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An Overview of Green Analytical Techniques in the Spectrometric Analysis of Environmental and Biological Samples

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ABSTRACT This literature survey presents in a nutshell different parameters for the effectiveness of the green spectrometric procedures, which have been applied to the determination of organics, inorganics, and metal ions in different matrices. The following issues were considered: the main aspects of miniaturization, reagent replacement, reduction of wastes, and on-line recovery and detoxification, which made the analytical procedures sustainable. Also, a discussion of analytical characteristics along with spectrometric methodologies and applications is included.

KEYWORDS Biological, environmental, green analytical techniques, spectrometric analysis

INTRODUCTION

Traditionally, analytical chemistry involves the use of solvents and reagents, which are frequently hazardous and put at risk both the human beings and environment. Green Analytical Chemistry is defined as environmentally benign analytical methodologies.^[1] It is a science-based nonregulatory and economically driven approach for attaining the goals of environmental protection.^[1,2] Green Chemistry (GC) is the application of a set of principles^[2] that reduces or eliminates the use or generation of hazardous substances in the design, manufacture, and use of chemical products. In practice, GC is taken to cover a much wider range of issues^[3] using and producing chemicals with minimum waste. GC also encompasses reducing other associated environmental impacts^[4] including reduction in the amount of energy used in chemical processes. In fact, GC is not different from traditional chemistry in as much as it embraces the same creativity and innovation that has always been central to classical chemistry. With an increase in environmental consciousness throughout the world, there is a challenge for chemists to develop new products, improved processes, and better services that achieve necessary social, economical, and environmental objectives. Since the nature of chemicals and types of transformation are widely varied, so are the GC solutions that have been proposed. Thus there is a constant demand to the development of greener, yet reliable, analytical

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procedures, because several current analytical methods employ highly toxic reagents, resulting themselves in a potentially negative environmental impact. For developing a new analytical procedure, the amount and toxicity of the wastes generated are as important as any other analytical feature.^[5] Although chemists are environmentally concerned, they hardly use the term "green." So, preliminary studies in this field used the terms "environmentally friendly" methods^[6] or "clean" methods.^[7] Nevertheless, after the publication of the review of Anastas^[8] on Green Analytical Chemistry (GAC), more publications are coming up related to the use of friendly methodologies. With the end in view, the present literature survey has been conducted, which will include analytical methodologies suitable to greener previously available methods to solve real problems.

Chemical analysis and monitoring play an important role in estimation to the extent of the influence of chemists upon the environment. Recently a large number of analytical methodologies have been introduced in practice including incremental improvements in established methods by changing or modifying reagents and solvents, reducing chemicals, or incorporating on-line detoxification steps. On the basis of the literature data and observation of current trends in chemical analysis and monitoring, it can be stated that rapid progress is being made in the development of those analytical methodologies that assure observation of the principles of GAC.^[9]

To our knowledge, only five reviews^[1,8,10–12] have been published on GAC although more works are being published on environmentally friendly methodologies. The present review will include an overview of green techniques, especially concerning spectrometry in the analysis of environmental and biological samples.

CLEAN PRETREATMENT METHODOLOGIES

Analytical procedures typically involve a number of equally relevant steps for sampling, sample preparation, isolation of target compounds, identification, quantification, and data handling. In many application areas, sample preparation is still the bottleneck of such procedures. This is especially true in the case of environmental and biological sample analysis where sophisticated and powerful hyphenated

systems for instrumental analysis of the final extracts contrast sharply with traditional high reagent consumption, large-scale, and labor-intensive procedures that are based on liquid–liquid extraction or Soxhlet extraction for sample pretreatment. Several analytical steps involved in such procedures are usually carried out off-line, which make them tedious and time-consuming, prone to loss of analytes, and at the same time prone to contamination, because of the continual manual manipulation of the extracts. In recent years, much effort has been devoted to eliminate these drawbacks. The principles of GC^[1,2] may be utilized to formulate the major features depicting the green analytical methodologies. The following targets are considered to be the vital ones^[13]: reduction of the amounts of reagents, elimination or reduction of the amount of solvents, and reduction of energy consumption, together with the minimization of the contact of the operator with samples and reagent and the detoxification of wastes.

It has been demonstrated that water at supercritical (400°C, 350 bar) and superheated (250°C, 50 bar) conditions can be used as an alternative to organic solvents, for extraction of polycyclic aromatic hydrocarbons (PAHs), n-alkanes, alkylbenzenes, and polychlorinated biphenyls (PCBs) from river sediment and soil samples.^[14–16] It has been also shown that water at temperatures above 100°C, under sufficient pressure to remain as a liquid, is capable of replacing organic-aqueous mixtures used in reversed-phase HPLC^[17–19] and steam water has been used as a mobile phase for gas chromatography.^[20]

A good number of green analytical procedures have been reported to extract and concentrate analytes. For example, in comparison to classical liquid–liquid extraction, extractions by using ultrasound,^[21] microwave-assisted treatment,^[22,23] supercritical fluid,^[19,24–26] membranes, and cloud-point^[27,28] have been reported in which amount of organic solvents used could be reduced or avoided.

Ultrasounds are used to extract analytes with a drastic reduction of solvents and energy consume or without the use of organic solvents. Just by using ultrasound water bath the analytes are homogenized and the supernatant, after centrifugation, is collected for analysis. Although the sonication-assisted approach has not yet been studied extensively, some applications^[21] have already demonstrated the

TABLE 1 Clean Pretreatment Methodologies

Analyte(s)	Matrix	Pretreatment	Ref.
Linear alkylbenzene sulfonates	Sediments	Soxhlet extraction with water using focused microwaves with an on-line preconcentration/derivatization/detection manifold through FI interface for fully automated screening	14
Linear alkylbenzene sulfonates	Sediments	Superheated water extraction with on-line preconcentration/derivatization/detection through FI interface	15
Nitrated polycyclic aromatic hydrocarbons	Soil	Static pressurized liquid extraction with a filtration-preconcentration system through a FI interface using water as leaching agent	16
Bioactive substances like proteins and peptides	Medical, pharmaceutical preparations	Used functional polymers like poly(N-isopropylacrylamide) as chromatography column modifier, using aqueous media as a mobile phase	17
Neosaxitoxin, saxitoxin, gonyautoxins	Shellfish	Separation on a μ Bondapak NH_2 column using water and acetate buffer as mobile phase	18
Flavanoid glycosides, amino acids	Medicinal plants	Accelerated solvent extraction using water and supercritical fluid extraction using CO_2 and 10% EtOH	19
Acetophenone, <i>m</i> -cresol	Aqueous solution	Solid phase extraction traps packed with polystyrene divinylbenzene or poly (divinylbenzene-co-N-vinylpyrrolidone) and their subsequent release using superheated water or steam	20
Oxytetracycline, sulphadimidine	Cow milk	Homogenization with an inorganic acid solution using an ultrasound homogenizer followed by centrifugation	21
Organophosphorus pesticides	Tomato, lettuce, pepper	Microwave-assisted micellar extraction using nonionic surfactants polyoxyethylene 10-lauryl ether and oligoethylene glycol monoalkyl ether	22
Polychlorinated biphenyls, chlorobenzenes	Fly ash	Microwave-assisted extraction	23
Antioxidant compounds	Vegetal materials	Extraction with supercritical CO_2	24
Organochlorine and organophosphorus pesticide multiresidues	Medicinal plants	Supercritical fluid extraction	25
Cocaine and its metabolites	Blood, urine	Supercritical fluid extraction	26
Phenoxy herbicides	Bovine milk	Liquid-liquid-liquid microextraction with a hollow fiber membrane	27
Volatile, semi-volatile organic compounds	Snow	Solid-phase microextraction using a divinylbenzene coated polydimethyl-siloxane fiber with a film thickness of 65 μm	28
Methanol	1,1-Dimethyl propyl methyl ether	Organic-organic separation by pervaporation using α -alumina supported NaY-zeolite membrane	31
Huperzine A and huperzine B	Huperzia serrata herbal extraction	Removal of impurities using Amberlite XAD-H using 1% H_2SO_4 followed by separation on polystyrene-based porous microsphere PST column while mobile phase consisted of water and ethanol	32
Phenolic compounds	Natural water	Multi-syringe FI system with on-line preconcentration using Amberlite XAD-4 SPE followed by elution with 0.1 M NaOH	33

Phenols	Soil	Microwave assisted micellar extraction using polyoxyethylene 10-lauryl ether	34
Phenols	Drain water	Headspace water-based liquid phase microextraction	35
Narasin	Poultry tissue	Solid phase extraction	36
Imidacloprid	Fruit and vegetables	Two stage solid phase extraction clean up on aminopropyl/florisil cartridges using binary mixtures of solvents	37
Organochlorine and organophosphorus pesticides	Herbal infusions of <i>Passiflora L.</i>	Headspace solid-phase microextraction using fiber coated with polydimethyl siloxane-poly(vinyl alcohol)	38
Floral oil	Rosa canina	Superheated water extraction followed by C ₁₈ -solid-phase extraction	39
Anthocyanins, total phenolics	Grape skin	Pressurized liquid extraction using methanol/acetone/water/HCl mixture found to be effective	40
Sodium saccharin and sodium cyclamate	Table-top sweeteners	Reagent free determinations	41
Malathion	Pesticides	Reagent free determinations	42
Tetracyclines	Milk	Solid phase extraction using Isolute C ₁₈ end-capped syringe column using water as eluent	43
Fumonisin	Maize products	Static extraction with methanol–water, acetonitrile–methanol–water–ethanol–water, and only water in reversed-phase liquid chromatography	44
Nitrated polycyclic aromatic hydrocarbons	Soil	Pressurized liquid extraction	45
2-Thiobarbituric acid	Palm olein	Thermal oxidation	46
Alkaloids	Seeds	Supercritical fluid extraction	47
Polycyclic aromatic hydrocarbons	Environmental solid samples	Pressurized liquid extraction	48
Diverse classes of biologically active compounds	Steroids, benzodiazepines, NSAIDs, tricyclic antidepressants, β -adrenergic blocking agents, mixtures of purines and pyrimidines	Extraction with ethoxynonafluorobutane	49
Fluorinated compounds	Waste stream from pharmaceutical production	Aerobic biodegradation	50
Metal ions	Anthracene, acenaphthene, biphenyl, naphthalene, triptycene, naphthalene derivatives of naphthol	Use of aqueous biphasic systems	51
Polycyclic aromatic hydrocarbons	Plant materials	Use of less toxic aliphatic alcohols as mobile phase	52
Natural products	Environmental solid samples	Supercritical fluid extraction	53
Organic pollutants		Pressurized extraction	54

potential of sonication for miniaturized, rapid, relatively inexpensive and quantitative dynamic extraction and on-line purification.

Microwave-assisted extraction (MAE) reduces or avoids the use of organic solvents for extraction. Even water is used as a safe and environmentally friendly solvent in microwave-assisted extraction. The evaluation of extraction efficiency shows that MAE has a high extraction efficiency compared to Soxhlet extraction when water content is lower than 60%.^[23] Furthermore, there is an hour to minute reduction in extraction time with MAE.^[29]

Supercritical fluid extraction (SFE), based on the utilization of a CO₂ under supercritical conditions, is a technology suitable for extraction and purification of a variety of compounds. The use of fluids under supercritical conditions was found to have substantial advantages in terms of higher efficiency and lower time consumption as compared with conventional techniques.^[19,24–26] Despite SFE being a miniaturized and solvent-free extraction method novel, robust, and often less expensive extraction techniques like pressurized liquid extraction (PLE) have emerged in the field of green analytical techniques. PLE, introduced in the mid-1990s,^[30] uses a typically dispersed sample in a drying or inert sorbent such as sodium sulphate. Hydromatrix or diatomaceous earth is packed in a stainless steel cell and, once inserted in a closed flow-through system, extracted with the selected solvent at temperatures above its atmospheric boiling point. Since the solvent must be kept liquid during extraction, relatively high pressures are also applied. The efficiency, rapidity, and moderate solvent consumption are the reasons for its widespread application of PLE.^[16]

During the last decade researchers have concentrated on carrying out various works with reduction/elimination of reagents and solvents. For example, extraction of surfactants,^[14,15] pesticides,^[22,25,27,38,42] antibiotics,^[21,43] phenols,^[33–35,40] alkaloids,^[26,47] bioactive substances,^[17,49] polycyclic aromatic hydrocarbons^[16,45,48,52] and other organic compounds,^[18,20,23,24,27,28,31,32,37,39,41,44,46,53] fluorinated compounds,^[50] and metal ions^[51] have been conveniently extracted from most of the environmental and biological matrices without the use of organic solvents.

Table 1 summarizes the main principles of different clean pretreatment methodologies proposed in the literature.

GREEN SPECTROMETRIC DETERMINATION PROCEDURES

The increasing demands for fast, well-balanced, cost-effective, and green analytical methods are a major incentive to improve the classical procedures used for measurement in real sample analysis. In most classical procedures, the use of rapid and powerful instrumental techniques for the final separation and detection together with the automation and miniaturization of procedures and instruments have reinforced the use of spectrometric methods as a green alternative. The efforts made in this field in the last 10–15 years have led to the adaptation of existing methods and the development of new techniques to save time and chemicals, and to improve overall performance. One way has been to develop at-line or on-line and frequently automated systems. In these approaches, miniaturization has been a key factor in designing integrated analytical systems to provide higher sample throughput and/or unattended operation.^[7] Micro- or miniature devices have been developed by various authors for flow analysis to obtain excellent performance. One of the advantages of miniaturization is small reagent consumption and a field-affordable size for sustainable environmental analysis. The miniature device is not only for operational usefulness, but also for the performance of the instrument.^[55] Miniaturized methods were preferred^[56] due to their low operating costs, environmentally friendly character, and suitability for hyphenated techniques. Additionally, on-line decontamination strategies have provided fully mechanized procedures that avoid collateral effects of the spectrometric measurements.

Table 2 provides some examples of clean spectrometric methods published in recent years with an explanation of the clean aspects of the used procedures and the main analytical features of methods employed. From these examples, it can be concluded that greener the spectrometric measurements not involves necessarily to sacrifice the performance of classical methods and thus it is compatible with the search for improved characteristics of methods and their sustainability.

On concerning the different methods proposed it can be seen that they can be classified as a function of their miniaturization, automation, or the incorporation of on-line decontamination or reagent recovery units.^[1]

TABLE 2 Green Spectrometric Determination Procedures

Analyte/sample	Clean methodology	Analytical characteristics	Ref.
Formetanate in mineral and tap water	On-line microwave assisted alkaline hydrolysis of analyte <i>m</i> -aminophenol followed by reaction with <i>p</i> -aminophenol (PAP) and KIO ₃ to form blue indophenol dye ($\lambda_{\text{max}} = 576 \text{ nm}$)	Calibration: up to 99.1 μM DL: 2.1 μM RSD: 4.3% Recoveries: 106.15 Sampling rate: 12/h	57
Propoxur in natural water	FIA alkaline hydrolysis of analyte to produce 2-isopropoxyphenol followed by treatment with <i>p</i> -aminophenol (PAP) and KIO ₄ to yield indophenol dye ($\lambda_{\text{max}} = 600 \text{ nm}$). The waste was irradiated at 254 nm in the presence of TiO ₂ to degrade excess PAP and reaction products to avoid environmental pollution	Calibration: up to 100 $\mu\text{g/mL}$ DL: 0.12 $\mu\text{g/mL}$ RSD: 0.8% Recoveries: > 99%	58
Cyclamate in sweeteners	Flow injection procedure exploits the reaction of analyte with nitrite in acidic medium followed by spectrophotometric determination of excess reactant by iodometry	Calibration: up to 3 mM/L DL: 30 $\mu\text{M/L}$ RSD: 1.7% Sampling rate: 60/h	59
Propy-phenazone and caffeine in pharmaceuticals	FI measurements on pharmaceuticals dissolved in chloroform were carried out by FTIR at 1595 cm^{-1} for Propyphenazone and at 1712 cm^{-1} for caffeine. A distillation unit was incorporated into the FI-manifold for on-line recycling of chloroform avoiding the accumulation of toxic waste	DL: 0.03 mg/mL Propyphenazone 1.5 mg/mL caffeine RSD: 1–2.1%	60
Resorcinol in waste	A stream of 50 $\mu\text{g/mL}$ mixed with a stream of 0.2 mM KIO ₄ and the resulting solution merged with 6 mM NaOH into which the analyte injected. The absorbance of the resulting mixture measured at 540 nm. The waste obtained was mixed with a slurry of 0.5 g/L TiO ₂ in 0.22 M HCl and rolled on an UV lamp and irradiated at 254 nm thus affecting detoxification	DL: 16 ng/mL RSD: 0.6% Sampling rate: 60/h	61
Chlorpyrifos in fruits	FI chemiluminescence reaction of the analyte with luminal and periodate both immobilized on an ion-exchange column	Calibration: 0.48–484 ng/mL DL: 0.18 ng/mL RSD: <3% Recoveries: 94.4–107.4%	62
Buprofezin in pesticide formulations	On-line extraction with acetonitrile followed by IR spectral measurement at 2091 nm avoids contact by the operator with toxic products	DL: 5 $\mu\text{g/mL}$ RSD: 0.06% Sampling rate: 30/h	63
Phenols in water	Flow manifold comprises 4 solenoid micro-pumps employed for reaction between sample, sodium nitroprusside, hydroxylamine hydrochloride, and buffer (pH 12.3) followed by spectrophotometric determination at 700 nm. The method avoids the use of 4-aminoantipyrine-chloroform	Calibration: 50–3500 nM/mL DL: 13 ng/mL RSD: 0.5% Recoveries: 92–105% Sampling rate: 65/h	64

(Continued)

TABLE 2 Continued

Analyte/sample	Clean methodology	Analytical characteristics	Ref.
Diuron in pesticide formulation	Near infrared based methodology was based on pesticide extraction with acetonitrile followed by measurement between 2021 and 2047 nm.	DL: 0.013 mg/g RSD: 0.03% Sampling rate: 120/h	65
Anionic surfactant in water	Multicommutation approach for spectrophotometric procedure using methylene blue followed by chloroform extraction provided a 35 times reduction of the waste containing organic solvents	Calibration: 0.2–1.7 mg/L DL: 1.7 µg/L RSD: 5.9% DL: 0.092 ng/mL	66
2,3,7,8-Tetrachlorodibenzo- <i>p</i> -dioxin	Solid–liquid extraction by using laser-excited time resolved shpol'skii spectroscopy		67
Dibenzo[a,l]pyrene in water	Solid–liquid extraction by using laser-excited time resolved shpol'skii spectroscopy	Calibration: 10 ng/mL DL: 0.003–0.015 ng/mL RSD: 3.2–6.4% Sampling rate: 4/h DL: 0.15 ng/note RSD: 6% Recoveries: 98–101% DL: 90 ng/mL RSD: 4% Recoveries: >78%	68
Cocaine in Euro bank notes	Analyte extracted with methanol by vortex agitation, evaporated, reconstituted in methanol, and analyzed by GC MS MS		69
Sulfamonomethoxine, sulfadimethoxine, and their N4-acetyl metabolity in chicken plasma	The sample mixed with 4 M ammonium sulphate solution, centrifuged, analyzed by HPLC on polyethylene glycol reverse-phase column with 0.001 M sodium acetate as mobile phase		70
Malondialdehyde in human serum	Micro-extraction of analyte thiobarbituric acid adduct in Aliquot 336 in ethyl acetate followed by spectrophotometric assay at 543.1 nm	Calibration: up to 10 µmol/L DL: 0.19 µmol/L RSD: 0.7–0.8% DL: 12 µg/mL	71
Malathion in pesticide formulations	Emulsifiable concentrates directly injected into 3 mL closed FIA manifold in which 2 mL CHCl ₃ recirculated and homogenized sample was measured by FTIR		72

Caffeine in tea	Extraction with ammonia and chloroform and direct measurement by FTIR requiring less requirement of organic solvent and less time consumption	DL: 1 µg/mL	73
Carbaryl	Flow system based on multicommutation and binary sampling for the spectrophotometric determination ($\lambda_{\max} = 596 \text{ nm}$) of the analyte after its alkaline hydrolysis to <i>p</i> -aminophenol.	DL: 26 µg/L Sampling rate: 70/h	74
Nitrates in natural water	FI system with anion-exchange column for separation of the interfering species, followed by treatment with HClO_4 and spectrophotometric determination at 201 nm	Calibration: 0.5–25 mg/L DL: 0.1 mg/L RSD: 0.7%	75
Iron in waters	The leaf extract in dilute HCl /acetate buffer (pH 4.8) being used as an alternative reagent to quantify iron using a FI system at 570 nm	Calibration: 1–10 µg/mL DL: 1 µg/mL RSD: 3–10% Recoveries: 95–97% Sampling rate: 20/h	76
Cd in environmental samples	On-line solid phase extraction using Chele $\times$ 100 column at pH 7 followed by FAAS	DL: 17 ng/mL	77
Te in milk	Multicommutation based on use of solenoid valves followed by HGAFS reduces the reagent consumption as well as generation of effluents	Recoveries: 100–104% Calibration: up to 0.5 ng/mL DL: 0.2 ng/L RSD: 2.1%	78
Hg in milk	Multicommutation followed by cold vapor AFS reduces waste generation	Sampling rate: 85/h DL: 0.011 ng/g RSD: 3.4%	79
Iodine value in olive oil	Parallel flow injection spectrophotometry ($\lambda_{\max} = 392 \text{ nm}$) using the matrix diluted at 1:50 in <i>n</i> -propanol and injected into 6 mM IBr in acetic acid carrier	Sampling rate: 70/h Calibration: 9–125 g iodine/100 g oil RSD: 0.4–1.1% Sampling rate: 60/h	80

Regarding the type of analytes considered different strategies can be found for both, organic and inorganic compounds with special strategies for the determination of metal ions.

Green Determination of Organics

Vibrational spectrometry methods, based on both near-infrared^[63,65] or middle-infrared^[60,72,73] and Raman spectrometry^[41,42] have been extensively used for green spectroscopy determination of organics based on the automation of measurements^[60,63,65,72,73] and the replacement of chlorinated solvents^[63,65] additionally than on the direct analysis of samples without any previous treatment.^[42]

On the other hand, the automation of UV-Vis measurements can reduce drastically the amount of reagents consumed in the spectrometric determination of organics^[57–59,61,64,66,72] and can incorporate on-line photodegradation processes for the detoxification of wastes^[57,58,61] or on-line recovery of solvents based on the use of distillation units.^[60]

Chromatographic-based determination methods can be greened through the replacement of toxic solvents^[70] and the improvement in sample pretreatment.^[69,19–28]

Green Determination of Anions

Green determination methods have been proposed in the literature for the spectrometric determination of nitrates in waters^[5] and ions in industrial oils.^[81]

An approach for performing continuous liquid–liquid extraction under high pressure and temperature^[81] has been applied for the separation of inorganic ions (e.g., Cl^- , F^- , SO_4^{2-}) from used industrial oils. Pressurized acidified hot water was used as the extractant. This simple method for anions extraction in used oils presents several positive aspects: (1) no complex pretreatment of the oil; (2) low cost of extractant (5% HNO_3); (3) low consumption of energy; (4) short extraction time (~ 10 min); and (5) high efficiency of the extraction process (79.4–97.1% for Cl^- , 79.2–100% for F^- , and 80.4–99.8% for SO_4^{2-}).

Green Determination of Metal Ions

The automation of classical atomic spectrometric methods for metal ions determination has been

proposed for greening these methodologies^[77–79] additionally than the use of alternative natural reagents such as chromophore agents.^[76]

Naphthol- and resorcinol-based azo dyes have been studied as metal ion extractants in aqueous biphasic systems as a function of pH. The distribution ratios of Fe(III), Co(II), and Ni(II) were enhanced by several orders of magnitude at high pH in contrast to the behavior of Cs(I), Cd(II), and Eu(III) whose partitioning behavior was largely unaffected by the presence of these extractants at any pH.^[51]

Continuous pressurized liquid–liquid extraction with 20% HNO_3 + 1 M KCl + 10^{-3} M EDTA has been developed for the extraction of metals (V, Ni, Zn, Fe, and Cu) from the oil resulting from recycled tires. Recoveries $>90\%$ have been obtained.^[82]

On the other hand, the green spectrometric determination of metal ions has incorporated on-line detoxification strategies like metal passivation^[79] thus incorporating approaches developed for large-scale remediation of soils and waters.

A GC approach was developed by Cathun et al.^[83] as an option for remediation of toxic mercury in the environment. It was found that organic and inorganic mercury pollutants could be mineralized in the environment with cyclodextrins. The bound mercury compounds resisted biodegradation and were found to be non-toxic to environmental microorganisms under laboratory conditions. The toxicity of the Hg-contaminated soil decreased to 80% after treatment with cyclodextrins. A solution of 1% cyclodextrins was deemed sufficient for inclusion of Hg in both soil and water and this methodology could be incorporated to greener flow injection methods employed for mercury speciation.

CONCLUSION

The ultimate value of Green Chemistry lies in its applicability for the new millennium. So the challenges to reduce the waste, the toxicity of chemicals, and the amount of energy used, while still providing the best output that the society needs, are overcome through Green Analytical Chemistry.

The increasing demand for faster, cost-effective, and environmentally friendly analytical methods is a major incentive to improve the classical procedures used for sample treatment in real sample analysis. Examples of application of Green Chemistry in the

spectrometric analytical methodologies have been presented. The principles of this approach include primary elimination or at least reduction of the amounts of reagents and solvents during laboratory work, particularly at the sample preparation stage, strong reduction of wastes, and on-line recovery or decontamination of analytical residues.

Thus, if we can develop an efficient methodology for chemical analysis (economically and technologically viable), which incorporates human and environmental safety as its core principle, then truly we can have sustainable green chemical analysis processing and in this sense it can be evidenced that spectrometry-based methods are themselves a green alternative^[12] and that based on the improvement of sample preparation and determination conditions the spectrometric methods can be additionally greened.^[1]

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