Green Strategies in Trace Analysis: A Glimpse of Simple Alternatives for Sample Pretreatment and Analyte Determination

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ABSTRACT Researches in green chemistry have mainly been focused on new synthetic rotes, aiming diminution of side products, replacement of toxic solvents, and minimization of energy consumption. However, there is a clear demand to the development of greener analytical procedures and challenges are magnified when trace analysis is concerned. This overview is focused on environmentally friendly strategies for sample pretreatment and measurement aiming determination of species in low concentrations, including tungsten coil atomic spectrometry, long pathlength spectrophotometry, flow-based methodologies, and greener strategies for analyte extraction, exploiting either retention on solid supports or surfactant-mediated processes.

KEYWORDS cloud-point extraction, Green Analytical Chemistry, long pathlength spectrophotometry, solid-phase extraction, tungsten coil atomic spectrometry

INTRODUCTION

Green Chemistry (GC) aims the development of chemical processes involving minimized use of toxic substances and waste generation.[1] It was shortly defined as "the use of chemistry for pollution prevention"[2] and expressed by means of twelve basic principles.[1] Researches in this field have focused mainly on new synthetic rotes in order to avoid side products based on the concept of atomic economy and replacement of organic solvents, in accordance with the trend to sustainable development. In this way, there is a clear demand to the development of greener analytical procedures, which becomes evident because a number of current analytical methods employ highly toxic reagents, resulting in a relatively large volume of toxic wastes. Disposal and treatment of these wastes are difficult, expensive, time-consuming, and often requires high energy consumption. General discussions on application of the concepts to GC to analytical chemistry have been presented by some authors.[1–5]

Several strategies can be adopted aiming greener analytical procedures, involving replacement of toxic reagents, minimized reagent consumption, recycling, and waste treatment. However, the development should be

TABLE 1   Green Strategies for Trace Analysis

Strategy	Typical application	Main characteristics
WCAAS and WCAES	Metals determination	High sensitivity with low power requirement and low sample consumption
Long pathlength spectrophotometry	Organic and inorganic species after chemical derivatization	High sensitivity without organic solvent use
Solid-phase extraction	Separation and preconcentration	Low consumption and exposure to organic solvents
Automation and miniaturization	Organic and inorganic species after chemical derivatization	Increase in sample throughput and waste minimization
Cloud point extraction	Extraction of hydrophobic species	Use of low toxicity surfactants
Microwave-assisted extraction with diluted acids	Extraction of analytes from solid samples	Reduction of time for sample preparation and low reagent consumption

carried out without critically affecting key analytical features, such as sensitivity, accuracy, and precision. This challenge becomes more serious for analytes in low concentration, especially in samples with complex matrices that need previous separation. In this situation, approaches that require toxic solvents, complex equipments with large energy demand, and large sample amounts are frequent.

This work is focused on an overview of some well-succeeded greener strategies for trace analysis. The approaches and the main characteristics are presented in Table 1. A general discussion and representative examples are presented in the next sections.

GREEN STRATEGIES FOR TRACE ANALYTE DETERMINATION

Tungsten Coil Atomic Spectrometry

There is no doubt that graphite furnace atomic absorption spectrometry (GFAAS) is a well established and important technique for determination of trace metals in a plethora of samples.[6] Additionally, GFAAS allows direct analysis of solids and recently its analytical capability is even increasing with commercial development of high resolution continuum source AAS equipment.[7] However, GFAAS has some drawbacks, such as the need of a high energy input for fast heating during the atomization step. This is not critical in a laboratory environment with proper availability of energy supply, but it implies that the equipment cannot be used in field applications. This aspect is aggravated by the

requirement of an additional system for cooling-down the graphite tube after reaching high atomization temperatures. Notwithstanding, energy is a serious resource and we must learn how to live without spending it freely in our worn out planet.

A simple alternative to overcome these limitations without any negative consequence in sensitivity is the use of a tungsten coil electrothermal atomizer.[8–10] Tungsten coil (150 or 250 W) can be extracted from commercial lamps and it presents attractive characteristics as an electrothermal atomizer, such as:

- Low chemical reactivity;
- Fast heating (i.e., up to $30\,K\,ms^{-1}$), by a low power supply;
- Proper physical properties, for instance due to its specific heat, tungsten coils can be cooled-down without any external refrigerating system;
- Extremely low cost due to mass production;
- Reduced background emission in ultraviolet spectral range.

Based on these characteristics, the idea of using tungsten coils as an atomizer in AAS is not new,[11,12] but its performance was negatively affected in the earlier days by limitations associated with slow data acquisition of extremely fast transient signals.[9] Nowadays, this aspect is totally overcome and short range temporal signals can be acquired either in area or in peak height.

In the nineties a series of researchers demonstrated the capability of tungsten coil AAS (WCAAS) for determining Pb in blood without any previous

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step of sample digestion.[11–13] In a more recent work, the superb performance of WCAAS for determining ytterbium in animal nutritional studies was demonstrated.[14] This work has shown that a refractory element that would form carbides in a graphite tube is efficiently atomized from a metallic surface. Previous work has emphasized this same performance for barium, which also forms refractory carbide in a graphite surface.[15]

More recently it was proposed that tungsten coil would also be used for atomic emission measurements,[16,17] and an even simpler instrument was designed without a radiation source and a power supply to feed it. The applicability of tungsten coil atomic emission spectrometry (WCAES) was fully demonstrated for rare earth analysis in environmental samples.[18]

These developments demonstrated that tungsten coil atomizers can be used in extremely simple and portable instruments and these are fully compatible with green strategies demanding low inputs of energy and consumables without any critical degradation of performance. However, it should be mentioned that interferences are generally severe in open atomizers due to the non-isothermal character and both WCAAS and WCAES require tailored procedures for calibration to circumvent these processes.

Long Pathlength Spectrophotometry

Molecular spectrophotometry is a widespread analytical technique for determination of a lot of analytes in different samples. Applications usually exploit chemical derivatization that often requires toxic reagents.[19] In addition, for trace analysis, a concentration step either of the analyte or of the reaction product is often necessary, resulting in additional waste generation. The former drawback can be circumvented by minimizing the reagent consumption by automation, miniaturization, or by using immobilized reagents, as discussed in the next sections. One of the more promising alternatives for improving sensitivity in molecular spectrophotometry involves the increase of the measurement optical path.

The Lambert–Beer's law establishes that the analytical response is directly proportional to the optical path of the measurement cell, which increases proportionally the number of absorbing species that interacts with the radiation beam. However, from a practical point of view, this strategy is usually limited to optical paths lower than 10 cm when conventional materials (e.g., glass or quartz) are used, in view of the excessive attenuation of the radiation power and increase in the cell volume.[20] These difficulties have been circumvented by using multi-reflexive or liquid-core waveguide (LCW) cells. The second alternative is more usual for measurements in liquid medium and devices with up to 5 m optical path with capillary dimensions (ca. 250 μL/m) are commercially available.[21]

LCW cells are constructed by a tube of a material with refractive index (RI) lower than the liquid inside it or, alternatively, by a fused-silica capillary covered with the material with RI lower than the liquid. Suitable materials for measurements in aqueous solutions are the fluoropolymers of the Teflon AF family, which presents RI in the range 1.29–1.31 (water RI = 1.33) and are transparent within 200 and 2000 nm.[22] Thus, according to the Snell's law, a cell filled up with water or a diluted aqueous solution can act as a waveguide and, depending on the angle of incidence, radiation can be constrained into the cell due to total internal reflection.

Long pathlength spectrophotometry (LPS) is a greener alternative for trace metal analysis by avoiding laborious pretreatment steps, which commonly involve toxic solvents. On the other hand, even when increase in sensitivity is not required, this strategy can result in greener procedures by processing samples after suitable dilution, allowing a proportional decrease in reagent consumption.

The potential of LPS to develop greener analytical procedures was demonstrated in the spectrophotometric determination of total phenols, exploiting the oxidative coupling of phenolic compounds with 4-aminoantipyrine in alkaline medium containing potassium hexacyanoferrate(III).[23] The use of a flow system designed with independently controlled solenoid vales allowed a 200-fold reduction in reagent consumption in comparison to the batch reference procedure. The 100-fold increase in the optical path permitted the direct determination of total phenols without liquid–liquid extraction. The detection limit was comparable with that attained by the procedure with chloroform extraction, which consumes up to 50 mL of the organic solvent and generates ca. 600 mL of waste per determination.[24]

Another representative example is chloride determination exploiting incorporation of a solid-phase reactor containing immobilized silver chloranilate in a flow

system.[25] Chloranilate ions were released from the minicolumn due to formation of AgCl and measured in a 100-cm optical path flow cell, resulting in analytical signals 75-fold higher. Waste generation was reduced to ca. 100 ng chloranilate per determination and the procedure is a greener alternative to the spectrophotometric procedure using mercury(II) thiocyanate.

The main limitations of LCW cells are the mechanical fragility, possibility of clogging of the capillary with solid particles in suspension and the increase of the blank signals proportional to the optical path when the reagents absorbs at the measurement wavelength. Adsorption of organic substances and retention of air bubbles were minimized by using fused silica capillaries covered with Teflon AF instead of tubes constructed directly with the fluoropolymer. On the other hand, the same experimental set-up can be used for measurements by fluorescence[26] or chemiluminescence,[27] with potential to maximize the amount of detected radiation with consequent increase in sensitivity. LCW cells have also been coupled to separation techniques[28] and used in devices for determination of traces of gaseous species exploiting the high permeability to Teflon AF.[22]

Multi-reflection cells also allow increasing the sensitivity and effective optical paths higher than 100 m were reported for measurements of gaseous species by infrared spectroscopy.[29] However, its use for measurements in liquid medium is limited. Some examples include cells for capillary electrophoresis[30] and flow injection analyis,[31] which increased 40- and 1.7-fold the sensitivity, respectively. The cells were constructed with fused silica[30] or glass[31] capillaries covered with silver, with windows for incidence of the radiation beam (from a He-Ne laser[30] or a light emission diode[31]) and transmission to the detector. The incident angle is a critical aspect, which affects the number of internal reflections, estimated as 44[30] and 19[31] for the fused silica and glass cell, respectively.

GREEN STRATEGIES FOR SAMPLE PRETREATMENT

Flow-Based Procedures and Miniaturization

Flow analysis has been extensively exploited to mechanize analytical procedures, improving the analytical performance mainly in relation to precision, reagent consumption, and sample throughput. Analyses are processed in closed systems, minimizing risks to the analyst and of sample contamination. As measurements are carried out without attaining chemical equilibrium conditions, kinetic discrimination can be easily implemented. However, measurements out of the steady state and the inherent sample dispersion in the carrier contribute to a generally lower sensitivity than achieved in batch procedures. On the other hand, flow systems have been largely used for analyte extraction and concentration, aiming improving selectivity and sensitivity, as well as for sample decomposition, including microwave-assisted acid sample digestion[32] and photochemical processes.[33] In general, the sample treatment can be carried out with lower reagent consumption and waste generation in comparison to the conventional alternatives. Some examples of the use of flow systems for separation and concentration are presented in the next section. The potential of flow systems to develop greener analytical procedures, by replacement of toxic reagents, waste minimization, and in-line treatment and recycling was emphasized in a previous article.[34]

Reagent consumption in flow-based methodologies can be further reduced by means of miniaturization, in agreement with the concept of micro-Total Analytical Systems (µTAS).[35] Researches in this field have emphasized the development of simpler and low-cost alternatives to develop microfluidic devices, generally based on polymeric materials. For example, the construction of a µ-FIA analyzer by deep UV lithography on two layers of urethane–acrylate polymers was recently described.[36] The device integrated the micro-channels and photometric detection with a light emitting diode and photodiode with a total volume of 7.0 µL. The potential to minimize reagent consumption and waste generation was demonstrated by chloride determination with mercury(II) thiocyanate, in which less than 2 µg Hg(II) was consumed per determination (ca. 300-fold lower than in the batch procedure) and only ca. 20 mL of waste was generated after an 8 hr working day. Miniaturization thus allows the development of green procedures even when toxic reagents are involved. A further example is the determination of the carbaryl pesticide by thermal lens spectrometry after derivatization and solvent extraction in a

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micro-flow system.[37] Two glass micro-chips were used to carry out the pesticide hydrolysis, diazotization, and extraction of the colored product in toluene. Despite the minimized consumption of the organic solvent (<300 nL per determination), an enrichment factor of 50 was achieved, yielding a detection limit of 70 nmol L^{-1}.

Liquid–Liquid and Solid-Phase Extraction

The direct determination of trace concentrations of metal ions or organic species in different samples by most analytical techniques is often difficult due to matrix effects, lack of sensitivity, or both. Preliminary separation and concentration of trace analytes from the sample matrix is thus frequently required.[38]

The most widespread techniques for separation and preconcentration are liquid–liquid[39] and solid–liquid[40] extractions. Typically, preconcentration is achieved by addition of a suitable reagent (e.g., a chelating agent) to an aqueous sample and extraction of the formed product to an organic phase or a hydrophobic solid phase. Alternatively, functional chelating groups may be previously immobilized into the sorbent when solid-phase extraction is employed.

Liquid–liquid extraction (LLE) is the earliest and classical method for metal preconcentration and matrix removal, and still has been applied in a certain extent, in spite of the inherent limitations, including large waste generation. Various greener alternatives have been developed, including accelerated solvent extraction (ASE), cloud-point extraction, ultrasound- and microwave-assisted extraction, supercritical fluid extraction (SFE), and membrane extraction. These strategies reduce both the use of organic solvents and the extraction times in comparison to traditional liquid–liquid extractions.[3]

Automation can greatly reduce the hindrances of batch liquid–liquid extraction,[41] such as the operation time, reagent and solvent amounts, and risks of human contact with organic solvents. A variety of flow systems have been proposed for automation of the liquid–liquid extraction process, including FIA,[42,43] segmented flow analysis (SFA),[44] mono-segmented flow analysis (MSFA),[45] SIA,[46] and multicommutation.[47] Liquid–liquid extraction in a single 1.3 µL-microdrop,[48] membrane extraction,[49] or in a

batch-type micro-scale liquid phase analyzer[50] are other ingenious alternatives for greener LLE.

Solid-phase extraction (SPE) offers a number of important benefits when compared with the classical LLE, such as higher enrichment factors, high recoveries, rapid phase separation, lower cost, and the facility for coupling to different detection techniques in on-line or off-line modes.[51,52] Additionally, SPE provides the possibility to eliminate solvents in the pretreatment process because the analyte can be directly extracted from the liquid sample onto the sorbent material, principally when the analytical measurements are performed directly on the solid support. This results in low consumption and exposure to organic solvents. A wide range of solid supports have been applied for solid-phase extraction, such as ion-exchange or chelating resins,[53] modified or bonded silica,[54] polyurethane foam,[55] and cellulose.[56] Some specific examples of greener strategies exploiting solid-phase extraction are presented next.

The reagent 1-(2-pyridylazo)-2-naphthol (PAN) was proposed for the solvent extraction and spectrophotometric determination of manganese, iron, cadmium, mercury, gallium, zinc, nickel, and yttrium.[57,58] The extraction procedure was evaluated with different toxic solvents: benzene, chloroform, carbon tetrachloride, and isoamilic alcohol.[58] On the other hand, organic solvents were not required when a chelating sorbent was obtained by adsorption of PAN on Amberlite XAD-4 for SPE to determine copper, zinc, iron, cadmium, nickel, and lead.[59] The elution was performed with diluted hydrochloric acid and metals were determined by flame atomic absorption spectrometry.

Komjarova and Blust compared liquid–liquid and solid-phase extraction for the determination of cadmium, copper, nickel, lead, and zinc in seawater.[60] Ammonium pyrrolidine dithiocarbamate (APDC) and diethyl ammonium diethyl dithiocarbamate (DDDC) were used as chelating agents. The comparison focused on investigation of analytical performance including recoveries for several species and concentration factors. Greener procedures can be designed by minimizing sample volume and careful selection of reagents, as shown in Table 2.[60]

SPE can be carried out in batch or in mechanized systems. Batch procedures are suitable when higher preconcentration factors are needed, but usually require large reagent and sample amounts. When

TABLE 2 Comparison of Liquid–Liquid and Solid-Phase Extraction Procedures for the Determination of Metals in Seawater Using APDC and DDDC as Chelating Agents[60]

Factor	Solvent extraction	Solid phase extraction
Elements with good recoveries (>85%)	Cd, Cu, Ni, Pb, Zn	Cd, Zn, Cu, Ni (UV oxidation may be required for Cu)
Sample volumes (mL)	200	50
Concentration factor	40	25
Time and labor consumption	High	Medium
Reagents/costs	Uses expensive, environmentally unsafe reagents	Environmentally safe and cheap

on-line systems are considered, the principal advantage is the possibility of automation, increasing precision and sample throughput, while minimizing both reagent/sample consumption and waste generation.[61] The complexity of the strategies can vary from simple coupling of mini-columns to autosamplers[62] to complex flow injection analysis (FIA), sequential injection analysis (SIA), multicommuted flow systems,[63] and that based on microdevices, as discussed in the previous section.

The decreasing in sample and reagents consumption can be exemplified by batch[64] and flow-based[65] preconcentration of zinc with polyurethane foam. Both methods were based on the solid-phase extraction of the zinc in the form of thiocyanate complexes with subsequent spectrophotometric determination with 4-(2-pyridylazo)-resorcinol (PAR). Sample and thiocyanate consumption were quite reduced when the flow system was utilized. Additionally, in the flow system a mini-column packed with foam was employed in various preconcentration cycles.

The increasing demand for environmentally friendly analytical methods is one of the major incentives to improve the classical procedures used for sample treatment.[66] A tendency that can be observed when a new sample preparation procedure is developed or for adaptation of existing methods is the possibility to save time and chemicals by miniaturization.[4] Consequently, the popularity of solid phase microextraction (SPME) has increased. SPME is based on the partitioning of analytes between the sample and a stationary phase, which is typically coated to the surface of a fused silica fiber.

Subsequently, analytes are thermally desorbed directly onto the injection port of a gas chromatograph or eluted with a suitable solvent for further analysis. Its simplicity of operation, solventlessness, and the availability of commercial fibers have made SPME become a tool routinely used for several applications.[67]

The determination of persistent organic pollutants (POPs), such as pesticides and polychlorinated biphenyls, in human tissue samples is an example of application of the SPME. There are several conventional extraction methods that have been reported for the determination of POPs, including Soxhlet extraction, in which long extraction time and substantial volumes of organic solvents are required.[68,69] The employment of polypropylene membrane in a SPME procedure reduced both the analysis time and solvent consumption.[70]

Metallic species can also be preconcentrated exploiting SPME. A method for speciation of alkyl-lead and inorganic lead(II) in aqueous samples was developed by derivatization with deuterium-labeled sodium tetraethylborate.[71] The obtained derivatives were extracted from the headspace by a SPME fiber for subsequent desorption and determination.

In the determination of persistent organic pollutants, new procedures involving extraction with acetonitrile followed by dispersive solid-phase extraction have gained attention.[72,73] This method, first reported in 2003 by Anastassiades and co-workers, has been named QuEChERS, which reflects its major advantages (Quick, Easy, Cheap, Effective, Rugged, and Safe).[72] The QuEChERS process involves an initial extraction procedure with acetonitrile followed by an extraction/partitioning step after the addition of a salt mixture. An aliquot of the raw extract is then cleaned up by dispersive solid-phase extraction and the final extract in acetonitrile is directly analyzed by chromatography. The procedures then inherently involve a minor number of steps for sample preparation and considerably reduce the use of solvents.

The QuEChERS procedure effectively covers a very wide range of analytes, including highly polar pesticides as well as highly acidic and basic ones.[74] For the analysis of pesticides residues in foods, the method results in faster sample analysis and significant reductions in solvent usage and hazardous

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waste production when compared with traditional methods. Schenck and Hobbs reported that the QuEChERS method for the analysis of pesticides in fruits and vegetables entails extracting the pesticide residues from 10 g of sample by vortex mixing with 10 mL of acetonitrile.[75] In a previous work, involving traditional solvent extraction, each sample portion was blended with 100 mL of acetonitrile for analytes extraction.[76]

Direct Measurements on Solid Phase

The ideal green analysis would run *in situ* without sampling, reagent addition, or extraction. Real-time measurements contribute to minimize costs[3] and can also yield more reliable results by avoiding errors due to sample contamination and loss of the analyte. Nondestructive techniques, such as infrared spectrometry and X-ray fluorescence (XRF), are also attractive to achieve environmentally friendly procedures, by minimizing the sample preparation steps and the consequent waste generation.

XRF spectrometry is a inherently green analytical technique because samples are not destroyed[77] during the X-ray excitation or fluorescence emission process and usually none reagent is required in sample preparation. However, preconcentration is often needed for trace metal determination because its sensitivity is relatively poor. Simultaneous multi-element analysis based on analytical measurements directly on a solid support is one of the advantages of XRF spectrometry. An example of this possibility is the simultaneous determination of copper and iron in automotive gasoline after preconcentration on cellulose paper.[56] In the proposed procedure, samples were spotted on the paper disk to form a uniform thin film, yielding a homogeneous and reproducible interface to the XRF instrument and avoiding drastic and time-consuming treatment, by the use of concentrated acids, heating, or treatment with organic solvents.

Near-infrared (NIR) spectrometry analysis has been also used for noninvasive and nondestructive determinations, generally with exploitation of multivariate calibration algorithms. Measurements can be performed directly on solid samples such as pharmaceutical tablets,[78] polymer beads,[79] pesticide formulations,[80] and soils[81] with minimal sample preparation, thus avoiding solvent use or

sample digestion, and without physical alteration of the sample.

Solid phase spectrophotometry (SPS), sometimes called optosensing, is other approach for direct measurements on solid supports. In this technique, a solid matrix is employed for preconcentration of the species of interest, being the measurements performed, via a non-destructive (molecular) spectroscopic detector, directly on a solid support.[82] Molecular absorption spectroscopy is clearly the most frequently used detection technique in SPS procedures due to its high flexibility for adaptation to a wide variety of analytical problems.[83] However, chemiluminescence, phosphorescence, or fluorescence can also be the basis of SPS measurements with advantages related to sensitivity. Additionally, some SPS procedures exploit detection by vibrational spectroscopy.

Usually two strategies have been employed. In the former, a chromogenic reagent is previously adsorbed on the solid phase and when the sample solution is placed in contact with the solid phase, the analytes are removed from the solution forming a product with the immobilized reagent.[84] In the second case, reaction between analyte and chromogenic reagent occurs previously and the formed compound is sorbed on the surface of the solid support.[85] SPS offers a simple way to attain low detection limits, being small amounts of samples and reagents usually employed. Reduction of reagent consumption was observed when 1-(2-tiazolylazo)-2-naphthol (TAN) was immobilized on C18-bonded silica support for the flow injection determination of zinc based on the reversible analyte retention.[86] A valuable reduction in the reagent consumption from 1 mg per determination in the batch procedure[87] to <1 μg per determination was achieved when SPS was employed.

A greener analytical procedure based on FI–SPS was also proposed for iron determination. Iron(II) was reversibly retained on TAN immobilized on C18-bonded silica.[88] The metal ion was eluted with a small volume of a diluted acid solution without removing the immobilized reagent, which can be used for at least 100 determinations. In this work, other chemicals (buffer and reducing agent) were carefully selected considering the analytical performance and toxicity. The FI–SPS procedure was 10-fold more sensitive in comparison to procedures

based on measurements in solution, in which higher sample and reagents volumes were employed.[89]

SPS also can also be employed for quantification of non-metallic species. The determination of sulfide based on the oxidative coupling of two molecules of *N,N*-dimethyl-*p*-phenylenediamine (DMPD) with H_2S, in the presence of Fe(III), with subsequent retention and measurement of formed methylene blue on C18 is an example.[90] The FI–SPS method involves lower reagents and sample consumption when compared with the batch procedure that includes a solid-phase preconcentration and spectrophotometric measurements in solution.[91] A 50,000 µL sample volume was necessary when the batch methodology was employed, while 500 µL was used by FI–SPS method.

The performance of different spectrophotometric procedures for determination of total phenols based on reaction with 4-aminoantipyrine was compared.[92] The reaction product was extracted with carbon tetrachloride or, in a greener alternative, with C18-bonded silica. Measurements with the second strategy were carried out after elution with methanol or directly on the solid support. Detection limits were estimated as 8, 11, and $0.4\,\mu g\,L^{-1}$, for LLE, SPE, or SPS, respectively. An improved detection limit is achieved by SPS because the inherent dilution in the elution step is avoided.

Solid surface luminescence, the analytical measurement of the fluorescence or phosphorescence of a component sorbed on solid materials, has been demonstrated to be a useful and rapid approach with application to biological, pharmaceutical, and environmental samples, without needing a pretreatment step in the analysis, reducing sample and reagents volumes. A solid-phase fluorescence spectroscopic batch procedure for salicylic acid in drug formulations was based on the sorption of the analyte from an aqueous solution on a Sephadex anion exchanger gel. The equilibrated gel was transferred to a 1 mm quartz cell and the native fluorescence of the sorbed analyte was directly measured. The procedure did not require any sample pretreatment other than its dissolution.[93]

Although native fluorescence has been the main approach used in solid surface measurements, phosphorescence and fluorescence of metal complexes have also been exploited. Lanthanide-sensitized luminescence is a widely used strategy to improve sensitivity and selectivity. The procedure consists on forming a chelate between the lanthanide ion and the analyte previously to its retention on the solid surface, allowing the concentration of the complex in the sensing support, with direct measurement of the luminescence signal.[94,95] The use of a flow-through solid-phase terbium-sensitized luminescence system, for example, was described for the determination of fluoroquinolone norfloxacin in biological fluids. A chelate between the terbium ion and the analyte was formed on-line previously to the sample injection into the carrier stream. The chelate was then transported toward the flow-through cell, in which it was retained on a cationic Sephadex resin, developing the corresponding luminescence signal. Afterward, an ethylenediaminetetraacetic acid solution was used as eluting agent, in order to regenerate the sensing zone.[95]

A solid-phase vibrational spectrometry-based methodology has been developed for caffeine determination in commercial energy drink samples. The Raman spectrum of caffeine, sorbed on a C18 solid-phase support packed into a glass tube of 5 mm i.d., was obtained directly between 3500 and $70\,cm^{-1}$. The authors emphasized that the procedure reduced the reagent consumption and waste generation when compared with those based on chromatography, thus being an environmentally friendly methodology, which eliminates the use of organic solvents, except the 3 mL of methanol per sample, reducing the waste generation to 42 mL per hour.[96]

Cloud-Point Extraction

The cloud-point phenomenon consists in phase separation when an aqueous surfactant solution is disturbed by heating, pressure, or addition of a suitable substance. The process yields two isotropic phases—one containing most of surfactant and hydrophobic species extracted from the solution (named surfactant rich phase) and a diluted aqueous phase containing surfactant close to the critical micelle concentration.[97] This strategy has been used for sample clean up and mainly to concentrate the analyte or the reaction product before analysis, which can be carried out by several techniques, such as atomic spectrometry, UV-vis spectrophotometry or capillary electrophoresis. The extraction process

TABLE 3   Comparison of Strategies to Improve Sensitivity in Total Phenols Determination by Reaction with 4-Aminoantipyrine (4-AAP)

Procedure	Detection limit ($\mu g\ L^{-1}$)	4-AAP consumption (mg)[a]	Waste[a]	Waste volume (mL)[a]	Ref.
LLE	1.0	20	$K_3[Fe(CN)_6]$ (80 mg), $CHCl_3$ (25–50 mL)	553	24
FIA-LPS	1.0	0.1	$K_3[Fe(CN)_6]$ (0.12 mg)	4.0	23
FIA-LLE[b]	8.0	—	$K_3[Fe(CN)_6]$, $CHCl_3$	—	92
FIA-SPE	11	0.8	$K_3[Fe(CN)_6]$ (2.4 mg), methanol (0.5 mL)	3.0	
FIA-SPS	0.4				
CPE	0.5	5	Triton X-114 (62 mg), Triton X-100 (40 mg), $K_3[Fe(CN)_6]$ (7.5 mg)	50	102

[a]Estimate per determination; [b]Reagent consumption and waste volume cannot be estimated; LLE—liquid-liquid extraction; CPE—cloud point extraction; FIA—flow injection analysis; LPS—long pathlength spectrophotometry; SPE—solid-phase extraction; SPS—solid-phase spectrophotometry.

has also been mechanized in flow-based systems.[98] In procedures involving analyte concentration, high enrichment factors (values from 10 to 100 are usual) are achieved in a single extraction by the quantitative transference of the hydrophobic species to a low-volume surfactant-rich phase. The process efficiency is favored by formation of the extractable species in a homogeneous medium, which is an advantage in comparison to conventional liquid–liquid extraction.

In addition to its analytical performance, cloud-point extraction is in agreement with the principles of Green Chemistry, because low amounts of low toxicity surfactants replace the usual toxic organic solvents. In addition, surfactants are non-flammable and present low volatility, minimizing risks in the extraction process.

Most of the applications of cloud-point extractions are focused on determination of metal ions previously to detection by UV-vis or atomic spectrometry.[99] The procedures generally involve formation of hydrophobic species by complexation with an organic ligand in a medium containing the surfactant. The cloud-point phenomenon is usually induced by increasing the temperature and the metal complexes are extracted to the surfactant-rich phase. Addition of a suitable solvent (e.g., ethanol) is often needed in order to diminish the viscosity (causing an inherent sample dilution) to make feasible sample introduction in the measurement system. In addition to the analyte concentration, minimization of matrix effects is also feasible.[100] Applications of the CPE to metal determination by spectroscopic techniques were recently revised.[101]

In analogy to the conventional procedure for total phenols determination, which exploits extraction of the reaction product in chloroform, a cloud-point extraction procedure was developed in which the product of the oxidative coupling with 4-aminoantipyrine was extracted with Triton X-114.[102] The analytical features compare favorably with the extraction with the organic solvent, yielding a preconcentration factor of 50 and a detection limit estimated as $0.5\ \mu g\ L^{-1}$.

Comparison of different strategies to increase sensitivity adopting the total phenols determination as model system is presented in Table 3. The potential of flow-based methodologies to reduce reagent consumption and waste generation is clearly demonstrated, as well as the increase in sensitivity by long pathlength spectrophotometry, avoiding the need of extraction of the reaction product and CPE to replace toxic organic solvents.

The potential of the cloud-point extraction for sample clean up was demonstrated in the determination of the insecticide trichlorfon in vegetables by HPLC-UV exploiting its catalytic effect on formation of 4-amino-4′-nitrobiphenyl.[103] The reaction product was separated and preconcentrated by CPE, yielding better recoveries (95.4–103%) than that achieved by SPE and elution with organic solvents (70.3–78.5%).

CONCLUSIONS AND TRENDS

Recent advances paved the way toward the development of sample preparation strategies and determination techniques based on reduced use of reagents, energy, time, and consequently with low generation of toxic residues. Surely this trend will be dominant in the coming decades and analytical chemistry will become an important ally for greener

approaches providing the tools to monitor the environment without negative consequences on planet-scarce resources.

The challenge to develop greener analytical procedures is higher for trace analysis, which usually requires sample treatment for improving sensitivity or elimination of matrix effects. Replacement of toxic reagents or direct measurements by non-destructive analytical techniques, the ideal strategies to attain green analytical methodologies, are not general approaches. However, greener procedures can be attained by minimizing the reagent amounts and waste generation, exploiting alternatives such as miniaturization, automation, and use of immobilized reagents in reversible systems. These strategies can yield significant results, especially for large-scale analysis, reducing costs related to analytical determination and waste treatment. The main trend to analyte determination is the improvement of detection capability and selectivity aiming the direct analyte determination.

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