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Review Article

Recent Advances in Green Analytical Chemistry

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ABSTRACT

Energy-efficient equipment, minimal waste production, and the use of hazardous chemicals and reagents are all encouraged by green analytical chemistry. Current innovations in analytical method development are mostly focused on shrinking sample preparation equipment, using less toxic solvents, and developing extraction processes that are solventless or solvent-minimized. The GAC's guiding principles provide a foundational framework for incorporating green practices into analytical processes. Despite these recommendations, some undesirable actions are unavoidable in many situations. In order to examine and, if feasible, lessen the impact of analytical techniques on the environment and workers, it is crucial to determine how green they are. A number of indicators have been created to assess how environmentally friendly analytical processes are. Important instruments for evaluating the environmental friendliness of analytical procedures are the Analytical Eco-Scale, Green Analytical Procedure Index, and Analytical Greenness Metric. Each of these metrics takes into account different aspects of the analytical process to estimate the procedure's green index. Among the most crucial instruments for evaluating the environmental impact of analytical processes are the Analytical Eco-Scale, Green Analytical Procedure Index, and Analytical Greenness Metric. Each of these metrics takes into account different aspects of the analytical process to estimate the procedure's green index. These metrics, their underlying theories, and instances of their use in particular analytical processes were all discussed in this review. From the viewpoint of the average reader or user, the benefits and drawbacks of various measures are discussed. We think this paper will stimulate a lot of fresh ideas and advancements in this field.

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INTRODUCTION

The term "green chemistry" describes the development of chemical products and procedures that minimize or do away with the usage of hazardous ingredients. The chemical product's life cycle (Fig. 1), includes its production, use, and eventual disposal, is encompassed by green chemistry. Green analytical chemistry's objective is to minimize or completely do away with hazardous and toxic reagents, solvents, and methods used throughout the analysis processes pre-treatment, determination, and preparation phases¹.

Chemical senescence. Since the goal of combined chemical measurement chemistry is to obtain direct chemical means for accurate bulk or surface analysis, whether it be the bulk surface of a solid, liquid, or signal, forming the proper data hand requires developmental measurements and scientific content that is handling Chemistry analyses provide a quantitative foundation for knowledge regarding chemical

systems, including theories, models, and development systems. This covers the creation and explanation of the chemical world's ubiquitous procedures for new laws, the speech of the guns, and the administration of the analytic administrative pre-critical in this sense, the Ne processes are eruptions, connected to several problems wherever the Sustainable Development paradigm is applicable to a sustainable society where science is involved².

The following definition is provided in the textbook issued by the European Federation of Chemical Societies Working Party on Analytical Chemistry: The scientific field of analytical chemistry creates and employs tools, techniques, and plans to find out what the make-up and characteristics of matter are in space and time³. This highlights the fact that developing techniques for chemical measurements in order to gather the required data is a key component of research in analytical chemistry. Precision and accuracy are key

components of measurement data quality and have a significant impact on data uncertainty measurements.

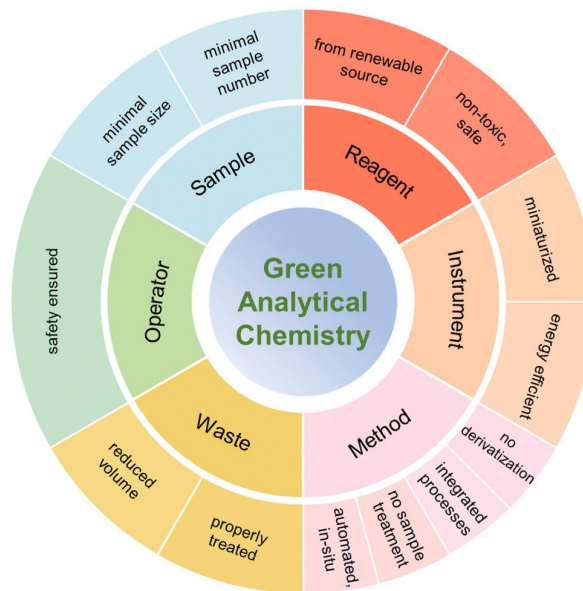


Figure 1: Green Analytical Chemistry

Lowering the determination limits, shortening the analysis time, and developing guidelines for the analysis of intricate or unknown sample metrics are frequently the outcomes of research aimed at improving these parameters. Accuracy and precision in data can help to make technically sound decisions about their science of chemical measurements. These fields are closely linked to the creation and provision of systems for both industry and government control and regulation, and they are crucial components of systems for ensuring and controlling quality⁴.

The basics of green chemistry and green analytical chemistry have been the subject of an intriguing discussion started by P.M. Nowak. "Can green chemistry have a theoretical basis as a science?" is the first question it poses. Green chemistry (as described by Anastas and Warner 5) and green analytical chemistry (as defined by Namlesnik) are notions that are primarily intended for processes, synthetic chemists, and method developers⁵. The issue is that these ideas contradict each other and lack coherence. To improve the formulation of the hierarchical order on the Unified Principles of Greenness, it has been proposed to construct Unified Greenness Theory and provide a mathematical explanation for it. This study, which focuses on the significant developments and patterns in analytical chemistry during the past 25 years, examines the impact of green chemistry principles out of chronological order. Among these advancements are trends in chemical measurements that are closely linked to green developments⁶.

History of Green Analytical Chemistry:

Origin of the Concept:

During Euro analysis VI in Paris in 1987, Malissa gave a presentation on paradigm shifts in analytical chemistry. The dissertation is centred on the many stages that historical chemistry covered. included the idea of the late 20th-century imposition of the ecological paradigm. These theories aligned well with the Pimentel report's conclusions, which was released in the United States in 1985 and discussed the effects of chemistry on Earth's health. After ten years. The

Analyst journal of the Royal Society of Chemistry in the United Kingdom introduced environmental analytical chemistry as a technique for analytical processes in an integrated approach to analytical chemistry that also considers the detrimental effects of analytical processes on the environment 7.

The use of chemical processes and procedures known as "green chemistry" aims to minimise or completely do away with the use of products, byproducts, feedstocks, reagents, and solvents, and other substances that are harmful to the environment or human health⁸. Put simply, it's the application of chemistry to the avoidance of pollution. The concepts and philosophy of Green Chemistry are the same as those that were previously established for analytical labs (GAC). However, the concept of improving analytical techniques by reducing solvent and reagent concentrations precedes theoretical advancements; the first GAC approaches for clean analytical techniques were described in 1995⁹. Environmental sensitivity has long been a feature of the analytical community. However, the new integrated approach to analytical chemistry 10 incorporated previous advancements in sample pre-treatment and measurement techniques in light of these novel concepts. Environmentally friendly analytical techniques known as GAC, or clean analytical chemistry, have seen a sharp increase in the number of scientific references in the CAS and SU databases in recent years.

Green Analytical Chemistry's Landmark:

There are three ways that the negative environmental effects of analytical procedures have been mitigated:

- A decrease in the quantity of solvents needed for sample prior to treatment.
- Decreased in the quantity and poisoning of chemicals and solvents used in the meat department, particularly through automation and miniaturisation.
- Creation of substitute direct analytical methodologies that do not need reagents or solvents.

GAC benchmarks for the years 1970–2007. The instruments that may be used to make a method greener differ from the conceptual milestones in this manner. It's noteworthy to observe that although the notions of Green Chemistry and GAC were developed in the 1990s, the means for implementing them originated in the 1970s, suggesting that theoretical ideas were not as advanced as experimental ones. In order to lower the quantity of solvent needed for the sample pre-treatment, the use of microwave radiation was initially suggested for sample digestion in a groundbreaking study in 1975¹¹.

However, in the middle of the 1980s, organic analytes were separated from a variety of sample cortices: In contrast to conventional convective heating techniques for preparation of the sample, microwave-assisted extraction (MAE) conserves solvent and is both quick and effective in terms of energy consumption.

MAE can be substituted with supercritical fluid extraction (SFE), which has as its foundation of the analyte extraction using a fluid in a supercritical environment. When SFE was developed in the middle of the 1980s, it avoided the drawbacks of organic solvents and solved the problems with solid-sample extraction. However, despite SFE has positive aspects, it fell short of chemical analysis experts' expectations¹². Similar to Soxhlet extraction, pressurised fluid extraction (PFE) uses solvents close to their supercritical zone, where high temperatures cause high rates of solvent diffusion and solute solubility.

While keeping the solvent below its boiling point, high pressure enables the solvent to enter the sample more thoroughly. PFE offers good extraction efficiency in a brief extraction period (15–20 min) and at low solvent quantities (15–40 ml). PFE, often referred to as accelerated solvent extraction (ASE), was initially created by Dione in 1996 and verified using an automated extraction system that was sold commercially¹³.

One crucial technique to prevent the usage of a lot of organic solvents in the preconcentration and extraction stages is solid-phase extraction, or SPE. It has been exclusively utilised for water sample enrichment, offering advantages over liquid-liquid extraction (LLE) in the following applications:

- Cutting back on the number of solvents utilised
- Emulsion formation does not impede extraction
- Effective extraction rates and
- Automation's simplicity.

Green Analytical Methodologies:

Examining GAC approaches includes a variety of tactics to reduce or completely eradicate the use of hazardous materials and the generation of debris. The creation of novel pathways to reduce the quantity of byproducts and replace hazardous solvents has been the primary emphasis¹⁴.

Approaches of Screening:

It is evident that reducing the number of samples that must be analyzed using conventional, non-green techniques and the amount of waste generated throughout the process are two of the GAC's objectives. But this decrease in the quantity

of samples for examination needs to be carried out in a safe, regulated manner. The so-called "screening methods" can be used to achieve this, which include methods for determining both those that enable the quick collection of semi-quantitative data and those that determine whether target analytes are present above or below a threshold. Information about every element in a sample. Generally speaking, screening techniques are qualitative, needing little to no sample treatment. The answer is utilized to make decisions right away, and traditional alternatives are needed for confirmation. A straightforward measurement that yields a "yes/no" result is the most basic description of a screening procedure. This eliminates the need to handle a large number of samples and restricts the use of conventional procedures for complete sample treatments to those samples that yield positive results.

It is noteworthy to acknowledge the significant endeavors undertaken by the community of scientists in this regard in the past several years. It is noteworthy to discuss immunoassays (IAs) in this regard. Originally created in 1960 to monitor insulin in blood¹⁵, IAs are currently typically utilized in clinical chemistry to determine whether biological samples include viruses, hormones, or medicines¹⁶.

The most used immunoassay technique is called ELISA. The decrease of hazardous wastes that results from completely substituting aqueous media for organic solvents is the primary benefit of those analytical screening methods that are grounded in biology. In addition, quick colorimetric tests are utilized to detect the existence of certain inorganic substances. We should discuss the several analytical methods frequently used for quick determination of a sample's elemental composition:

- X-ray fluorescence, which requires no pretreatment and offers outstanding qualitative or semi-quantitative data:
- Emission spectrometry of plasma atoms linked inductively the most sensitive and selective methods for multi-elemental determination of many components in a single sample are inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma atomic emission spectrometry (ICP-AES).
- Mass spectrometry (MS), which has several benefits for sensitively determining organic contaminants and selectively determining substances. delivering high-sensitivity, quickly-sequential information on several chemicals.
- Ion-mobility spectrometry (IMS), which is frequently used to detect chemicals from pyrolysis, screen explosives at airports, and monitor stack-gas emissions in enterprises. Additionally, it is used to identify compounds, such as warfare agents, for the military industry¹⁷.

Replacement of Toxic Reagents:

Without requiring further purification, Leaf extract from guavas has been employed as a substitute natural reagent for the FI measurement of Fe. According to a proposal, chlorophyll derived from pea leaves can be used as a natural fluorometric reagent to determine mercury levels by suppressing fluorescence when Hg²⁺ is present. The introduction of the GAC technique for stripping voltammetry

has made the substitute of Hg-based electrodes a popular issue. The many suggested electrode materials.

On-Line Decontamination of Wastes:

Along with more conventional goals (such sensitivity, accuracy, precision, and LODs), special focus should be made on evaluating the environmental effect of new technologies, as previously discussed in the context of GAC 1994. The various flow techniques that were suggested required more work to detoxify the wastes produced. In order to obtain clean waste, online waste treatment essentially entails adding a decontamination step following analytical analysis.

Online waste detoxification was proposed in 1999 and involved the use of:

- Degradation by heat:
- Detoxification via oxidation.
- Photodegradation and.
- Biodegradation¹⁸.

Reagent Free Methodologies:

The most environmentally friendly analytical decisions may be made using methods that rely on direct measurements of untreated materials. One reagent-free approach that has been employed is FT-Raman spectrometry. The quantitative

determination of various analytes is carried out directly on the sample, whether it be liquid or solid, by using ordinary glass vials as sample containers. This eliminates the requirement for sample handling and the operator's exposure to potentially hazardous materials. Additionally, waste generation and reagent consumption are avoided. This method has been used to the examination of sweetener formulations¹⁶ and the measurement of iprodione in solid-pesticide formulations¹⁹. Chemometrics development has backed Level.

Photoacoustic Fourier transform infrared spectroscopy (PAS-FT-IR) is another example of a solvent-free technology that was used to measure Mancozeb in agrochemicals⁹. The technique comprised measuring solid sample transmittance spectra directly. Additional reagent-free techniques suggested in the literature include the use of sample matrix as a reductant in photo-induced mercury cold/chemical vapour generation (PI-CVG). It was proposed to employ atomic fluorescence to identify traces of mercury in wine or spirits samples. The novel technique is predicated on the reduction of mercury using UV-irradiated wine ethanol. To accomplish the reagent-free aim, actual sample analysis was done using the standard-addition method^{20,21}.

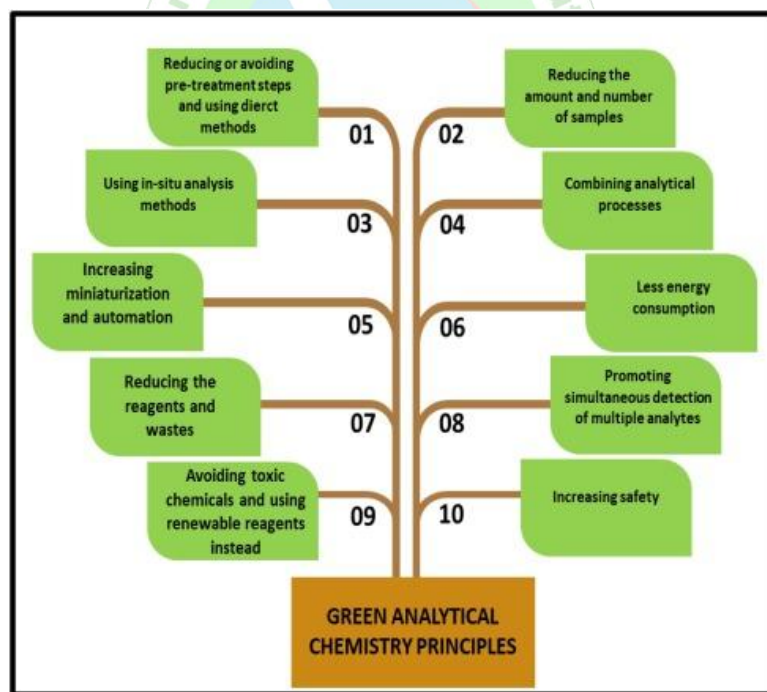


Figure.2: Principals of Green Analytical Chemistry

Key Components of Green Analytical Chemistry:

The goal of the discipline of GAC research is to create analytical processes that produce fewer harmful compounds and are more sustainable. Green chemistry aims to make chemical reactions and processes more ecologically friendly, and this is the foundation of GAC. Among the essential elements of GAC are:

- Cutting back on chemical use: Get rid of or use less chemicals, such as additives, reagents, solvents, and preservatives.
- Reducing energy usage: Make use of less energy
- Waste management: Handle analytical waste appropriately.
- Improving safety: Provide the operator with a safer method.
- Atom economy: Atom economy-related design techniques
- Minimizing devices: Reduce the size of analytical devices

- Cutting down on time: Reduce the amount of time it takes to complete an analysis and receive findings.

Impact of Green Analytical Chemistry:

Pharmaceutical Analysis:

Green chemistry is now something that the chemical and pharmaceutical businesses and laboratories need to take into consideration beyond only their analysis. Ecologically sound reasoning includes the selected methodology, reagents, accessories, staff qualification, and time to assess the product's effectiveness. HPLC is the preferred technique for identifying the active pharmaceutical components and looking into contaminants and degradation products (HPLC). Acetonitrile and/or methanol are used as organic solvents in the majority of these procedures. Additionally, many choose buffer solutions. This is unavoidable. Nonetheless, the majority of them do not employ buffer solutions in the mobile phase and have never even tried to utilize an additional organic solvent in addition to the acetonitrile/methanol combination. Why? Ignorance of the consequences, ease of use, or accommodations?

Environment:

Before being put back into the enclosure, the residues produced by the chemical-pharmaceutical lyres need to be pre-treated. However, the cost of this procedure varies greatly based on the solvent and level of toxicity. For instance, the incineration of acetonitrile results in trash that exacerbates acid rain. The toxicity of the solvent has a detrimental impact on humans even when we use a procedure to reduce waste.

Population:

The present chemistry affects the people on several fronts and in various ways. Patients who frequently get their prescription drugs from pharmacies or health facilities are impacted by the reagents and analytical methods used by analysts or chemical-pharmaceutical operators. A costly process results in an expensive product that is sold. A more costly product is produced on the market using an expensive process and accessories, which are not necessarily essential. An even more costly product is produced on the market using an expensive procedure that requires multiple steps and accessories, some of which are not essential.

Company:

The principles of analytical chemistry and the direction to be taken in the extraction of light chemistry are outlined in the Platea Pharmaceutical Comp Template. The collaboration between formation and training in chemistry must ensure that a better world is provided until better people and communities are in place. A company that embraces this contemporary and modern mindset will undoubtedly flourish. The contemporary des but participants in it of attitude. There will be high-ranking officials in it, and the goal is to make the entire supply chain sustainable, environmentally friendly, and cleannot just the finished product.

Future:

World leaders have already initiated this theoretical process through the 1972 United Nations Conference on the Human Environment in Stockholm, the 1982 Nairobi Conference,

the 1992 United Nations Conference on Environment and Development in Rio de Janeiro, the 2002 World Summit on Sustainable Development in Johannesburg, the 2012 United Nations Conference on Sustainable Development in Rio de Janeiro, and the 2015 Paris Agreement. A venue for academics and business people, the "Green & Sustainable Chemistry Conference" allows them to present their work, exchange ideas, and promote learning²².

Benefits of Green Analytical Chemistry:

Human Health:

- Cleaner Air: Less exposure to dangerous chemical releases into the atmosphere means fewer lung injuries.
- Cleaner Water: There is less hazardous chemical waste discharged into the water, making it safer to consume and use for recreational purposes.
- A reduction in the need for personal protective equipment, a decrease in the usage of harmful chemicals, and an increase in worker safety in the chemical sector (e.g., fires or explosions).
- Safer food: removal of persistent toxic chemicals that can enter the food chain; pesticides that are only harmful to specific pests and that dissolve fast after application.
- Minimal exposure to harmful substances as hormone disruptors.

Environment:

- Many chemicals end up in the environment as a result of disposal, accidental releases (like emissions during manufacturing), or deliberate releases (like pesticides) during use. Green chemicals either decompose into innocuous substances or are recovered for use in the future.
- Plants and animals are less harmed by toxic compounds in the environment.
- A lower chance of global warming, ozone depletion, and smog formation.
- There is less chemical disturbance of ecosystems.
- Reduced use of landfills, especially for hazardous waste.

Economy and Business:

- Chemical processes that require less feedstock to create the same amount of output yield higher yields.
- Fewer synthetic phases, which often allow for increased plant capacity, less energy and water use, and faster product manufacturing.
- Permit a waste product to take the place of a feedstock that was purchased.
- Improved performance, requiring less product to accomplish the same goal.
- Increased rivalry between chemical producers and their clientele.

Recent Developments in Green Analytical Chemistry:

Software's of Green Analytical Chemistry:

ECO-Footprint:

Ecological Food Enteral Footprint Analysis (EFA) is an accounting tool that Rees and Wackernagel introduced at the beginning of the 1990s. It describes how much of a certain resource (ecosystem services) is needed for a given amount of consumption for a particular building project or in an industrial activity. Additionally, the EF describes how the ecosystem can replenish all the resources utilized in a given region for the creation of products and services by absorbing post-consumer waste. The EF measurement is expressed in global hectares (Gha) per person.

The region's industrial operations or population density will be more ecologically friendly if the EF value is lower. Six primary ecological land-use categories forest, fisheries, arable, built-up, grazing, and energy-producing land are taken into account when evaluating the EF. In addition to general EF, particular EF for certain issues impacting ecosystems is now gaining popularity. Examples of particular EF include: Chemical Trace.

The following material footprints are available: energy, land, water, carbon, nitrogen, and phosphorus. Unique method for estimating the general EF parameters. Three primary aspects are taken into account by these methods: the footprints of biological resources, energy, and built-up land. Between 1997 and 2011, China's technological advancements and economic progress were evaluated using this methodology.

E-Factor:

Sheldon has created a quick and easy metric called E (environmental factor) to assess the environmental effect of industrial operations, founded on the notion that the finest answers are typically the most straightforward. The total weight (in kilograms) of waste generated during an industrial or technological process per kilogram of a product is known as the E-Factor. The process will be less wasteful, more sustainable, and greener the closer the E-factor number is to zero. It should be noted, therefore, that the E-Factor can be computed with or without the process water included, based on its possible applications²³. The reported E-Factor values for a few chosen chemical industry sectors. This may also be applied to assess the environmental effects of a particular industrial process, such as the manufacturing of a certain electronic gadget. The pharmaceutical industry has higher E-factor values than other chemical industry sectors. This is because a multi-stage reaction is required to produce a very high-purity product, which generates a lot of waste. Furthermore, the use of very pure reagents is necessary for the manufacturing of pharmaceuticals.

Green Metrics Applied to Organic Synthesis:

When it comes to laboratory and industrial organic synthesis, Green chemistry's tenets have the most impact. High selectivity and the use of readily available, reasonably priced substrates for minimal steps in the synthesis process are essential for a perfect synthesis. These synthesis pathways should also be defined as being more ecologically friendly and sustainable. It is necessary to use green substrates, green reagents, and green reaction conditions while designing the synthesis of novel molecules. Green chemistry generally seeks to achieve organic synthesis. Decrease in the amount of waste and by-products produced at each stage of the synthesis process. Removal of hazardous solvents and chemicals. Substituting environmentally friendly solvents

with water, supercritical fluids, ionic liquids, etc. The usage of catalysts; for example, reducing energy use is a major issue in the production of green organics and could be achieved by heating photocatalysts conventionally^{24,25}. An increase in response efficiency and a decrease in rate volume are two further advantages of irradiation, ultrasonication, or irradiation using alternate energy sources.

CONCLUSION:

There are currently no recognized and commonly used metrics for green analytical chemistry. Although certain greenness criteria have been devised, they fall short of meeting the current demands. In addition to collecting intricate environmental effect data about analytical reagents or methods, they should be simple to conduct and comprehend. There are still a lot of important gaps because the scientific field is still in its infancy. It is necessary to establish concepts for assessing analytical reagents, analytical techniques, and even the environmental performance of entire analytical labs. Development of solvent selection methods, digesting chemicals, and derivatization agent assessment systems relevant to analytical chemistry is required. When choosing a solvent and reagent for optimization operations. Analytical methods' effects on the environment must be considered. Ionic liquids, bio-based solvents, and deep eutectic solvents are examples of new compounds that have been applied in analytical chemistry recently. Before making any comments regarding their greenness, these chemicals must be carefully and thoroughly evaluated. Although life cycle assessment (LCA) has been applied sparingly in the field of green chemistry, analytical chemistry has yet to employ it for evaluation. The many examples demonstrate how life cycle assessment (LCA) provides a comprehensive understanding of the activity's environmental impact. The most thorough method for evaluating the application of analytical reagents or processes appears to be life cycle assessment (LCA).

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