



Experimental and chemometric strategies for the development of Green Analytical Chemistry (GAC) spectroscopic methods for the determination of organic pollutants in natural waters



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ABSTRACT

The development of Green Analytical Chemistry (GAC) methods is one of the most active areas of Green Chemistry. Especially relevant are GAC methods devoted to the detection and quantification of environmental pollutants, because they should not pollute the environment more than the analyte to be determined. While considerable attention has been paid to develop environmentally friendly alternatives for the first stage of the global analytical process (e.g., sample preparation techniques), relatively fewer works are dedicated to implement green approaches for obtaining the analytical signal. Current strategies that are based on the principles of Green Chemistry for the determination of common organic pollutants in natural waters are detailed. The review collects and discusses selected publications from about the last 5 years relating to the topic, highlighting the role of multivariate calibration as a modern and very useful tool to achieve the pursued objectives.

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Abbreviations: ALS, alternating least-squares; BTZ, bentazone; CA, calix[n]arene; CBZ, carbamazepine; CD, cyclodextrin; CIP, ciprofloxacin; COW, correlation optimized warping alignment algorithm; DAD, diode array detector; DAI, daidzein; EDDP, 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine; EEFMs, excitation-emission fluorescence matrices; EEPiFM, excitation-emission photoinduced fluorescence matrix; E3, estriol; E2, 17 β -Estradiol; EE2, 17 α -Ethinylestradiol; E1, estrone; FLD, fluorimetric detection; GAC, Green Analytical Chemistry; GC, gas chromatography; GC-MS/MS, gas chromatography-mass spectrometry; GEN, genistein; LC, liquid chromatography; LC-DAD, liquid chromatography coupled to diode array detector; LC-MS/MS, liquid chromatography coupled to tandem mass spectrometry; LOD, limit of detection; MCL, maximum contaminant level; MCR, multivariate curve resolution; MCR_{tril}, multivariate curve resolution with trilinearity constraint; MDA, 3,4-Methylenedioxyamphetamine; MDEA, 3,4-Methylenedioxyethamphetamine; MDMA, 3,4-Methylenedioxymethamphetamine; MET, methamphetamine; MLC, micellar liquid chromatography; MW, mineral water; N-PLS/RBL, multidimensional partial least squares/residual bilinearization; OFL, ofloxacin; PAH, polycyclic aromatic hydrocarbon; PARAFAC, parallel factor analysis; PIF, photoinduced fluorescence; PX, piroxicam; PLS, partial least-squares; PSE, pseudoephedrine; RDSE, rotating disk sorptive extraction; RS, river sediment; RW, river water; SDS, sodium dodecylsulfate; SPS, solid-phase spectroscopy; SW, surface water; SWATLD, self-weighted alternating trilinear decomposition; TBT, tributyltin; TW, tap water; U-PLS/RBL, unfolded partial least squares/residual bilinearization; US-EPA, United State Environmental Protection Agency; UW, underground water; W, water; WW, wastewater; WWTP1, wastewater treatment plant influent; WWTP2, wastewater treatment plant effluent

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1. Introduction

The term Green Chemistry emerged from the Pollution Prevention Act that was enacted in 1990 in the United States, and refers to the design of chemical products and processes that reduce or eliminate the use or generation of hazardous compounds (US-EPA, 2015).

Although in early years Green Chemistry was mainly oriented to the planning of organic synthesis, the application of Green Chemistry concepts was gradually extended to other areas such as analytical chemistry. In fact, with the purpose of generating environmentally friendly methods without affecting their accuracy, sensitivity, and reproducibility, in the late 1990s the Green Analytical Chemistry (GAC) concept arose. In 1998, Anastas and Warner proposed the twelve principles of the Green Chemistry (Anastas and Warner, 1998) and, in 2001 Namieśnik selected those having priority for the development of GAC methods (Namieśnik, 2001). These principles include the reduction or elimination of the use of organic solvents, the reduction of gaseous, liquid and solid wastes, the disposal of toxic or eco-toxic reagents, and reduction in power consumption. In 2013, Gałuszka et al. proposed twelve principles as a guide for the development of new environmentally friendly methods (Gałuszka et al., 2013), and many researchers began to offer novel strategies to implement these new concepts (de la Guardia and Garrigues, 2014), including the idea that the simpler the analytical procedure, the greener (Koel, 2016). It is important to point out that chemists have different tools to assess the greenness of analytical procedures (Gałuszka et al., 2012; Tobiszewski et al., 2015a, Tobiszewski, 2016).

A variety of approaches can be used to reduce environmental pollution caused during the whole analytical process. These strategies focus on the various stages of this process, which can be summarized in: (1) sample collection and preparation, (2) acquisition of analytical signals and (3) data processing (Molina-Díaz et al., 2010).

Sample preparation is, perhaps, the analytical step that has received more attention in developing greener approaches for the determination of environmental pollutants, and numerous reviews and articles have been published on the subject (Gałuszka et al., 2012; Tobiszewski et al., 2010; Farré et al., 2010; Armenta et al., 2015). This fact is not surprising because: (1) sample pre-treatment is considered the most polluting step since the use of organic solvents is required for removing interferences and for concentrating the target compounds, which are generally present in trace levels (Tobiszewski et al., 2010), and (2) the most frequent methods for pollutant determination are chromatographic, which generally require rigorous clean-up and extraction processes of the environmental samples.

Among green extraction methods which avoid a large consumption of organic solvents we can mention: solid-phase-extraction with adsorption membranes, liquid-phase-extraction, stir-bar sorptive-extraction, ultrasound-assisted-extraction, supercritical-fluid-extraction, subcritical-water extraction, solid-phase-microextraction, thin-film-microextraction, dispersive liquid-liquid-microextraction, and microextraction in packed syringe (Tobiszewski et al., 2009, 2010; Duarte et al., 2014; Spietelun et al., 2013).

In comparison to the numerous GAC protocols for sample pre-treatment, relatively few articles are devoted to green acquisition of the analytical signals. In the present review, we will discuss different strategies employed in spectroscopic methods, especially those based on molecular luminescence, and those variables capable to positively modify the intensity of the signals in order to decrease or avoid the use of organic solvents.

Finally, the relationship between the last stage of the analytical process (data treatment) and Green Chemistry was consolidated from the introduction of multivariate calibration in quantitative analysis, and a brief explanation of this type of calibration will be given below (Mas et al., 2010).

It is desirable that Green Chemistry principles are taken into account in the entire analytical procedure, especially considering that in many cases the different stages are closely related. For example, the acquisition of second- or third-order data during the measurement step leads to their chemometric processing and successful results can be obtained without an exhaustive treatment of the sample. In other words, the correct choice of the method and data treatment results in a drastically simplified sample processing step.

2. Multivariate calibration

Multivariate calibration methods involve the use of mathematical models that relate multivariate instrumental signals with analyte concentrations or sample properties (Massart et al., 1997). In contrast to zeroth-order (univariate) calibration, where a single instrumental response per sample is recorded and analyzed, first-, second- and third-order (multivariate) calibrations work with multiple signals for each sample (Olivieri and Escandar, 2014). In fact, calibrations can be classified as shown in Table 1.

Zeroth-order calibration is performed with instruments that produce a single response per sample (e.g. absorbance or fluorescence emission at a single wavelength). First-order calibration is carried out with data for a single sample which can be arranged as a vector (e.g. UV-vis spectrum, fluorescence emission spectrum, etc). Besides, second-order calibration is performed with matrix data for a given sample (e.g. excitation-emission fluorescence matrices (EEFMs), absorption or fluorescence spectra evolving during kinetics of a chemical reaction, etc). If second-order data for a set of samples are joined into a three-dimensional array, the resulting object is known as a three-way data array. Finally, when additional modes are introduced, higher-order data are obtained. It should be noticed that two equivalent nomenclatures are used for describing data and the corresponding calibrations. For example, one could refer to either second-order or three-way calibration; the former expression focuses on the number of modes of a single sample (two modes, second-order data) whereas the latter on the number of modes of a sample set (three modes, three-way data).

Specifically, in second-order calibration methods the analyzed instrumental response is a data matrix per sample. Although there are many different protocols for second-order data generation, excitation-emission fluorescence matrix (EEFM) data and chromatographic data with spectral detection are, by far, the most

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