Chapter 15
Green Analytical Chemistry: Summary of Existing Knowledge and Future Trends

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Abstract Analysis of recent publications in Green Analytical Chemistry shows the current trends and future needs in this area. The main issues are related to search for cheaper, more efficient, more accurate, greener and miniaturized alternatives. Miniaturization is perhaps, the most notable current trend in analytical chemistry. Rapid developments and improvements in instrumentation have led to an impressive range of benchtop technology and portable devices. In addition, an important issue that has been explored by many authors is metrics of Green Analytical Chemistry, such as Analytical Eco-Scale or Green Analytical Procedure Index. Implementation of interdisciplinary methods is an emerging trend in Green Analytical Chemistry. Employment of multicriteria decision analysis, a technique which is used in environmental management, to Green Analytical Chemistry is a very popular and common trend. Another important issue that will determine the future of Green Analytical Chemistry is education and popularization of this concept in the society. This chapter summarizes contemporary problems and gives the future perspectives of Green Analytical Chemistry.

Keywords Trends in Green Analytical Chemistry · Green solvents · Green extraction techniques · Green metrics · Education · Teaching Green Analytical Chemistry

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J. Płotka-Wasylka and J. Namieśnik (eds.), *Green Analytical Chemistry*, Green Chemistry and Sustainable Technology,
https://doi.org/10.1007/978-981-13-9105-7_15

15.1 Introduction

The importance and scope of use of analytics and bioanalytics are constantly growing due to the need to obtain reliable analytical information about the processes taking place in various material objects of different origins and their composition. At this point, one can ask yourself how many known chemical compounds may be present in the tested samples. The answer to this question can be found in Chemical Abstracts. The relevant data are summarized in Table 15.1. The number of chemical compounds whose basic properties are known is constantly growing.

Two groups of chemists are responsible for this:

- chemists employed in laboratories and industrial facilities where research on new synthesis processes and the production of various types of chemicals on an increasingly larger scale are carried out,
- chemical analysts who develop new analytical procedures and use control and measurement instruments ensuring the ability to detect, identify and quantify an increasingly wider range of analytes at a lower and lower level of content in samples characterized by complex and often variable composition of the matrix.

The increase of the tonnage production and the variety of chemicals produced (in pure form or in the form of appropriate chemical products) makes the human habitat increasingly saturated with chemical compounds. Thus, the immediate human environment is often referred to as a chemosphere. The OECD report provides relevant data and forecasts on the growth in the production of chemicals and the increase in global population growth (Fig. 15.1). According to these data, the manufacturing of chemical products increases by 3% annually when there is a 0.77% increase in population density. Taking the above into account, the need arose to develop a new

Table 15.1 Information on the numbers of existing chemical compounds as well as chemical reactions based on Chemical Abstracts

	02.12.2014	09.09.2015	22.04.2016	17.08.2017	07.08.2018
Number of known chemical substances (organic and inorganic)	65,844,568	66,324,359	66,644,872	67,273,974	67,752,102
Number of known chemical reactions (single-step and multi-step)	76,343,169	82,348,277	88,175,941	100,490,924	110,147,030
Number of chemical compounds available in trade	86,820,549	104,517,210	110,378,650	131,745,000	146,466,171
Number of chemical compounds subject to legal regulations	312,274	344,630	345,575	387,170	389,931

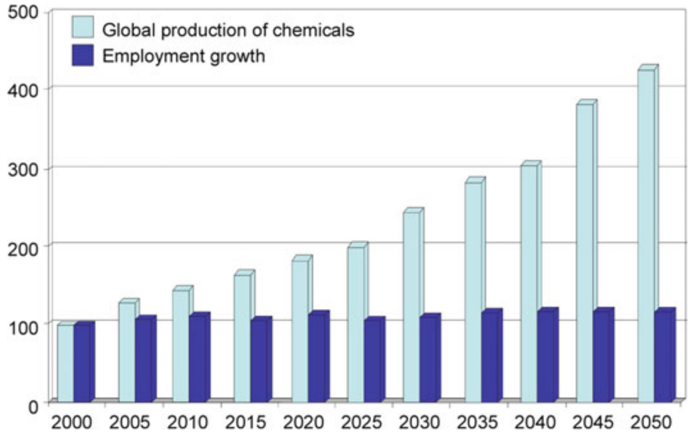


Fig. 15.1 Schematic representation of the relationship between employment growth and production of chemicals based on the OECD report [1]

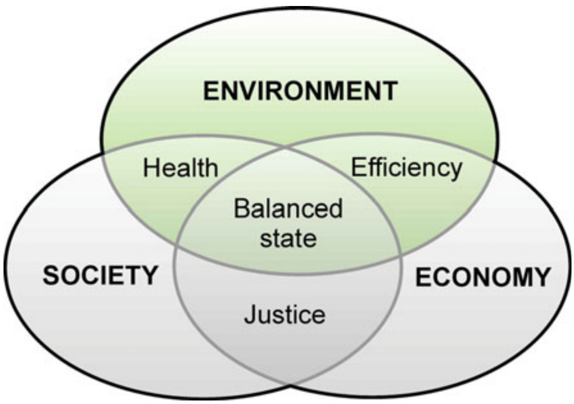
philosophy regarding meeting the social demand for various types of chemical products. It is related to the implementation of the concept of sustainable development.

When satisfying the consumption needs of the human population, the protection of the environment against degradation and rapacious exploitation must be taken into account, as well as protection of health and life of employees involved in various stages of the process of manufacturing consumer goods. The change in philosophy described above is illustrated on the diagram shown in Fig. 15.2.

This approach to the process of manufacturing consumer goods is described in the form of rules of conduct. Literature provides information on the following principles:

- 12 Principles of Green Chemistry [2]
- 12 Principles of Green Chemical Technology [3]
- 12 Principles of Green Chemical Engineering [4].

Fig. 15.2 Schematic presentation of the premises constituting the basis for changing the way of activity of chemists and technologists



For the descriptive assessment of activities related to the introduction to the analytical practice of the concept of sustainable development, the 3R concept [5] is used:

- Reduce
- Replace
- Recycle.

Another code of conduct is the ten eco-commandments for earth citizens developed by prof. Menke Gluckert [6].

In addition to these general rules of conduct regarding chemistry and chemical technology, the principles of Green Analytical Chemistry [7] were published, and later also the principles of particular groups of analytical techniques, such as green chromatography or green spectroscopy techniques. The implementation of the principles of green chemistry and Green Analytical Chemistry is the reason why the set of criteria for the selection of analytical methodology, which can be used to perform a specific analytical task, must be expanded. All those who are involved in the development of new methodologies (procedures) are aware that the following criteria should be taken into consideration:

- Accuracy,
- Precision,
- Selectivity,
- Detection limits.

If the principles of Green Analytical Chemistry are taken into consideration, the impact on the environment and human health becomes the fifth parameter in the assessment of the usefulness of analytical procedures [8]. The heart of Green Analytical Chemistry is schematically presented in Fig. 15.3.

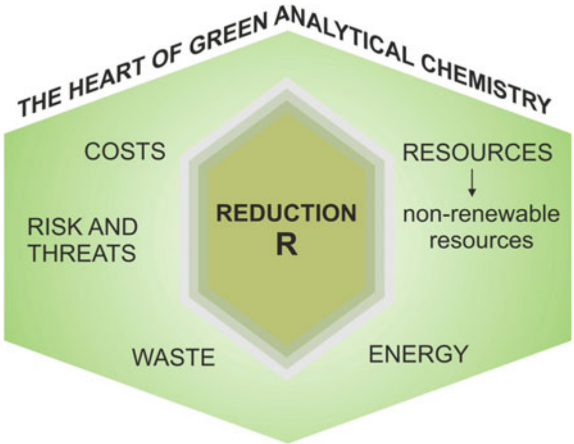


Fig. 15.3 The heart of Green Analytical Chemistry

15.2 Current Trends in Green Analytical Chemistry

Analysis of recent publications concerning Green Analytical Chemistry shows the current trends and future needs in this area. Articles published since 2018 have focused mostly on improvements of analytical procedures aiming at greening the selected steps of the analytical process. These improvements include:

- using an alternative, more environmentally friendly solvents [9–18],
- greening extraction procedures [19–30],
- promoting multi-analyte techniques [31–35],
- reducing reagent volume by application of miniaturized techniques [22, 36–39],
- introducing new components as stationary and mobile phases in chromatography [40, 41],
- eliminating sample treatment [32, 42–46],
- simplifying analytical protocols [47, 48],
- greening sample digestion [49] and derivatization [50],
- using mathematical modelling and chemometrics in greener analytical methods [51, 52].

Some authors have also recently reported on the development of new methods [53–58] or have promoted non-destructive analytical methods [59] and natural reagents [60].

One of the current trends in Green Analytical Chemistry is developing simple and cheap methods for the qualitative and/or quantitative determination of different analytes and parameters that are useful for certain applications. An example of this approach is paper-based analytical devices that can be used in pharmaceutical sciences in gene delivery formulations [61] and determination of amino acids in gym supplements [62]. They can also be used in food chemistry for the determination of antioxidant capacity of tea and vegetable oils [63, 64]. Food adulteration is another area where simple green methods can be employed. Digital images and chemometric tools were successfully used for quantification of fat content in chicken burgers [65]; whereas, liquid–liquid microextraction coupled with mobile phone-based photometric detection was used for the determination of anionic surfactants in milk [66]. Sitanurak et al. [67] proposed using the paper-based device for quantification of hypochlorite in bleach and disinfectants. An interesting green alternative to conventional analytical methods was proposed by Kiwfo et al. [68] who used a noodle-based analytical device as copper (Cu^{2+}) and acid–base assay.

An important issue that has been explored by many authors since 2012 is the metrics of Green Analytical Chemistry. The first tool proposed for the assessment of the greenness of analytical procedures was Analytical Eco-Scale developed by Gałuszka et al. [7]. Both the use and introduction of new metrics were the topic of numerous studies in 2018 [33, 69–74].

Implementation of interdisciplinary methods is an emerging trend in Green Analytical Chemistry. Tobiszewski and Orłowski [75] employed multicriteria decision analysis, a technique which is used in environmental management, to Green Analytical Chemistry. Combining method development in the pharmaceutical analysis (a quality by design approach) with Green Analytical Chemistry has recently been postulated by Saroj et al. [76].

15.3 Future Directions of Development of New Analytical Procedures and Measuring Instruments

In many research and R&D centres, work is underway to develop new analytical procedures designed for studying various types of material objects. In these procedures, improvements are being made at the stages of detection, separation, identification and quantification of the broadest possible spectrum of analytes. As mentioned before, these new methodological solutions should undergo an assessment of environmental nuisance and impact on the health and life of analytical staff. For this purpose, various tools are used to obtain qualitative or quantitative information about the pro-environmental nature of the proposed methodological solution.

An analysis of literature data might be the basis for distinguishing the development directions of new analytical solutions that to a greater or lesser extent meet the requirements resulting from the principles of Green Analytical Chemistry:

- searching for new non-matrix techniques for preparing samples for analysis,
- introduction of new types of solvents to the analytical practice (the so-called green solvents), the impact of which does not have an adverse effect on either the environment or the health and life of analysts,
- application of additional factors affecting the acceleration of the reaction or the extraction process,
- development of new types of control and measurement devices ensuring the possibility of performing in situ tests (without time delay),
- new solutions in the so-called direct analytical techniques. Such solutions are particularly attractive because the analysis of the tested material does not require any sample preparation. Table 15.2 presents basic information about the different groups of measuring instruments that can be used for direct detection and/or determination of analytes,
- the use of reagents produced from renewable raw materials,
- development of remote measurement techniques (remote sensing). Information on the morphological classification of remote sensing methods is presented in Table 15.3.

In the field of remote sensing techniques, both passive and active devices are used. The latter are equipped with their own sources of radiation, while the operation of the former is based on the use of radiation from external sources (e.g. solar radiation). In practice, active devices have a broader scope of application.

Table 15.4 summarizes information on three analytical techniques equipped with monochromatic radiation sources.

Table 15.2 Basic information on analytical instruments used in direct analyses of different types of samples

Method	Technique	Example of application
Colorimetry	Dry test Wet test	Determination of metal ions in water Determination of metals in vegetables and fruits Determination of nitrates in vegetables
Potentiometry	Ion Selective Electrodes—ISE	Measurement of pH (Glass electrode) Determination of metals in surface water
Activation analysis	(Instrumental) Neutron Activation Analysis—(I)NAA	Determination of metals in environmental samples
Atomic Absorption Spectroscopy	Graphite Furnace Atomic Absorption Spectroscopy—(GFAAS) Quartz Furnace Atomic Absorption Spectroscopy—(QFAAS)	Determination of metals in solid and liquid environmental samples
Inductively Coupled Plasma Mass Spectrometry	Laser Ablation Inductively Coupled Plasma- Mass Spectrometry (LA-ICP-MS)	Determination of major and trace elements in different samples
Infrared Spectroscopy	Fourier-Transform Infrared Spectroscopy (FTIR)	Analysis of samples of different matrix composition
Nuclear Magnetic Resonance Spectroscopy	Nuclear Magnetic Resonance Spectroscopy (NMR)	Analysis of samples of different materials
Emission Spectroscopy	Laser-Induced Breakdown Spectroscopy (LIBS)	Real-time elemental analysis in a wide range of samples
X-ray Fluorescence	Wavelength-Dispersive X-ray Fluorescence (WD-XRF) Energy-Dispersive X-ray Fluorescence (ED-XRF)	Simultaneous determination of many elements in solid and liquid samples
Raman Spectroscopy	Raman Spectroscopy (RS) Surface-Enhanced Raman Spectroscopy (SERS)	Analysis of samples of different matrix composition
Laser-Induced Breakdown Spectroscopy	Laser-Induced Breakdown Spectroscopy (LIBS)	Analysis of chemical composition of different materials
Immunoanalysis	Immunoanalysis (IMA) Enzyme-Linked Immunosorbent Assay—ELISA	Detection and determination of selected dioxins and dioxin-like compounds in environmental samples

(continued)

Table 15.2 (continued)

Method	Technique	Example of application
Fluorescence	Laser-induced fluorescence (LIF) UV light-emitting diode induced fluorescence (UV LED)	Real-time screening of traces of polycyclic aromatic hydrocarbons in surface water and soil samples. A possibility of the use of UV LED in monoaromatic hydrocarbon prospection studies
Ion-Mobility Spectrometry	Ion-Mobility Spectrometry (IMS)	Detection of high energy materials (explosives, propellants) and drugs
Photoelectron Spectroscopy	X-ray Photoelectron Spectroscopy (XPS)	Detection and quantification of all elements except for hydrogen. Determination of types of bonds between elements on the surface of samples
Electron Paramagnetic Resonance Spectroscopy	Electron Paramagnetic Resonance Spectroscopy—EPR (Electron Spin Resonance Spectroscopy—ESR)	Used in solid-state physics for determination of free radicals, in chemistry for studying reaction rates, in biology and medicine for monitoring of spin labelling, in archaeology for dating of tooth enamel
Methods of surface analysis	Secondary Ion Mass Spectrometry (SIMS)	Analysis of surface of different materials (mapping of analytes on the surface of samples)
	Electron Spectroscopy for Chemical Analysis (X-ray Photoelectron Spectroscopy)—ESCA (XPS)	
	Scanning Electron Microscope (Energy-Dispersive X-ray Spectroscopy)—SEM (EDS)	
	Auger Electron Spectroscopy (AES)	
	Ion Scattering Spectroscopy (ISS)	
Mass spectrometry	Direct Analysis in Real Time-Mass Spectrometry (DART-MS)	Analysis of liquid and solid samples
	Selected Ion Flow Tube-Mass Spectrometry (SIFT-MS)	Analysis of gaseous mixtures Determination of volatile compounds
	Desorption Electrospray Ionization Spectrometry (DESI-MS)	Direct analyses of liquid samples Detection of chemical warfare agents
	Proton Transfer Reaction-Mass Spectrometry (PTR-MS)	Real-time simultaneous determination of volatile organic compounds

(continued)

Table 15.2 (continued)

Method	Technique	Example of application
	Membrane Inlet Mass Spectrometry (MIMS)	Determination of volatile compounds that permeate through the membrane in gaseous and liquid samples
	Direct Inlet Probe-Atmospheric Pressure Photo Ionization-Mass Spectrometry (DIP-APPI-MS)	Identification and determination of sample components adsorbed on the surface of a sampler introduced into an ionization chamber.
	Direct Infusion-Mass Spectrometry (DI-MS)	Used in metabolomic studies of liquid samples
	Matrix-Assisted Laser Desorption/Ionization-Mass Spectrometry (MALDI-MS)	Analysis of samples with different matrix composition for determination of biologically active compounds (oligonucleotides, carbohydrates, lipids and others)
	Surface-Enhanced Laser Desorption/Ionization-Time of Flight-Mass Spectrometry (SELDI-TOF-MS)	Analysis of biological material samples (tissues, blood, urine, etc.) for identification of proteins
Remote sensing techniques	Light Detection and Ranging (LiDAR)	Analyses of air samples
	Sonic Detection and Ranging (SODAR)	Measurements of air humidity
Sensor matrix	Electronic nose (e-nose)	Analysis of gaseous samples (air, breath, headspace phase)
	Electronic tongue (e-tongue)	Analysis of liquid samples

Table 15.3 Morphological classification of remote sensing methods

Methods	Passive	Active
Ground	Photographic Photoelectric measurements Correlation spectrometer	Radio measurements LiDAR measurements SODAR measurements
Aerial	Photographic and thermovision Radiometric measurements Correlation spectrometer	SLAR SAR LiDAR measurements
Satellite	Multispectral imaging Microwave measurements Photometric measurements	LiDAR measurements Large-range Radar measurements

Table 15.4 Basic information on monostatic devices with a source of monochromatic radiation

Analytical technique	A brief description of the principle of operation
Differential Optical Absorption Spectroscopy—DOAS	The light radiation beam is directed from the transmitter to the receiver. The length of the optical beam's path is known The intensity of the beam changes due to contact with atmospheric components After returning to the receiver, the beam is directed through a fibre optic cable to the central unit equipped with a computerized spectrometer The computer allows collecting characteristic data on a beam of radiation up to 100 times per second
Differential Absorption LiDAR—DIAL	It is a device in which two laser beams of different lengths pass through a gas cloud (along the same path) If the radiation length of one of the beams is equal to the radiation length best absorbed by a specific component, and the radiation of the second beam is not absorbed at all, the difference in radiation intensity of both beams (after returning to the receiver) is proportional to the amount of the absorbing component
Light Detection and Ranging—LiDAR	It is a pulsed laser system used in a similar way to a radar system. In this case, the return time of the reflected beam of radiation is measured, and on this basis the distance from the cloud of the substance reflecting the radiation or the distance from a fixed obstacle is determined

- development of new procedures for assessing the environmental nuisance and toxicological risk of the activity of chemical analysts.

15.4 Ongoing Challenges and Future Trends in Teaching GAC

Nowadays, many efforts are being made in order to include the GAC concept to education, including the field of analytical chemistry, where twelve GAC principles play the main role. There is no doubt that the understanding and awareness of these principles and other evolving related ideas require special teaching of GAC as part of the curriculum at undergraduate and graduate levels. In fact, making analytical chemistry more environmentally friendly is a basic approach that combines old and new analytical chemistry ideas and as such, it should be transmitted into the teaching of GAC [77].

Education in Green Analytical Chemistry balances between ethical and chemical aspects; therefore, the main role of teachers is to convince the students that chemistry not only poses a risk for the planet, but also shows great promise for human health care as well as a sustainable environment. Therefore, teaching GAC should be a social responsibility, as it is undoubtedly one of the pillars of modern chemistry [78], and in particular of analytical chemistry [79], which is due to the fact that virtually every area of life today depends on the data obtained and transmitted via chemical research. Analytical chemistry should be socially responsible, because the data and knowledge that it provides affect every element of the reality that surrounds us [77]. Green Analytical Chemistry is an appropriate platform for teaching and promoting social responsibility because it is a social movement itself [80]. If we would like to have analytical chemists who are responsible, socially sensitive, and who would take care of the metrological quality of data and information, we must educate them from the very beginning, from primary school through high school to university. However, it is not a good idea to create separate chapters in chemistry textbooks or to have guest lectures given by humanists. Rather, it should be done by integrating chemical instrumentation and nomenclature with social and ethical themes [81].

An important objective in teaching analytical chemistry is to change the chemistry students' attitude. In addition, the attitude of future generations towards chemistry and its impact on the environment should also be changed. For a long time, some of the green chemistry principles have been included in teaching analytical chemistry, since they are essential for increasing safety and reducing lab costs. However, these efforts were not mandatory; they only depended on the ethical preferences of teachers and lab staff [77]. Therefore, additional efforts should be made to educate teachers about conveying the message of sustainability in analytical chemistry teaching. It should be quite clear that the GAC principles should be an integral part of solving analytical problems, an obligation, and in no case a matter of choice. As pointed out in a recent paper [82], there are several concepts for teaching Green Analytical Chemistry, which are presented in Fig. 15.4.

New ideas in teaching Green Analytical Chemistry include the greening of analytical methods as well as the development of new green methodologies. Safety concerns regarding laboratories and waste have become the reason for developing new ideas of improving the safety in such a working environment and successfully reducing the amount of waste or decontaminating it [77]. 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 [83]. It needs to be stated that analytical chemistry gives the opportunity for innovations in teachings and science, in the context of waste treatment or by using new reagents that increase students' understanding of and sensitivity to the environmental consequences of their scientific choices.

Unfortunately, there are many gaps and areas for improvement in GAC teaching and research. Firstly, the teaching style itself, such as presentations on how to

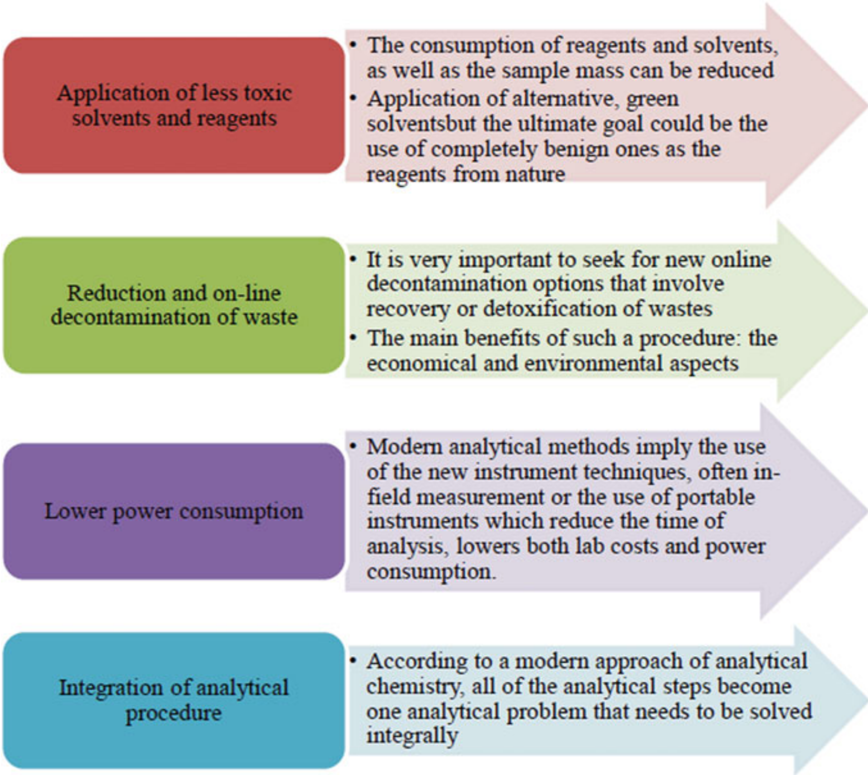


Fig. 15.4 Outline of the studies discussed in the present sub-chapter focused on the use of DES in the extraction and/or digestion/dissolution processes

understand the laws of analytical chemistry, reaction recording style, etc. should be changed. Besides the gaps in education and teaching, there are also ones in the literature and research. The simplest example is that several false "greenness" claims exist in the chemical literature. Many researchers state that a given analytical procedure is green based only on one of the Twelve Principles of Green Analytical Chemistry. Such a proceeding shows a very narrow point of view rather than a multi-dimensional global approach which considers all reagents, materials and energy consumption, as well as the environmental impact of any waste and by-products manufactured. A good example of such a proceeding is a declaration that a given procedure/reaction is "solvent-free" or "solventless". This, undoubtedly, should be changed, and it is the teachers' responsibility to show their students when they can consider a procedure "green".

Widespread success in these and related fields may lead to re-writing undergraduate textbooks as the paradigm shift evolves [82]. Finally, quantification of energy consumption, as well as the costs of an appropriate methodology, has received little attention from both research and teaching perspectives. In addition, several current

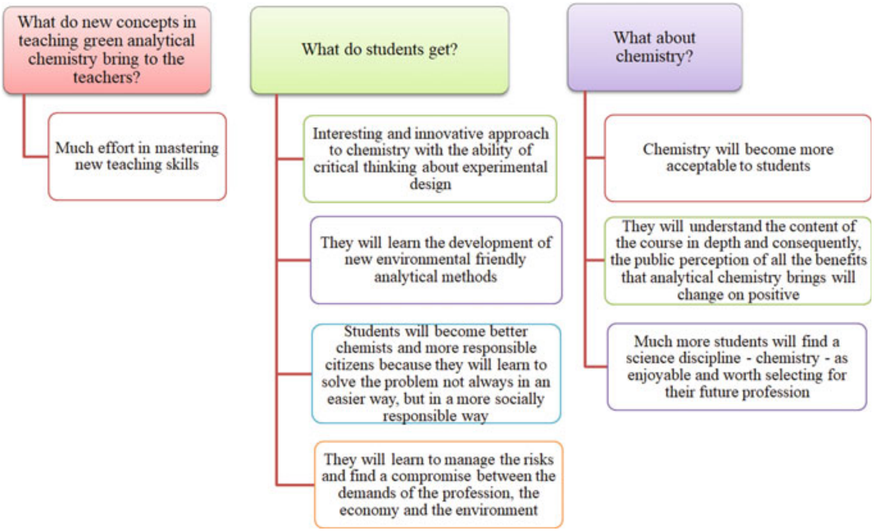


Fig. 15.5 Questions concerning introduction of Green Analytical Chemistry into teaching practice

trends in extraction techniques focused on finding solutions to minimize the use of solvents. Thus, new microextraction techniques are still introduced into analytical practice. These modern methods need to be known for students. Therefore, new textbooks, as well as scholarly materials, will be published in the coming years.

Summarizing the above information, some questions should be asked:

- What do the new concepts in teaching Green Analytical Chemistry bring to the teachers?
- What do students get?
- What about chemistry?

The answers are presented in Fig. 15.5.

15.5 Future Perspectives of Green Analytical Chemistry

A fast progress in Green Analytical Chemistry could not be possible without active participation of analytical chemists in developing new, more environmentally friendly approaches to the analytical process or its phases. Of many different areas of interest in Green Analytical Chemistry, two seems to play a major role in the development of this concept, namely, greening of analytical laboratories and life cycle assessment of reagents and instruments.

Greening of analytical laboratories. Principles of Green Analytical Chemistry set general guidelines for making chemical analysis safer and more environmentally friendly. A successful implementation of these principles on a laboratory scale may be easier during designing of a new facility, but in the case of existing laboratories, it requires changes which may generate high costs and make the concept of Green Analytical Chemistry a wishful thinking.

A green analytical laboratory can be defined as a laboratory in which Green Analytical Chemistry principles are implemented and constant efforts are being made in order to assure minimum environmental impact through evaluation of the greenness of analytical procedures and selection of the most environmentally friendly options. However, the greening of analytical laboratories can be implemented on different levels of the analytical process, from reagents to methods and procedures to instruments.

From cradle to grave—from reagents to waste. Analytical processes should be perceived similarly to industrial processes in which life cycle assessment is performed. A new approach "from reagent to waste" should be implemented because reagents used in chemical analyses are part of the analytical waste. A green approach to the analytical waste problem is to eliminate it or minimize its amount. More efforts are needed in order to develop methods of recovery of resources from analytical waste. So far, the recovery of americium and plutonium from analytical waste has been performed [84–86]. A possibility of recovering elements other than radionuclides should be examined in the future. Recovery of platinum group elements and rare earth elements seems to be economically viable. A life cycle assessment of analytical instruments should also be adapted to Green Analytical Chemistry.

Another important issue that will determine the future of Green Analytical Chemistry is education and popularization of this concept in the society [77, 82]. This can be achieved through making Green Analytical Chemistry an integral part of a curriculum at different education levels. Simple, but spectacular methods, i.e. those based on smartphone detection, can be presented during science festivals and workshops open to the public. All these efforts will be crucial for a wider interest and continuous progress in Green Analytical Chemistry.

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