Non-invasive analysis of solid samples

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Within the Green Analytical Chemistry paradigm, the best alternative for greening the methods of analysis comprises the direct determination of sample composition and/or sample properties without any chemical sample treatment, and, of course, it would be preferable not to have any physical treatment before acquisition of the information desired.

In this review, we evaluate the state of the art in, and available alternatives for, analysis of solids without prior sample treatment, starting from the non-invasive quality control of products or processes through to the use of portable instruments for *in situ* determinations and the development of methods based on image analysis. We evaluate the advantages of such methodologies from the viewpoints of both environmental and operator risk.

Keywords: Direct solid-sample analysis; Environmental risk; Green Analytical Chemistry (GAC); Image analysis; *In situ* determination; Non-invasive method; Operator risk; Portable instrumentation; Sample treatment; Solid sample

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1. Green Analytical Chemistry

Green Analytical Chemistry (GAC) can be defined as analytical chemistry that takes care of the risks to the environment and operators of side effects of analytical methods and processes, and, as a consequence, tries to avoid or, at least, to reduce these deleterious effects [1–3]. GAC involves a new paradigm for method development and method evaluation, which considers, as well as the main analytical characteristics of methods (e.g., accuracy, sensitivity, selectivity or precision), the energy and the reagents consumed, the waste generated and the toxicity of reagents and solvents used.

GAC is analytical chemistry, but considered with new eyes, which look simultaneously at the best quality of data and preserving the environment. In such a frame, it is clear that greening old analytical practices is an urgent task and, as clearly shown in many recent review papers, simplification, automation, miniaturization and reagent replacement are some of the tools available to do it [4–6]. The present review therefore focuses on simplification of the analytical procedures as the best alternative for greening a method because, by leaving out the chemical sample pretreatment, improving the in-field measurement and doing determinations as directly as possible, many environmental and operator risks can be avoided as, at the same time, can methodological risks concerning sample contamination and analyte losses.

As can be seen in Fig. 1, to move classical methods of analysis, based on a complete scheme of operations, to direct ones, it is possible to improve the methods from fundamental and environmental perspectives, and offer, at the same time, exciting business opportunities. We can therefore see that the use of portable instrumentation makes it possible to move the measurement systems to the sample or the process, thus providing suitable in-field signals to be transformed into data to build problem-solving models without the need for reagents or solvents and reducing the energy consumed. Also, remote sensing and non-invasive measurements are very important for the acquisition of accurate results without analyte contamination or loss.

From a practical point of view, it is necessary to establish clearly the differences between direct measurements of samples with the instrument and secondary measurements. In this sense, it is also essential to take into consideration that some techniques, which can be very useful for intact analysis [e.g., near-infrared (NIR) or Raman spectroscopy], require

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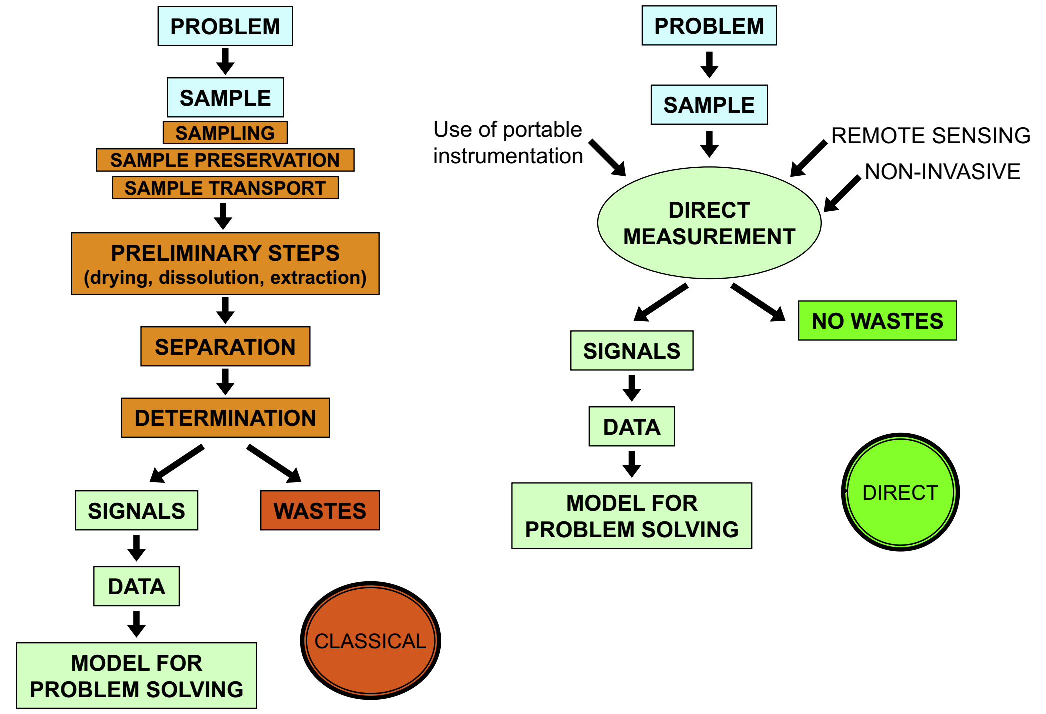

Figure 1. Direct solid analysis methods compared with traditional methods and tools for direct solid analysis.

prior intensive work with analysis of reference materials and chemometric data treatment.

In the following sections, we set out these principles taking into consideration the recent scientific literature published and reviewed in this field.

2. Variability of solid samples and analytical information required

The term solid sample practically covers all that we can see, with the exception of air or gaseous samples, water and other liquid samples, so, on thinking about direct analysis of solid samples, we must consider environmental samples (e.g., soil and biota), clinical samples (e.g., tumors and tissues), any kind of solid food, and the majority of pharmaceutical and industrial samples, which must be analyzed for different reasons (e.g., environmental or clinical diagnosis, or process or quality control). It is therefore clear that there is no single conception involved in the analytical demands regarding solids.

As summarized in Fig. 2, there are two main analytical questions about solids concerning solid homogeneity and composition, and, for the latter, we must separately consider mineral (or inorganic) sample composition and organic composition.

As direct alternatives to access the homogeneity and particle size of solids, electron microscopy offers excellent tools to verify those points, the single problem being the need to take a small portion of the sample to be introduced to the microscope, thus causing some minor sample damage, which also creates some trouble concerning data representativity [7].

However, in the case of sample composition, vibrational spectroscopy [8] and X-ray fluorescence [9] offer direct methodologies to establish clearly the concentration of major and minor components, based on the specific signals corresponding to the sample elements or bonds present in the structure of the target molecules. However, the availability of portable instrumentation for X-ray fluorescence, mid-infrared (MIR), NIR and Raman spectroscopy makes it easy to obtain this kind of information. Unfortunately, these techniques are not sensitive enough to provide direct evidence on the composition of solid samples at trace and ultra-trace levels, and, because of that, for these determinations, we need to use atomic spectroscopy, chromatography or electroanalytical methods, which all involve the dissolution or extraction of samples or, at least in the case of mineral composition at trace level, laser ablation of samples.

It is also possible to obtain direct information on the trace composition of solids based on unspecific spectroscopy signals, which could be affected by the presence of traces of elements and/or molecules, and could be modeled through the use of reference data obtained from dissolution of a sample calibration set and the spectroscopy signals. Based on the models built in this way, the direct analysis of new solid samples could be done by introducing the sample signals into prior mathematical models [10,11].