Solid-phase spectroscopy from the point of view of green analytical chemistry

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In the 1990s, the concept of green chemistry (GC) emerged with the aim of minimizing the environmental impact of activity in chemistry. Nowadays, green analytical chemistry (GAC) receives increasing attention as an important trend in analytical chemistry and an emerging area of GC in the laboratory. Analytical methods based on spectroscopy are amongst those that dominate GAC.

In this article, we discuss the contribution of solid-phase spectroscopy (SPS) to the development of GAC methodologies, from its first conception (batch mode) to developments based on implementing SPS with flow-analysis methodologies. Using the GAC concept, we present and comment upon relevant examples of strategies and types of configuration, in order to give readers insight into the features and the potential of SPS in the emerging field of GAC.

Keywords: Batch mode; Bead-injection spectroscopy; Flow analysis; Flow-injection analysis; Flow-through optosensor; Green analytical chemistry; Multi-commutation; Multi-syringe flow-injection analysis; Sequential-injection analysis; Solid-phase spectroscopy

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1. Introduction

Green analytical chemistry (GAC) is currently an important trend in analytical chemistry [1] and an emerging area of green chemistry (GC) in the laboratory, receiving increasing importance and attention. It is apparent that, at the beginning of the twenty-first century, analytical chemistry methodologies are more closely related to GC principles [2], e.g.:

- minimizing reagent consumption and waste generation;
- use of safer solvents and auxiliaries;
- minimizing the potential of chemical accidents by means of a safer chemistry; and,
- miniaturizing analytical systems (i.e. development of microfluidics field).

Analytical chemistry has therefore become an area of application of GC principles [3]. For these reasons, its introduction into chemical education is currently also increasing [4].

According to GC principles, in developing a ''greener'' analytical procedure, the following should be taken into account:

a) chemical wastes (in an ideal situation) should not be produced;
b) if chemical wastes are produced (a more realistic situation), they should not be toxic and their amounts should be minimized and recycled; and,
c) the amount and the toxicity of solvents and reagents used in the steps of sample pre-treatment and measurement should be reduced, mainly by automation and miniaturization.

The main different steps of the analytical process (sample collection, sample preparation, separation, detection, and data evaluation) make different contributions to environmental pollution and there are different potential ways to make them greener and closer to GC principles [3,5].

The trends in new sample-preparation methods that minimize the amount of reagents and organic solvents contribute to improving the environmentally-friendly features of those methodologies that cannot be applied directly to samples with no sample treatment (see [1,5]).

Nevertheless, when the use of reagents is unavoidable and their substitution is not feasible, the best alternative is minimization of their consumption. At this point, automation of analytical procedures by means of flow-injection (FI) methodologies plays an important role in the GC context.

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However, and in spite of the progress of some areas of analytical chemistry (e.g., electrochemistry) that are developing relevant approaches to address the current challenges of GC [6], spectroscopic methods currently dominate the area of GAC [7]. One of the spectroscopic methodologies that has contributed to developing greener analytical methods is solid-phase spectroscopy (SPS), first proposed by Yoshimura et al. [8]. The same Yoshimura later proposed the first analytical automated application [9] implementing SPS with flow-based automatic systems.

Since then, there have been several developments and advances in this field. The first methods based on flow analysis with SPS detection were called flow-through optosensors, and mostly used the classical FI analysis (FIA) technique. Recently, FIA has been replaced by other methodologies such as sequential-injection analysis (SIA), multi-commutation FIA (MCFIA) and multi-syringe FIA (MSFIA).

In this article, we discuss in detail the contribution of SPS to the development of GAC methodologies, from its first conception (batch mode) to further development based on the implementation of SPS with different flow techniques. The latter approach based on flow methodologies represents (from the GAC point of view), a reliable automatic alternative for reducing solvent, sample and reagent consumption, minimizing waste generation, saving time compared to batch mode, showing very good analytical features in terms of sensitivity, selectivity and precision and the ability to perform straightforward multi-component analysis.

We present relevant examples of strategies and configurations developed in this field and we comment using the GAC concept in order to give the readers a view of the potential of SPS in the emerging field of GAC [1,5,10–13].

2. Solid-phase spectroscopy (SPS)

Yoshimura et al. [8] described for the first time a photometric procedure based on immobilization of the target species (analyte or a suitable reaction product) on an appropriate solid support (usually microbeads from a polymeric or a non-polar sorbent material or ion-exchange resins) by establishing an equilibrium between the active sites of the sorbent and the target species in solution. Beads are then collected by filtration and transferred to an appropriate measurement cell as a suspension with a few mL of solution. The analytical spectroscopic property from the target species, typically absorbance or fluorescence, directly retained on the solid support is measured and related to the sample-analyte concentration [14,15]. Although Yoshimura first called this methodology ''ion-exchange colorimetry'', from a more generic point of view, it should more appropriately be called SPS.

The first applications of the SPS principle were trace-metal-ion analyses in water samples using ion-exchangers as solid supports and either UV and Vis spectrophotometric or fluorimetric [8,15,16] detection. Anionic and cationic species were determined using one of the following three different approaches, depending on the nature of the sample analyte and the derivatizing reagent [17].

A. The solid microbeads are added to the sample solution together with the derivatizing reagent (if used). This procedure is recommended when the color reaction is highly selective for the analyte and the

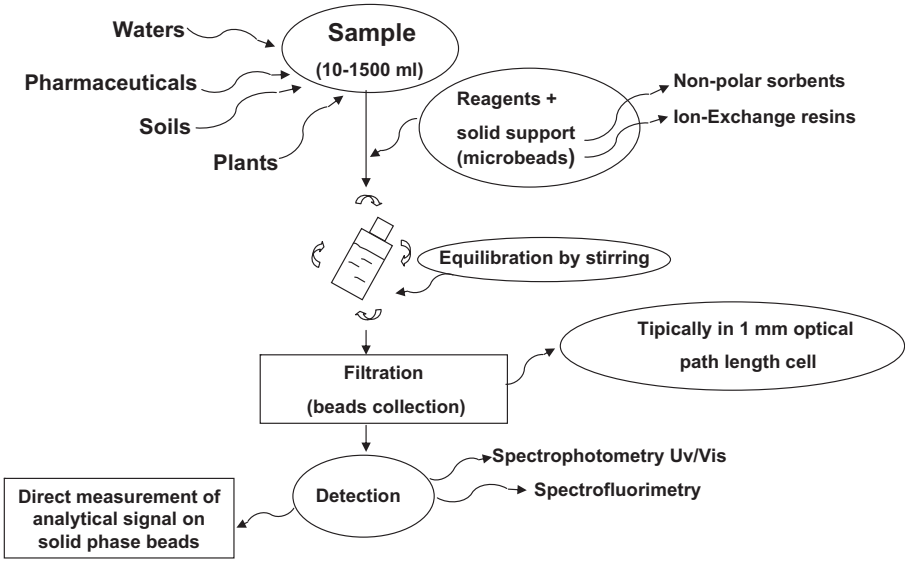

Figure 1. Methodology of solid-phase spectroscopy in batch mode.