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Green Analytical Chemistry, Sustainable Methods for Chemical Analysis - A Review

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Abstract- Green Analytical Chemistry (GAC) is an emerging branch of analytical science that applies the twelve principles of green chemistry to chemical measurement in order to reduce environmental and human health impacts. By minimizing the use of hazardous reagents, conserving energy, and preventing the generation of dangerous waste, GAC provides a framework for eco-friendly analytical procedures that maintain high accuracy and precision. Recent innovations emphasize the use of green solvents water, supercritical carbon dioxide, ionic liquids, and other bio-based alternatives alongside energy efficient methodologies such as microwave assisted and ultrasound assisted techniques that accelerate reaction kinetics and lower power demands. Non-intrusive, real-time monitoring combined with chemometric approaches optimizes resource utilization and data acquisition. The field has moved from reducing solvent volumes in sample pretreatment to direct analytical methods that require little or no solvent or reagent, further shrinking the ecological footprint. Progress in green instrumentation, including miniaturized and portable devices, microfluidic lab-on-a-chip systems, and automated platforms, has likewise decreased sample and energy consumption. To assess and guide these efforts, standardized tools such as NEMI (National Environmental Methods Index), AES (Analytical Eco-Scale), and GAPI (Green Analytical Procedure Index) have been developed to evaluate the "greenness" of analytical methods and promote global comparability. Despite these achievements, challenges remain. Balancing sensitivity, selectivity, and detection limits with sustainability goals is complex, and universally accepted metrics for environmental performance are still evolving. Looking forward, artificial intelligence, machine learning, and digital-twin modeling promise to further streamline workflows, minimize waste, and enable dynamic optimization of analytical processes. This review will examine these developments in detail, discussing green solvents and sample preparation strategies, energy-efficient analytical techniques, miniaturized instrumentation, chemometric and real time monitoring tools, and established greenness assessment metrics, while highlighting current limitations and future directions for sustainable chemical analysis.

I. INTRODUCTION

Before the 1990s, the environmental consequences of chemical procedures were rarely a major consideration. The emphasis then rested largely on developing analytical methods that were highly sensitive and dependable. During the 1990s and early 2000s, however, concerns about toxic chemical emissions and the growing need for sustainable practices began to gain traction. This shift gave rise to the concept of green chemistry, which soon started to shape many branches of chemistry, including analytical chemistry.

Green chemistry (GC), introduced by Paul Anastas and John Warner in 1998, focuses on designing, producing, using, and ultimately disposing of chemical products and processes in ways that minimize or eliminate hazardous substances. The goal is to achieve sustainable and environmentally sound practices. Green Analytical Chemistry (GAC) builds on these ideas, offering safer and more efficient approaches for detecting and quantifying chemicals without harming the environment or human health.
Incorporating GC into analytical chemistry education is now essential for environmental accountability, regulatory compliance, resource efficiency, cost savings, and innovation. As environmental regulations tighten, understanding GAC ensures that

future chemists can design methods that meet modern ecological standards.

Today, with sustainability and environmental responsibility taking center stage, familiarity with GAC principles is increasingly critical. The twelve sustainability driven principles of GAC provide a framework for creating effective and eco-friendly processes. These principles address areas such as energy conservation, waste minimization, and the selection of safer materials.

As markets and industries shift toward greener solutions, chemists who apply GAC concepts can gain a competitive advantage while supporting environmental protection. Applying these principles benefits a wide range of sectors from research and manufacturing to public health and environmental management. By embracing GAC, analytical chemistry can evolve into a discipline that actively supports a sustainable future, delivering benefits to industry, society, and the planet alike.

The extraction of organic substances is typically conducted using organic solvents, applicable to both liquid (liquid–liquid extraction, LLE) and solid samples (Soxhlet extraction, ultrasonic extraction). Typically, micro-components are removed, necessitating solvents of high purity, which correspondingly incurs a significant cost. Moreover, numerous substances are hazardous, potentially carcinogenic, and their disposal poses significant challenges. Traditional extraction methods typically include multiple stages, including the purifying of the extract, resulting in increased analyte losses and extended sample preparation durations. The drawbacks of traditional extraction procedures, particularly their reliance on substantial amounts of organic solvents, have prompted the innovation of novel methods characterized by their rapidity and minimal solvent consumption.

GAC aims to develop eco-friendly alternatives, and one of the promising techniques in this field is solid-phase micro extraction (SPME). As a solvent-free sample preparation method, SPME aligns with the principles of green chemistry by eliminating the need for harmful solvents and minimizing waste production. The versatility of SPME has enabled its effective use in several analytical sample preparation fields including environmental analysis, food analysis, forensic investigation, pharmaceutical analysis, and biomedical research. It integrates sampling, extraction, concentration, and sample introduction into a single step. Its capacity to provide straightforward, extremely sensitive, rapid, and solvent-free extraction of analytes from gaseous, liquid, and solid samples enhances its use for trace-level detection of chemicals, even within complex matrices. As compared to traditional techniques like solid phase extraction, SPME offers several advantages for its simplicity, versatility, minimum solvent usage, and reduced sample handing process. However, several areas still require further research, such as the development of suitable methods for complex matrices, new types of coating materials, and the detection of multiple compounds by a single device.

The 12 principles of green Analytical chemistry

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Waste Prevention: It is far better to avoid creating waste than to handle or clean it up afterward. The emphasis is on designing chemical processes that generate minimal waste from the outset, reducing the burden and cost of disposal or remediation.

Atom Economy: Synthetic strategies should be planned so that nearly all starting materials end up in the final product. Maximizing the incorporation of raw materials minimizes by-products and improves overall efficiency.

Less Hazardous Chemical Syntheses: Whenever possible, reactions should use and produce substances with little or no toxicity. Selecting milder reagents and safer pathways lowers risks to both the environment and human health.

Designing Safer Chemicals: Compounds should be engineered to perform their intended function while exhibiting the lowest possible toxicity. Considering potential hazards during molecular design leads to effective yet inherently safer products.

Safer Solvents and Auxiliaries: Because solvents and auxiliary agents often have significant environmental impacts, their use should be minimized or replaced with less harmful options whenever feasible.

Energy Efficiency: Chemical transformations should require the least possible energy. Ideally, reactions occur at ambient temperature and pressure, cutting both environmental impact and operating costs.

Use of Renewable Feedstocks: Whenever practical and economical, raw materials should come from renewable sources rather than finite ones. This lessens dependence on depleting resources and lowers the overall ecological footprint.

Reduce Derivatives: Unnecessary steps such as protection/deprotection or temporary chemical modifications should be avoided. Limiting derivatization decreases reagent use and reduces waste generation.

Catalysis: Catalytic reagents, which can drive reactions repeatedly, are preferred over stoichiometric reagents. Catalysts increase selectivity, reduce energy needs, and help limit waste formation.

Design for Degradation: Products should be designed to break down into harmless substances after their useful life. Planning for benign degradation prevents long-term accumulation in the environment.

Real-Time Analysis: Analytical methods should allow continuous monitoring of reactions so that potential hazards are detected and managed before harmful substances are formed.

Safer Chemistry: Choose materials and process conditions that lower the likelihood of accidents such as explosions, fires, or leaks. Building safety into the chemistry itself enhances reliability and protects workers and the environment.

Importance of GAC in reducing environmental impact and promoting sustainability

Reducing hazardous pollution: Traditional analytical methods often rely on toxic chemicals and solvents that threaten both human health and ecosystems. Green Analytical Chemistry (GAC) addresses this by emphasizing the use of safer, low-toxicity reagents and environmentally benign solvents. For example, biodegradable reagents or water-based solvents can replace conventional organic solvents that frequently contaminate water supplies. Many older techniques generate persistent by-products that are difficult to break down, whereas GAC promotes reactions that yield harmless, biodegradable residues, minimizing long-term environmental impact. In addition, incorporating real-time monitoring enables early detection and control of pollutants at their source, preventing harmful emissions before they can cause damage.

Reducing chemical waste: Conventional analytical methods often produce substantial amounts of chemical waste, particularly from hazardous solvents and reagents. Green Analytical Chemistry (GAC) tackles this by minimizing the use of chemicals during analysis, which in turn reduces the need for complex waste management. Techniques such as supercritical fluid chromatography (SFC), microwave-assisted extraction (MAE), and solid-phase microextraction (SPME) greatly cut solvent consumption. Many green approaches also require smaller sample volumes, lowering the quantities of reagents and solvents needed. This significantly decreases both the overall waste generated and the environmental burden of disposal. Unlike traditional methods that often demand large sample sizes and extensive preparation, GAC promotes in-situ and real-time analysis, allowing samples to be examined immediately and reducing extra handling, processing, and transportation further minimizing chemical waste.

Lowering energy consumption: Many traditional analytical techniques, such as distillation or certain forms of chromatography, operate under high temperatures or pressures and therefore demand considerable energy. Green Analytical Chemistry

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(GAC) promotes energy efficient approaches that can be performed at ambient conditions or with reduced power. For example, microwave-assisted processes use significantly less energy than conventional heating methods while delivering faster results. GAC also encourages the use of compact, high-efficiency instruments like lab-on-a-chip systems that require minimal energy and resources to run. These smaller devices not only conserve power but also provide rapid, precise analyses with reduced waste.

Use of renewable materials and reagents: Green Analytical Chemistry (GAC) promotes the selection of sustainable, biodegradable, and renewable inputs to decrease dependence on finite resources. For example, bio-based solvents derived from plant materials can replace traditional petroleum-based solvents. GAC also emphasizes choosing reagents and materials that can be recycled or reused, lowering overall resource consumption and reducing the need for scarce chemicals or metals. Many green analytical methods incorporate solvent recovery or the reuse of solid-phase extraction cartridges, extending their life cycle. In addition, GAC supports closed-loop systems that continually reclaim and recycle solvents and reagents, minimizing waste generation and environmental impact.

Emphasis on green solvents and solvent-free methods: Green Analytical Chemistry (GAC) advocates the use of solvents that are non-toxic, biodegradable, and environmentally benign. Hazardous, volatile options such as hexane or chloroform are increasingly replaced by safer alternatives like water, ionic liquids, deep eutectic solvents, hydrotropes, or supercritical carbon dioxide. GAC also advances solvent-free analytical techniques such as solid-phase microextraction (SPME) and other dry analytical approaches which minimize chemical waste and significantly cut the need for harmful reagents during sample extraction and analysis.

Regulatory Compliance: Organizations adopting green analytical techniques are better positioned to meet increasingly strict environmental regulations. This includes reducing hazardous waste generation, lowering emissions, and ensuring safe disposal practices in line with international standards. GAC principles can be applied across diverse fields such as forensics, environmental monitoring, food safety, and pharmaceuticals where minimizing the ecological footprint of chemical analyses is crucial for both regulatory compliance and sustainability goals. By integrating GAC methods, these industries can cut their overall environmental impact and actively contribute to a greener, more sustainable future.

The 10 guidelines for preparing green samples

1. Favour in situ sample preparation
2. Use safer solvents and reagents
3. Target sustainable, reusable, and renewable materials
4. Minimize waste
5. Minimize sample, chemical and material amounts
6. Maximize sample throughput
7. Integrate steps and promote automation
8. Minimize energy consumption
9. Choose the greenest possible post-sample preparation configuration for analysis.
10. Ensure safe procedures for the operator.

Green analytical techniques employed in pharmaceutical analysis

Green Chromatographic Techniques:
Chromatography is widely used in pharmaceutical analysis but often relies on hazardous solvents that generate significant waste. Green chromatography addresses this by improving sustainability and minimizing solvent use. Supercritical Fluid Chromatography (SFC) employs nontoxic, recyclable CO_2, reducing solvent consumption, costs, and waste. However, innovations are still needed to lower energy demands, enhance sample transfer, and support multi-detection with high mass spectrometric sensitivity. Reversed-Phase Chromatography (RPC) can also be made greener by replacing harmful solvents such as methanol and acetonitrile with safer alternatives like ethanol, isopropanol, acetone, ethyl acetate, propylene carbonate, and water. These substitutions improve laboratory safety, reduce waste disposal costs, and lessen environmental impact without sacrificing performance. Additionally, Miniaturized Chromatography reduces solvent and sample volumes by over 90% compared to conventional LC, cutting time, cost, waste, and energy consumption. Beyond environmental and health benefits, miniaturization improves ion sensitivity, decreases dilution, and enhances mass spectrometric efficiency.

Solid-Phase Microextraction (SPME): SPME is an environmentally friendly sample preparation technique that minimizes reliance on hazardous solvents, aligning with green chemistry principles. With its very small extraction phase volume, the method produces minimal laboratory waste, requires little to no solvents, and offers fast, straightforward sample preparation. Its microextraction nature significantly reduces waste while enabling unique opportunities for in vivo sampling, avoiding labor-intensive procedures. The technique is easily automated, reducing manual handling and improving efficiency, making it highly practical for routine analysis. Additionally, SPME is well-suited for direct monitoring of environmental water and air, offering a simple, robust, and field-compatible option for on-site chemical analysis. These qualities make SPME an efficient, sustainable alternative to traditional extraction methods.

Green Spectroscopic Techniques: Near-Infrared (NIR) Spectroscopy is an inherently green method that reduces reliance on hazardous chemicals and solvents. It allows rapid, solvent-free analysis, such as checking solvent purity without sample preparation. By minimizing solvent use, NIR spectroscopy offers a sustainable alternative to traditional wet-chemistry methods. It also supports environmentally friendly recycling by improving sorting accuracy, reducing material demand, and lowering disposal costs through solvent recovery.

Raman Spectroscopy is another eco-friendly approach designed to simplify analysis and shorten research times. It aids in crop monitoring, plant stress diagnosis, and sustainable agricultural practices. Raman spectroscopy enables real-time monitoring of solvent concentration during exchange or distillation, reducing solvent consumption and improving process efficiency. By eliminating delays linked to offline analysis, it saves reactor time, enhances process understanding, and supports industrial sustainability. Additionally, Raman spectroscopy facilitates recycling applications, such as precise large-scale sorting of waste plastics.
Voltametric and Electrochemical Methods: Voltammetry is valued for its simplicity, portability, low cost, and high sensitivity. Portable voltametric sensors allow on-site, rapid analysis with minimal sample preparation. Screen printing technology has further advanced the field by enabling mass production of disposable screen-printed electrodes (SPEs) at low cost, offering versatility, reproducibility, and reduced waste. Electrochemical methods also support sustainability by replacing hazardous reagents with safer alternatives, thereby minimizing pollution. They play a vital role in advancing green energy practices through efficient energy conversion and storage. For example, fuel cells use electrochemical reactions to generate cleaner energy with fewer emissions, while batteries improve renewable energy storage, helping balance solar and wind intermittency. By lowering the environmental footprint of synthesis and enabling greener energy technologies, electrochemical methods align closely with the principles of Green Analytical Chemistry (GAC).

The three greenness assessment tools are briefly described here.

1) NEMI (National Environmental Method Index)
The Methods and Data Comparability Board (MDCB) developed the NEMI, which hosts the largest ecological analytical database. This tool provides free access to environmental methods through www.nemi.gov (accessed February 14, 2021). Keith et al. (2007) offered a detailed explanation of the instrument.

As illustrated in Figure 2, the NEMI is depicted as a circle known as the *greenness profile*, divided into four equal quadrants. The first quadrant represents PBT (persistent, bioaccumulative, and toxic), the second highlights acute toxicity, while the third and fourth correspond to corrosivity and waste generation, respectively. Each section can be shaded green to indicate compliance with green chemistry principles, or left blank if not.

The greenness profile accounts for critical parameters such as waste volume, pH, and the presence of substances with specific hazardous properties. This visual tool enables analysts to compare different analytical methods and evaluate their level of eco-friendliness and overall greenness.

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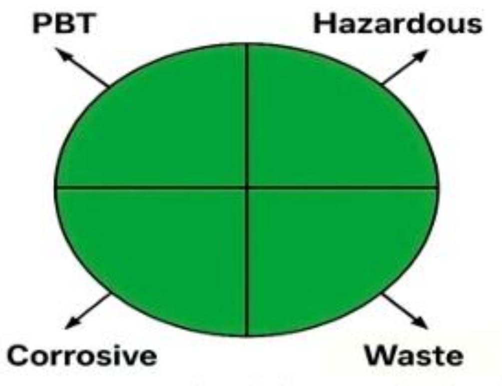


Figure 2

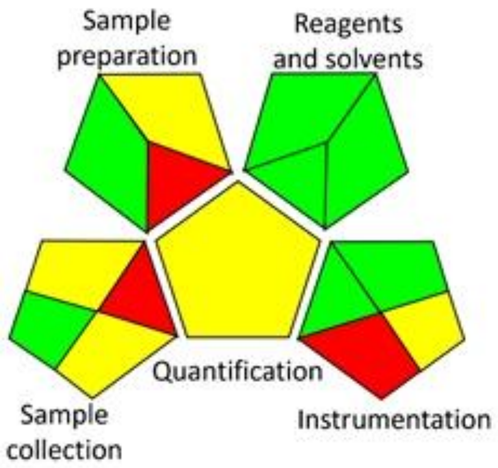
2) Analytical Eco-Scale Assessment (ESA): The Analytical Eco-Scale Assessment is a scoring system designed to evaluate how environmentally friendly an analytical process is. The scale begins with 100 points, representing the most eco-friendly method with no penalties. Penalty points are subtracted based on factors such as the use of hazardous solvents, excipients, additives, energy consumption, and other environmental impacts.

As shown in Figure 2, the final score determines the level of greenness:

- > 75 points → the method is considered *green*
- 50–75 points → the method is considered *acceptable*
- < 50 points → the method is deemed *inadequate*

Penalty points are assigned according to the hazard level of chemicals involved. For instance, a chemical with no hazard pictogram receives zero penalty points (non-hazardous), while less hazardous chemicals are assigned one penalty point.

3) Green Analytical Procedure Index (GAPI): The Green Analytical Procedure Index, introduced by J. Płotka-Wasylka in 2018, is a modern tool designed to evaluate the environmental impact of analytical processes, covering every stage from sample collection to the final result. According to the GAPI framework, an analytical procedure typically begins with sample collection, followed by a phase that safeguards the sample from undesirable chemical or physical changes. The final phase involves the application of analytical techniques for detection and quantification. GAPI employs a pictogram to visually represent the ecological impact of each stage in the process. This pictogram uses a colour code green, yellow, and red to classify the degree of environmental friendliness, making it possible to quickly assess which stages are greener and which pose more environmental concerns.



4) Analytical Greenness Calculator (AGREE)

The Analytical Greenness Calculator (AGREE) is a comprehensive and user-friendly evaluation method that provides an informative, easily interpretable result. Its assessment criteria are based on the 12 principles of Green Analytical Chemistry (GAC), which are integrated into a single 0–1 scale score.

- The most important advantages of the AGREE tool can be listed as follows
- It is more comprehensive as it includes all the principles of green analytical chemistry.
- It is more flexible as it allows users to make some modifications.
- It allows easy analysis of the positive and negative aspects of the method thanks to the detailed pictogram.
- It gives both qualitative and quantitative results.
- The software is easy to use and gives fast results.

One advantage of AGREE is the availability of freeware software, making it highly accessible and simple to apply across different analytical contexts.

II. CONCLUSION

As interest in green analytical chemistry (GAC) continues to grow, there is a need for new and improved approaches to evaluate analytical processes. GAC metrics provide valuable tools for comparing different method parameters and steps, allowing identification of less environmentally friendly components that can be optimized to meet sustainability standards.

Among these tools, the Analytical Eco-Scale stands out as a practical semi-quantitative instrument for both laboratory applications and teaching. It is simple, quick to use, and applicable to both established and newly developed processes, offering clear evaluation criteria.

Growing concerns about the environmental impact of chemical and analytical practices particularly the use of hazardous solvents and reagents have made greenness assessment a priority. Since the introduction of the concept of "green chemistry" in recent decades, the field of analytical chemistry has increasingly embraced systematic evaluation methods to promote safer, more sustainable practices.

Author's Contribution

The authors collectively contributed to the development of this comprehensive review on green analytical chemistry. Each author played a significant role in manuscript preparation. Their combined efforts have provided valuable insights into the advancement of greenness assessment tools and their applications in analytical chemistry.

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