding the fundamentals and the analytical applications of electrochemistry. This experiment presents new educational values regarding the replacement of classical methods with a “greener” electrochemistry by substituting the mercury electrodes with bismuth-coated screen-printed electrodes in the determination of quinine in tonic water. In addition, students are exposed to some of the essential problems of experimental analytical chemistry and a real-world sample, which makes the experiment more interesting [70].

Green or greener principles can be skillfully applied in teaching with flow analysis methods. Simple handling, versatile tools for automation of wet chemistry procedures is a special way that can enhance green chemistry experiment or any other experiment can make „greener“.

An experiment that comprises a flow-injection spectrophotometric method for the determination of creatinine is described for introducing the green analytical chemistry to undergraduate students. This procedure allows a reduction of reagent consumption by 60% compared to the corresponding batch procedure. Creatinine is determined in real or synthetic urine samples by UV–Vis spectrophotometry. Subsequently, the wastes are photochemically degraded by UV radiation. This aproach highlights two key requisites of an ideal green analytical method: minimization of reagent consumption and waste management [71].

The spectrophotometric method based on sequential injection analysis (SIA), aiming at determining Fe ions by the application of the natural reagent, is suggested for the courses of analytical chemistry in undergraduate studies. The students have goal to design SIA method through experiments optimization and finally take advantage of this method in the analysis of real samples. SIA is the second generation of flow systems and offers good analytical characteristics due to their simplicity, high analytical frequency and capacity to reduce reagent consumption when compared with FIA or batch procedure. This method is interesting for students, inexpensive and meets basic principles of green analytical chemistry [72].

In this review, some interesting experiments were described, for which their authors selected the keyword "green analytical chemistry". All the examples, mainly for graduate and undergraduate studies, reported above are the result of the commitment of scientists and teachers in the field of analytical chemistry with the aim of enriching existing or introducing new content into the curricula of green analytical chemistry. Experiments meet some of the basic principles of green analytical chemistry: contribute to the reduction of the sample and the consumption of reagents and solvents, the replacement of toxic chemicals, the new „green“ treatment of sample, the treatment or waste reduction and energy saving.

6. Summary

Nowadays, chemistry curricula as well as the education of chemistry teachers should more accurately reflect to the significance of education and sustainable development, but should also support and promote the development of human identity, which is undoubtedly correlated with the environment. This is also correct for Analytical Chemistry. Obviously, the new concepts in teaching green analytical chemistry include the greening of analytical methods and the development of new green methodologies. Teaching analytical chemistry should include the way of thinking about the analytical problems as well as their solutions in terms of sustainability. Few aspects should be emphasized; the classical figures of merit well known from the past and evaluating the persistent, bioaccumulative and toxic characteristics of some solvents and reagents, the application of hazardous or corrosive agents or solvents and the analytical wastes generation.

Although, there are texts that help teachers to understand the basic principles of green chemistry, discussing the way of introducing them into the teaching process, lab manuals for green analytical chemistry are seldom available. In addition, a few scientific papers problematize the teaching green analytical chemistry in specialized educational journals. Thus, there is a growing need to expand the range of pedagogical materials from the same chemical subdisciplines most notably to the analytical/environmental and physical chemistry. Therefore, we believe that this manuscript is of high importance and can help readers in the future practice.

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