

# Green analytical chemistry—theory and practice

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This *tutorial review* summarises the current state of green analytical chemistry with special emphasis on environmentally friendly sample preparation techniques. Green analytical chemistry is a part of the sustainable development concept; its history and origins are described. Miniaturisation of analytical devices and shortening the time elapsing between performing analysis and obtaining reliable analytical results are important aspects of green analytical chemistry. Solventless extraction techniques, the application of alternative solvents and assisted extractions are considered to be the main approaches complying with green analytical chemistry principles.

## Introduction

“Sustainable development”, like the earlier “protection of the environment” or “ecology”, has become a very popular term. “Protection of the environment” itself, however, is not a discipline with a long tradition. Contemporary environmental awareness probably stems from the famous “U Thant Report”, presented at the 23rd session of the United Nations in 1969. Further tentative references to sustainable development can be found in the proceedings of the Stockholm conference in 1972. A clear formulation of the idea came to light in the 1980s. The works of the United Nations Commission on Environment and Development, established in 1983, should also be mentioned. This commission prepared the “Brundtland Report”, published in “Our Common Future”. It is from this book that the well-known definition of sustainable development comes: a form of development that meets the needs of the present without compromising the ability of future generations to meet their own needs.<sup>1</sup> Sustainable development is thus people-centred: it aims at improving the quality of human

life. So, the starting point is focused on human beings, in contrast to many ethical viewpoints on the environment. This seems correct, since sustainable development demands certain limitations to human activities.<sup>2</sup>

The above definition of sustainable development is also a normative concept: it gives us standards (rules) upon which to base judgments.<sup>2</sup> Sustainable development concerns the common area of three spheres: society, the market and the environment (see Fig. 1).

Among the factors influencing a sustainable state, pride of place must go to manufacturing technologies, which in many cases involve chemical activities at both the industrial and the laboratory scale. The crucial role of chemists is endorsed by data in the OECD report on the rate of chemical production compared to the increase in the global human population (Fig. 2). These data also substantiate the hypothesis about the ongoing chemicalisation of the homosphere.<sup>3</sup>

We are becoming increasingly concerned about the state of the environment. It would, therefore, be appropriate to examine those activities of chemists and chemical engineers that can significantly influence the state of the environment at both the industrial and the laboratory scale.

As a consequence of the ever-increasing quantities of products and consumer goods “needed” in everyday life, the

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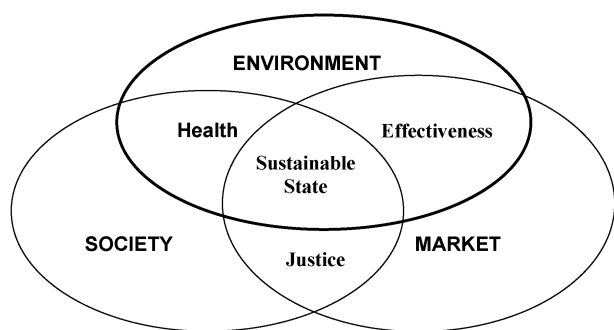
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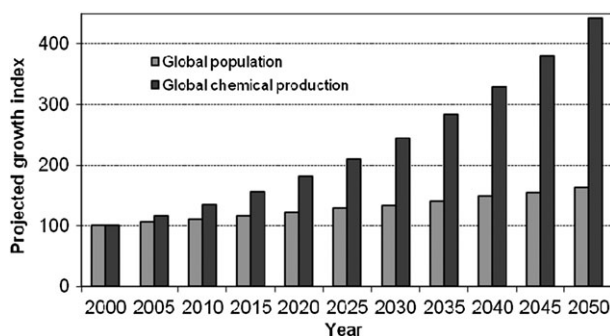


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**Fig. 1** Sustainable development as the common area of three spheres (economy—society—environment).



**Fig. 2** Comparison of predicted changes in global population and production of chemical goods at the global scale. Assumptions: the production of chemical goods increases by 3% annually, the global population increases at a rate of 0.77% per year.

label *Homo technologicus* has frequently been applied to contemporary humankind. This insatiable demand for various products is met by rapid developments in manufacturing technology. These may exploit the environment and its resources very wastefully; alternatively, they may be



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*trace constituents in samples with complex matrix compositions, the design and testing of customised analytical units and measuring devices, and the production of new types of matrix-free reference materials. Author and editor of 8 books, author and co-author of over 300 papers and over 400 reports and communications published in conference proceedings, and 10 patents.*

environmentally friendly, by making use of low waste technologies and closed media cycles, and by recycling wastes and by-products.<sup>4</sup>

The small-scale activities of chemists, such as laboratory experiments, can also have a negative influence on the environment, *e.g.*, through the uncontrolled disposal of chemical wastes and spent reagents.

For all the above reasons the chemical community has been developing different activities over a period of several years; these may be considered on two planes:<sup>5</sup>

- the teaching of basic aspects of environmental science at all levels of education, resulting in the production of specialists capable of handling and solving existing and potential environmental problems, and also in an increase of pro-environmental awareness among the general public;

- a fresh approach to typical chemical activities, leading to the environmentally more friendly use of facilities. In recent times, this approach has been embraced on an ever larger scale, and the term *green chemistry* has been coined to describe it. Indeed, a new scientific journal has adopted “green chemistry” for its name and is gradually becoming a forum for the exchange of views and expertise among a growing number of chemists.

A variety of terms are used to emphasise the possibility of using chemical processes in environmentally friendly ways.

The most common ones are:

- Green Chemistry
- Environmentally Benign Chemistry
- Clean Chemistry
- Atom Economy
- Benign by Design Chemistry
- Ecological Chemistry
- Environmentally Friendly Chemistry
- Sustainable Chemistry
- Ecochemistry

Much information is available on the principles of green chemistry. They were first explicitly stated as “the 12 principles of green chemistry” in 1998 by Anastas and Warner.<sup>6</sup> Another paper (Winterton<sup>7</sup>) describes the principles for implementing “green” chemical syntheses on a technological scale.

The two terms “ecotechnology” and “ecological engineering” are also used in the literature, but often in diametrically opposing contexts.<sup>8</sup> A special topic issue on green-sustainable chemistry was published in 2007 in the IUPAC journal “Pure and Applied Chemistry”.<sup>9</sup> A special issue on this topic also appeared in the “Review Chemistry Journal” in that same year.<sup>10</sup>

## Green analytical chemistry

Environmental demands and ecotoxicological considerations call for action in two principal directions:<sup>11</sup>

- the search for environmentally friendly technologies that are characterised by low, if not zero, emissions of pollutants;
- the trend towards determining a broad spectrum of analytes at low concentrations (ppb or even ppt) in samples with a complex matrix composition.

The second approach has been facilitated by the introduction of a new generation of highly sensitive analytical

devices and methods, and by the development of new sample preparation procedures, that is, sample treatment prior to the final determination stage.

This line of action becomes particularly significant in modern environmental analysis, but these new detectors are insufficiently sensitive to determine the majority of analytes in environmental samples.<sup>12</sup> For this reason, it has become a matter of urgency to optimise the stages and operations associated with sample preparation.

In this respect, sample preparation involves:

- isolating the analytes from the original matrix and moving them to a recipient (secondary) matrix of simpler composition (analyte enrichment is optional);
- releasing analytes, previously kept in a suitable trap, at the isolation and/or enrichment stage;
- removing excess solvent, and drying, purifying and fractionating the extracts.

These steps are usually followed by chromatographic techniques, which are routinely used to separate mixtures into individual chemical species prior to the final determination. The operations involved in sample preparation are usually tedious and time-consuming and are difficult to automate.

Of special significance to environmental analysis are sample preparation methods in which liquid solvents are used in reduced amounts or even completely eliminated from the analytical procedure.<sup>13</sup> Furthermore, the number of operations and processes involved in the sample preparation stage should be kept to a minimum.

The isolation and/or preconcentration of analytes from samples with a complex matrix composition is a very important stage in trace and environmental analytical procedures.

The work of analytical laboratories is closely scrutinised to minimise their negative impact on both the abiotic environment and humans. We can talk about “green analytical chemistry”.<sup>14</sup> This is intended to develop tools for comparing the environmental impacts of different analytical activities. Life cycle assessment is one such tool: it can be applied not only to industrial goods but also to a comparative assessment of the environmental nuisance caused by individual chemicals, operations, analytical techniques and entire analytical

procedures.<sup>15</sup> Parameters like the EHS (Environmental—Health—Safety) Indicator and CED (Cumulative Energy Demand) may be applied during such an assessment.

Fig. 3 illustrates schematically the differences between the terms frequently used to describe analytical activities. It is important to realise that these terms are not synonymous.

Analytical chemistry and monitoring play important roles in assessing the influence of chemists on the environment.<sup>16</sup> There are already a vast number of analytical methods and techniques, and the number of determinations is increasing very rapidly. By way of illustration, we may cite the more than 3500 analytical procedures approved by the US Environmental Protection Agency for the determination of more than 4000 analytes in samples of different types of water, *i.e.*, surface water, drinking water and wastewater; and water is just one of the four “elements” of the environment. Now, since analytical activities can be carried out in environmentally friendly or unfriendly ways, the development of green chemistry as a whole will be at risk without the coexistence of green analytical chemistry, alternatively referred to by the terms “clean analytical chemistry” and “conscientious analytical methods”.<sup>17</sup>

There are a number of literature reviews<sup>7,11,18–24</sup> discussing different aspects of introducing the sustainable development concept to analytical chemistry laboratories.

The aforementioned 12 principles of green chemistry may be invoked to formulate the main features of green analytical chemistry. The following should be treated as top priorities:

- the elimination (or at least, the significant reduction) of reagents, particularly organic solvents, from analytical procedures;
- reduced emissions of vapours and gases, as well as liquid and solid wastes generated in analytical laboratories;
- the elimination of highly toxic and/or eco-toxic reagents from analytical procedures (*e.g.*, the substitution of benzene with other solvents);
- reduced labour and energy consumption of analytical procedures (per single analyte).

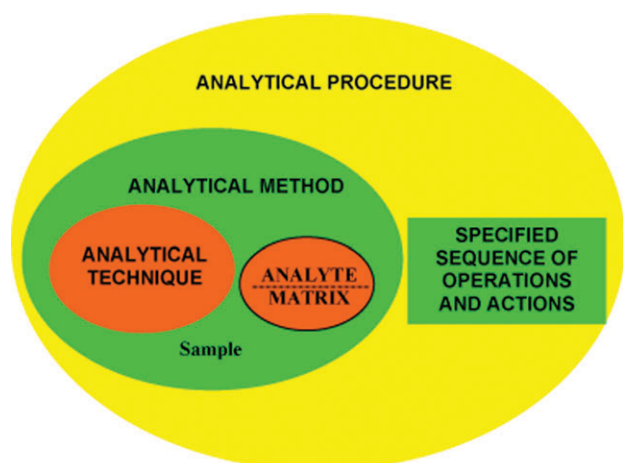
A further important parameter, characterising the analytical methods applied to obtain reliable information about the chemical composition of material objects and the processes taking place in them, is the time elapsing between the collection of a representative sample and the desired information becoming available. There are four ways of locating analytical devices with respect to the material object to be examined and the time elapsing between successive analytical measurements (see Fig. 4).

## Challenges in green analytical chemistry

The challenges to the introduction of sustainable development principles to analytical laboratories are shown in Fig. 5.

## Green sample preparation techniques

The literature data and observation of current trends in analysis and monitoring indicate that progress has been particularly rapid in the development of precisely those methods and techniques ensuring compliance with green analytical chemistry principles; solvent-free sample preparation techniques are of special value.



**Fig. 3** Schematic presentation of the dependencies among the terms often used to describe the analytical process.

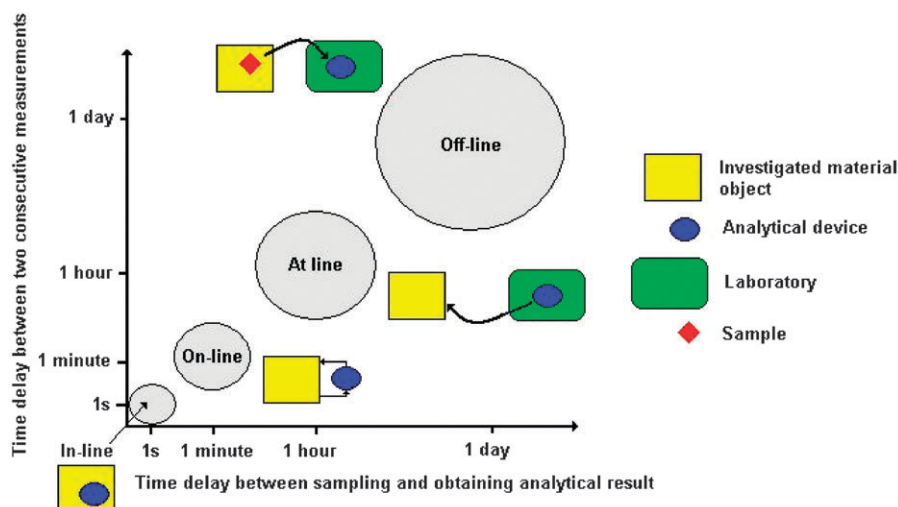


Fig. 4 The effect of locating an analytical device with respect to the object on the time delay in obtaining analytical information.

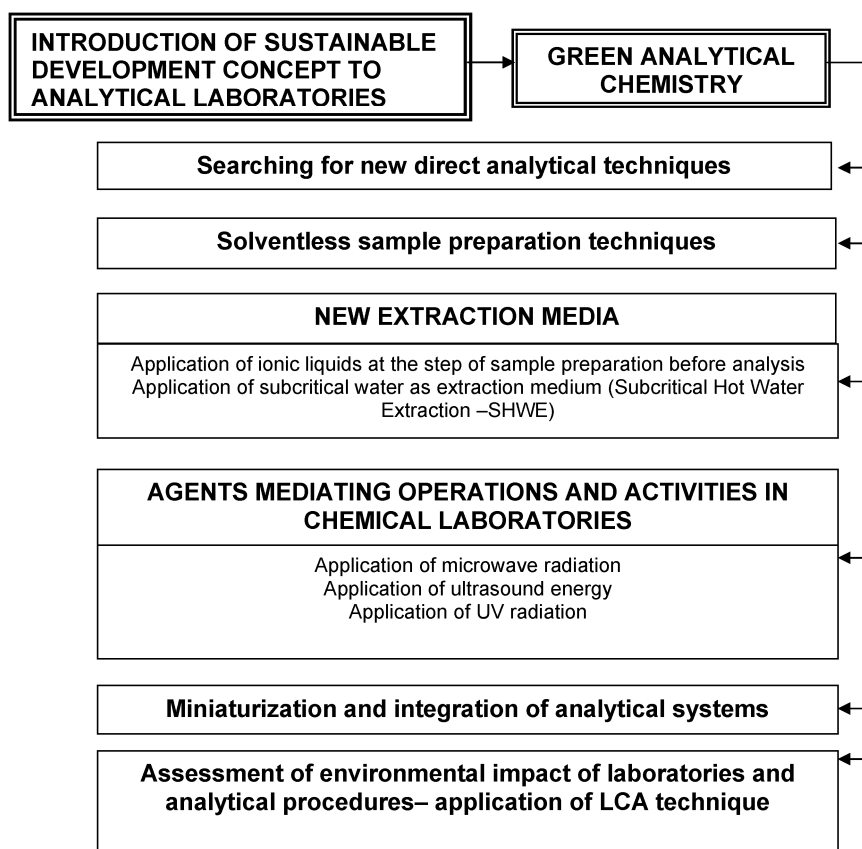


Fig. 5 Methodological challenges connected with the introduction of sustainable development principles to analytical chemistry laboratories.

Solid phase extraction (SPE) is a routine technique in sample preparation.<sup>25</sup> Table 1 classifies the different methodological versions of SPE. Some of them should be treated as examples of the solventless approach to sample preparation.

### Membrane extraction

The use of different membrane materials in various configurations for the extraction of a broad range of analytes from gaseous

and aqueous matrices has become popular in recent years. However, the low polarity of the membrane limits the number of target compounds and renders the technique unsuitable for the analysis of polar components.<sup>26</sup> Although synthetic membranes may be made of very different chemical compounds and may display different properties, they can be classified as microporous membranes, homogeneous membranes (also known as dense membranes) made from metal, glass, polymer or liquid, ion-exchange membranes, and asymmetrical membranes.



**Table 1** Classification of solid phase extraction (SPE) techniques

No.	Classification parameter	Additional information
1.	The origin of the sorbent	<ul style="list-style-type: none"> <li>• Natural</li> <li>- Activated carbon</li> <li>• Synthetic</li> <li>- Porous polymers</li> </ul>
2.	The nature of the sorptive material	<ul style="list-style-type: none"> <li>• Inorganic sorbents</li> <li>- Silica gel</li> <li>- Aluminium oxide</li> <li>- Florisil</li> <li>• Organic sorbents</li> <li>- Polyurethane foams (PUF)</li> <li>- Porapacks (P, R, S, Q)</li> <li>- Chromosorbs (101–108)</li> <li>- Tenax-TA</li> <li>- Tenax-GC</li> </ul>
3.	Surface development	<ul style="list-style-type: none"> <li>• Nonporous sorbents</li> <li>• Porous sorbents</li> </ul>
4.	Pore diameter	<ul style="list-style-type: none"> <li>• Narrow pores</li> <li>• Wide pores</li> </ul>
5.	Sorbent grain size	<ul style="list-style-type: none"> <li>• Macrograins</li> <li>• Micrograins</li> <li>• Nanograins</li> </ul>
6.	Mode of extraction	<ul style="list-style-type: none"> <li>• Dynamic</li> <li>• Passive (passive dosimeters)</li> <li>• Denudation</li> </ul>
7.	Geometric form of sorption bed	<ul style="list-style-type: none"> <li>• Tube filled with sorption material bed</li> <li>• Extraction discs</li> <li>• Denudation trap</li> <li>• Extraction fibres (SPME)</li> <li>• Stir-bar sorptive extraction (SBSE)</li> <li>• Sorbent added to medium (dispersive extraction)</li> </ul>
8.	Connection of sorption system with measuring device	<ul style="list-style-type: none"> <li>• Off-line</li> </ul>
9.	Volume of medium passing through sorbent	<ul style="list-style-type: none"> <li>• On-line</li> <li>• High-volume samplers (HVS)</li> </ul>
10.	Release of sorbed analytes	<ul style="list-style-type: none"> <li>• Low-volume samplers (LVS)</li> <li>• Elution with organic solvent</li> <li>• Thermal desorption</li> <li>• Elution with supercritical fluid</li> </ul>
11.	Application of extraction in analytical procedures	<ul style="list-style-type: none"> <li>• Sample collection from medium</li> <li>• Purification of extracts</li> <li>• Purification of laboratory media (water, gases)</li> </ul>
12.	Physical phenomena invoked at the analyte trapping stage	<ul style="list-style-type: none"> <li>• Adsorption</li> <li>• Interphase partition</li> <li>• Exclusion</li> <li>• Immunoaffinity</li> </ul>

Semi-permeable porous and non-porous membranes are used to separate the components of gaseous and liquid mixtures. These latter membranes were developed jointly by chemical engineers, materials scientists and polymer technologists. They do not have “pores” in the conventional sense; their selectivity is based on differences in the solubility and diffusion properties of the various components in a mixture. Separation is based on the different permeation of analytes through, *e.g.*, a polymer or liquid membrane material. This process can be divided into three stages: adsorption of molecules on the outer surface of the membrane; dissolution of the adsorbed molecules and diffusion through the membrane

material; desorption or evaporation of the molecules on the other side of the membrane to the receiving medium (carrier gas, absorbing solution, solid sorbent).

In membrane-based processes, separation is the result of differences in the transport rates of chemical species across the interface. Transport through membranes is a non-equilibrium process in which flow can be related to the force that generated it. These forces are due mainly to:<sup>26</sup>

- Differences in concentration. The International Union of Pure and Applied Chemistry (IUPAC) recommends the term “dialysis” for all processes caused by these forces. The separated species may be gases or liquids.

- Differences in pressure. The three separation processes through membranes in which transport is induced by the application of pressure are microfiltration, ultrafiltration, and reverse osmosis or hyperfiltration. They differ in the size of solutes retained by the membrane:

- between 0.1 and 1 nm in reverse osmosis
- between 1 and 10<sup>4</sup> nm in ultrafiltration
- between 10<sup>4</sup> and 10<sup>6</sup> nm in microfiltration

- Differences in electrical potential. There are two processes based on the application of differences in electrical potential:

- electrodialysis. The system comprises a series of anionic and cationic exchange membranes arranged alternately between an anode and cathode. Electrodialysis can be used with both neutral and charged membranes;

- Donnan dialysis. This employs a charged membrane, but no external potential difference is applied. One of the two solutions separated at the membrane has a lower concentration of all species than the other one, giving rise to a flow of one of the species (whose charge allows it to pass through the membrane). In this way a difference in potential is generated that must be compensated by the passage of ions from the zone of lower concentration to that of higher concentration (against the gradient).

Overall, permeation is a function of the dissolution of the analyte in the membrane material, which means that the partition coefficient of a given analyte between the donor phase (sample matrix) and the membrane is a significant parameter limiting the mass transportation rate. Therefore, non-porous membranes are relatively non-selective. In contrast, porous membranes are considered to be selective, the diameter of membrane pores being crucial for ensuring selective transport of analytes. However, not only diffusion itself but also dissolution in the membrane material plays a role in analyte transportation.

Suitable membrane devices can be utilised directly, through the contact of a gaseous or liquid sample with an appropriate polymer (silicone rubber or Teflon) membrane, while the other side of the membrane is flushed with a stream of suitable gas. The gas mixture produced in this way is directed straight to the measuring instrument. Solid or liquid samples can be analysed indirectly when the gaseous phase above the sample is in contact with the membrane. Membrane extraction can be carried out using suitable tubes (hollow fibre membranes) or flat film membranes made of a semi-permeable material.<sup>27</sup> The first attempts to adopt this approach date back to the 1980s. A nitrogen stream is used as carrier gas for removing the analytes from the outer surface of a flat membrane in contact

with a liquid sample. The analytes are subsequently collected on a sorbent bed and upon desorption are finally determined.

Membrane techniques may be applied to the extraction of volatile analytes into a carrier gas stream from a sample of a particular volume in a container (static technique), and from the sample stream (dynamic technique).<sup>28</sup>

An extraction membrane can also serve as an inlet device. The classic example is a mass spectrometer equipped with a sampling interface in the form of a semi-permeable membrane. In this case, introduction of volatile organic analytes to the mass spectrometer occurs through a polymer membrane (usually a silicone membrane), which is highly permeable to lipophilic organic compounds but is impermeable to water and hydrophilic, polar and/or high-molecular weight compounds. A membrane serving as an interface may be either flat or tubular.

## Assisted analyte extraction

### Microwave radiation

This may be used for accelerating sample heating, sample drying, determining water content (microwave *moisture balance*), fixing biological material samples, sample ashing and melting, exciting analytes in plasma (*MIP*), increasing the rates of chemical reactions, evaporating aqueous solutions, thermally stabilising wastes, heating chromatographic columns (in *GC*) and extracting analytes (Microwave Assisted Extraction—*MAE*). The almost routine utilisation of microwave radiation in chemical laboratories has spawned the term Microwave Enhanced Chemistry (*MEC*).

### Ultrasound

According to the literature, ultrasound is used in the following processes: sample mineralisation, sample dissolution, homogenisation, emulsion formation, filtration, chemical reactions (derivatisation), reagent generation, glassware cleaning, sample degassing, filtration, and analyte extraction (Ultrasound Extraction – *USE*).

### Alternative media in laboratory practice

Table 2 provides information on “green” media applicable in analytical laboratories for different purposes.

### Supercritical fluids

Of the many potential supercritical fluids, supercritical carbon dioxide (*scCO*<sub>2</sub>) and supercritical water (*scH*<sub>2</sub>*O*) are the ones

**Table 2** “Green” media used in analytical laboratories

Medium	Area of utilisation
Supercritical fluid	Extraction agent Mobile phase in chromatography
Ionic liquid	Extraction agent Reaction medium
Superheated water (water in a subcritical state)	Extraction agent
Inert gas	Extraction agent Mobile phase in gas chromatography

most likely to fulfil the requirements of green chemistry, particularly the former. It is non-flammable, readily accessible (from renewable feedstock or the power industry) and very cheap. Its critical parameters ( $T_k = 31.1\text{ }^\circ\text{C}$ ;  $P_k = 7.38\text{ MPa}$ ) are easily achievable, and because *CO*<sub>2</sub> has a low heat of evaporation, its utilisation leads to energy savings. *ScCO*<sub>2</sub> can dissolve both nonpolar compounds and some polar ones (e.g. methanol, acetone) at efficiencies comparable with those of halogenated solvents.<sup>29</sup>

Supercritical water, also used as a solvent, is non-flammable, widely accessible and cheap. It has low viscosity and diffusivity, and can dissolve many polar compounds.

Despite their many advantages, methods utilising supercritical fluids are rarely used because they are technically complex: the extraction parameters have to be controlled with precision as the solubility of compounds in a supercritical fluid is very sensitive to changes of pressure and temperature.<sup>30</sup>

### Ionic liquids

The search for new, environmentally friendly reaction media has drawn attention to ionic liquids (ILs), which have very interesting and promising parameters.<sup>31</sup> Ionic liquids are not new to science: the first one—ethylammonium nitrate (*EAN*) (m.p.  $14\text{ }^\circ\text{C}$ )—was synthesised by P. Walden. An interesting feature of ionic liquids is that properties like melting point or miscibility with organic solvents or water can be designed to meet chemists’ needs.<sup>32</sup> ILs have other advantages, for example:

- small amounts of wastes are generated (in production and use),
- they can be re-used many times,
- high reaction efficiency and selectivity at room temperature,
- they can dissolve catalysts (particularly metal complexes),
- they can dissolve both inorganic compounds (including some minerals and carbon) and organics (from simple solvents to polymers, wood and cellulose),
- thermal stability (their decomposition temperature is often  $200\text{--}250\text{ }^\circ\text{C}$ ),
- most are non-flammable and have a negligible vapour pressure.

The properties of ILs make them interesting compounds for many different applications: organic synthesis, catalysis, biocatalysis, enzyme reactions, solvent extraction, electrochemistry, electrolytes in batteries, electrolytes for dye-synthesised solar cells, elements of polymer gel electrolytes, in metal deposition, surfactant aggregate formation, high surface tension materials and tissue preservation. They are also used as the stationary phase in gas chromatography. The range, quality and rapidly increasing number of publications in the past few decades are evidence enough that significant efforts are being made to utilise ILs in green chemistry.<sup>33</sup>

Ionic liquids are not ideal, however. Their biggest disadvantage at present is that they are produced only in small quantities, so they are expensive. In addition, ILs constitute a potential threat to the aquatic environment (the imidazolium cation has toxicological properties similar to those of dichloromethane or toluene). This threat stems from its low biodegradability, as well as the formation of new, even more toxic, ionic pairs with other organic ions present in the aquatic environment or the

soil. Moreover, combustion of ILs produces toxic gases like  $F_2$  or HF, which pollute the environment when released into it. Obtaining high purity ionic liquids is also problematic because of the presence of salts, colour or odour.<sup>34</sup>

## Miniaturisation of analytical devices

The search for faster and cheaper alternatives to laboratory-based analysis has been intensive, and throughout the 1980s chemical sensors were seen by many as the way forward.<sup>35</sup> This approach is attractive because measurements can be made quickly and easily. Though designed to measure a specific analyte, sensors often do not handle interferents well and get contaminated quickly, so the potential originally envisaged for them has not been realised.

In recent years, researchers have looked for solutions with the advantages of sensors but also the versatility and reliability of conventional instruments. At present, the most promising technology for achieving this involves carrying out chemical analysis on a very small scale by shrinking the standard laboratory techniques to fit onto a “chemical chip”. This process of miniaturisation has transformed electronics and computing, and many see the potential for similar advances in chemical analysis. Miniaturisation is set to produce a generation of analytical instruments that will be cheaper, faster and more flexible, but no less efficient than the ones in use today.

The lab-on-a-chip concept is not new: the idea of making miniature separation columns goes back to the late 1970s when S. Terry and co-workers at Stanford University demonstrated a working GC on a silicon wafer.<sup>36</sup> This pioneering device included a column, injector and valves and was capable of separating a mixture of organics within ten seconds. Although the device’s resolution was relatively poor, the potential for improvement was obvious, and this paper became a landmark in the lab-on-a-chip world. Nowadays, GC-MS systems (*e.g.*, analyser, ion traps, cylindrical ion traps, quadrupole mass separators or time-of-flight (TOF) mass spectrometers) have been miniaturised. The wafer-based design enables large-scale production: all parts are fabricated in a single piece of silicon, eliminating the need to align the units to each other. The vacuum requirements are significantly relaxed and carrier gas consumption is reduced because of the small size of the unit.<sup>37,38</sup>

Even so, it was another decade before serious interest in microfabricated separation systems was revived, when A. Manz and co-workers at the Ciba-Geigy laboratories (Switzerland) proposed the “miniaturised total analysis system” or  $\mu$ TAS as an alternative to chemical sensors for continuous monitoring.<sup>39</sup> To demonstrate how such systems could be built, Manz’s group made capillary electrophoresis channels on glass chips and showed that separation of two fluorescent dyes could be achieved more quickly than was possible using a standard system.<sup>40</sup>

Capillary electrophoresis is particularly suitable for microfabrication because no valves or pumps are needed to propel the sample through the column. With chromatography, on the other hand, the need for pumps and valves remains and this presents significant technical challenges.<sup>41</sup> Although microfabricated pumps are available, it is difficult to design

one capable of generating the pressure needed to force a liquid through a very small channel. Producing a workable chromatograph on a chip will also require solutions to such problems as making reproducible and stable stationary phases for packed and open tubular columns, creating the pressure needed to pump fluids through the column at a constant flow rate, accurately and reproducibly injecting sub-nanolitre volumes, creating detection systems able to measure the very small quantities of analytes, and minimising dead volumes. Work on miniaturised chromatography is still in progress.<sup>42</sup>

The idea of the “electronic tongue” project is based on the development of new types of poorly selective chemical sensors displaying cross-sensitivity to multiple components in liquids, and their application in an array.<sup>43</sup> The “electronic tongue” can be defined as an analytical instrument that includes an array of non-selective chemical sensors with partial specificity towards different solution components and an appropriate pattern recognition instrument capable of quantitative and qualitative analysis.<sup>44</sup>

In a recent development, separation techniques have been successfully integrated into the concept of the total chemical analysis system—TAS.<sup>45</sup> The combination of all sample handling and measurement steps into a single package incorporating a high level of automation makes the TAS an ideal approach for the continuous monitoring of different types of analytes. TAS periodically transforms chemical information into electronic information.<sup>46</sup> Sampling, sample transport, any necessary chemical reactions, separations and detection are all performed automatically. Much of the sample pretreatment serves to eliminate most interferents, so the detector or sensor in a TAS does not need to be highly selective.

The concept of miniaturised total chemical analysis system extends this approach.<sup>47</sup> A miniaturised TAS would be of benefit since it could consist of several system elements, each designed to protect the subsequent element of the downstream system from components of the sample matrix. Compared with utilising a sensor alone, the use of such a TAS system should result in increased durability. At the same time, the performance required of any single component of the system could be less than that required of a sensor alone. Equally intriguing, perhaps, is the fact that to the user, the system would seem very much like a stand-alone sensor, but its performance would be under the user’s dynamic control. This would considerably improve the flexibility of a  $\mu$ -TAS device, resulting in superior performance for chemical analysis compared to the stand-alone sensor approach. While such devices may not always be able to compete with benchtop-scale laboratory equipment in terms of sensitivity and selectivity, integrated systems may prove superior in terms of speed of analysis and production costs.

Complete miniature modules aim to achieve:

- total system size of the same order of magnitude as the transducer;
- true on-chip referencing and multicomponent sensing by single-chip sensing-pad arrays;
- low system complexity;
- minimal costs of (mass) production;
- ruggedness as a result of the built-in-alignment of sensor parts;

**Table 3** Main trends in miniaturisation of analytical systems

Approach	Examples
New types of sensors and biosensors	Supramolecular sensors
Systems of sensors	Electronic nose Electronic tongue
Microsystems	$\mu$ -Total analysis Systems ( $\mu$ -TAS) Lab-on-a-chip

- standardised waveguides, sensing pads and schemes suitable for a wide variety of applications.

The development of the “electronic nose” and the “electronic tongue” was prompted by the desire to model, substitute and enhance human olfactory and tasting abilities. The design of these devices is based on the biological principles of organising sensor systems—arrays of non-specific chemical sensors with subsequent image recognition by a neural network. Many modern achievements in neural computing are widely applied in sensor science for the “electronic nose” and “electronic tongue” systems. Such systems can therefore be considered a specific branch of the development of artificial intelligence and/or a field in the application of the “electronic brain”.

The history of the “electronic nose” as an intelligent multisensor started in 1982, the term itself becoming widely accepted around 1990. Such “noses” usually provide a quantitative recognition of gas mixtures. Table 3 lists the main trends in the miniaturisation of analytical systems.<sup>48</sup>

### Spot tests

In environmental and medical analysis (*e.g.*, in a hospital) there is a great demand for fast methods of obtaining analytical information on material objects. Such information is one of the crucial elements upon which decisions are based.<sup>36</sup> Therefore, quick tests should be easy and simple to use, easily available, of low unit cost, usable in self-measurement mode (by patients), possibly for different objects (drinking water, vegetables, fruit).

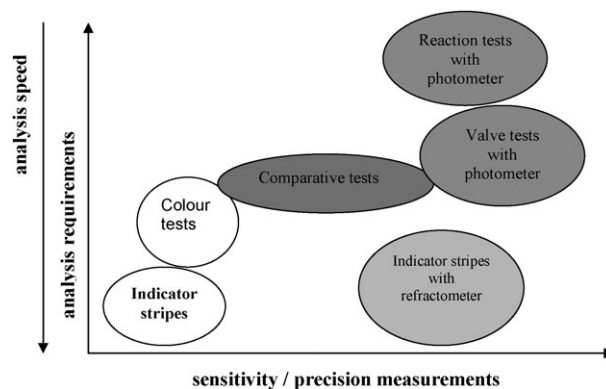
There is still a lot of ambiguity in the nomenclature relating to quick tests; different terms are used to denote the same things, which can be a source of error or misunderstanding.

The terms “quick test” and “rapid test” usually refer to types of tests with the following features in common:

- rapid measurement of a target parameter (concentration of analyte, pH, *etc.*);
- kits containing a complete set of reagents, vessels, and possibly other equipment necessary for carrying out the analysis;
- the analysis can be performed in the field.

Based on their principle of operation, there are three types of tests commonly applied in laboratory practice:<sup>36</sup>

- *dry tests*. This test is based on an adsorptive material saturated with a reagent mixture, which ensures the conditions necessary for detecting and determining a target compound or ion. This field testing material, as it is known, can be fixed to a supporting material, usually made from some white plastic (PS, PUC, polyester), to produce a test strip. The dry test can be in a form appropriate to an automatic reflectance reading unit, *i.e.*, in the form of a slide in Kodak tests. The same tests can



**Fig. 6** The characteristics of test kits, the speed of analysis, complexity and sensitivity of equipment.

take the form of plates where the test field is shielded by a plastic cover or the tubes are packed with a support-coated reagent.

- *semi-dry tests*. A semi-dry test is a test to which at least one liquid reagent is added. Such a design is most often dictated by chemical reasons, though it happens that technological requirements are the cause.

- *wet tests*.

Test methods have been developed for many analytes: metal ions, anions, dissolved oxygen and chlorine, hydrogen peroxide, ammonia, pesticides, nitrite, nitrate, petroleum products (*e.g.*, in water), sulfur dioxide, hydrogen sulfide, ozone and many other gases (*e.g.*, in air).<sup>36</sup> Fig. 6 characterises those test kits important from the green analytical chemistry point of view.

### Passive devices

The use of passive samplers (dosimeters) is a modern approach to the analysis of atmospheric, indoor and workplace air pollution. Simple in design and use, and relatively cheap, they do not require any power supply and facilitate the simultaneous detection of vapours of many compounds.<sup>48</sup>

Passive samplers are also often known as diffusive samplers: they are capable of collecting samples of gas or vapour pollutants from the atmosphere at rates controlled by physical processes like diffusion through a static air layer or permeation through a membrane, but which do not involve the active movement of air through the sampler. Compared with conventional pump samplers, passive samplers have the advantages of not needing power sources or bulky and expensive pumps, being more acceptable for wearing as personal dosimeters, and simplicity of operation.<sup>36</sup>

Passive samplers, therefore, offer the most attractive alternative to active sampling techniques<sup>49</sup> and are routinely used to measure time-weighted average (TWA) exposure to airborne pollutants. Moreover, their use to control workplace airborne health hazards can substantially reduce the cost of analyses. Modern passive devices are similar in size, weight and convenience to the well-known radiation dosimeters. They are especially important to health professionals like surgeons, dentists, nurses and veterinarians, who use them for determining exposure to waste anaesthetics. Personal charcoal tube (CT) samplers, active devices that run on battery-powered



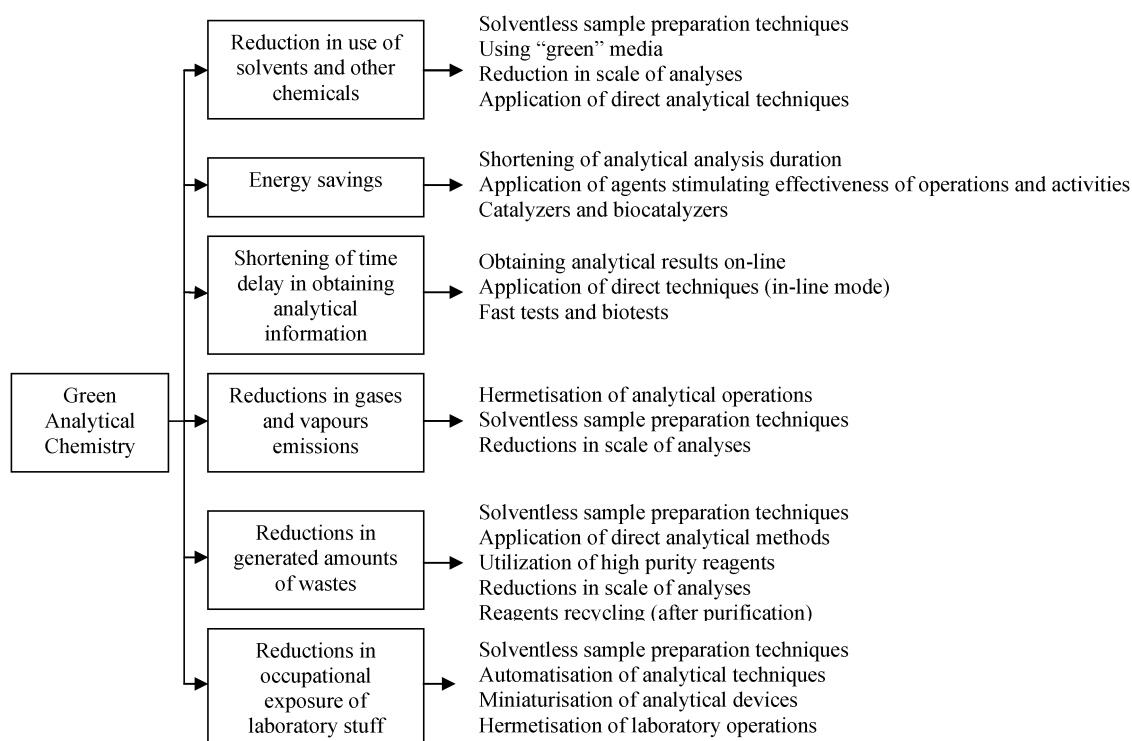


Fig. 7 Methodological approaches in "green" chemistry with special emphasis on the sample preparation step.

pumps, require specially trained personnel in order to obtain valid results and do not fulfil the mobility and sterility requirements of operating rooms. Their main disadvantages are their relatively high unit cost, the need to periodically replace or repair the pumps (which usually have a relatively short service period/lifetime), a sampling time limited by battery lifetime, workers' reluctance to wear the heavy active units during the working day, and the noise generated by the pump.

The practical applications of passive samplers are continually expanding. During the last ten years new types of passive dosimeter have been designed to sample different types of contaminants from water.

## Conclusions

From the above considerations we may conclude that the environmental impact of analytical methodologies and the individual exposure of laboratory staff can be reduced. Fig. 7 summarises the approaches demonstrating the "green" character of particular analytical methods.

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