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Non-destructive Spectroscopy combined with chemometrics as a tool for Green Chemical Analysis of environmental samples: A review

Ainara Gredilla *, Silvia Fdez-Ortiz de Vallejuelo, Nerea Elejoste, Alberto de Diego, Juan Manuel Madariaga

Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country, UPV/EHU, P.O. Box 644, 48080 Bilbao, Basque Country, Spain

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ABSTRACT

The design of environmentally friendly analytical techniques and the modification of methods that are in use are important issues to be addressed in *Green Analytical Chemistry*. Potential applications of non-destructive spectroscopic techniques to achieve these principles are discussed in this review. Special emphasis is placed in environmental samples. Taking into account the current tendency to combine the analysis of environmental samples by non-destructive spectroscopic techniques and chemometrics, the most important applications concerning this task are also compiled. Although multiple objectives are pursued, regression techniques, frequently in combination with infrared spectroscopy, stand out, with around 300 references since 2009. More than half of these publications deal with the design of models to predict properties of soils. Nonetheless, the combination of regression techniques and non-destructive spectroscopy is continuously progressing, and they have been applied, for example, in the analysis of different environmental samples by remote or *in-situ* multispectral sensors with satisfactory results.

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Abbreviations: AAS, Atomic Absorption Spectrometry; ANN, Artificial Neural Networks; ARIMA, AutoRegressive Integrated Moving Average Modelling; ATR, Attenuated Total Reflectance; BP-ANN, Back Propagation Artificial Neural Networks; BRT, Boosted Regression Tree; CA, Cluster Analysis; CARS-PLS, Competitive Adaptive Reweighted Sampling Partial Least Squares; DRIFT, Diffuse Reflectance Infrared Fourier Transform; EC-MLR, Equidistant Combination Multiple Linear Regression; ED-XRF, Energy Dispersive X-ray Fluorescence; EDXRFS, Energy Dispersive X-ray Fluorescence Scattering; FA, Factor Analysis; GA-PLS, Genetic Algorithm Partial Least Squares; GRNN, Generalized Regression Neural Networks; ICP-AES, Inductively Coupled Plasma Atomic Emission Spectrometry; ICP-MS, Inductively Coupled Plasma Mass spectrometry; IR, Infrared; k-NN, k-Nearest Neighbour; LDA, Linear Discriminant Analysis; LS-SVM, Least Squares Support Vector Machine; LWR, Locally Weighted Regression; MCR, Multivariate Curve Resolution; MCR-ALS, Multivariate Curve Resolution Alternating Least Squares; MIR, Middle Infrared; MLR, Multiple Linear Regression; MW-PLS, Moving Window Partial Least Squares; NIR, Near Infrared; PARAFAC, Parallel Factor Analysis; PCA, Principal Component Analysis; PCR, Principal Component Regression; PLS, Partial Least Squares; PLS-BPNN, Partial Least Squares Back Propagation Neural Networks; PLS-DA, Partial Least Squares Discriminant Analysis; SEM-EDX, Scanning Electron Microscopy Energy Dispersive X-Ray; SML, Stepwise Multiple Linear; SPA-MLR, Successive Projections Algorithm Multiple Linear Regression; SPA-LS-SVM, Successive Projections Algorithm Least Squares Support Vector Machine; SPA-PLS, Successive Projections Algorithm Partial Least Squares; STATIS, Structuration des Tableaux A Trois Indices de la Statistique; SVM, Support Vector Machine; UVE-GA-PLS, Uninformative Variable Elimination Genetic Algorithm Partial Least Squares; UVE-PLS, Uninformative Variable Elimination Partial Least Squares; VIS-NIR, Visible-Near Infrared; XRD, X-ray Diffraction; XRF, X-ray Fluorescence.

* Corresponding author. Tel.: +34 946015445; Fax: +34 94601 3500.
E-mail address: ainara.gredi@gmail.com (A. Gredilla).

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1. Green chemistry concept

Currently, the traditional perception of Chemistry by the society is not positive. The Industrial Revolution brought about a drastic and unrestrained development of heavy industry. As the generated waste was directly discharged into the environment without prior treatment, numerous water bodies, soil plots and the atmosphere itself resulted seriously damaged. At that time, therefore, it was difficult to separate Chemistry from pollution. Nowadays we perceive Chemistry in a radically different way, and the stigma once attached to it is gradually disappearing. This new perception promotes Chemistry as a tool for the protection and improvement of the environment. In 1990, Paul Anastas and John Warner proposed the concept of *Green Chemistry* [1]. They defined *Green Chemistry* as a new philosophy based on eliminating, or at least reducing, the use or generation of hazardous substances in the design, synthesis and application of chemical products.

The *Green Chemistry* concept aims to unify the interests of the market, the society and the environment, nonetheless, chemical analysis is undoubtedly one of its principal areas of application. Particularly in this specific field, apart from reducing the use of hazardous agents, the decrease in energy consumption and generation of waste products is of special interest [2]. Thus, the development of new environmentally friendly analytical techniques and the modification of already existing methods are key points in the progress of the *Green Analytical Chemistry* concept.

2. Classical chemical analysis

The classical approach of an analytical process includes four main steps: *i)* sampling, *ii)* sample (pre)treatment, *iii)* analyte separation and finally *iv)* analyte detection. All of them could involve a considerable consumption of energy and produce a significant amount of hazardous substances.

Provided that the reagents used for cleaning purposes are carefully selected and handled, the sampling step should not constitute an important threat to the environment. Moreover, the use of passive sampling techniques instead of traditional approaches (active sampling) optimises the process in terms of time and money [3].

The pretreatment of solid, liquid and gaseous samples is usually a long and expensive process. Sometimes, it involves harmful steps for the environment. Pretreatment of a liquid, for example, often includes filtration, preconcentration and clean-up of the sample. The environmental effects derived from the pretreatment of solid samples are even stronger. In the classical approach, the analytes must be extracted into a liquid phase. The process usually takes a long time and there is a high risk to contaminate the sample and/or to degrade or transform the analyte [4].

The separation of analytes is mostly attempted by chromatographic and electrophoretic techniques. For detection, mass spectrometry and optical spectroscopy are the most popular approaches [5,6]. Separation and detection, however, are not nowadays critical stages concerning *Green Chemistry* criteria.

3. Non-destructive spectroscopy

Non-destructive spectroscopy has been studied in depth during the last years in order to overcome the drawbacks that, concerning the principles of *Green Analytical Chemistry*, result from the use of traditional analytical techniques [7]. The non-destructive spectroscopic techniques provide analytical information without damaging the sample and in most of the cases, in addition, sample treatment (extraction or digestion) is not required. In the view of *Green Chemistry,* this is indeed the most important advantage of non-destructive spectroscopy. Sampling can be also avoided, since *in situ* analyses are susceptible to be done using portable equipment [8]. Moreover, non-destructive spectroscopy potentially enables the simultaneous analysis of several analytes in a single run, with a consequent saving of reagents and time.

Vibrational techniques (Infrared (IR) and Raman spectroscopy) and X-ray fluorescence (XRF) are amongst the non-destructive spectroscopic techniques that have attracted more interest in the last years. They all rely on the interaction between electromagnetic radiation and matter, and the information obtained depends on the source of the energy used to irradiate the sample. Although the information obtained by IR could be classified as the poorer one, its applicability is by far the most important [9,10]. Numerous reviews such those of Moros et al. [7] and Armenta et al. [11] have compiled the most important works based on IR. Even though signals frequently overlap, Near Infrared (NIR, 780–2500 nm) is still the most used technique. Middle Infrared (MIR, from about 700 nm to 2500 nm) have also numerous applications, but the use of Far Infrared (FAR, 400 nm and 700 nm) is still limited.

Traditionally, dispersive instruments have been used to obtain infrared spectra, but as they were only able to measure one wavelength at each time, the use of Fourier Transform Infrared (FT-IR) spectrometers has been continuously increasing over time. A FT-IR spectrometer is able to collect all wavelengths simultaneously and, consequently, most of the IR instruments commercialised nowadays are FT-IR spectrometers.

Transmittance is the pioneering and most straightforward IR mode, however, applications based on the measurement of reflected light can be used for samples that there are difficult to analyse by the conventional transmittance methods. Reflectance methods can be divided into three principal categories: Attenuated Total Reflectance Spectroscopy (ATR), Specular Reflectance Spectroscopy and Diffuse Reflectance Spectroscopy (DRS). The information obtained from all of them is comparable if the differences emerging from the way the infrared light beam is absorbed by the sample are appropriately corrected. ATR spectroscopy is based on the total internal reflection phenomenon. Depending on the ATR cell, liquid, solid or gas samples can be analysed. Specular Reflectance Spectroscopy and DRS are based on external reflectance, so that the radiation reflected from a surface is measured in both cases. Specular reflection is defined as light reflected from a smooth surface at a definite angle, whereas DRS is based on the reflection produced when energy penetrates the surface of a sample and this tend to reflect light in all directions. Since DRS is usually coupled with Fourier transformation for a more appropriate interpretation of the signals, it is commonly known as DRIFT. Applications of DRIFT are by far more abundant than those of specular reflectance spectroscopy [7].

Raman Spectroscopy is considered a non-destructive technique because the power of its laser can be modulated according to the sample that is being analysed to avoid the thermodescomposition of the sample. Raman Spectroscopy provides us with revealing information, since the spectrum obtained is characteristic of each molecule of the sample area that is being analyzed. However, the application of this technique is still limited for quantitative analysis because the pretreatment of the spectra could be tedious.

XRF, unlike vibrational techniques, provides us with elemental information of the sample. It has been largely used in medical and environmental applications with satisfactory results [12]. In recent times, many attempts have been done to combine vibrational and elemental spectroscopic techniques. The combination of Scanning Electron Microscopy coupled to Energy Dispersive X-Ray Spectroscopy (SEM-EDX) and Raman spectrometry is a successful example of this combination [13].

Despite the multiple applications of the abovementioned spectroscopic techniques, this review will only focus in the analysis of environmental samples such as soils (including rocks and sediments), water, air particles, and biota (animals and plants mainly).

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