International Journal of Pharmaceutical research and Applications
Volume 11, Issue 3, May-June 2026, pp:79-86 www.ijprajournal.com ISSN: 2456-4494

Green Approaches in Analytical Chemistry Principle and Its Application

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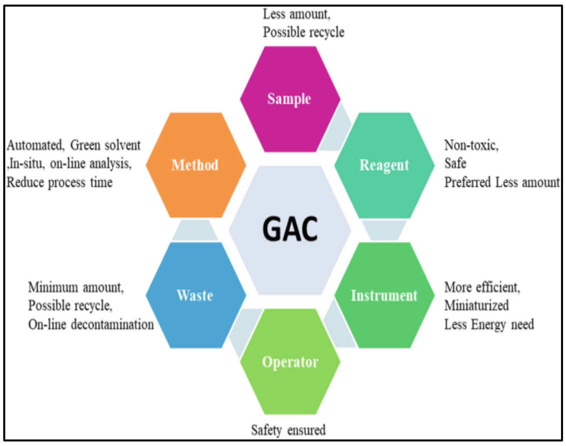
Date of Submission: 23-04-2026 Date of Acceptance: 03-05-2026

Abstract: Green Analytical Chemistry (GAC) is a developing approach which applies green chemistry principles to reduce environmental and health risks. This review outlines the key principles, progress, and uses of GAC, highlighting its importance in sustainable chemical analysis. The 12 principles of GAC emphasize minimizing sample sizes, reducing energy consumption, avoiding toxic reagents, and encouraging waste reduction while preserving analytical effectiveness. Techniques like solid-phase microextraction, supercritical fluid chromatography, and various spectroscopic methods have greatly improved the eco-friendliness of analytical processes. The concept of White Analytical Chemistry aims to balance environmental sustainability, analytical efficiency, and economic viability. Some tools such as the Ecological Footprint and E-Factor are introduced as measures to assess the environmental effects of analytical techniques. The application of GAC in synthesis, drug development, and material science showcases its practical importance in decreasing pollution and enhancing efficiency. Although there are challenges in maintaining sensitivity and precision, ongoing innovations in green solvents, miniaturized methods, and automation are advancing the field. Overall, GAC signifies a significant shift towards environmentally conscious analytical practices that align with global sustainability objectives.

Keywords: Green Analytical Chemistry, Waste reduction, Green solvents, miniaturization.

I. INTRODUCTION:

Green Analytical Chemistry (GAC) is a developing field that incorporates green chemistry principles into analytical techniques to minimize the environmental and health effects typically linked to chemical analysis [1].



GAC focuses on reducing the use of harmful reagents, lowering energy use, and preventing hazardous waste production in order to align analytical methods with sustainability objectives. Its foundation is based on the 12 principles of green chemistry, which offer a detailed framework for creating and applying eco-friendly analytical methods [2]. These principles highlight the importance of waste reduction, utilizing renewable materials, enhancing energy efficiency, maximizing atom economy, and eliminating hazardous substances, all of which are essential for transforming the role of analytical chemistry in the current environmental and industrial contexts [3].

Green Analytical Chemistry (GAC) is primarily characterized by the purposeful creation and execution of analytical methods designed to minimize or completely remove the use and production of harmful substances, thus reducing negative impacts on human safety, health, and the environment. The development of GAC is driven by a rising awareness of environmental issues worldwide and heightened regulatory demands, while also aligning with the core principles of green chemistry [4].

The scope of GAC goes beyond just environmental advantages; it promotes a comprehensive method for chemical analysis. By emphasizing real-time monitoring of reactions during the process, GAC allows industries to identify and resolve inefficiencies or dangerous by-products before they worsen, thereby stopping pollution at its source. The use of chemometric tools improves the accuracy and effectiveness of these techniques, facilitating strong data analysis while reducing resource consumption. This move towards a proactive approach, as opposed to a reactive one, underscores the revolutionary impact of GAC on traditional analytical chemistry practices.[5]

Twelve principles were suggested as overarching guidelines for making analytical methods more environmentally friendly. The initial principle advocated for the use of direct analytical techniques to eliminate the need for sample preparation. Additionally, the report indicated that any "green" actions implemented during the sample preparation phase (such as reduced energy consumption, ensuring operator safety, and using non-toxic or renewable reagents) adversely affected the accuracy, precision, selectivity, sensitivity, and detectability of the analytical process [6]. his assumption was not thoroughly considered, especially given the analytical capabilities of established sample preparation technologies available at that time. For instance, solid-phase microextraction (SPME), which does not require solvents or reagents, significantly outperformed direct analytical methods and could effectively sample complex materials [7].

The 12 principles of GAC can be summarized as follows:

1. Employ direct analytical methods to eliminate the need for sample preparations.
2. Aim for a reduced sample size and fewer samples.
3. Conduct measurements in situ.
4. Combine analytical processes and operations to conserve energy and lower reagent usage.
5. Opt for automated and miniaturized techniques.
6. Steer clear of derivatization.
7. Limit the production of analytical waste and ensure proper waste management.
8. Favor multi-analyte or multi-parameter methods over single-analyte approaches.
9. Strive to minimize energy consumption.
10. Prefer reagents sourced from renewable materials.
11. Remove or substitute toxic reagents.
12. Enhance operator safety [8,9].

The idea of White Analytical Chemistry (WAC), introduced by Nowak et al., highlights a crucial principle [10]. WAC advocates for a harmonious integration of environmental safety, analytical effectiveness, and practical economic considerations [11,12]. This integration is frequently articulated through the "red" (analytical performance), "green" (environmental impact), and "blue" (cost and practicality) characteristics, which collectively determine the method's whiteness [13].

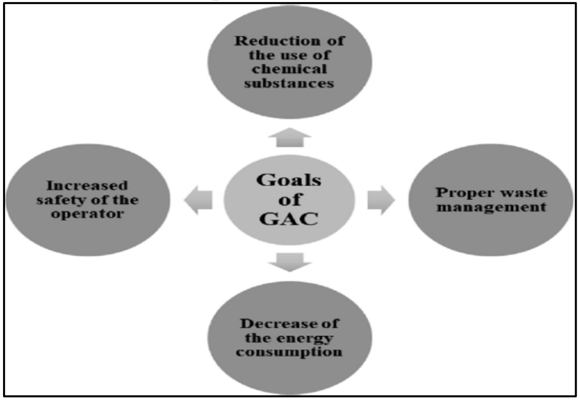
The first principle of Green Analytical Chemistry (GAC) is often misunderstood, leading to the incorrect belief that skipping the sample preparation step is environmentally friendly, disregarding the advancements in "green" technologies in the field. It also overlooks situations where direct analysis is impractical, necessitating conversion of samples into an analyzable format (such as solids or complicated matrices like food or biological samples). Furthermore, the “dilute-and-shoot” method frequently involves diluting samples by ratios ranging from 1:1 to 1:100[14,15].

In 1987, during Euroanalysis VI in Paris, Malissa shared his thoughts on shifts in paradigms within analytical chemistry [16]. His dissertation traced the historical evolution of chemistry, highlighting the emergence of the ecological paradigm at the close of the twentieth century. These concepts aligned closely with the findings of the Pimentel report, released in the USA in 1985 [17], which addressed the effects of chemistry on the planet's health. A decade later, The Analyst journal published by the Royal Society of Chemistry in the UK introduced Environmental Analytical Chemistry as a framework for analytical practices that incorporates consideration of the environmental repercussions of such practices [18].

The Concept of Green Chemistry: During the 1980s, environmental concerns became a significant focus for nearly all industries. To address the challenges of pollution, toxicity, health risks, and industrial accidents related to chemical manufacturing, the idea of green chemistry emerged in response to stringent environmental regulations. The term "green chemistry" was first introduced in 1991 by Anastas P. T. as part of an Environmental Protection Agency (EPA) initiative. Green chemistry refers to the development of chemical products and processes that reduce or eliminate the use or creation of hazardous or toxic substances. Table 1 illustrates the development of green chemistry [19,20].

Objectives of the Review

The main goals of this review are to offer a thorough examination of GAC principles and their applications, highlight recent advancements in the field, and address the challenges and future directions. It seeks to consolidate existing research to provide a clear understanding of how GAC principles are applied in various analytical methods. For example, Gadipelly et al. (2015) investigated the role of green solvents in analytical chemistry, showcasing significant decreases in hazardous waste production. By analyzing such research, this review will shed light on the practical advantages and potential drawbacks of GAC, informing future research and development in this domain.[21].



Here are the current opportunities for Analytical Chemistry to contribute to societal progress:

1)engaging in the advancement of knowledge and the development of theories;

2)advocating for the necessity of new regulations and policies;

3)creating standards and specifications;

4) assessing the environmental safety of new methods, processes, and products.

Analytical Chemistry carries out the following roles:

1) analyzes qualitative and quantitative data regarding the nature, quantity, and identity of elements and molecules in our surroundings;

2) delivers adequate information with the necessary analytical sensitivity, selectivity, and precision to aid in decision-making and problem-solving;

3)offers tailored information based on the needs of the end-users of chemical data [22].

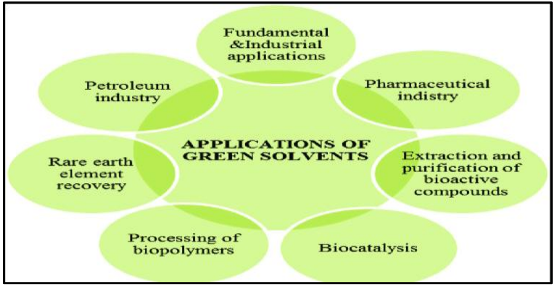
Applications: 1. **Synthesis of nitriles from aldehydes:** This method avoids harmful solvents, results in quicker reactions, and achieves high yields. It is characterized as a simple, clean, and environmentally friendly process [23].

2. **Synthesis of graphene from biomass:** Graphene is utilized in various applications such as electronics, batteries, and sensors. The green technique also incorporates plant or biomass waste [24].

3. **Synthesis of 1- amidoalkyl-2- naphthols:** enabling cost-effective, eco-friendly, and large-scale production for pharmaceutical compounds. Additionally, it employs natural catalysts like tannic acid, eliminating the need for solvents, which decreases both expenses and pollution—making it vital for drug development [25].

4. **Synthesis of spiro heterobicyclic rings:** Another green method uses a non-toxic iodine catalyst with microwave technology, ensuring faster results while minimizing pollution and increasing yields[26].

5. **Synthesis of methacrylate-based hydrogels crosslink:** Furthermore, in drug delivery and biomedical applications, this green approach employs water instead of chemicals, ensuring safety and biocompatibility [27].



Eco-Footprint

In the early 1990s, Rees and Wackernagel developed a tool called the Ecological Footprint (EF) or Ecological Footprint Analysis (EFA), which assesses the demand for specific resources (ecosystem services) needed to sustain a certain level of consumption in industrial processes or building projects. Additionally, the EF measures an ecosystem's capacity to absorb waste generated by consumers and to offset the resources utilized in the production of goods and services within a given area. The EF is quantified in global hectares (gha) per person, with lower EF values indicating more environmentally sustainable industrial practices or consumption patterns in the region. The EF evaluation encompasses six primary ecological land-use categories: forest land, fishing grounds, arable land, urban areas, grazing land, and land designated for energy production [28,29,30,31,32,33,34,35,36,37].

Examples of specific Environmental Footprints (EF) include the Chemical Footprint (Sala and Goralczyk, 2013) [38], Material Footprint (Laakso and Lettenmeier, 2015) [39], Energy Footprint (Vujanovic et al., 2014) [40], Land Footprint (Hsien H. Khoo, 2015) [41], Water Footprint (Mansardo et al., 2014) [42], Carbon Footprint (Rodriguez-Caballero et al., 2015) [43], Nitrogen Footprint (Singh and Bakshil, 2015) [44], and Phosphorus Footprint (Wang et al., 2011) [45].

E-Factor

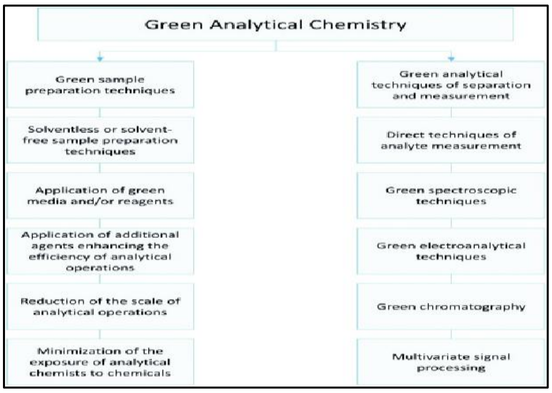
Sheldon has created a straightforward and quick metric to assess the environmental impact of industrial processes, known as the E-Factor (environmental factor). This metric is defined as the total weight of all waste produced during an industrial or technological process (measured in kilograms) for each kilogram of product. A lower E-Factor value (E-Factor ~0) indicates less waste generation, making the process more sustainable and environmentally friendly. It's important to note that the E-Factor can be calculated with or without including the water used in the process, depending on the intended application[46,47,48,49,50].

The higher E-Factor values observed in the pharmaceutical industry, compared to other sectors of the chemical industry, are primarily due to the demand for extremely high-purity products in multi-step reactions, which generate numerous by-products (waste). Furthermore, the production of pharmaceuticals necessitates the use of high-purity reagents. One significant drawback of the E-Factor as a measure of the environmental impact of technological processes is that it overlooks both the hazards and the environmental risks associated with the resulting waste. Two notable examples of the successful application of the E-Factor for assessing the sustainability of technological processes in the pharmaceutical sector include the synthesis of sildenafil citrate (Viagra™) [51].

An Overview of Sample Preparation Techniques and Their Influence on the Greenness of Analytical Methods:

Numerous sample preparation techniques serve as trusted approaches for analytical chemists. Over time, these traditional methods have developed to enhance their efficiency and accuracy. However, certain techniques, such as liquid-liquid extraction (LLE) and Soxhlet extraction, are being reassessed due to their incompatibility with the principles of Green Analytical Chemistry (GAC). The sample preparation and extraction stages often represent the most environmentally harmful aspects of analytical procedures [52]; therefore, laboratories and industries striving for greener practices often target these stages for improvement. Nonetheless, while seeking greener options, it's crucial that the quality of analysis remains uncompromised. In essence, any new method should be more environmentally friendly while maintaining or surpassing the analytical performance of its predecessors.

Initial endeavors to create greener methods incorporated various forms of heat, pressure, and 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) have notably increased the environmental friendliness of extraction compared to older methods [53].



Solid-Phase Microextraction

Principles: Solid-phase microextraction is a method that employs a solid support layered with an extraction coating [54]. This narrow layer, which ranges from 7 to 250 µm thick, acts as the extraction medium, allowing analytes to move from the sample matrix into the coating by partitioning into its bulk or onto its porous active surface until equilibrium is achieved. The quantity of analyte extracted using this approach is influenced by the balance between the sample matrix and the extraction phase.

The extracted amount at equilibrium is given by the equation

n^{eq} = KesVeVs\KesVe+Vs *Cs
where Kes is the distribution coefficient of the analyte between the matrix and extraction phase, Ve is the volume of the extraction phase, Vs is the volume of the sample, and Cs is the initial concentration of the analyte in the sample.

In cases where the sample volume is significantly larger than the combined total of the distribution coefficient and the extraction phase volume, the equation can be reduced to \(n_{eq} = K_e s \cdot V_e \cdot C_s\). This simplification facilitates accurate quantification and optimization of extraction, even when the sample volume is not precisely known. For instance, one could quantitatively analyze the constituents of river water despite the unpredictable volume of water present. It's important to highlight that solid-phase microextraction is a non-exhaustive method, relying on partitioning equilibria [55].

Green Analytical Methods
Green Chromatography: Chromatography plays a significant role in analytical chemistry, with various environmentally friendly approaches emerging:
Supercritical Fluid Chromatography (SFC): This method utilizes supercritical fluids, like carbon dioxide, as mobile phases, leading to lower solvent usage and enhanced efficiency [56].
High-Performance Liquid Chromatography (HPLC): Recent innovations in HPLC focus on incorporating more environmentally friendly solvents and stationary phases that reduce waste and toxicity.
Spectroscopic Techniques: Several spectroscopic methods, including UV-Vis, IR, and Raman spectroscopy, have been adapted to align with green analytical practices:
Near-Infrared (NIR) Spectroscopy: NIR is a non-destructive approach requiring minimal sample preparation, which helps decrease waste and saves time.
Laser-Induced Breakdown Spectroscopy (LIBS): LIBS allows for quick analysis of solid samples with minimal sample preparation and avoids hazardous reagents.
Electrochemical Methods: Electrochemical techniques offer an eco-friendly alternative for analyzing a variety of substances [57].
Types of Green Analytical Solvents:
Water: Water is an abundantly available and non-toxic solvent that is essential in many industrial processes, including chemical extractions and as a medium for reactions. Its utility in green chemistry is enhanced by methods such as aqueous biphasic systems, which broaden its applications.
Supercritical Fluids:
Supercritical carbon dioxide ($scCO_2$) is a frequently utilized environmentally friendly solvent. Due to its non-toxic characteristics, recyclability, and relatively gentle operational conditions, it is widely employed in various processes like decaffeination, material extraction, and industrial cleaning.
Ionic Liquids:
Ionic liquids are made up of organic cations paired with inorganic anions. They are notable for having negligible vapor pressure and customizable physical and chemical properties, making them commonly used in separation technologies, catalytic processes, and electrochemical applications.

Chemistry:
Solvent-free methods:
Eliminate the need for organic solvents, which can be harmful and non-renewable.
For example: solid phase microextraction (SPME).
Miniaturized analytical methods:
Utilize minimal sample and reagent quantities, thereby minimizing waste.
For instance: microfluidic systems and microextraction with packed sorbents.
In site and on-site analysis:
Evaluate samples directly at the source to prevent transportation and degradation.
Examples include biosensors and FTIR spectrometers.
Adoption of green solvents:
Substitute toxic solvents with eco-friendly alternatives.
Examples are water, ethanol, and supercritical CO2.

Energy-efficient methods:
Lower energy usage during analysis[58].

II. Conclusion:

Green Analytical Chemistry marks a significant advancement in analytical science, prioritizing sustainability without sacrificing quality. By utilizing eco-friendly methods, minimizing hazardous waste, and enhancing energy efficiency, GAC effectively tackles environmental and health issues. Innovations like green solvents, cutting-edge extraction techniques, and real-time analysis have broadened its use across various sectors. Nevertheless, challenges persist in achieving a balance between precision and environmental advantages. Ongoing research, technological improvements, and regulatory backing are crucial for the complete integration of GAC principles. In the end, GAC sets the stage for a safer, more sustainable future in analytical chemistry.

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