Development of Solvent-Free Analytical Methods for Trace Pollutant Detection in Water Systems Using Green Chemistry Principles

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Abstract

The imperative for pristine water resources necessitates advanced analytical methodologies capable of detecting trace pollutants with high sensitivity and specificity. Conventional analytical procedures often rely on hazardous solvents, generate significant waste, and consume substantial energy, contrasting with contemporary sustainability goals. This article synthesizes developments in solvent-free analytical methods for trace pollutant detection in water systems, grounded in green chemistry principles. It critically examines innovations across sample preparation, instrumental techniques, and advanced sensing platforms, including solid-phase microextraction (SPME), green chromatographic approaches, biosensors, and nanomaterial-enabled strategies. The environmental and health advantages of these approaches are considered alongside their analytical performance characteristics, such as sensitivity, selectivity, and regulatory alignment. Identified challenges encompass operational complexities, economic considerations, and scalability. The article culminates in a synthesis of current progress, recognizing existing limitations, and offering future perspectives for research, policy, and practical implementation to foster more sustainable and effective water quality monitoring globally.

Keywords: Green Analytical Chemistry; Solvent-Free Methods; Trace Pollutant Detection; Water Quality; Solid-Phase Microextraction; Biosensors; Nanotechnology; Environmental Monitoring.

1 Introduction

Water quality assessment remains a critical global concern, driven by increasing anthropogenic pressures and the pervasive presence of trace pollutants. The reliable detection and quantification of these contaminants are fundamental to environmental protection and public health. Traditional analytical workflows, while effective, frequently involve methodologies that are resource-intensive and generate considerable chemical waste, prompting a re-evaluation of current practices within the scientific community. The need for more sustainable analytical solutions has spurred innovations in green chemistry principles.

1.1 Emerging Contaminants and the Need for Trace Detection in Water Systems

Emerging contaminants (ECs) represent a diverse group of chemical substances increasingly identified in aquatic environments, including pharmaceuticals, personal care products, pesticides, and industrial chemicals [1]. These compounds, even at nanogram or microgram per liter concentrations, pose potential ecological and human health risks due to their persistence, bioaccumulation, and toxicity [2][3]. Their widespread occurrence stems from various sources, including industrial discharges, agricultural runoff, and treated wastewater effluents, which often prove inadequate for their complete removal [4]. Consequently, continuous monitoring and the development of highly sensitive and selective analytical methods are essential for their detection and management [5]. The expansion of analytical capabilities has led to an increase in the identification and frequency of EC detections, underscoring the urgent requirement for refined detection strategies [2]. Effective strategies are needed to bridge the gap between their environmental prevalence and comprehensive health risk assessments, particularly for compounds where toxicity data remains limited [2].

1.2 Limitations of Conventional Analytical Methods

Traditional analytical methods, while providing robust quantification of pollutants, frequently suffer from inherent limitations that restrict their sustainability and applicability for trace detection. These methods often involve extensive sample preparation steps, such as liquid-liquid extraction (LLE) or solid-phase extraction (SPE), which are labor-intensive, time-consuming, and require significant volumes of organic solvents [6]. The reliance on hazardous reagents and the generation of substantial chemical waste contradict contemporary environmental stewardship principles [7]. Moreover, conventional techniques often necessitate specialized laboratory infrastructure and highly trained personnel, limiting their deployment in remote locations or for rapid, on-site screening [8][9]. The complexity and cost associated with these traditional approaches impede routine monitoring, particularly for the vast array of ECs present at ultra-low concentrations. Despite ongoing advancements in analytical instrumentation, the sample preparation stage frequently remains a bottleneck, emphasizing the need for innovative, more efficient, and environmentally conscious alternatives [10][6].

1.3 The Promise of Green Chemistry Principles

Green Chemistry provides a transformative framework for developing analytical methods that minimize environmental impact while maintaining high performance [11]. The application of its principles to analytical chemistry, known as Green Analytical Chemistry (GAC), focuses on reducing or eliminating hazardous substances from the entire analytical process, from sample collection to data interpretation [12]. This paradigm shift encompasses strategies such as solvent reduction or complete elimination, waste minimization, energy efficiency, and the use of safer reagents and materials [13]. By integrating GAC principles, new analytical methods can achieve comparable or superior sensitivity and selectivity to conventional techniques, but with a significantly reduced ecological footprint [14][15]. The adoption of green methodologies is not merely an environmental consideration but also offers operational benefits, including reduced costs associated with solvent purchase, waste disposal, and enhanced laboratory safety. This

approach underpins the development of solvent-free techniques, representing a significant advancement towards sustainable environmental monitoring [12][15].

1.4 Review Methodology

This study adopts a structured narrative review approach to synthesize recent advancements in solvent-free analytical methods for trace pollutant detection in water systems. Relevant literature was identified through systematic searches in major scientific databases including Scopus, Web of Science, and ScienceDirect. Keywords such as "green analytical chemistry," "solvent-free extraction," "SPME," "biosensors," and "water pollutants" were used in various combinations.

Inclusion criteria focused on peer-reviewed articles published between 2015 and 2023, emphasizing experimental validation, environmental applications, and methodological innovation. Studies lacking analytical validation or environmental relevance were excluded. The selected literature was categorized into thematic areas including sample preparation, instrumentation, biosensing technologies, and quality assurance.

This structured approach ensures comprehensive coverage of the field while maintaining analytical rigor and reproducibility.

This study contributes to the existing body of knowledge by providing an integrated synthesis of solvent-free analytical methodologies across multiple technological domains, including microextraction, chromatographic innovation, biosensing, and nanotechnology. Unlike prior reviews that focus on isolated techniques, this work presents a cross-disciplinary evaluation, linking methodological advances with sustainability metrics and real-world applicability in water monitoring systems.

2 Thematic Review: Advances in Solvent-Free Analytical Methods

The evolution of analytical chemistry increasingly emphasizes sustainability, driving the development of methods that minimize environmental impact without compromising performance. Solvent-free analytical methods represent a core component of this shift, offering pathways to detect trace pollutants efficiently and responsibly. This thematic review explores recent advancements across various facets of solvent-free analysis, from foundational principles to specific techniques and applications.

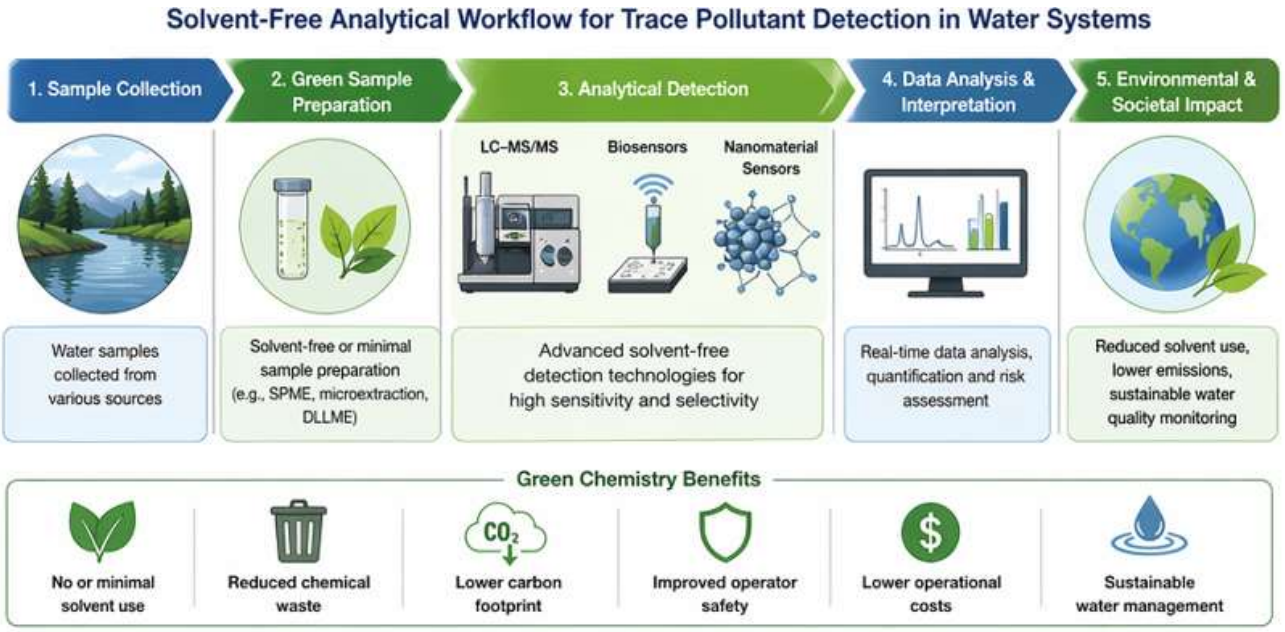

Figure 1. Solvent-Free Analytical Workflow for Trace Pollutant Detection in Water Systems

Figure 1 illustrates a comprehensive solvent-free analytical workflow for trace pollutant detection in water systems, structured across five key stages: (1) sample collection, (2) green sample preparation using solvent-free or microextraction techniques such as SPME and DLLME, (3) analytical detection employing advanced platforms including LC-MS/MS, biosensors, and nanomaterial-based sensors, (4) data analysis and interpretation for real-time quantification and risk assessment, and (5) environmental and societal impact assessment.

The workflow emphasizes the integration of green chemistry principles, highlighting benefits such as reduced solvent consumption, minimized chemical waste, lower carbon footprint, improved laboratory safety, and enhanced sustainability in water quality monitoring.

2.1 Green Chemistry in Analytical Method Development

Integrating green chemistry principles into analytical method development offers a strategic approach to mitigate the environmental burden of chemical analysis. This integration extends beyond mere solvent reduction to encompass the entire life cycle of an analytical procedure, from reagent selection to waste management. The objective centers on creating analytical processes that are inherently safer, more efficient, and economically viable [16].

2.1.1 Principles of Green Analytical Chemistry

Green Analytical Chemistry (GAC) builds upon the twelve principles of green chemistry, adapting them specifically for analytical applications [13][11]. Key tenets include minimizing or eliminating the use of hazardous reagents and solvents, reducing energy consumption, and preventing waste generation [13] . This framework encourages

innovation in sample preparation techniques, favoring microextraction, solventless extractions, and the use of benign alternatives such as water or supercritical fluids [17]. Additionally, GAC promotes the development of real-time, in-situ monitoring to reduce sample transport and storage requirements, thereby decreasing the overall environmental footprint [13]. The integration of green metrics, such as the Green Analytical Procedure Index (GAPI) and Analytical Greenness Evaluator (AGREE), enables systematic assessment of a method's environmental friendliness [18]. These tools facilitate transparent comparison and selection of more sustainable analytical protocols, guiding researchers toward practices that align with environmental protection and resource efficiency [19].

2.1.2 Drivers for Sustainable Analytical Practices

The increasing global emphasis on environmental protection and public health serves as a primary driver for adopting sustainable analytical practices. Regulatory frameworks, such as the European Union's Water Framework Directive, mandate rigorous monitoring of water quality, compelling laboratories to seek more efficient and environmentally sound methods for detecting pollutants [20]. Furthermore, heightened awareness among stakeholders, including industries and consumers, regarding the ecological impact of chemical processes fuels the demand for greener alternatives. Economic incentives also play a role, as reducing solvent consumption and waste disposal costs can translate into significant operational savings. The continuous advancement in analytical technology, particularly in miniaturization and automation, supports the development of greener methods by enabling reduced sample sizes and reagent volumes [8][21]. These combined pressures and opportunities accelerate the transition towards more sustainable and responsible analytical chemistry worldwide.

2.2 Innovations in Solvent-Free Sample Preparation Techniques

Sample preparation, historically the most solvent-intensive and time-consuming stage of analytical workflows, has seen significant innovation towards solvent-free or solvent-minimized approaches. These advancements are central to green analytical chemistry, reducing environmental impact and enhancing analytical efficiency. The focus on miniaturization and direct extraction methods represents a strategic shift in handling complex matrices like water [10][6].

2.2.1 Solid-Phase Microextraction (SPME) and Related Technologies

Solid-phase microextraction (SPME) is a leading solvent-free sample preparation technique, integrating sampling, extraction, and sample introduction into a single step [22][23][24]. This method utilizes a fused silica fiber coated with an extracting phase that directly adsorbs analytes from the sample matrix (liquid or headspace) [25][24]. The adsorbed analytes are then thermally desorbed into a gas chromatograph or liquid desorbed into a high-performance liquid chromatograph [24]. SPME eliminates the need for bulk solvents, significantly reducing waste and simplifying the overall analytical process [23][24]. Recent developments include novel fiber coatings, such as metal-organic frameworks and covalent organic frameworks, enhancing selectivity and extraction efficiency for a wide range of pollutants [26]. Variations like stir-bar sorptive extraction (SBSE) and thin-film microextraction (TFME) offer increased sorptive capacity and faster

equilibrium times, further improving method performance [23]. SPME has been successfully validated through inter-laboratory comparison tests, demonstrating its reliability for routine analysis of organic compounds at trace levels in environmental matrices [22][24]. Its portability also enables on-site sampling, reducing sample degradation and improving data integrity [23][24].

2.2.2 Miniaturized and Alternative Solvent Systems

Beyond complete solvent elimination, significant progress has been made in miniaturizing traditional extraction techniques and exploring alternative, benign solvents. Dispersive liquid-liquid microextraction (DLLME), for instance, dramatically reduces solvent consumption by employing microliter volumes of extraction and disperser solvents [27]. This method often achieves lower limits of detection compared to conventional liquid-liquid extraction for various environmental pollutants [27]. Another innovation involves the use of miniaturized passive samplers, which effectively concentrate contaminants from water over extended periods using minimal or no active pumping [21]. These devices, sometimes 3D-printed, offer a cost-effective and practical means for large-scale monitoring programs [21]. Furthermore, research into greener solvents, such as ionic liquids, deep eutectic solvents, and supercritical fluids, presents promising avenues for reducing the toxicity and environmental footprint of analytical extractions [11]. These alternative media offer tunable properties that can enhance extraction efficiency and selectivity while aligning with green chemistry principles [17].

2.3 Instrumental Techniques for Trace Pollutant Detection

The advancement of analytical instrumentation has paralleled the drive for greener methodologies, enabling highly sensitive and selective detection of trace pollutants. Integration of green chemistry principles with instrumental techniques focuses on reducing reagent consumption, energy usage, and hazardous waste generation, while enhancing analytical performance. This evolution supports both regulatory compliance and environmental stewardship.

Table 1. Comparative Performance of Solvent-Free vs Conventional Analytical Methods

Method	**Solvent Usage**	**LOD (ng/L)**	**Analysis Time**	**Environmental Impact**	**Field Deployable**
LLE + GC-MS	High	10–50	Long	High	No
SPE + LC-MS	Moderate	1–10	Moderate	Moderate	Limited
SPME + GC-MS	None	0.1–5	Short	Low	Yes
DLLME	Low	0.5–5	Short	Low	Limited

Biosensors	None	0.001–1	Very Short	Very Low	Yes
Nanomaterial Sensors	None	0.0001–0.1	Very Short	Very Low	Yes

This comparison highlights the superior environmental performance and competitive analytical sensitivity of solvent-free approaches relative to conventional techniques.

2.3.1 Green Chromatographic Approaches

Chromatographic techniques are central to pollutant analysis, and significant efforts have focused on making them greener. Supercritical Fluid Chromatography (SFC) uses supercritical carbon dioxide as the primary mobile phase, drastically reducing organic solvent consumption and waste compared to High-Performance Liquid Chromatography (HPLC). Miniaturized Liquid Chromatography (LC) systems, including micro-HPLC and capillary electrophoresis, achieve similar separations with significantly lower mobile phase volumes. Gas Chromatography (GC) has also seen green advancements using alternative, safer carrier gases like hydrogen and nitrogen, replacing helium where feasible. These green chromatographic approaches maintain high sensitivity and accuracy while reducing the ecological impact, making them suitable for routine analysis laboratories. Hyphenated techniques, such as LC-MS/MS, continue to offer ultra-trace sensitivity and high selectivity for complex matrices, and their greenness is improved by optimizing sample preparation steps and miniaturizing the analytical flow [21] .

2.3.2 Spectroscopic and Electroanalytical Methods

Spectroscopic and electroanalytical methods provide powerful, often solvent-free, platforms for trace pollutant detection. Laser Ramanspectroscopy, for example, enables both qualitative and quantitative analysis of molecular pollutants in water without contact, accommodating dissolved, undissolved, organic, and inorganic species. This technique relies on pre-established databases of pure molecular samples for accurate identification and quantification. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and its tandem variant (ICP-MS/MS) are critical for elemental analysis, offering exceptional sensitivity for heavy metals and other trace elements in aqueous samples [28]. Green spectrophotometry, employing plant-based extractants and biodegradable solvents, has been explored for trace heavy metal detection, demonstrating sensitivity comparable to traditional methods while reducing environmental harm. Portable electrochemical sensors offer another avenue for on-site, rapid, and solvent-free detection of heavy metals and other contaminants, utilizing minimal sample volumes and exhibiting high sensitivity and selectivity [9].

2.4 Biosensors and Nanotechnology-Based Detection Platforms

The integration of biosensors and nanotechnology offers significant advancements in solvent-free trace pollutant detection, providing highly sensitive, selective, and often portable solutions for water quality monitoring. These platforms leverage biological

recognition elements or unique nanomaterial properties to detect contaminants, minimizing the need for extensive sample preparation and hazardous reagents.

2.4.1 Emerging Biosensors for Water Quality Monitoring

Biosensors represent a promising biotechnological alternative for monitoring emerging contaminants (ECs) in aquatic environments, addressing the limitations of high cost, complexity, and labor-intensive traditional analytical techniques. These devices typically comprise a biological recognition element (e.g., enzymes, antibodies, DNA, receptors) coupled with a transducer that converts a biological interaction into a measurable signal [29]. Biosensors offer advantages such as high sensitivity, selectivity, rapid response times, and potential for on-site, real-time monitoring [9][8]. Optical and electrochemical biosensors are particularly prevalent, designed to detect a range of pollutants including heavy metals, pesticides, bacteria, and toxins [9][8] . Innovations in biosensor technology include the development of portable and multifunctional devices that enhance their applicability for field conditions, simplifying environmental assessments and public health safeguards [9] .

2.4.2 Nanomaterial-Enabled Detection Strategies

Nanotechnology significantly enhances the performance of biosensors and other detection platforms by leveraging the unique physical and chemical properties of nanomaterials. Nanomaterial-based sensors offer superior sensitivity, selectivity, and miniaturization capabilities for detecting a wide array of water contaminants, including heavy metals, anions, and microorganisms [30][31][32]. These materials, such as graphene, gold nanoparticles, and carbon nanotubes, provide high surface-area-to-volume ratios, enabling greater interaction with analytes and improving detection limits [32]. For instance, graphene-based immunosensors demonstrate high resistivity and stability, detecting lead ions in water at ultra-low concentrations (0.01 ppb). Similarly, gold nanoparticle biosensors exhibit high sensitivity to mercury ions, with detection limits reaching 0.005 ppb. Nanomaterial integration facilitates the creation of portable, cost-effective, and field-deployable devices, allowing for rapid and accurate on-site analysis [33][9]. This convergence of nanotechnology and biosensing is transforming water quality monitoring, offering practical solutions for systematic environmental assessment [33][34].

Table 2. Comparison of Biosensor Types for Water Pollutant Detection

Sensor Type	**Target Pollutant**	**Detection Limit**	**Advantages**	**Limitations**
Electrochemical	Heavy metals	ppb–ppt	High sensitivity	Fouling
Optical	Organic pollutants	ppb	Fast response	Interference
Immunosensors	Pesticides	ppt	High selectivity	Cost

Emerging Solvent-Free Analytical Technologies for Trace Pollutant Detection

Technology	Principle	Target Analytes	Detection Limit (LOD)	Advantages	Applications
SPME	Adsorption/absorption of analytes on a coated fiber followed by desorption in the injector	PAHs, Pesticides, Pharmaceuticals, Phenols	0.1–5 ng/L	• Solvent-free • Simple & fast • High enrichment factor	Surface water, Drinking water, Wastewater
DLLME	Dispersive liquid–liquid microextraction using microdroplets	Heavy metals, Dyes, Phenols, Pharmaceuticals	0.5–5 ng/L	• Low solvent use • High recovery • Inexpensive	Industrial effluents, Groundwater, Sea water
Electrochemical Biosensors	Recognition of target analyte by bioreceptor and electrochemical signal transduction	Heavy metals, Pesticides, Endocrine disruptors	0.001–1 ng/L	• High sensitivity • Real-time detection • Portable	On-site monitoring, Drinking water, Aquaculture
Nanomaterial-Based Sensors	Enhanced interaction and signal generation using nanomaterials	Pharmaceuticals, Dyes, Endocrine disruptors	0.0001–0.1 ng/L	• Ultra-sensitive • Wide linear range • Multi-analyte	Environmental monitoring, Food safety, Drinking water
Raman Spectroscopy	Molecular fingerprinting based on Raman scattering	Microplastics, PAHs, Pesticides, Pharmaceuticals	1–100 ng/L	• Non-destructive • Minimal preparation • Rapid analysis	Surface water, Sediments, Wastewater

Figure 2. Overview of Emerging Solvent-Free Analytical Technologies for Trace Pollutant Detection

Figure 2 provides a comparative overview of key solvent-free analytical technologies, including solid-phase microextraction (SPME), dispersive liquid-liquid microextraction (DLLME), electrochemical biosensors, nanomaterial-based sensors, and Raman spectroscopy.

The figure summarizes each technology based on operational principle, target analytes, detection limits (LOD), advantages, and practical applications. Nanomaterial-based sensors and biosensors demonstrate ultra-low detection limits (down to ppt levels), while SPME and DLLME offer robust and scalable solutions for routine environmental analysis.

2.5 Quality Assurance and Reference Materials in Green Analytical Methods

Ensuring the reliability and accuracy of analytical results, particularly for trace pollutant detection, requires robust quality assurance (QA) protocols. Within green analytical methods, this imperative extends to validating new techniques and utilizing appropriate reference materials while adhering to sustainability principles. The need for traceable and reliable data is growing, reflected in the increasing importance of ISO/IEC 17025 accreditation [35].

2.5.1 Certified Reference Materials and Method Validation

Certified Reference Materials (CRMs) are indispensable for validating green analytical methods, establishing metrological traceability, and ensuring data comparability across laboratories [36][35]. CRMs provide a benchmark against which the accuracy and

precision of new, solvent-free techniques can be assessed [37][38]. Method validation, a systematic process to confirm that a method meets specified performance requirements, typically involves evaluating parameters such as specificity, linearity, accuracy, precision, limits of detection (LOD), and limits of quantification (LOQ)[39]. For green methods, validation also encompasses assessing their environmental impact, often using greenness metrics like AGREE or GAPI. The development of green analytical methods for pharmaceuticals and environmental analysis, validated according to guidelines such as ICH Q2(R1), demonstrates satisfactory performance while minimizing environmental impact. The use of CRMs is fundamental for internal quality control, external quality control, and proficiency testing programs, which are essential components of a comprehensive quality assurance system [37][38].

2.5.2 Challenges in Reference Material Preparation for Trace Pollutants

The preparation and certification of CRMs for trace pollutant detection, especially for emerging contaminants in complex water matrices, present unique challenges. A primary difficulty lies in ensuring homogeneity and stability of target analytes at ultra-trace levels within the matrix over time [36][40]. Many emerging pollutants are unstable or prone to degradation, complicating long-term storage and distribution of CRMs. Furthermore, the sheer diversity of ECs, including various organic and inorganic species, necessitates a broad range of CRMs covering different chemical classes and environmental matrices [36][41]. The certified values for many elements, particularly rare earth elements or technology-critical elements not regulated by current monitoring standards, are often absent in existing CRMs, requiring researchers to rely on published literature values [28]. Specific matrix effects inherent to water samples (e.g., salinity, pH, organic matter content) can also interfere with accurate certification processes. Strategies for preparing water matrix CRMs for organic analytes, such as polycyclic aromatic hydrocarbons and pesticides, have been explored through proficiency testing schemes, revealing the applicability and suitability of different approaches [20]. These ongoing efforts are critical to provide essential tools for method validation and quality control in greener analytical chemistry [42].

3 Analysis: Impact and Implications of Solvent-Free Analytical Methods

The transition to solvent-free analytical methods represents a significant paradigm shift, offering extensive benefits and posing distinct challenges. This section evaluates the broader impact of these innovations, considering their environmental, health, analytical, operational, and economic dimensions, along with their practical application in real-world scenarios.

3.1 Environmental and Health Benefits of Solvent-Free Approaches

Solvent-free analytical methods deliver substantial environmental and health benefits by aligning with green chemistry principles. Eliminating or significantly reducing hazardous organic solvents minimizes the generation of toxic waste, thereby decreasing the environmental footprint of analytical laboratories [12]. This reduction translates directly into less air pollution from volatile organic compounds and reduces contamination risks to

soil and water bodies. From a health perspective, diminishing reliance on hazardous solvents improves laboratory safety by reducing exposure risks for analytical chemists, leading to a safer working environment. The development of methods using benign materials, such as plant-based extractants, further enhances their eco-sustainability. These methods also often consume less energy, contributing to overall resource efficiency and reducing greenhouse gas emissions associated with chemical manufacturing and disposal. The shift towards solvent-free methodologies represents a concrete step towards a more sustainable and responsible analytical practice, fostering an ecosystem where analytical needs are met with minimal ecological harm.

3.2 Analytical Performance, Sensitivity, and Regulatory Compliance

Solvent-free analytical methods have demonstrated robust analytical performance, often achieving sensitivity and selectivity comparable to, or even surpassing, conventional techniques. Miniaturized extraction techniques like DLLME can yield detection limits significantly lower than traditional liquid-liquid extraction for various environmental contaminants [27]. Solid-phase microextraction (SPME) provides consistent, quantifiable results for low-concentration analytes, making it suitable for trace analysis [24]. Many green methods, particularly those coupled with advanced detectors like LC-MS/MS, achieve ultra-trace sensitivity (e.g., sub-ng/L or fg on-column detection limits for ECs), which is crucial for monitoring pollutants at environmentally relevant concentrations [21]. The specificity of these methods is often enhanced by novel sorbent phases or selective biological recognition elements in biosensors, allowing accurate identification of target analytes in complex matrices [26]. Crucially, developed green methods are validated according to established guidelines, ensuring satisfactory specificity, accuracy, precision, and robustness for regulatory compliance [38]. The development of portable and on-site detection capabilities supports rapid screening and informed decision-making in regulatory enforcement and environmental management [8].

The analytical sensitivity of detection systems can be formally expressed as:

$$LOD = (3 \times \sigma) / S$$

where σ represents the standard deviation of the blank signal and S denotes the slope of the calibration curve. Solvent-free methods often exhibit improved signal-to-noise ratios due to reduced matrix interference, thereby lowering σ and enhancing detection sensitivity.

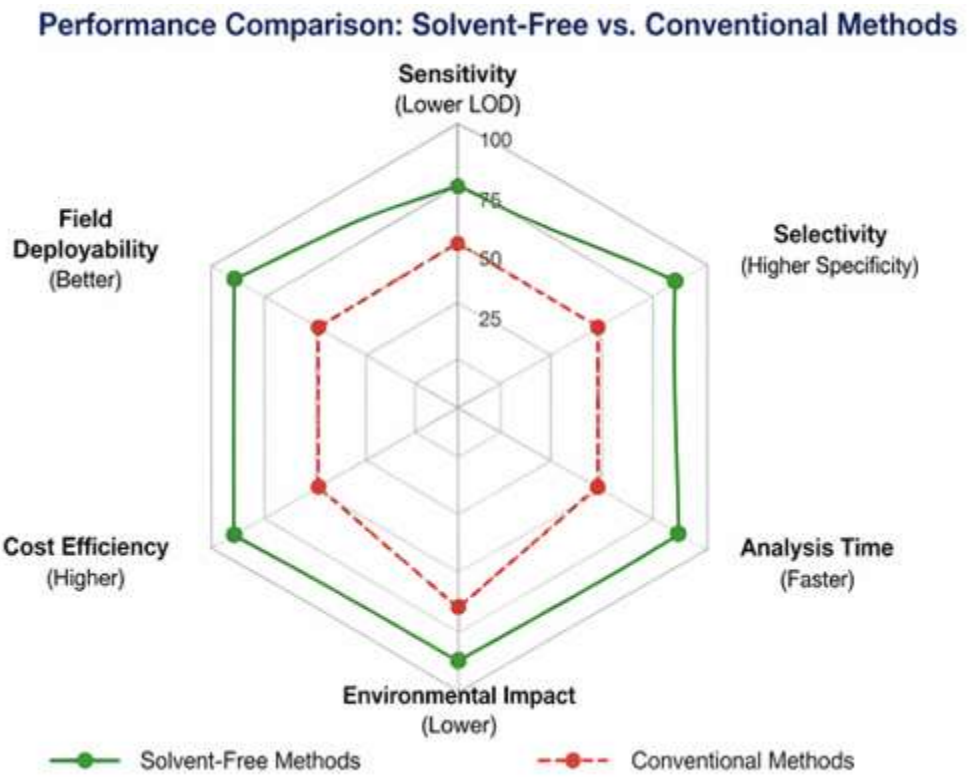

Figure 3. Comparative Performance Analysis of Solvent-Free and Conventional Analytical Methods

Figure 3 presents a comparative radar chart evaluating solvent-free analytical methods against conventional solvent-based techniques across key performance metrics, including sensitivity (limit of detection), selectivity, analysis time, environmental impact, cost efficiency, and field deployability.

Solvent-free methods demonstrate superior performance in environmental sustainability, analysis speed, and field applicability, while maintaining competitive sensitivity and selectivity. The reduced ecological footprint and operational efficiency underscore their suitability for modern environmental monitoring applications.

3.3 Operational, Economic, and Scalability Challenges

Despite their advantages, solvent-free analytical methods encounter operational, economic, and scalability challenges. The initial capital investment for specialized equipment, such as automated SPME systems or advanced biosensor platforms, can be higher than for conventional setups, potentially deterring adoption in some laboratories. While these methods reduce solvent costs and waste disposal expenses in the long term, the upfront expenditure can be a barrier. Operational complexities may also arise from the need for specialized training for new techniques and the optimization of novel extraction phases or biosensor components. The development and validation of new CRMs for these methods, particularly for diverse and unstable emerging contaminants, remain resource-intensive and technically demanding [36][28]. Scalability can be an issue for certain highly specialized or custom-built devices, limiting their widespread implementation for large-

scale monitoring programs. However, advancements in miniaturized passive samplers and portable biosensors offer pathways for broader deployment, as they provide cost-effective and practically efficient means for extensive chemical characterization [21][9].

3.4 Case Studies: Application in Real-World Water Monitoring Programs

The practical application of solvent-free methods in real-world water monitoring programs illustrates their effectiveness and potential. One notable example includes the use of miniaturized passive samplers for monitoring contaminants of emerging concern (CECs) in river systems [21]. A 3D-printed passive sampler device, combined with highly sensitive LC-MS/MS, enabled the identification of almost double the number of CECs compared to traditional grab samples in river water, demonstrating its superior ability to characterize chemical contamination over time [21]. This miniaturized workflow proved cost-effective and efficient for large-scale monitoring programs, especially downstream from wastewater treatment plants [21]. Another case involves the deployment of on-site sampling techniques like SPME for rapid assessment. These methods, with their portability, allow for immediate analysis, reducing sample degradation and providing timely data for environmental assessments, such as those related to atmospheric pollutants washed out by rainfall into water bodies [23][43]. Moreover, the use of various analytical tools, including indicative methods correlating with microscopy, has been tested on operational ships for ballast water compliance monitoring, revealing promising rapid methods that require less expertise [44]. These examples underscore the evolving capabilities of solvent-free and green analytical approaches to address complex environmental challenges effectively.

Despite the demonstrated advantages of solvent-free analytical methods, a critical limitation lies in their standardization and regulatory acceptance. Many emerging techniques lack harmonized validation protocols across laboratories, which may hinder their adoption in compliance-driven environments. Furthermore, while biosensors and nanomaterial-based systems offer exceptional sensitivity, issues related to long-term stability, reproducibility, and calibration drift remain unresolved. Addressing these challenges requires coordinated efforts between academia, regulatory bodies, and industry stakeholders to establish standardized validation frameworks and performance benchmarks.

3.5 Graphical Abstract Description:

The graphical abstract illustrates a solvent-free analytical workflow beginning with water sample collection, followed by green sample preparation (SPME/microextraction), advanced detection (LC-MS, biosensors, nanomaterials), and real-time data output. Environmental benefits such as reduced solvent use, lower emissions, and improved sustainability are highlighted alongside analytical performance metrics.

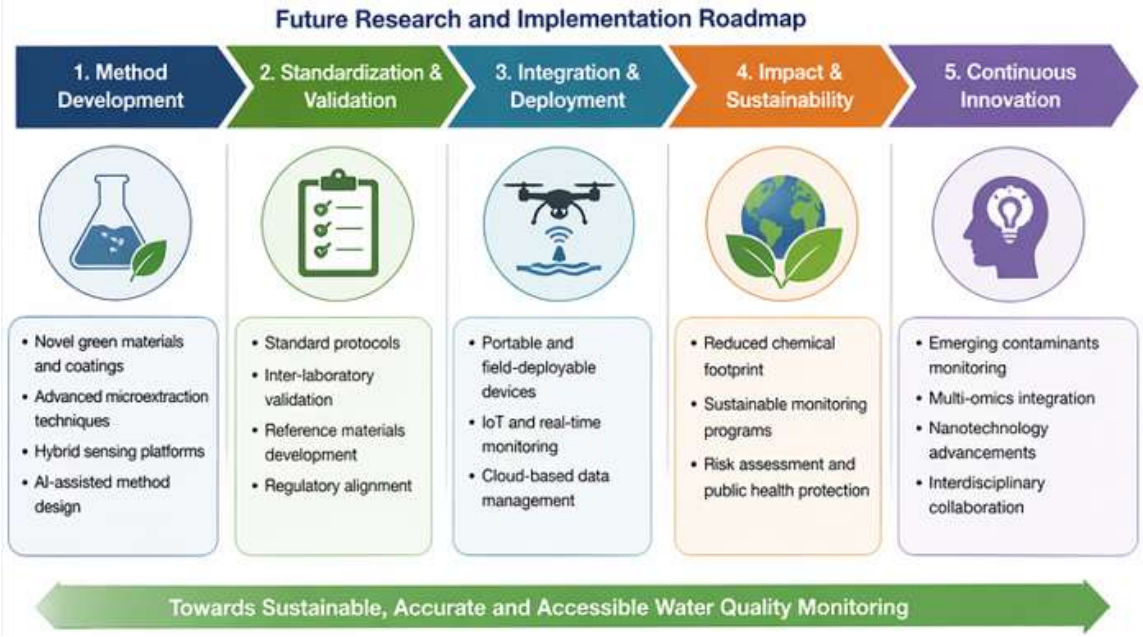

Figure 4. Future Research and Implementation Roadmap for Solvent-Free Analytical Methods

Figure 4 outlines a strategic roadmap for advancing solvent-free analytical methods, encompassing five key phases: (1) method development through novel green materials and hybrid sensing platforms, (2) standardization and validation via inter-laboratory studies and reference material development, (3) integration and deployment through portable devices and IoT-enabled monitoring systems, (4) impact and sustainability focusing on reduced environmental footprint and improved public health outcomes, and (5) continuous innovation driven by emerging contaminants, nanotechnology advancements, and interdisciplinary collaboration.

This roadmap highlights the pathway toward scalable, accessible, and sustainable water quality monitoring systems.

4 Conclusion

The development of solvent-free analytical methods for trace pollutant detection in water systems, guided by green chemistry principles, represents a pivotal advancement in environmental monitoring. These innovations address the critical need for highly sensitive, selective, and sustainable approaches to safeguard water resources and public health. The comprehensive review of existing techniques demonstrates a clear trajectory towards minimizing environmental impact while enhancing analytical performance.

4.1 Synthesis of Advances, Limitations, and Future Perspectives

Significant progress has been made in solvent-free sample preparation, with techniques like solid-phase microextraction (SPME) offering integrated extraction and introduction, thereby eliminating substantial solvent use [22]. Miniaturized extraction and alternative solvent systems further reduce chemical footprint and waste [17]. Instrumental techniques,

including green chromatographic approaches like SFC and miniaturized LC, along with advanced spectroscopic and electroanalytical methods, provide robust detection capabilities with reduced energy and reagent consumption. Biosensors and nanomaterial-enabled platforms offer portable, real-time, and ultra-sensitive detection, crucial for on-site monitoring of emerging contaminants [9]. These advancements collectively reduce laboratory waste, enhance safety, and lower operational costs. However, limitations persist, including the initial capital investment for specialized equipment, the complexity of method development and validation for novel matrices, and the ongoing challenge of developing certified reference materials for a rapidly expanding list of emerging pollutants [36]. Future perspectives include the continued integration of artificial intelligence and machine learning for data interpretation, the development of more robust and universal extraction phases, and enhanced modularity for field-deployable systems. A sustained focus on multidisciplinary research will accelerate the transition towards fully sustainable and accessible water quality analysis.

4.2 Recommendations for Research, Policy, and Practice

To further advance solvent-free analytical methods, several key recommendations emerge for research, policy, and practical implementation.

- **Research:**
    1. Prioritize the development of novel, highly selective, and stable sorbent materials for microextraction techniques that can handle diverse pollutant classes and complex matrices.
    2. Investigate the integration of advanced data analytics and machine learning with biosensor and nanomaterial platforms to improve detection accuracy and reduce false positives in real-time monitoring.
    3. Focus on developing cost-effective and easily reproducible manufacturing processes for miniaturized devices and portable analytical systems to enhance accessibility and scalability.
    4. Conduct more inter-laboratory validation studies for green analytical methods, particularly for emerging contaminants, to establish their broad applicability and regulatory acceptance.

- **Policy:**
    1. Establish clear regulatory guidelines and incentives for adopting green analytical chemistry practices in environmental monitoring laboratories, potentially through subsidies or tax breaks for green technology investments.
    2. Support the development and availability of certified reference materials specifically tailored for trace emerging contaminants in water, addressing current gaps in metrological traceability [28].

3. Promote international collaboration to standardize green analytical methods and quality assurance protocols, facilitating global data comparability and effective cross-border environmental management.

- **Practice:**
    1. Implement comprehensive training programs for analytical chemists on new solvent-free techniques and green chemistry principles to foster wider adoption and expertise.
    2. Encourage the use of green metrics (e.g., AGREE, GAPI) in routine laboratory operations to systematically evaluate and improve the environmental performance of analytical methods.
    3. Facilitate partnerships between academic institutions, industry, and regulatory bodies to accelerate the translation of innovative green analytical research into practical, widely deployable solutions.

These concerted efforts will collectively drive the evolution of analytical chemistry towards a more sustainable and impactful future, ensuring cleaner water systems globally.

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