

GREEN ANALYTICAL TECHNIQUES, SOLVENTS AND SAMPLE PREPARATION STRATEGIES FOR EFFECTIVE BIOACTIVE COMPOUND ANALYSIS

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ABSTRACT

As environmental consciousness grows in analytical chemistry, there is a rising demand for eco-friendly sample preparation techniques. Green analytical chemistry emphasizes the creation of environmentally responsible analytical methods, advocating for direct analysis approaches that reduce sample processing, thereby lowering energy and reagent usage and minimizing waste production. Sample preparation and extraction are pivotal stages in developing analytical methods that can be optimized to adhere to green analytical chemistry principles. Techniques like solid-phase microextraction (SPME) and liquid-phase microextraction (LPME) offer a sustainable alternative by miniaturizing the pre-concentration step, contrasting traditional large-scale extraction methods. Despite their promise, these microextraction methods are not yet widely adopted in standard analytical practices, even though they are commonly used as benchmarks in the field. It is important to note that microextractions can replace large-scale

extractions in routine methods, aligning with green analytical chemistry principles. This review assesses the environmental friendliness, benefits, and drawbacks of prevalent SPME and LPME techniques suitable for gas chromatography, focusing on aspects such as

automation, solvent usage, safety, reusability, energy efficiency, time efficiency, and ease of handling.

KEYWORDS: Green analytical chemistry, Extraction techniques, Liquid-liquid extraction, Solid-phase extraction, Sample preparation, Greenness assessment.

INTRODUCTION

Analytical chemistry has long been aware of the environmental consequences of its practices. The foundational principles of Green Chemistry were introduced by Anastas and Warner in 1999.^[1] Since then, these principles have been evaluated and refined by researchers for Green Analytical Chemistry (GAC).^[2,6] Ideal green analytical methods, based on Green Chemistry principles, should include:

- Direct, automated, miniaturized, and multi-analyte approaches.
- Use of minimal sample sizes, fewer processed samples, and simplified pre-treatment.
- Reduced chemical consumption and waste production.
- Lowered hazards and risks.
- Improved work safety and environmental sustainability.

The Green Analytical Procedure Index (GAPI) assesses all stages of an analytical method, including sampling, sample preparation, reagents, instrumentation, and determination, using a multicriteria decision analysis approach.^[7] It creates a visual symbol with five pentagrams, each representing a different step of the analytical process.^[8]

Green analytical features

Analytical Chemistry, as a science focused on obtaining detailed information about sample composition, must adhere to specific principles to ensure the accuracy of both qualitative and quantitative analyses. The methods used should aim to acquire selective information about target analytes, free from interference by matrix components or similar compounds. Additionally, the methods must be sensitive enough to detect and quantify target compounds in the selected sample with precision and robustness. Therefore, the primary analytical features of a procedure designed to address an analytical problem include accuracy, sensitivity, selectivity, and precision, alongside representative information obtained through a well-designed sampling program. However, it is also important to consider the robustness of measurement conditions and practical aspects such as speed, cost, and environmental impact, as these factors can influence the overall effectiveness of the method.^[9] In this context, the

green aspects of a method have become a critical criterion for evaluating and comparing different methodologies. Green properties emphasize minimizing the environmental impact of analytical methods while maximizing operator safety. This includes reducing reagent and energy consumption, minimizing equipment usage, and limiting waste generation. Nevertheless, it is essential to recognize that the greenest method is not merely the one with the lowest environmental footprint, but the one that effectively solves the analytical problem with the least overall impact on the environment. Several systems have been developed to assess and compare the effectiveness of green chemistry techniques against traditional methods, providing a framework for evaluating their environmental and practical benefits.^[10,14]

These systems are grounded in the 12 Principles of Green Chemistry, which have been adapted and redefined as the 12 Principles of Green Analytical Chemistry. Many undergraduate and graduate programs have begun integrating green chemistry principles into their curricula, adapting them to traditional and widely used chemical techniques. Similarly, numerous research groups are striving to transform their testing methods to align with the principles of green chemistry.^[13,19] Analytical chemistry is one of the fields actively working to incorporate green chemistry principles into its instrumentation and methodologies. One of the most significant challenges in this area is the development of more sustainable and efficient sample preparation techniques.^[20]

Therefore, the development and implementation of green extraction methods are essential to address many of the pressing challenges in modern analytical determinations. The aim of this manuscript is to highlight the latest advancements in green sample treatment methodologies developed in recent years, with a particular focus on those designed to minimize environmental impact and reduce risks to operators. These innovative methodologies have been assessed from a green chemistry perspective, utilizing the AGREE prep green metric tool to evaluate and quantify the greenness of current sample treatment approaches.^[21]

Overview of sample preparation strategies and their impact on analytical methods greenness

A myriad of sample preparation strategies exist as reliable, go-to methods for analytical chemists. Throughout the history of the field, these traditional methods have evolved to become increasingly efficient and precise. Despite their widespread use, some of these techniques such as liquid-liquid extraction (LLE) and Soxhlet extraction—are now being

reconsidered because they do not align with the principles of Green Analytical Chemistry.^[22] Notably, the preparation and extraction stage of an analytical procedure is often the most environmentally harmful component. Early efforts to develop greener methods employed various forms of heat, pressure, or radiation to enhance the extraction process. Techniques such as ultrasound-assisted extraction (UAE), pressurized solvent extraction (PSE), microwave-assisted extraction (MAE), and supercritical fluid extraction (SFE) significantly improved the environmental sustainability of extraction compared to traditional methods.

UAE involves exposing the sample to ultrasound waves, which agitate the molecules and accelerate the extraction process, thereby enhancing extraction efficiency. PSE operates by utilizing solvents near their supercritical region, where elevated temperatures enable more efficient extraction. MAE employs microwaves to rapidly heat both the solvent and the sample within a sealed container, offering a more efficient extraction process while minimizing the volume of solvents needed, as it is more environment friendly and safe to use.^[23]

Another sample preparation method, known as Quick, Easy, Cheap, Effective, Rugged, and Safe, involves extracting analytes using an organic solvent, separating the phases through the addition of a salt, and purifying the supernatant via dispersive solid-phase extraction (dSPE). As the name implies, these kits perform the same analysis but on a smaller scale.^[24,25]

Solid phase extraction

Solid-phase extraction (SPE) is a widely used method for sample preparation. In this technique, solutes are adsorbed onto a short column containing a compatible solid sorbent after an aqueous sample is passed through it.^[26] The target analytes are then eluted from the sorbent using small volumes of highly eluting organic solvents leading to their concentration and enrichment. SPE utilizes small quantities of solvent and generates minimal waste, making it an environmentally friendly technique. It can be automated using simple, cost-effective equipment, enhancing laboratory throughput while improving accuracy and precision. Despite its advantages, SPE has certain limitations that must be addressed to ensure effective analyte extraction. One issue is the potential unevenness of the packing material's bed, which can reduce extraction efficiency. This problem can be mitigated by using commercially available cartridges. Additionally, some traditional sorbents exhibit low selectivity, leading to insufficient retention of highly polar compounds. Another challenge is the competition for retention between analytes and the sample matrix, which can significantly

impact analyte recovery. Therefore, thorough optimization of the process is essential to achieve successful and reliable analyte extraction.^[27]

Solid phase micro extraction

Solid-phase microextraction (SPME) integrates the processes of extraction and enrichment into a single, solvent-free technique, simplifying sample preparation. This method was first developed in 1990 by Arthur and Pawliszyn. It employs a silica fiber coated with a suitable adsorbent phase which directly extracts analytes from the sample and concentrates them on the fiber's coating. This approach eliminates the need for solvents and streamlines the extraction process.^[28] SPME is a technique that employs an extraction phase coated onto a solid support. This thin coating layer, typically ranging from 7 to 250 µm in thickness, acts as the extraction phase, where analytes diffuse from the sample matrix into the coating.^[29] This occurs either by partitioning into the bulk of the coating or by adsorbing onto its porous active surface until equilibrium is achieved. The amount of analyte extracted by this method depends on the equilibrium established between the sample matrix and the extraction phase.^[30]

Extractions in green analytical chemistry

Microwave assisted extraction

Microwave-assisted extraction (MAE) is a technique that utilizes microwave energy to heat a sample, inducing changes in the cellular structure of the material. These changes enhance the release and extraction of target compounds from the sample matrix.^[31] In recent decades, MAE has gained considerable recognition as an effective method for extracting bioactive compounds from various sources, especially in the context of valorizing by-products generated from agro-industrial processes.^[32] The full range of microwave frequencies, spanning from 300 MHz to 100 GHz, can be utilized for extraction. The conventional microwave ovens typically operate at a fixed frequency of 2.45 GHz. The key advantages of MAE include rapid heating and the ability to achieve high temperatures and ease of operation. One limitation is the restricted heating efficiency of certain solvents due to their dielectric properties.^[33]

Microwave devices consist of four primary components namely the magnetron, waveguide, applicator (which holds the sample) and circulator. Depending on how microwave energy is delivered to the sample, MAE devices can be classified into two categories: multimode systems and single-mode systems. Multimode systems disperse microwave radiation within a

cavity enabling uniform treatment of multiple samples simultaneously. In contrast, single-mode systems focus microwaves directly on the sample resulting in more efficient and targeted extraction. Multimode systems are used with closed vessels, allowing for the application of high pressure during extraction, whereas single-mode systems are often associated with open vessels operating at atmospheric pressure.^[34]

Ultrasound assisted extraction (UAE)

UAE utilizes ultrasound energy and various solvents to efficiently extract target compounds from different plant matrices. Ultrasounds are mechanical waves with frequencies exceeding 20 kHz, which is beyond the audible range of human hearing (20 Hz to 20 kHz). These waves consist of alternating compression and rarefaction cycles that propagate through solid, liquid, or gas media, causing molecular displacement and dislodgement. When high-intensity sound waves are applied, the negative pressure during the rarefaction phase can exceed the intermolecular forces holding molecules together, pulling them apart and generating cavitation bubbles. These bubbles grow through coalescence and eventually collapse during the compression phase, creating localized hot spots and extreme conditions.^[35] The collapse of cavitation bubbles produces shockwaves, and the resulting inter-particle collisions lead to the fragmentation of cellular structures. Due to the limitations of traditional and other modern extraction methods, such as high capital costs, significant energy consumption, and the use of hazardous organic solvents, the application of ultrasound for extraction has gained considerable attention over the past decade. UAE is a technique that incorporates ultrasound during the extraction process, making it an attractive option as it is considered a clean, efficient, and environmentally friendly approach.^[36]

Supercritical fluid extraction

Supercritical fluid extraction (SFE) is an environmentally friendly, simple, and fully automated analytical technique. Often referred to as an "environmentally benign sample preparation method," SFE typically employs non-toxic solvents such as supercritical carbon dioxide or water. With its short extraction times, lower operating pressures and temperatures, and the ability to preserve the integrity of food's functional components, SFE significantly minimizes the risk of activity loss in sensitive compounds.^[37] Carbon dioxide, nitrous oxide, ethane, propane, n-pentane, ammonia, and sulfur hexafluoride are among the most commonly used supercritical fluids. Due to its non-abrasive, non-explosive, and non-toxic properties, CO₂ is the most widely utilized gas in SFE. The key advantages of SFE include its

quantitative accuracy, simplicity, rapid extraction times, high selectivity, and environmentally friendly nature, making it a preferred method for various applications.^[38]

QuEChERS extraction methodology

QuEChERS is widely recognized for its rapidity, simplicity, cost-effectiveness, efficiency, robustness, and safety.^[39] The QuEChERS method is considered a green extraction technique due to its minimal use of organic solvents compared to other extraction methods. It consists of two key phases: solvent extraction and sample clean-up. During the solvent extraction phase, the sample is vigorously shaken with a buffer (to protect base-sensitive analytes), anhydrous magnesium sulfate, and sodium chloride (to induce salting-out). The sample clean-up phase is crucial for removing interfering matrix components, such as carbohydrates and fatty acids. This phase employs rapid dSPE, utilizing magnesium sulfate (to absorb residual water) and a weak anion exchanger called primary secondary amine (PSA) as the dispersive SPE sorbent, thereby enhancing the purity of the extract.^[40]

Alternative green solvents for sample preparation

Water is the most environmentally friendly, cost-effective, sustainable, and non-toxic solvent available. Maceration, the simplest and most widely used extraction technique, often employs water as the solvent. The properties of water can be finely adjusted by incorporating specific additives. For instance, both micellar and hydrotropic extractions require the addition of a surfactant or a hydrotrope, respectively, to water. These amphiphilic compounds enhance the solubility of hydrophobic substances in aqueous environments by forming micelles or aggregates, thereby improving extraction efficiency. Natural Deep Eutectic Solvents (NADESs) are mixtures of naturally occurring solid compounds that have melting points significantly lower than those of their individual components. This unique characteristic arises primarily from the formation of intermolecular hydrogen bonds between hydrogen bond donors and acceptors. As solvents, NADESs are environmentally friendly, sustainable, and easily recyclable, making them an attractive alternative in green chemistry applications.^[41,42]



Figure 1: Advantages of green solvents.

Deep Eutectic Solvents

Deep eutectic solvents (DES) are emerging as promising alternatives to traditional volatile organic solvents. Composed of natural components such as organic acids, amino acids, sugars, alcohols, and cholinium derivatives, DES are considered the most environmentally friendly and sustainable substitutes for ionic liquids. They are formed by combining a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), resulting in a significant reduction in the mixture's melting point due to strong hydrogen bonding. DES offer advantages over ionic liquids, including easy production without chemical synthesis and the availability of inexpensive natural components. They are known for their diverse liquid states, biodegradability, strong solubilization capabilities, adjustable polarity, and low volatility. However, they are more viscous and less chemically inert than ionic liquids, which can slow mass transfer in extraction or dissolution processes. This drawback can be mitigated by adding water during preparation or as a diluent, which reduces increased Van der Waals forces, hydrogen bonds, and electrostatic interactions. DES have been used as eco-friendly solvents for extracting various solutes, aiding in the monitoring of contaminants in real-world samples.^[43]

Surfactants and Hydrotropes

Surfactants are amphiphilic compounds containing both hydrophobic and hydrophilic segments, allowing them to dissolve in both organic and aqueous phases. Above the critical micellar concentration (CMC) in water, surfactant molecules form micelles with polar heads exposed to water and nonpolar chains at the core. In nonpolar fluids, they form reverse micelles with polar heads at the center. Surfactants can adsorb onto inorganic surfaces, forming either a monolayer or a bilayer.^[44] In a monolayer, ionic surfactant head groups are attracted to oppositely charged mineral oxide surfaces, while nonpolar chains interact with solution molecules to form a second layer in bilayer aggregation. This configuration allows organic molecules to dissolve in the organic core formed by nonpolar chains.^[45]

Hydrotropes are amphiphilic green solvents that dissolve hydrophobic substances in aqueous solutions through a mechanism distinct from micellar solubilization. They consist of an ionic group (hydrophilic head) and a benzene-substituted molecule (hydrophobic part). Unlike surfactants, their hydrophobic portion is too small to form micelles spontaneously. Hydrotropes can aggregate at a minimum hydrotrope concentration (MHC), increasing the solubility of hydrophobic substances in the aqueous phase. Due to their non-toxic, affordable, and chemically inert nature, hydrotropes have been used to extract certain chemicals.^[46]

Greener Sample Preparation Considerations

Recent advancements in sample preparation demonstrate a commitment to greener methods, with trends in analytical chemistry focusing on automation, integration of steps, miniaturization of equipment, and innovative materials. The aim is to replace hazardous substances with alternatives that pose minimal environmental, health, and safety (EHS) risks. However, improvements are still needed, particularly in using bio-based solvents instead of petroleum-derived ones. The bio-derived nature of these solvents does not always eliminate EHS concerns.^[47] The development of environmentally friendly solvents should ensure comparable analytical performance. The creation of advanced materials for sample preparation often involves compounds with undesirable EHS properties. Greener sample preparation would benefit from focusing on sustainable synthetic processes. Analytical system miniaturization has progressed significantly, with solvent-less and reagent-less techniques becoming common due to simplified sample preparation. Smaller sampling and preparation equipment is expected to handle complex point-of-need analyses.^[48] Automation remains a key goal, with microfluidic and mesofluidic systems gaining attention. These

systems integrate unitary phases, aligning with the fourth principle of GAC.^[49] Although analysis time is crucial, it is not explicitly addressed in the 12 GAC principles. This is especially important in scenarios requiring numerous analyses, such as clinical testing. More emphasis should be placed on speeding up extraction processes. The development of multiplexed systems for simultaneous target analyte identification is encouraged, along with vanguard-rearguard methodologies for efficient decision-making when processing large sample volumes.^[50] These techniques aim to screen and confirm positive or inconclusive samples, reducing the number of samples processed, saving energy, reagents, and solvents, and minimizing waste. Despite their potential, vanguard-rearguard strategies are underutilized, and more focus should be placed on developing screening techniques that incorporate sample preparation for enhanced sensitivity and selectivity.^[51]

Future Trends and Challenges

The future of green analytical techniques in green chemistry is dynamic and rapidly advancing. Current trends include the development of miniaturized technologies, such as benchtop and portable devices, which reduce reagent use and waste. There is an increasing emphasis on metrics like the Analytical Eco-Scale and Green Analytical Procedure Index to assess the eco-friendliness of methods. Emerging trends highlight interdisciplinary approaches, with multicriteria decision analysis from environmental management being applied to green analytical chemistry. Education and popularization of green analytical chemistry concepts are vital for future growth.

Challenges in green analytical chemistry involve creating more efficient, accurate, and cost-effective methods, finding new renewable feedstocks to replace traditional reagents and solvents, and developing smart materials to enhance sensitivity and selectivity in sample preparation. The future outlook suggests a shift towards more accessible, affordable, and environmentally friendly analytical chemistry. Overall, the future of green analytical techniques in green chemistry is promising, with ongoing research and innovation addressing challenges and expanding sustainable practices.

CONCLUSION

Green analytical techniques are transforming analytical chemistry by offering sustainable, eco-friendly, and efficient methods for sample preparation, analysis, and data interpretation. These techniques reduce waste, minimize solvent use, and promote renewable energy

sources. The integration of green analytical techniques into green analytical chemistry has led to significant advancements in.

1. **Miniaturization:** Lower reagent use and waste generation.
2. **Solvent Reduction:** Replacing toxic solvents with eco-friendly alternatives.
3. **Energy Efficiency:** Utilizing renewable energy sources and reducing energy consumption.
4. **Sample Preparation:** Developing efficient, selective, and sensitive methods.

The adoption of green analytical techniques in green analytical chemistry has broad implications for:

1. **Environmental Sustainability:** Lower environmental impact and pollution.
2. **Human Health:** Reduced exposure to toxic chemicals and reagents.
3. **Economic Benefits:** Lower costs related to waste disposal and solvent use.

In conclusion, green analytical techniques are crucial for developing sustainable analytical practices, and their integration into green analytical chemistry is essential for promoting environmental stewardship, human health, and economic benefits.

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