Polish Journal of Environmental Studies Vol. 14, No 4 (2005), 389-395

Review

Green Chemistry — Current and Future Issues

W. Wardencki*, J. Curyło, J. Namieśnik

Department of Analytical Chemistry, Chemical Faculty, Gdańsk University of Technology, Narutowicza 11/12 ,
80-952 Gdańsk-Wrzeszcz; Poland

Received: May 5, 2004
Accepted: December 10, 2004

Abstract

The beginning of green chemistry is frequently considered as a response to the need to reduce the damage of the environment by man-made materials and the processes used to produce them. A quick view of green chemistry issues in the past decade demonstrates many methodologies that protect human health and the environment in an economically beneficial manner. This article presents selected examples of the implementation of green chemistry principles in everyday life in industry, the laboratory and in education. A brief history of green chemistry and future challenges are also mentioned.

Keywords: green chemistry, green analytical chemistry, clean chemistry, atom economy, sustainable development.

History

The term green chemistry was first used in 1991 by P. T. Anastas in a special program launched by the US Environmental Protection Agency (EPA) to implement sustainable development in chemistry and chemical technology by industry, academia and government. In 1995 the annual US Presidential Green Chemistry Challenge was announced. Similar awards were soon established in European countries. In 1996 the Working Party on Green Chemistry was created, acting within the framework of International Union of Applied and Pure Chemistry. One year later, the Green Chemistry Institute (GCI) was formed with chapters in 20 countries to facilitate contact between governmental agencies and industrial corporations with universities and research institutes to design and implement new technologies. The first conference highlighting green chemistry was held in Washington in 1997. Since that time other similar scientific conferences have soon held on a regular basis. The first books and journals on the subject of green chemistry were introduced in the 1990s, including the *Journal of Clean Processes and Products* (Springer-Verlag) and *Green Chemistry*, sponsored by the Royal Society of Chemistry. Other journals, such as *Environmental Science and Technology* and the *Journal of Chemical Education*, have devoted sections to green chemistry. The actual information also may be found on the Internet.

The Idea of Green Chemistry

The concept of green chemistry has appeared in the United States as a common research program resulting from interdisciplinary cooperation of university teams, independent research groups, industry, scientific societies and governmental agencies, which each have their own programs devoted to decreasing pollution.

Green chemistry incorporates a new approach to the synthesis, processing and application of chemical substances in such a manner as to reduce threats to health and the environment. This new approach is also known as:

- Environmentally benign chemistry
- Clean chemistry
- Atom economy
- Benign-by-design chemistry

---

*Corresponding author: e-mail: wawar@chem.pg.gda.pl

Green chemistry is commonly presented as a set of twelve principles proposed by Anastas and Warner [1]. The principles comprise instructions for professional chemists to implement new chemical compounds, new syntheses and new technological processes.

The first principle describes the basic idea of green chemistry — protecting the environment from pollution. The remaining principles are focused on such issues as atom economy, toxicity, solvent and other media using consumption of energy, application of raw materials from renewable sources and degradation of chemical products to simple, nontoxic substances that are friendly for the environment.

The 12 Principles of Green Chemistry

1. Prevention

It is better to prevent waste than to treat or clean up waste after it has been created.

2. Atom Economy

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Syntheses

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals

Chemical products should be designed to effect their desired function while minimizing toxicity.

5. Safer Solvents and Auxiliaries

The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. Design for Energy Efficiency

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. Use of Renewable Feedstocks

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce Derivatives

Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. Catalysis

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for Degradation

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. Real-time analysis for Pollution Prevention

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

The selected examples for implementing the 12 principles in laboratory and industry are presented in Table 1.

Table 1. Examples of implementation of green chemistry principles into practise.

Nr	Principle	Examples:
1	Prevention	Use of solvent-less sample preparation techniques [2]
2	Atom Economy	Hydrogenation of carboxylic acid to aldehydes using solid catalysts
3	Less Hazardous Chemical Syntheses	Adipic acid synthesis by oxidation of cyclohexene using hydrogen peroxide [3]
4	Designing Safer Chemicals	New, less hazardous pesticide (e.g. Spinosad) [4]
5	Safer Solvents and Auxiliaries	Supercritical fluid extraction, synthesis in ionic liquids [5]
6	Design for Energy Efficiency	Polyolefins – polimer alternative to PWC (polimerization may be carried with lower energy consumption) [6]
7	Use of Renewable Feedstocks	Production of surfactants [7]
8	Reduce Derivatives	On-fiber derivatization vs derivatization in solution in sample preparation [8]
9	Catalysis	Efficient Au(III)-catalyzed synthesis of b-enaminones from 1,3-dicarbonyl compds. and amines [9]
10	Design for Degradation	Synthesis of biodegradable polymers [10]
11	Real-time analysis for Pollution Prevention	Use of in-line analyzers for wastewater monitoring
12	Inherently Safer Chemistry for Accident Prevention	Di-Me carbonate (DMC) is an environmentally friendly substitute for di-Me sulfate and Me halides in methylation reactions [11].

Examples of Implementation of Green Chemistry Principles Into Practise

In some industrial chemical processes, not only waste products but also the reagents used for the production, may cause a threat to the environment. The risk of exposure to hazardous chemical compounds is limited in daily work by protective equipment such as goggles, breathing apparatus, face-guard masks, etc. According to the principles of green chemistry, a threat can be eliminated in a simpler way, by applying safe raw materials for production process.

Large amounts of adipic acid [$HOOC(CH_2)_4COOH$] are used each year for the production of nylon, polyurethanes, lubricants and plasticizers. Benzene — a compound with convinced carcinogenic properties — is a standard substrate for the production of this acid. Chemists from State University of Michigan developed green synthesis of adipic acid using a less toxic substrate. Furthermore, the natural source of this raw material — glucose — is almost inexhaustible. The glucose can be converted into adipic acid by an enzyme discovered in genetically modificated bacteria [12]. Such a manner of production of this acid guards the workers and the environment from exposure to hazardous chemical compounds.

Green chemistry tries, when possible, to utilize benign, renewable feedstocks as raw materials. From the point view of green chemistry, combustion of fuels obtained from renewable feedstocks is more preferable than combustion of fossil fuels from depleting finite sources. For example, many vehicles around the world are fueled with diesel oil, and the production of biodiesel oil is a promising possibility. As the name indicates, biodiesel oil is produced from cultivated plants oil, e.g. from soya beans. It is synthesized from fats embedded in plant oils by removing the glycerine molecule (Fig. 1) — a valuable raw material for soap production.

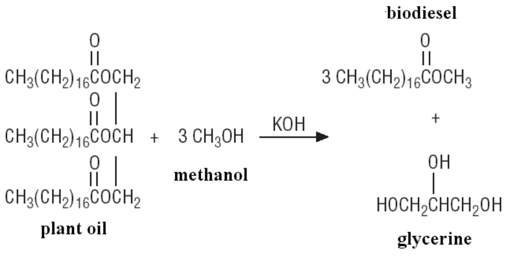

Fig. 1. Reaction for biodiesel oil production

Biodiesel oil also can be obtained from wasted plant oils, e.g. oils used in restaurants. In the technological process, a potential waste product is transformed into valuable fuel. (Combusted biodiesel oil smells like fried potatoes.) The advantages of using biodiesel oil are obvious. It's fuel from renewable resources and contrary to normal diesel oil, the combustion of biodiesel does not generate sulphur compounds and generally does not increase the amount of carbon dioxide in the atmosphere. CO_2 formed in the combustion of fuel was removed earlier by plants [12].

The great threats to the environment are organic solvents applied in many syntheses. They are released into the environment by a volatilization process, especially in the case of volatile organic compounds (VOCs) and as a result of leakage. The emission of such compounds is significant because in many syntheses their amounts exceeds the amount of reagents. The new solutions for practical synthesis aim at complete elimination of solvents or to substitute the compounds belonging to VOCs by cheap technological media, harmless for humans and the environment.

The use of supercritical fluids (SCFs) in chemical processes is becoming more and more prevalent [13-17]. The term "supercritical fluids" comprises the liquids and gases at temperatures and pressures higher than their critical temperatures and pressures (Fig. 2). Above the critical point the liquid-vapour phase boundary disappears while the formed phase exhibits properties between those of gas and liquid. High compressibility of supercritical fluids in the vicinity of the critical point makes it easy to adjust density and solution ability by a small change of temperature or pressure. Due to this, the supercritical fluids are able to dissolve many compounds with different polarity and molecular mass. Among many possible supercritical fluids, fulfilling the green chemistry demands as the reaction media are carbon dioxide ($scCO_2$) and water (scH_2O).

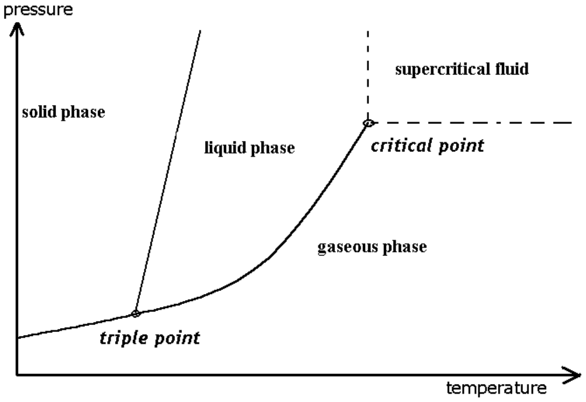

Fig. 2 Phase diagram showing supercritical fluid region.

Carbon dioxide as a supercritical fluid is most frequently used as medium for reactions. It is inflammable, easily available (from natural sources, from power engineering) and cheap. Its application gives considerable energy savings because the critical point is easy to reach due to a low evaporation heat of CO_2. Carbon dioxide as a supercritical fluid dissolves non-polar compounds and some polar (e. g. methanol, aceton) like fluorocarbon solvents. The discovery of a new surfactant with high surface activity in supercritical carbon dioxide opened a way to new processes in textile and metal industries and for dry cleaning of clothes. Micell Technologies Company offers technology for removal of stains using liquid carbon dioxide instead of the perchloroethylene more commonly applied [18].

Most of the common liquids (e.g., water, ethanol, benzene, etc.) are molecular. That is, regardless of whether they are polar or non-polar, they are basically made up of molecules. However, since the early 1980s an exciting new class of room-temperature liquids have become available. These are the ambient-temperature ionic liquids. Unlike the molecular liquids, regardless of the degree of association, they are basically constituted of ions. This gives them the potential to behave very differently from conventional molecular liquids when they are used as solvents.

Room-temperature ionic liquids are considered to be environmentally benign reaction media because they are low-viscosity liquids with no measurable vapor pressure. However, the lack of sustainable techniques for the removal of products from the room-temperature ionic liquids has limited their application. Professors Brennecke and Beckman have shown that environmentally benign carbon dioxide, which has been used extensively, both commercially and in research for the extraction of heavy organic solutes, can be used to extract nonvolatile organic compounds from room temperature ionic liquids [19]. They found that extraction of a material into carbon dioxide represents an attractive means for recovery of products from ionic liquids because:

(a) CO_2 dissolves in the ionic liquid to facilitate extraction, and
(b) the ionic liquid does not dissolve appreciably in the CO_2,

so that the product can be recovered in pure form. The research groups of Professors Brennecke and Beckman have shown that ionic liquids (using 1-butyl-3-methylimidazolium hexafluorophosphate as a prototype) and CO_2 exhibit extremely unusual, and very attractive, phase behavior. The solubility of CO_2 in ionic liquids is substantial, reaching mole fractions as high as 0.6 at just 8 MPa. Yet the two phases do not become completely miscible, so CO_2 can be used to extract compounds from the ionic liquids. Most importantly, the composition of the CO_2-rich phase is essentially pure CO_2, and there is no measurable cross-contamination of the CO_2 by the ionic liquid. Moreover, nonvolatile organic solutes (using naphthalene as a prototype) may be quantitatively extracted from the ionic liquid with CO_2, demonstrating the tremendous potential of ionic liquid/CO_2 biphasic systems as environmentally benign solvents for combined reaction and separation schemes.

Green Analytical Chemistry

Development of analytics and environmental monitoring leads to better knowledge of the state of the environment and the processes that take place in it. Due to the introduction into an analytical practice new methodologies and new measuring techniques for identification and determination of trace and micro-trace components in samples with complex compositions have enabled the discovery of the following important facts:

— acidifying the particular elements of the environment,
— the existence of stratospheric ozone depletion phenomenon,
— designation of long term trends in changes of trace components in atmospheric air,
— increase of concentration level of so called persistent organic pollutant (POPs), i. e. compounds belonging to dioxins (PCDD, PCDF), polychlorinated biphenyls (PCBs) and others,
— examination of pollutant bioaccumulation in tissues of organisms on different steps of the trophic chain.

This branch of analytical chemists creates many challenges. The most important are as follows:

— low and very low concentration levels of analytes,
— the existence of time and space fluctuations of analytes in the investigated media,
— a broad range of concentration of analytes belonging to the same group of compounds,
— the possibility of the presence of interfering compounds, frequently with similar chemical structure and properties.

The irony is that the analytical methods used to assess the state of environmental pollution may in fact be the source of emission of great amount of pollutants negatively influencing the environment. This is connected with the necessity of using considerable amounts of chemical compounds in successive steps of applied analytical procedures. Sampling and especially preparation for their final determination is frequently connected with the forming of large amounts of pollutants (vapours, wastes of reagents and solvents, solid waste). Therefore, it is necessary to introduce the rules of green chemistry into chemical laboratories on a large scale. There is an urgent necessity to evaluate the used analytical methods not only in respect for the reagent, instrumental costs and analytical parameters but also on the basis of their negative influence on the environment. A good tool for such evaluation may be Life Cycle Assessment (LCA). It can be stated that green analytical chemistry is the essential element of green chemistry. The constant development of a new solventless technique is a good example of the activities in this field. The following direct analytical techniques (a preparation step is not necessary) may be treated as the typical examples of procedures that are more friendly for the environment:

— X-ray fluorescence,
— surface acoustic wave (SAW) used during determination of volatile organic compounds (VOCs),
— immunoassay.

Also, the other techniques in which the amount of reagents and solvents is limited (calculated per one analytical cycle) belong to environmentally benign procedures, e.g.:

- — solid phase extraction (SPE),
- — accelerated solvent extraction (ASE),
- — solid phase microextraction (SPME)
- — liquid-liquid microextraction (MLLE), and other microextraction techniques,
- — ultrasonic extraction,
- — supercritical fluid extraction (SFE),
- — extraction in automated Soxhlet apparatus,
- — vacuum distillation of volatile organic compounds,
- — mass spectrometry with membrane interface (MIMS).

The extraction of pesticides from soil samples using accelerated solvent extraction is a good example of an analytical procedure fulfilling the rules of green chemistry [20]. This procedure is characterized by many advantages in comparison to classical extraction techniques used for extraction of analytes from complex matrices. The main advantages considering green chemistry are as follows:

- — reduction of used solvents (up to 95%),
- — shortening of analysis time (from 16 hours to 10 minutes),
- — savings of energy (the heating of extraction cell of ASE instrument to 100°C by 10 minutes in comparison to 16 hours heating of a plate in Soxhlet apparatus),
- — decreasing exposure to solvents due to shortening of extraction time and to smaller amounts of applied solvents),
- — similar analytical characteristics (precise and analyte recoveries) for smaller sample (ASE).

This procedure can be treated as an alternative to commonly used extraction in Soxhlet apparatus.

The ability to rapidly assess or monitor the disposition of environmental contaminants at purported or existing hazardous waste sites is an essential component of green chemistry. Soil samples have to be collected from surface to ground water and then shipped off-site for analysis with waiting periods exceeding months. Soil samples, which represent approximately half the total number, are extracted with solvents, then further separated using additional solvent to produce chemical-specific fractions. Each fraction is then analyzed by an appropriate method. The proposed technology by Professor Albert Robbat from Tufts University is aimed at reducing or eliminating solvent usage during the sample collection and sample analysis process by collecting and detecting organic pollutants at depth without bringing the actual soil sample to the surface. A thermal extraction cone penetrometry probe coupled to an ultra-fast gas chromatography/ mass spectrometer (TECP-TDGC/MS) has been developed to collect and analyze subsurface organic contaminants in situ. The TECP is capable of heating the soil to 300°C, which is sufficient to collect volatile and semivolatile organics bound to soil, in the presence of soil-water content as high as 30%. Rather than using solvents to extract organics from soil, the TECP uses heat, then traps the hot vapor in a Peltier-cooled thermal desorption GC sample inlet for on-line analysis. In addition, the proposed technology reduces solvent usage when decontaminating sample collection probes and utensils used to homogenize samples. No other technology exists that is capable of thermally extracting organics as diverse as PCBs, explosives, or PAHs under these conditions. When combined with the ION Fingerprint Detection™ software, ultra-fast TDGC/MS is capable of analyzing complex environmental samples in less than 5 minutes [19].

The next important challenge of green analytical chemistry is in-process monitoring. Developing and using the in-line or on-line analyzers allow us to determine analytes in real time, enabling us to detect disturbances in the course of a process in the initial steps. Such means of analysis gives rapid information and a chance for proper reaction — stopping the technological process or changing the operational parameters, and improves overall efficiency.

The application of green chemistry rules during designing greener analytical methods is a key to diminish negative effects of analytical chemistry on the environment [2, 21]. The same ingeniousness and novelty applied earlier to obtain excellent sensitivity, precision and accuracy is now used to abate or eliminate the application of hazardous substances in environmental analytics.

Teaching of Green Chemistry.

The main rule: *Teaching must be in harmony with practice.*

The question of how to educate the future generation of chemists possessing the skill and knowledge to practice environmentally friendly chemistry lies in the center of educational materials related to green chemistry [22].

Education is especially important in the popularization of green chemistry. It is realized both at the level of academia and on the level of pro-environmental education for broad circles of society. Young chemists are currently acquainted with new methods of organic compound syntheses instead of traditional methods and with new analytical chemistry techniques allowing them to assess the state of environmental pollution in an increasing number of high schools. Different international institutions, i.e. the American Chemical Society (ACS) and Polish Chemical Society (PTChem), are active in publishing materials that promote the rules and achievements of green chemistry. The green chemistry program should lead to sustainability by designing and using the methods in which natural raw materials will be economically processed, rational usage of energy sources, elimination of hazardous gaseous, liquid and solid wastes and by introduction of safety products for man. The popularization of green chemistry in schools, among the workers at plants of chemical industry and distributors of chemical products is also very important. The broad usage of green chemistry achievements will enable us to balance eco-development profitable for society, economy and the environment. The numerous educational materials, available currently on market [23] and on the Internet, are very useful in everyday teaching of green chemistry principles, e.g.:

Green Chemistry Resources, ACS homepage:
www.acs.org/education/greenchem
Green Chemistry Institute:
chemistry.org/greenchemistryinstitute
EPA Green Chemistry Program:
www.epa.gov/greenchemistry
Green Chemistry, a journal of the Royal Society of Chemistry:
www.rsc.org/is/journals/current/green/greenpub.htm
Green Chemistry Network:
chemsoc.org/networks/gcn
Chemical Education Foundation:
www.chemed.org
Chemical Industry Education Centre:
www.york.ac.uk/org/ciec

Conclusions

Green chemistry is not a new branch of science. It is a new philosophical approach that through application and extension of the principles of green chemistry can contribute to sustainable development. Presently it is easy to find in the literature many interesting examples of the use of green chemistry rules. They are applied not only in synthesis, processing and using of chemical compounds. Many new analytical methodologies are also described which are realized according to green chemistry rules. They are useful in conducting chemical processes and in evaluation of their effects on the environment. The application of proper sample preparation techniques, (e.g. SPME, SPE, ASE) allows us to obtain precise and accurate results of analysis.

Great efforts are still undertaken to design an ideal process that starts from non-polluting initial materials, leads to no secondary products and requires no solvents to carry out the chemical conversion or to isolate and purify the product. However, more environmentally friendly technologies at the research stage do not guarantee that they will be implemented on an industrial scale. Adoption of environmentally benign methods may be facilitated by higher flexibility in regulations, new programs to facilitate technology transfer among academic institutions, government and industry and tax incentives for implementing cleaner technologies.

Furthermore, the success of green chemistry depends on the training and education of a new generation of chemists. Student at all levels have to be introduced to the philosophy and practice of green chemistry.

Finally, regarding the role of education in green chemistry:

THE BIGGEST CHALLENGE OF GREEN CHEMISTRY IS TO USE ITS RULES IN PRACTICE.

The presented problem is strictly related to the activity of the Centre of Excellence in Environmental Analysis and Monitoring (CEEAM, www.pg.gda.pl/chem/ CEEAM/) sponsored by EU funds in the frame of the 5th Frame Program.

References

1. ANASTAS P. T., WARNER J. C. Green Chemistry: Theory and Practise. Oxford University Press, Oxford **1998**.
2. NAMIEŚNIK J., WARDENCKI W. Solventless sample preparation techniques in environmental analysis. J. High Resol. Chromatogr. **23**, 297, **2000**.
3. SATO K., AOKI M., NOYORI R. A "Green" Route to Adipic Acid: Direct Oxidation of Cyclohexenes with 30 percent hydrogen peroxide. Science. **281**, 1646, **1998**.
4. http:// www.epa.gov/greenchemistry
5. BARDLEY D., DYSON P., WELTON T. Room temperature ionic liquids. Chem. Rev. **9** (5), 18, **2000**.
6. ROMANO U., GARBASSI F. The environmental issue. A challenge for new generation polyolefins. Pure Appl. Chem. 72, 1383, 2000.
7. NICOLAS N., BENVEGNU T., PLUSQUELLEC D. Surfactants from renewable resources. Actualite Chimique **11-12**, 70, **2002**.
8. STASHENKO E. E., PUERTAS A. M., SALGAR W., DELGADO W., MARTINEZ J. R. Solid-phase microextraction with on fibre derivatization applied to the analysis of volatile carbonyl compounds. J. Chromatogr. A. **886**, 175, **2000**.
9. ACARDI A., BIANCHI G., DI GIUSEPPE S., MARINELLI F. Gold catalysis in the reaction of 1,3-dicarbonyls with nucleophiles. Green Chemistry. **5** (1), 64, **2003**.
10. SCOTT G. Green polymers. Polym. Degrad. Stab. **68** (1), 1, **2000**.
11. TUNDO P., SELVA M., MEMOLI S. Dimethylcarbonate as a green reagent. ACS Symp. Ser., **767** (Green Chemical Synthesses and Processes), 87, **2000**.
12. MERRILL M., PARENT K., KIRCHHOFF M. Green Chemistry. Stopping Pollution before it starts. Chem Matters. **April**, 7, **2003**.
13. JESSOP P. G., LEITNER W. Chemical synthesis using supercritical fluids. Wiley-VCH Weinheim, **1999**.
14. SARRADE S., GUIZARD C., RIOS G. M. New applications of supercritical fluids and supercritical fluids processes in separation. Separation and Purification Technology. **32** (1-3), 57, **2003**.
15. BRANNEGAN D. R., ASHRAF-KHORASSANI M., TAYLOR T. L. Supercritical fluid extraction of ethoxyquin from a beef matrix. Chromatographia. **54** (5/6), 399, **2001**.
16. WOLSKI T., LUDWICZUK A. Extraction of natural products with supercritical gases. Przem. Chem. **80**, 286, **2001**.
17. SKOWROŃSKI B., MORDECKA Z. Polish installation for supercritical extraction of hops. Przem. Chem. **80**, 521, **2001**.
18. http://www.micell.com
19. The Presidential Green Chemistry Challenge Awards Program. Summary of 2000 Award Entries and Recipients, www.epa.gov/greenchemistry, August **2001**.

20. U. S. EPA Method 3545
21. WARDENCKI W., NAMIEŚNIK J. Some remarks on gas chromatographic challenges in the context of green analytical chemistry. Pol. J. Envir. Stud., **11**, 185, **2002**.
22. HJERESEN D. L., SCHUTT D. L., BOESE J. M. Green chemistry and education. J. Chem. Educ. **12**, 1543, **2000**.
23. LANCASTER M. Green Chemistry. An Introductory Text. Royal Society of Chemistry, Cambridge, **2002**.