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The role of green extraction techniques in Green Analytical Chemistry

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ABSTRACT

Greening extraction techniques to improve the sensitivity and the selectivity of analytical methods is the sustainable alternative to classical sample-preparation procedures used in the past. In this update, we review the main strategies employed in the scientific literature to reduce deleterious side-effects of extraction techniques. We demonstrate that the evolution of sample-treatment procedures is focused on the simultaneous improvement of the main analytical features of the method and its practical aspects, including the economic case.

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1. The green wave

In a changing world, with the tremendous impact of human presence, the urgent need for sustainability of all of our activities has accelerated the evolution from the chemurgical paradigm to the ecological paradigm in which the environmental side effects of our chemical activities must be seriously taken into consideration [1]. Green Chemistry [2–4] and Green Analytical Chemistry (GAC) [5–9] evolved from the academic sphere to the real world, so there is a tremendous research activity on greening all aspects concerning the analysis of any kinds of sample, not only those for environmental studies. We are absolutely convinced that GAC will be really useful in the years ahead. The application of cheap, fast and environmentally safe procedures in environmental, clinical and food analysis will improve the quality of life in developing countries [10]. So, it can be seen that GAC has been the key tool to move from the chemurgical paradigm to the ecological paradigm in analytical chemistry and to create sustainable tools for challenges in the increasing demand in analysis for a clever combination of environment-friendly and cheap methodologies (see Fig. 1).

Based on the 12 principles of GAC [11], many green methods were proposed in recent years, and scientific journals have published special issues regarding GAC practice in research and applied laboratories, as can be observed in Table 1, so creating a wave that modified the concepts and the practice of analysis.

In summary, GAC has been well accepted by the scientific community. However, the change from qualitative to quantitative observation of the green character of analytical methodologies has evolved much more slowly than the scientific production in the field. In this sense, Life Cycle Assessment (LCA), a holistic tool encompassing all environmental exchanges (i.e., resources, energy, emissions, and waste) occurring during all stages of the life cycle of activities, is a useful tool, especially when applied to products or services for which the life-cycle concept and its stages are clearly defined [12]. An additional semi-quantitative criterion was developed by the Green Chemistry Institute (GCI) of the American Chemical Society (ACS). The criterion was applied to the National Environmental Methods Index (NEMI), a free Internet-searchable database of environmental methods [13]. The profile criterion was based on four key terms concerning reagents employed as:

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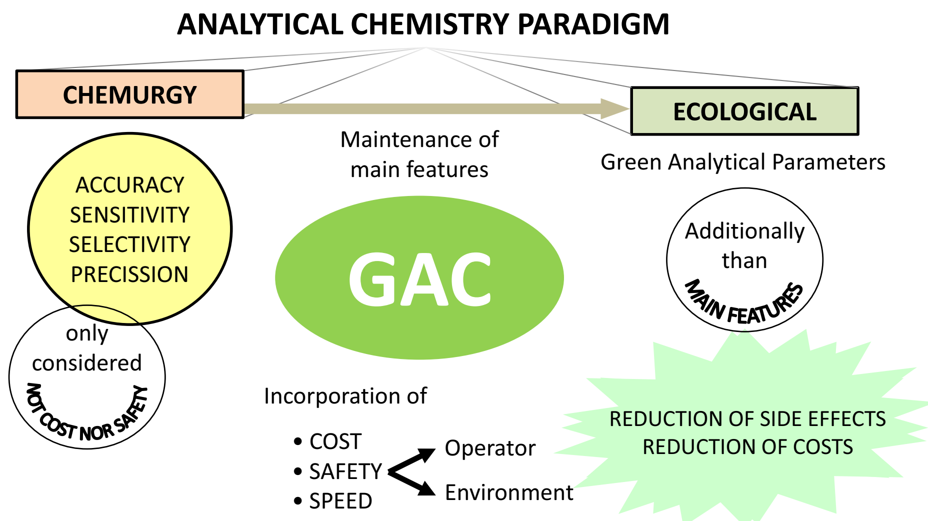

Fig. 1. Green Analytical Chemistry: shift from chemurgical paradigm to ecological paradigm.

(1) persistent, bioaccumulative and toxic (PBT);
(2) hazardous;
(3) corrosive; and,
(4) the amount and the nature of waste.

A similar criterion includes energy as a key point to be considered [14]. The addition of energy as a criterion is important due to the high reliance on non-renewable resources for production of electrical energy.

In recent years, an ecological scale was developed for the evaluation of analytical methods based on the introduction of penalty points [15]. According to it, a 100 score corresponds to a completely eco-friendly methodology, but subtracting penalty points of the method due to the volume and the toxicity of reagents consumed, energy consumed, emissions, operator hazard and waste generation. Methods are classified according to the eco-scale as:

- excellent green analysis (>75 points);
- acceptable green analysis (>50 points); and,
- inadequate green analysis (<50 points).

More recently, a new criterion was proposed to relate the penalty-point values to the volumes of reagents consumed and wastes generated using mathematical expressions and to associate the eco-scale value to a category class (A–G) in a so-called Green Certificate [16].

Table 1
Special issues of journals on Green Analytical Chemistry

Journal	Special issue (no. of papers)	Year, vol. (no.)
The Analyst (RSC)	Environmentally Conscientious Analytical Chemistry (5)	1995, 120 (2)
Spectroscopy Letters	Green Spectroscopy and Analytical Techniques (18)	2009, 42 (6–7)
Trends in Analytical Chemistry	Green Analytical Chemistry (10)	2010, 29 (7)
Analytical and Bioanalytical Chemistry	Green Analytical Methods (7)	2012, 404 (3)

2. Greening analytical procedures

Remote sensing and direct measurements on untreated samples are the green dream of analysts and many strategies have been developed for the analysis of target compounds based on the use of spectroscopy and electroanalytical signals [17] and image processing [18]. However, in most analytical methodologies, sample treatment is an unavoidable step and the use of a classical methodology, similar to that in Fig. 2 (sampling, sample transport and sample preparation before the acquisition of analytical measurements) is absolutely necessary. Typical sample-treatment methods include homogenization, filtration, centrifugation, clean-up, analyte extraction, preconcentration and/or derivatization. On evaluating the environmental impact of methods, sample preparation is, by far, the most challenging step regarding both the main features and the green parameters of the methods. Sample dissolution and analyte extraction involve the use of reagents and energy, and special care must be taken to select the procedure as simple as possible at room temperature, and the least hazardous reagents. In this context, options for greening methods must be based on avoidance of the use of toxic reagents and a strong reductions in consumption of energy and reagents, waste generation, time taken and operator effort. As a result, minimization and automation have been the basic tools for greening the analytical methods.

3. Facing the problem of sample treatment

Sample treatment has been the focus of intensive research from the GAC perspective in the past 20 years, since it is the bottleneck of analytical procedures.

It is worth stressing that the sample-preparation step largely determines the quality of the results obtained and is the main source of systematic errors and random lack of precision of analytical methodologies. The sample-treatment step must guarantee a quantitative recovery of target analytes, avoiding contamination and providing matrix isolation as far as possible, in order to reduce potential interferences and matrix effects during the measurement step.

We should notice that there is no universal sample-preparation technique suitable for all types of sample, and that sample preparation depends on the matrix, the nature of analytes and the final