

From the 'Colourless' to the 'Green' Analytical Chemistry

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In the early 1990's, there was a widespread movement within the chemistry community, with special consciousness on the impact that chemistry was having in both human health and environment. Since then, the chemistry community has focused its efforts in developing less hazardous processes for human health and the environment. This way of doing chemistry was named as 'Green Chemistry'. According to Anastas' definition, "Green Chemistry is the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feedstocks, products, byproducts, solvents, reagents, etc. that are hazardous to human health or the environment". Analytical Chemistry is one of the branches of chemistry where major efforts are being made to follow the rules of Green Chemistry. These efforts focus on the development and validation of new analytical methods that reduce or eliminate the use and release of hazardous substances in all the steps of the analytical process. This goal may be achieved either by developing new analytical methods as a whole, or by adapting well established analytical methods that are not environmentally-friendly and making them greener. This movement in the Analytical Chemistry, where the operator's safety and environmental consciousness are considered as important as the analytical performance is now known as 'Green Analytical Chemistry'. Different approaches can be followed in order to "do" Green Analytical Chemistry and they can be grouped within three main topics: the use of chemicals (including solvents); the generation of wastes; and the consumption of energy.

Regarding the use of chemicals, it should be emphasized that an ideal situation might be that in which no reagent/solvents are used during any of the steps of the analytical procedure. In this sense, some strategies can be followed, such as 1) *in situ* measurements and/or direct analysis, e.g., by using X-ray fluorescence spectrometry (XRF), Near Infrared Spectrometry (NIR), and laser spectrometry. However, the reality is quite the opposite of this utopian situation. Therefore, low-toxicity chemicals should be used instead of more hazardous ones, and in any case, they should be used by employing the minimum quantity needed. Thus, in this sense it is recommendable to use: 2) environmentally friendly chemicals, e.g., by replacing hazardous organic solvents involved in sample solution by more innocuous ones (halogenated solvents could be replaced by nonhalogenated ones, even ionic liquids; methanol, which is widely used in chromatography could be replaced by ethanol); 3) alternative extraction techniques to the classical liquid-liquid Extraction (LLE) or Solid-Phase Extraction (SPE), with low-consumption solvent or solvent-less techniques, such as Supercritical Fluid Extraction (SFE), Pressurized Fluid Extraction (PFE), among others, or even Solid-Phase Microextraction (SPME) and Liquid-Phase Microextraction (LPME); 4) automation, which also contributes to reduction of the amounts of chemicals, e.g., Flow Injection Analysis (FIA), especially with the merging zones approach, Sequential Injection Analysis (SIA), and multicommutation-based flow systems do reduce the amounts of consumed reagents even more. Moreover, if reagents are immobilized in an inert support and packed into a solid-phase reactor, the consumed amount is even more reduced; and finally; 5) reduction of the working scale would also reduce the amounts of chemicals to be used e.g., LPME constitutes a miniaturization of conventional LLE, where the amounts of organic solvents have been reduced from several mL to few μ L; also the use

of miniaturized systems, especially the so-called micro-total analysis systems; (TAS), where reagents are consumed in the nL range.

The generation of wastes is closely related to the chemicals used in the analytical procedure. Thus, all the previous discussion about the use of chemicals should be extrapolated to the generation of wastes. In general terms, a lower use of chemicals results in a lower generation of wastes. In this sense, miniaturization should reduce considerably the amounts of generated wastes. Typical examples are the above-mentioned miniaturization of LLE by LPME; or capillary Liquid Chromatography (LC) working with flow-rates of the order of nL/min; L/min instead of conventional LC working with mL/min flow rates. On the other hand, recycling and reusing the generated organic wastes could be a good approach by means of distillation of the bulk organic waste obtained by LC or LLE procedures. Another strategy, proposed by some authors, is the on-line waste treatment, by means of flow manifolds. The general strategy is to introduce an additional step after the measurement step in order to destroy the toxic species in the effluent. This additional step can be achieved by chemical, photochemical, thermal or microbiological degradation of the organic species. However, metal ions are nondegradable, and the strategy could consist in chemical or physical adsorption, precipitation or co-precipitation.

Regarding energy consumption, it should be said that an excess of consumption could cause both environmental and economical impacts. In this sense, Green Analytical Chemistry demands low energy-consumption analytical methods. Thus, if direct analysis can be carried out, this would avoid energy consumption in sample pretreatment and/or preparation. If not, some strategies could be followed in order to achieve this goal. For example, pressurized fluid extraction uses temperatures around 100°C or more for short periods of time (around 10 min) whereas conventional leaching of analytes with organic solvents by means of a hotplate or Soxhlet extraction might use less temperature but larger periods of time (even hours), resulting in an increase of the energy consumed. Supercritical fluid extraction, and microwave and ultrasounds assisted extraction could also reduce the time (and energy) of an extraction process. On the other hand, during the measurement step, the consumption of energy is an important issue, since an instrumental analytical technique, which needs electrical energy at least, is usually employed. Thus, low-consumption analytical techniques are preferred. Thus, fast chromatography, either liquid or gas chromatography, which boasts of less run time analysis,

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and thus less energy-consumption, is an alternative to conventional chromatography. On the other hand, the high throughput achieved by using FIA methodologies also results in saving energy, since the acquisition instrument, as simple as a spectrophotometer, is operated a shorter time. Nevertheless, it should be mentioned that the use of miniaturized systems like; TAS reduces even more the consumption of energy, compared with conventional flow methodologies.

Once at this point, it should be strongly emphasized that most of the published 'green' analytical methodologies just fulfill partly on these three topics, and strictly speaking, a real green analytical method should satisfy these three topics as a whole rather than individually. This

means, no use of chemicals, or at least use of innocuous chemicals, or use of very little amounts of hazardous chemicals (when no substitution can be achieved), no generation of toxic wastes or generation of the minimum as possible, and finally no high energy-consumption. Nevertheless, some methodologies clearly closer to this ideal situation can be found. A detailed discussion of these articles can be found in some interesting specialized reviews and books dealing with Green Analytical Chemistry, to which more interested readers are referred.

Finally, I would not like to finish this Editorial without encouraging analytical chemists to concise on the need to contribute to Green Analytical Chemistry and thus to make efforts in this line.