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(REVIEW ARTICLE)

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Green nanomaterial-based electrochemical sensors for monitoring pharmaceutical residues and heavy metals in water: A comprehensive review of analytical design, validation, and sustainability

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Abstract

Rapid monitoring of pharmaceutical residues and heavy metals in water requires analytical methods that combine sensitivity, selectivity, portability, low cost, and reduced environmental burden. Conventional centralized techniques such as ICP-MS, AAS, HPLC, and LC-MS/MS remain essential reference approaches for confirmatory analysis, but their infrastructure demand and sample-preparation requirements limit routine field deployment. This comprehensive narrative review synthesizes a working set of core peer-reviewed articles and guidance documents selected from 2012-2026, together with earlier foundational references in electrochemistry, green chemistry, and detection-limit terminology. The review focuses on nanomaterial-modified screen-printed electrodes and related electrochemical platforms for aqueous matrices. Carbon nanomaterials, noble and non-noble metal nanoparticles, metal oxides, MOFs, COFs, molecularly imprinted polymers, aptamers, and renewable biopolymers are compared according to their roles in conductivity, adsorption, catalysis, selectivity, antifouling performance, and sustainability. Heavy metals are mainly addressed through anodic stripping voltammetry and related pulse techniques, whereas pharmaceutical residues are commonly monitored using differential pulse voltammetry, square-wave voltammetry, amperometry, or impedimetric sensing. The manuscript also explains how pharmaceutical validation principles such as ICH Q2(R2) and ICH Q14 can be adapted to environmental sensors through a fit-for-purpose target profile, matrix-matched validation, real-sample recovery, robustness testing, and comparison with reference methods. Numerical examples for LOD calculation and Analytical Eco-Scale scoring are included to improve reproducibility and green-chemistry transparency. The major remaining challenges include dissolved oxygen effects, matrix fouling, electrode batch variability, volatile organic contaminants, nanomaterial disposal, and insufficient reporting of raw calibration data. All figures are original three-dimensional schematic illustrations prepared to clarify analytical workflows, electrode architecture, optimization, platform comparison, and practical method development.

Keywords: Green Analytical Chemistry; Screen-Printed Electrodes; Electrochemical Sensors; Nanomaterials; Pharmaceutical Residues; Heavy Metals; Water Analysis; Validation; Eco-Scale; Vancouver References.

1. Introduction

Analytical chemistry has evolved from the isolated single end-point measurement towards integrated systems, which cover sustainable sampling, selective preconcentration, signal amplification, digital processing, and defensible decision making. This trend is greatly impacted by green chemistry, calling on chemists to minimize the use of hazardous reagents, energy consumption, production of wastes, and superfluous analytical procedures [1,2]. In water-quality monitoring, the demand for fast and sensitive methods is further raised by trace heavy metals and pharmaceutical residues, both of which can be found at trace levels and in complicated matrices. This review rests on the conceptual framework of green analytical chemistry. Direct analysis, miniaturization, use of safer reagents, generation of less waste, automation, operator and environmental safety, and low-energy consumption are all fundamental components

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of the 12 principles of green analytical chemistry [2]. There are recent analytical tool proposals, such as Analytical Eco-Scale, Green Analytical Procedure Index, AGREE, AGREEprep and comparative greenness tools, that allow to evaluate environmental and practical parameters in the method selection instead of only the sensitivity or detection limit [3-8]. The thinking of metrology and regulation also informs contemporary practice in analytical chemistry. ICH Q14 provides information on science- and risk-based analytical procedure development, whereas ICH Q2(R2) outlines the principles of validation to confirm the acceptability of an analytical procedure for the purpose for which it is intended [9,10]. Although these guidelines are written to be applicable to drug regulatory dossiers, these concepts of specificity, range, accuracy, precision, robustness and procedure lifecycle are also applicable to environmental sensors, when matrix effects and the risks associated with field-use are specifically considered. Electrochemical sensing is especially suitable for decentralized water monitoring because electrical signals are generated directly at the electrode-solution interface. Fundamental electrochemical principles, including mass transfer, electron-transfer kinetics, interfacial double-layer behavior, and redox reactions, support amperometry, potentiometry, voltammetry, stripping voltammetry, and electrochemical impedance spectroscopy [13,14]. The complete green analytical workflow proposed in this review is summarized in Figure 1.

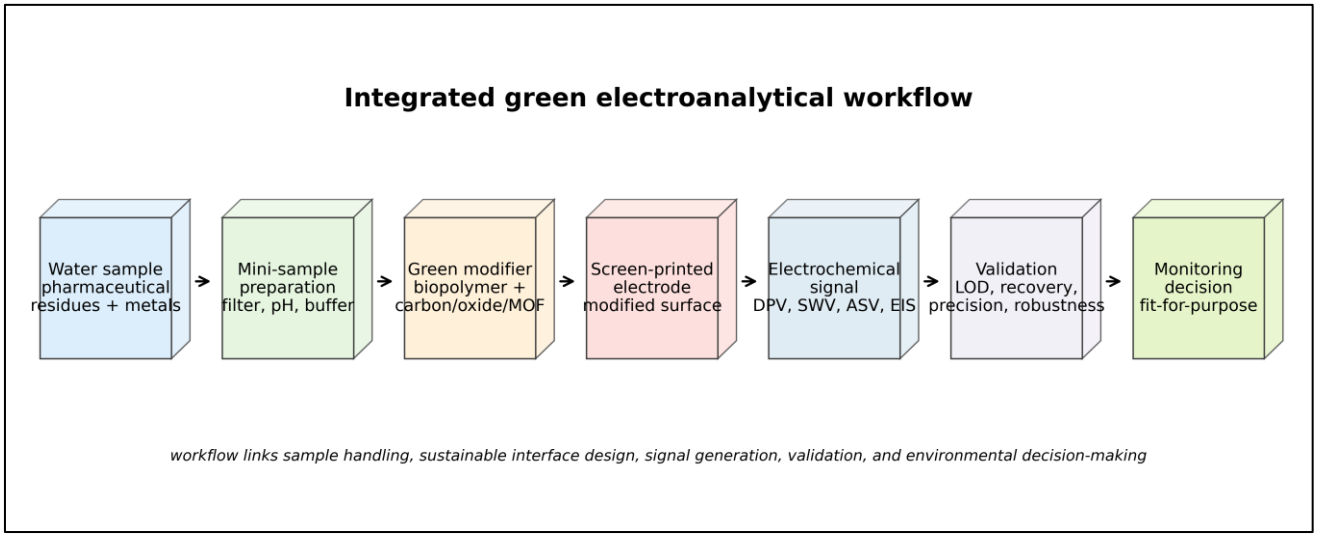

Figure 1 Three-dimensional schematic workflow for green nanomaterial-based electrochemical analysis of pharmaceutical residues and heavy metals in water. The figure links sample handling, sustainable interface construction, electrochemical signal generation, validation, and monitoring decisions.

2. Review Methodology and Scope

This review is conceived as a narrative review with a focussed search strategy and not as a systematic meta-analytical review. Systematic searches were conducted in Scopus, Web of Science, PubMed, ScienceDirect, ACS Publications, RSC journals, SpringerLink, MDPI journals and Google Scholar. The key words were: green analytical chemistry, electrochemical sensor, screen-printed electrode, nanomaterial-modified electrode, heavy metal ions, Pb(II), Cd(II), Hg(II), Cu(II), pharmaceutical residues, antibiotics, anti-inflammatory drugs, water samples, MOF electrochemical sensor, COF electrochemical sensor, molecularly imprinted polymer, biopolymer sensor, validation, Eco-Scale, GAPI and AGREE. The range of publication years was 2012-2026. because this time span includes the conceptualization of green analytical metrics, the fabrication of modern screen-printed electrodes and the latest nanostructured sensor literature. Previous citations were only included if they were reporting foundational theory, e.g. principles of green chemistry, basics of electrochemical or concepts of detection limit [1,11,13,14]. After consideration of analytical relevance, applicability to aqueous matrices, reporting of method performance and contribution to sensor design and/or validation, a working set of over 50 core references was retained for synthesis. Inclusion criteria were: (i) electrochemical or electroanalytical sensing platforms; (ii) target analytes belonging to heavy metal ions or pharmaceutical residues; (iii) use of water, wastewater, drinking water, surface water, food/water extract, or spiked environmental matrices; (iv) clear electrode-modification strategy; and (v) reporting of at least one analytical figure of merit such as linear range, LOD, recovery, selectivity, precision, or stability. Exclusion criteria were: purely toxicological papers, adsorption-removal studies without analytical detection, non-aqueous matrices without relevance to water monitoring, studies without sufficient method description, and articles focused only on material synthesis without sensor validation.

The review is structured on the basis of four questions of analysis: (i) the green nanomaterials involved in improving the generation of electrochemical signals; (ii) the best electrode architectures for heavy metal and pharmaceutical residues; (iii) the reporting style for validation, greenness and uncertainty, and (iv) the technical challenges that hinder consideration from proof-of- concept papers to regular environmental monitoring. Since the studies vary in matrix, electrode size, pretreatment, calibration range, deposition conditions, and statistical treatment, the tables highlight design rationale and comparative trends rather than attempt to rank all studies based on one numerical metric.

3. Analytical Principle of Nanomaterial-Based Electrochemical Sensing

In electrochemistry the electrode is more than a conductor: it is a microenvironment within which mass transport, adsorption, catalysis, recognition, and electron transfer are interconnected [1]. Due to the high surface-to-volume ratio, tunable functional groups, nanoscale porosity, catalytic sites, and conductive pathways, nanomaterials have the ability to modificate the environment at this scale. These properties become all the more essential when the analyte level is low, the sample matrix is complicated, or the redox process is sluggish at a bare electrode [15,16]. Anodic stripping voltammetry is by far the most sensitive technique for heavy metals. The procedure involves preconcentration in general, in which the metal ions are reduced, complexed or accumulated on the surface of the modified electrode; and the metal is stripped from the electrode surface back into the solution by an anodic scan. Peak current is proportional to concentration, while peak potential aids in identification. Bismuth films [15-17], antimony films [18-20] gold nanoparticles [21], carbon nanomaterials [22], chitosan composites [23], ion-imprinted polymers, MOFs, COFs and other porous structures [24] have been reported to enhance preconcentration, and improve peak definition. For pharmaceuticals residues, sensor response is a function of molecular structure and redox activity. Differential pulse voltammetry and square-wave voltammetry are also very popular techniques as they enhance faradaic signal in relation to capacitive current. Carbon nanomaterial could improve electroransfer and pi-pi interaction; metal oxides and MOFs could catalyze oxidation or reduction; and MIPs or aptamers could enhance molecular recognition in complex water matrices [25–28]. This manuscript uses the term screen-printed electrodes consistently for miniaturized printed electrochemical platforms. These electrodes are compatible with portable potentiostats and small sample volumes, and they can be modified by drop-casting, electrodeposition, ink formulation, or layered nanocomposite construction. Their practical value lies not only in low cost, but also in rapid on-site testing and high-throughput screening [17,18,52,53].

4. Green Modifier Materials and Three-Dimensional Electrode Architecture

The sustainability and analytical performance of a sensor are determined by the choice of modifier material and by the way functional layers are organized at the electrode-solution boundary. A typical architecture includes a conductive substrate, carbon ink or conductive layer, biopolymer binder, nanocarbon network, catalytic or porous nanomaterial, and recognition layer such as a MIP, aptamer, ion-imprinted polymer, MOF, or COF. Figure 2 presents this concept as a three-dimensional layered interface.

The architecture should be selected according to the analytical target. Metal ions benefit from films rich in donor groups such as amine, hydroxyl, carboxyl, sulfur, nitrogen, or oxygen sites. Pharmaceutical residues benefit from molecular cavities, hydrogen bonding, hydrophobic microdomains, pi-pi interactions, and electrocatalytic redox centers. Excessive film thickness may improve adsorption but reduce electron transfer and mass transport; therefore, optimization must balance sensitivity, selectivity, fouling resistance, adhesion, and reproducibility.

Sustainable materials such as chitosan, cellulose, alginate, lignin derivatives, hemicellulose, gum Arabic, and biochar can provide renewable functional groups for metal binding, film formation, and antifouling protection [21,23,29,30]. However, the term green should be used carefully. A natural material is not automatically green if its preparation involves high temperature, toxic reducing agents, large solvent volumes, or poor stability. Therefore, material selection should be evaluated together with the whole analytical procedure using Eco-Scale, GAPI, AGREE, or related metrics [3-8].

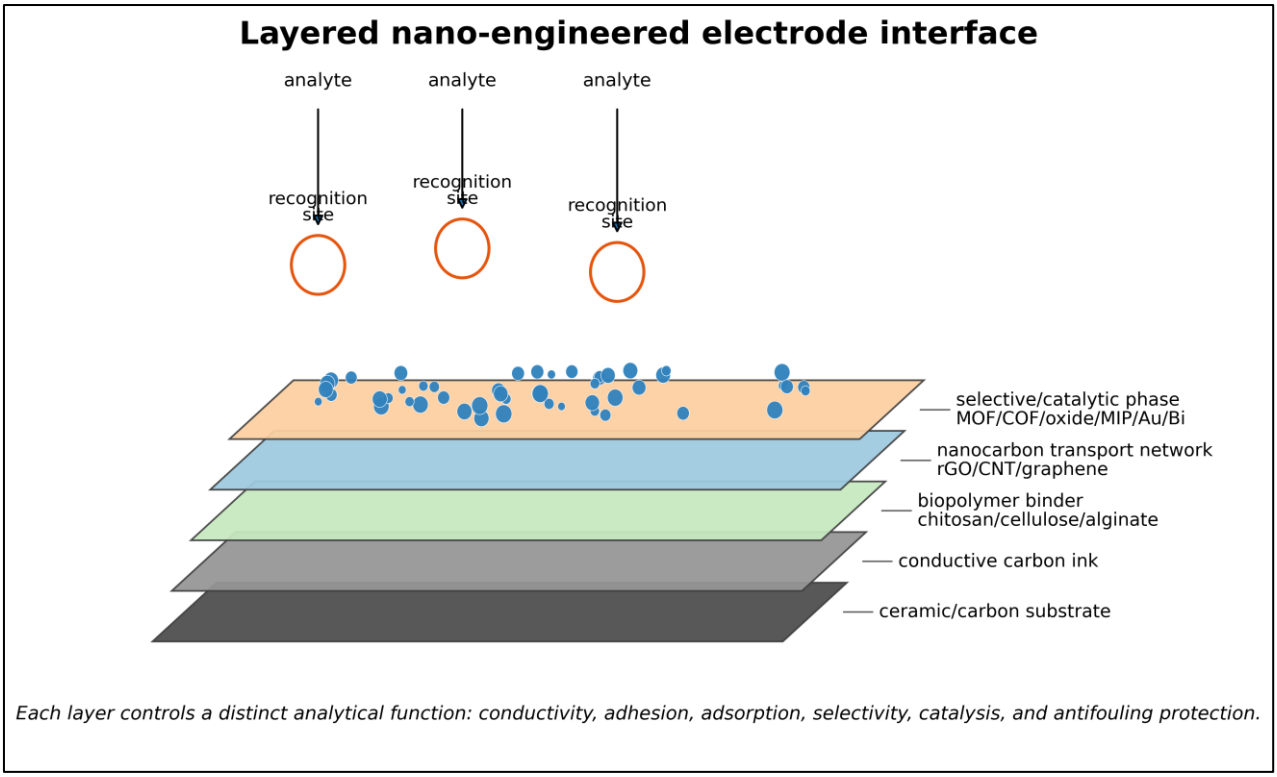

Figure 2 Three-dimensional schematic of a nano-engineered electrode interface. The drawing shows how substrate, conductive carbon ink, biopolymer binder, nanocarbon network, selective/catalytic phase, nanoparticles, and recognition sites cooperate to control adsorption, conductivity, selectivity, catalysis, and antifouling behavior.

The main modifier classes and their analytical functions are summarized in Table 1, while Table 2 explains the role of each layer shown in Figure 2.

Table 1 Green nanomaterial classes used in electrochemical sensing and their analytical functions.

Modifier / interface	Main analytical role	Best target class	Strength	Limitation
Graphene, rGO, CNTs, graphene quantum dots	Conductive network; surface area; pi-pi interaction	Pharmaceutical residues and metals	Fast electron transfer and flexible functionalization	Aggregation and batch-to-batch variability
Bismuth and antimony films/nanoparticles	Stripping-voltammetry deposition sites	Pb(II), Cd(II), Zn(II), selected metals	Mercury-free alternatives with sharp stripping peaks	Sensitive to pH, chloride, deposition conditions, and film renewal
Gold nanoparticles and gold films	Electrocatalysis, noble-metal affinity, aptamer support	Hg(II), Cu(II), As species, biomolecular targets	High conductivity and strong receptor immobilization	Cost and possible nonspecific adsorption
Metal oxides: Fe3O4, ZnO, TiO2, MnO2, La2O3	Adsorption, catalysis, magnetic handling, redox mediation	Metals and selected pharmaceutical residues	Chemical stability and low cost	Poor conductivity unless hybridized with carbon
MOFs and COFs	Porous preconcentration; tunable cavities; functional linkers	Heavy metals and pharmaceutical residues	High surface area and customizable chemistry	Water stability, conductivity, and synthesis complexity

Biopolymers: chitosan, cellulose, alginate, gum Arabic	Chelation, green binder, film formation, antifouling support	Metals, drugs after functionalization	Renewable and rich in functional groups	Swelling, low conductivity, and storage instability
MIPs, ion-imprinted polymers, aptamers	Selective molecular or ionic recognition	Pharmaceutical residues, Hg(II), Pb(II), selected ions	Improved selectivity in complex matrices	Template removal, cost, and matrix-induced loss of affinity

Table 2 Functional explanation of the electrode layers illustrated in Figure 2.

Layer in Figure 2	**Main function**	**Useful materials**	**Failure risk if poorly optimized**
Substrate / base electrode	Mechanical support and electrical connection	Screen-printed carbon, glassy carbon, graphite, gold	Poor adhesion or variable active area
Conductive carbon ink or layer	Provides electron pathway and low background resistance	Carbon ink, rGO, CNTs, graphite, carbon black	High resistance, high capacitive current, or cracking
Biopolymer binder	Film stability, chelation, and green immobilization	Chitosan, cellulose, alginate, gum Arabic	Swelling, diffusion barrier, or poor repeatability
Nanocarbon transport network	Surface area and fast electron transfer	Graphene, rGO, CNTs, graphene quantum dots	Aggregation or uncontrolled roughness
Selective/catalytic phase	Analyte accumulation, catalysis, recognition, and peak separation	Bi, Sb, Au, ZnO, MnO2, MOF, COF, MIP	Leaching, fouling, weak selectivity, or slow kinetics
Surface recognition sites	Specific binding of ion or molecule before signal readout	MIP cavities, ion-imprinted sites, aptamers, functional groups	Cross-reactivity or loss of binding after repeated use

5. Heavy Metal Monitoring

Heavy metals continue to be priority analytes, as many of this class of elements are persistent, non-degradable, bioaccumulative, and toxic in trace quantities. Lead, cadmium, mercury, arsenic, chromium, nickel, and copper are routinely analyzed in samples of drinking water, industrial wastewater, agricultural runoff, surface water, and seawater. Reviews on heavy metal detection also point out the desirability for methodologies that are rapid and sensitive, and low-cost potentially compatible with centralized spectrometric techniques [15-22]. Electrochemical sensors modified with nanomaterials are the most attractive for detecting heavy metals as they integrate the preconcentration and the signal readout steps. However, the nature of modifier materials is very different. Antimony and bismuth generally improve stripping sensitivity in case of Pb(II) and Cd(II); au enhances conductivity and affinity towards mercury and receptor immobilization; carbon materials enhance charge transfer and surface area but require functional moieties for selectivity; chitosan, cellulose and alginate increase chelation ability but need conductive composites; and MOF/COF materials offer porosity and tunable binding sites and may require integration with carbon to surmount conductivity constraints [19-24,36-50]. These discrepancies are outlined in Table 3. Recent advances in the field span the introduction of paper-based sensors, biopolymer-modified electrodes, screen-printed devices, flexible sensors, IoT-enabled platforms and MOF/COF-nanocomposite interfaces [16-24,36-40]. Multi-metal analysis in simultaneous mode is still problematic as peak overlap (or formation of intermetallic compounds), competing deposition, dissolved oxygen, chloride, carbonate, and natural organic matter may cause peak current distortion. Practical approaches should therefore be conducted in the presence of optimal supporting electrolyte, pH, deposition potential, deposition period, modifier concentration, oxygen-controlling tactic and in tolerable level of interferences.

Table 3 Comparative roles of major modifiers for heavy-metal electrochemical sensing**.**

Modifier	Sensitivity tendency	Selectivity tendency	Best use	Main limitation
Bismuth film / Bi nanoparticles	High for Pb(II), Cd(II), Zn(II) in ASV	Moderate; depends on deposition and ligand environment	Mercury-free stripping platforms	Film renewal, pH sensitivity, overlapping peaks
Antimony film / Sb nanoparticles	High for Cd(II), Pb(II), Zn(II), often in acidic media	Moderate; good stripping behavior under optimized conditions	Alternative to Bi in multi-metal ASV	Possible oxidation-state instability and matrix dependence
Gold nanoparticles / gold film	High for Hg(II), As species, Cu(II), receptor-based sensors	High when combined with aptamer, thiol, or MIP recognition	Noble-metal affinity and biomolecule immobilization	Cost and nonspecific adsorption
Carbon nanomaterials	Moderate to high after functionalization	Low to moderate alone; improved with chelators/MIPs	Conductive scaffold for hybrid sensors	Aggregation and insufficient selectivity alone
Chitosan	Improves accumulation through amine/hydroxyl groups	Moderate; good for cationic metals but not fully selective	Green chelating binder in hybrid films	Swelling and poor conductivity
Cellulose / nanocellulose / alginate	Improves adsorption and film sustainability	Moderate; depends on functionalization	Renewable binder and antifouling matrix	Hydration effects and limited conductivity
MOF/COF and porous hybrids	High when pores and ligands enrich target ions	High if linker chemistry is tailored	Multi-metal preconcentration and structured recognition	Water stability and electron-transfer limitations

6. Pharmaceutical Residue Monitoring

Pharmaceutical residues are introduced in the water system through domestic wastewaters, hospital wastewater, pharmaceutical industry wastewater, livestock farming, and inefficient elimination in the wastewater-treatment plants. Monitoring at an analytical level is challenging because concentrations are potentially low, compound classes are chemically diverse and matrix components such as natural organic matter (NOM), surfactants, disinfectant by-product, salt and transformation products can interfere on electrode response. Recent reviews emphasize electrochemical sensors and biosensors as promising tools for the determination of pharmaceutical residues in environmental waters due to their potential for miniaturization and surface modification with selective nanostructures [25-28]. The electrochemical response for antibiotics could include the oxidation of phenolic, piperazinyl, quinolone, amino or heteroaromatic moiety, depending on the class of the compound. Several tetracyclines and fluoroquinolones require pH-dependent adsorption and oxidation, some sulfonamides show weaker signals unless the surface of the electrode is catalytically modified, and b-lactams might need indirect or enzymatic procedures due to the poor direct electroactivity. Carbon/MOF/MIP composites can enhance the preconcentration and molecular recognition [25-28]. When it comes to analgesic and anti-inflammatory pharmaceutical residues, paracetamol and diclofenac can be detected by direct oxidation, most commonly at modified carbon electrodes, but ibuprofen and naproxen are known for having stronger adsorption and may be determined by use of electrocatalytic surfaces or subjected to sample pretreatment. Hormonal and endocrine active residues typically need aptamer, MIP or immuno-recognition layers as ultra-trace level and nonspecific adsorption constitute the greatest challenges. These cases testify that pharmaceutical sensing must be constructed/classify according to redox chemistry, molecular size, pKa, hydrophobicity and behavior in matrix rather than one universal shape/model for electrodes. In practical water analysis, pharmaceutical sensors should be evaluated not only in buffer but also in tap water, river water, wastewater, bottled water, or effluent extracts. Recovery studies, standard addition, interference testing, comparison with chromatographic reference methods, and electrode-to-electrode reproducibility are needed to demonstrate fitness for purpose. Fouling is a major barrier because drug oxidation products and organic matter can passivate the surface. Antifouling layers, hydrophilic polymer coatings, filtration, dilution, standard addition, and pulsed electrochemical cleaning can reduce this problem.

7. Analytical Validation and Adaptation of ICH Principles to Environmental Sensors

Validation should demonstrate that a method is suitable for its intended use. For a nanomaterial-based environmental sensor, this means more than reporting a calibration equation. The validation package should include selectivity, working range, linearity or validated nonlinear response, sensitivity, LOD, LOQ, accuracy/recovery, repeatability, intermediate precision, electrode-to-electrode reproducibility, robustness, stability, matrix tolerance, and real-sample applicability.

ICH Q2(R2) is valuable because it provides a structured vocabulary for analytical validation, but it was prepared for analytical procedures used in pharmaceutical registration applications [10]. Therefore, direct transfer to environmental water sensing is not sufficient. The principles should be adapted by defining an environmental analytical target profile: target analyte, matrix type, decision concentration, sample-preparation conditions, expected interferences, acceptable uncertainty, field or laboratory use, and required confirmation strategy. Accuracy becomes recovery in real water or agreement with ICP-MS/LC-MS/MS; precision must include independent electrode batches; specificity must include matrix ions, dissolved organic matter, and coexisting pharmaceuticals; and robustness must test pH, ionic strength, dissolved oxygen control, deposition time, and storage conditions.

ICH Q14 is also useful because it encourages science- and risk-based analytical procedure development [9]. In an environmental sensor, critical method variables may include nanomaterial loading, film thickness, drying temperature, electrolyte composition, deposition potential, deposition time, pulse amplitude, pH, sample filtration, and oxygen-removal or oxygen-tolerance strategy. These variables should be studied through risk assessment and design of experiments when possible, not only by one-factor-at-a-time optimization.

LOD and LOQ should be calculated transparently. A common slope-based approach is LOD = 3.3 x SD_blank / slope and LOQ = 10 x SD_blank / slope. For example, if the calibration slope for Pb(II) is 0.245 microampere per microgram L-1 and the standard deviation of ten blank measurements is 0.006 microampere, then LOD = 3.3 x 0.006 / 0.245 = 0.081 microgram L-1 and LOQ = 10 x 0.006 / 0.245 = 0.245 microgram L-1. This calculation should be supported by low-level validation samples and not reported as a theoretical number only [11].

Recommended validation evidence for publication-quality environmental electrochemical sensors is summarized in Table 4.

Table 4 Validation elements for adapting ICH-style principles to environmental electrochemical sensors.

Validation element	Environmental adaptation	Minimum evidence to report	Common weakness
Specificity / selectivity	Test realistic ions, organic matter, surfactants, oxygen, and coexisting drugs	Interference ratios, mixed-analyte tests, matrix comparison	Only unrelated interferents are tested
Linearity and range	Use matrix-matched calibration or standard addition when matrix effect is strong	Replicates, residuals, confidence intervals, range definition	High R2 reported without residuals
LOD / LOQ	Calculate from blank or low-level replicates plus slope; verify near decision level	Formula, blank SD, slope, n, low-level recovery	LOD calculated from unreported data
Accuracy / recovery	Spike real water samples; compare with reference method when possible	Recovery %, RSD %, standard addition, ICP-MS or LC-MS/MS comparison	Only buffer results reported
Precision	Separate repeatability, electrode-to-electrode, day-to-day, and batch-to-batch precision	Independent electrodes and independent days	Repeated scans on one electrode only
Robustness	Deliberately vary pH, deposition time, oxygen control, nanomaterial dose, storage	Factorial design or robustness table	No robustness test

Stability and fouling	Measure retained response after storage and repeated scans in real matrix	Short/long storage, cycling, fouling recovery	Freshly prepared electrodes only
Greenness and safety	Apply Eco-Scale, GAPI, AGREE; include nanomaterial disposal plan	Metric score plus waste and reagent details	Green claim without quantitative metric

8. Greenness Metrics and Numerical Eco-Scale Example

Green analytical chemistry metrics should be used to prevent unsupported claims. Analytical Eco-Scale assigns penalty points to factors such as hazardous reagents, energy use, waste, occupational risk, and procedure complexity; the final score is calculated as 100 minus the total penalty points [3]. GAPI gives a pictorial evaluation across the complete analytical process from sampling to final determination [4]. AGREE converts the 12 principles of green analytical chemistry into a multi-criteria score and software-assisted output [5]. These tools are complementary because each emphasizes different aspects of the method [3-8].

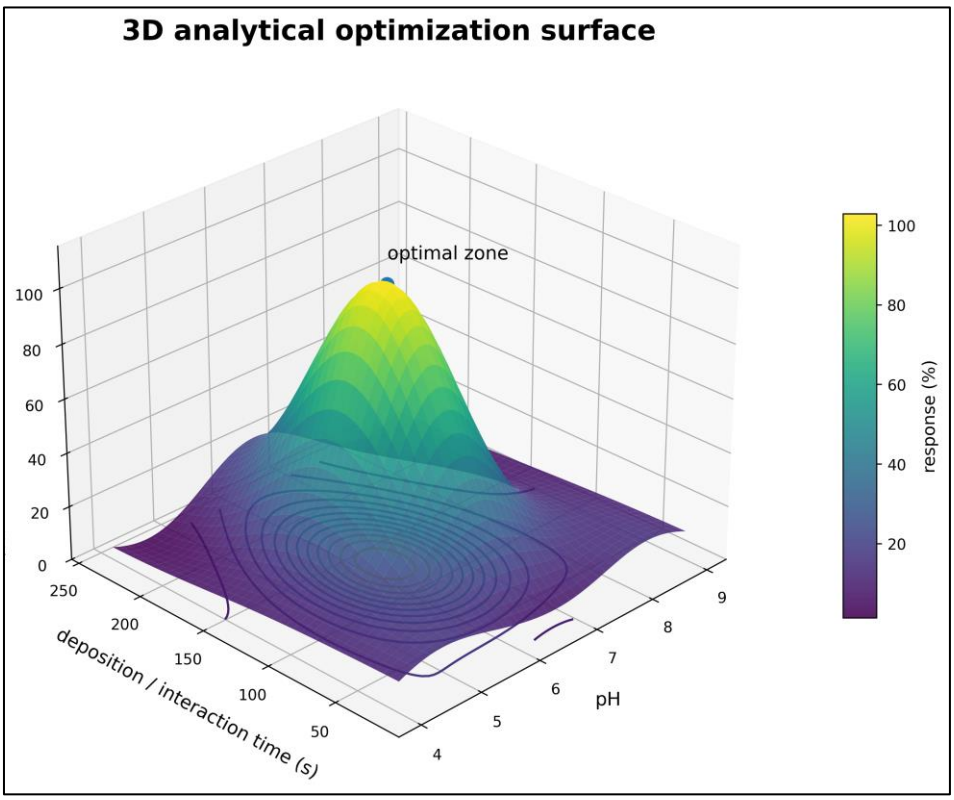

Figure 3 Three-dimensional response-surface illustration showing how pH and deposition/interaction time can influence normalized electrochemical current response. In practical optimization, similar surfaces can include signal intensity, recovery, waste, time, and robustness as simultaneous objectives.

As an illustrative Eco-Scale example, consider a screen-printed electrode method for Pb(II) in filtered tap water using 1.0 mL sample, acetate buffer, bismuth film, no organic solvent, room-temperature measurement, and a portable potentiostat. A possible penalty assignment is: buffer/reagent hazard = 2, bismuth salt = 2, waste volume below 10 mL = 1, energy demand = 0, sample pretreatment by filtration = 1, operator risk = 1, and no derivatization = 0. Total penalty points = 7; therefore Eco-Scale score = 100 - 7 = 93. This would indicate an excellent green profile, but the score should be recalculated if nitric-acid digestion, organic extraction, toxic solvents, large sample volumes, or non-reusable nanomaterials are introduced.

Figure 3 shows why green optimization must consider several variables simultaneously. Increasing deposition time can improve sensitivity but also increases analysis time and may worsen fouling. Increasing nanomaterial loading can improve surface area but may increase background current and waste. A response-surface or design-of-experiments approach can identify an operational zone that balances signal, time, material consumption, and robustness.

9. Comparative Position of Electrochemical Sensors

Nanomaterial based EC sensors should be considered as complementary rather than a substitution tool for traditional laboratory methods. However, ICP-MS, AAS, HPLC, and LC-MS/MS are indispensable for multi-element quantification, speciation, complex unknown screening, and confirmatory analysis. Their drawbacks are mostly a result of cost, required infrastructure, portability, and the burden of sample preparation as well as delayed feedback during analysis in high-volume monitoring. Electrochemical sensors can yield fast, low volume, and portable measurements, but need thorough validation for matrix effects, electrode-to-electrode variability, selectivity issues, and long-term stability [39,40]. Figure 4 illustrates a semi-quantitative appreciation based on relative scores from 1 to 10 (weak and unfavorable performance being 1 and strong and favorable performance being 10) with respect to the stated descriptor. Sensitivity, selectivity, portability, low cost, low waste, and field readiness are the factors. These scores are not absolute metrics and should not be considered as global indicators of performance as they are illustrative values based on literature and guided by common strengths and limitations of electrochemistry versus ICP-MS, AAS, chromatographic methods and portable sensors as reported in reviews [15-22,25-28,39,40]. The detail of the exact scoring system is provided in Table 5.

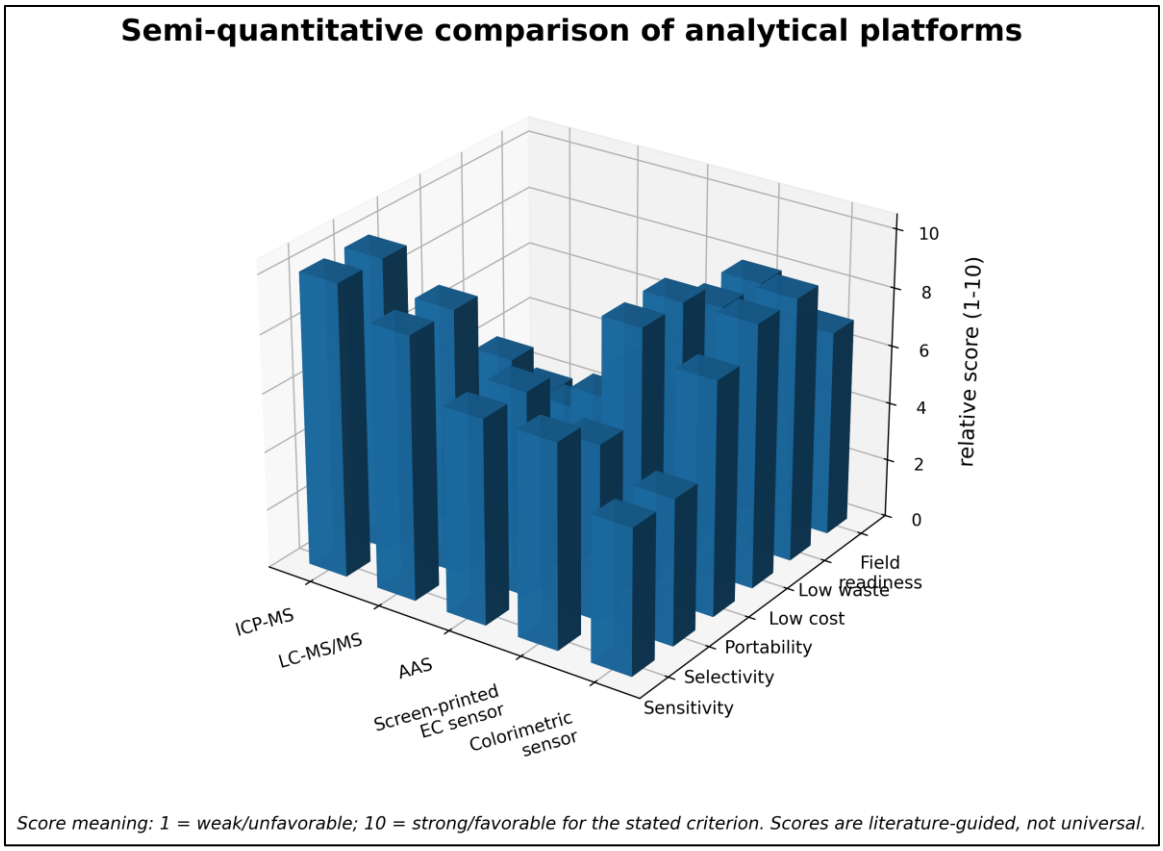

Figure 4 Three-dimensional semi-quantitative comparison of selected analytical platforms for environmental water monitoring. Relative score: 1 = weak/unfavorable; 10 = strong/favorable; scoring logic is summarized in Table 5.

Table 5 Scoring basis used for the platform comparison in Figure 4.

Criterion	Meaning of high score	Reason electrochemical sensors score strongly	Reason reference methods remain important
Sensitivity	Low LOD and useful response near environmental decision levels	Nanostructures and stripping voltammetry can reach trace levels	ICP-MS/LC-MS/MS usually provide lower or more traceable detection capability
Selectivity	Ability to distinguish target from interferents and matrix species	MIP, aptamer, ion-imprinted, and array strategies can improve selectivity	Reference methods provide chromatographic, mass, or elemental discrimination
Portability	Possibility of on-site or near-site analysis	Screen-printed electrodes and portable potentiostats are field-compatible	Large instruments require laboratory infrastructure
Low cost	Lower capital and per-test cost	Small devices and low sample/reagent consumption	Reference methods require expensive instrumentation and maintenance
Low waste	Small solvent/sample volume and limited pretreatment	Microvolume tests can minimize waste	Digestion, extraction, and chromatographic solvents may increase waste
Field readiness	Suitability for rapid screening and high sampling frequency	Can support on-site decisions after validation	Confirmatory evidence is still needed for regulation and legal decisions

10. Representative Sensor Platforms and Literature Patterns

Representative literature demonstrates several recurring design patterns. Reduced graphene oxide-chitosan/poly-L-lysine nanocomposites have been used for simultaneous stripping determination of Cd(II), Pb(II), and Cu(II), illustrating how carbon conductivity and biopolymer/amine functionality can work together [41]. Ion-imprinted chitosan-graphene oxide composites demonstrate how template-directed recognition can improve selectivity for a target ion [42]. Flexible copper-biopolymer sensors show the movement toward adaptable and field-compatible platforms [43]. Gold nanoparticle-functionalized beta-cyclodextrin-graphene hybrids show host-guest and nanometal enhancement effects [44].

Other examples highlight the growing range of interfaces. Gum Arabic nanoparticle films have been applied for rapid in-situ heavy-metal detection in real samples [45]. Bismuth-doped carbon xerogel in a chitosan matrix has been reported for sensitive voltammetric detection of Pb(II) and Cd(II) [46]. Conductive polypyrrole nanoparticles, chitin-grafted polyaniline, and AuNP-aptamer biosensors demonstrate that conductive polymers and biomolecular receptors can support both accumulation and selectivity [47-49]. COF and MOF/carbon hybrids add porous preconcentration and tunable functional sites, with recent studies extending beyond the earlier COF/MWCNT platforms toward newer COF and MOF-based heavy-metal sensors [36-38,50].

Across these studies, the most important analytical trend is hybridization. Single materials rarely deliver all necessary properties. Carbon materials supply conductivity, metal or oxide nanoparticles supply catalysis and deposition sites, biopolymers supply chelation and film formation, MOFs/COFs supply porosity and tunability, and MIPs or aptamers supply selectivity. Representative design patterns and their analytical risks are organized in Table 6.

Table 6 Representative design patterns for nanomaterial-based electrochemical sensors.

Design pattern	Core components	Best analytical target	Why it works	Key risk
Conductive chelating film	rGO/CNT + chitosan or polyamine polymer	Cd(II), Pb(II), Cu(II)	Combines electron transfer with metal binding	Peak competition and film swelling
Ion-imprinted nanocomposite	Template ion + polymer + GO/CNT	Single metal ion in complex matrix	Recognition cavity improves selectivity	Incomplete template removal and slow diffusion
Host-guest amplification	beta-cyclodextrin + AuNP + graphene	Metals and aromatic pharmaceutical residues	Inclusion/adsorption plus catalytic nanoparticles	Nonspecific inclusion of matrix compounds
MOF/COF-carbon hybrid	MOF/COF + MWCNT/rGO/carbon black	Pharmaceutical residues and metals	High porosity plus charge transport	Water stability and conductivity limitation
Biopolymer nanoparticle film	Gum Arabic/chitosan/cellulose + metal/oxide NPs	Field metal screening	Renewable binder and high adsorption capacity	Batch variability and long-term storage
Aptamer or MIP nanoelectrode	Aptamer/MIP + AuNP/CNT/graphene	Hg(II), antibiotics, hormones	Specific recognition with amplified transduction	Bio-recognition stability and cost
Flexible / IoT platform	Flexible substrate + carbon thread/SPE + wireless readout	On-site multi-metal screening	High sampling frequency and portable data capture	Calibration transfer and field robustness

11. Challenges, Environmental Safety, and Future Directions

Although many studies have demonstrated excellent sensitivity, their application in environmental monitoring in the field is still very limited. The first hurdle is real-sample complexity. Natural water and wastewater are rich in dissolved organic matter, chloride, carbonate, surfactants, suspended solids, microorganisms, disinfection byproducts, and other electroactive materials. These chemicals may complex with metals, contaminate electrodes, shift peak potentials, and modulate pharmaceutical oxidation mechanisms. Consequently, the performance in buffer needs to be considered as only a proof of concept. Dissolved oxygen is an important variable, yet widely neglected. Oxygen reduction may increase background current, shift baselines, and interfere with low potential determinations. Nitrogen purging provides better precision in laboratory but simplicity in field is compromised. Environmental sensor studies, as a rule, should clarify if oxygen was eliminated, permitted, or compensated for by background subtraction, choice of potential window, protection of membrane, or signal processing method. The second gap is reproducibility. The response may be affected by nanomaterial synthesis, drop-casting volume, drying conditions, ink formulation, electrode size, humidity, and storage temperature. Several articles that report the repeatability for repetitive scans on a single electrode give limited information about the repeatability for separate fabricated batches. In future work, the electrode-to-electrode RSD, the batch-to-batch variability, the storage stability and an acceptance criterion for discarding faulty SPEs should be announced. The third gap is selectivity in mixtures. Rarely do environmental samples contain one analyte alone. Simultaneous deposition of several ions, superposition and overlapping of oxidation peaks of drugs, degradation products and matrix elements are some of the issues that take this technique to the next level. Further promising strategies include multi-electrode arrays, molecularly imprinted layers, ion imprinted polymers, chemometric deconvolution, machine-learning classification, and complementary electrochemical screening with confirmatory chromatographic or spectrometric methods. Volatile organic contaminants add another challenge. Many volatile organic

compounds are not strongly electroactive at common aqueous electrodes, may evaporate during sample handling, and may require headspace, membrane extraction, adsorptive preconcentration, or indirect sensing. When a study claims broad water-pollutant monitoring, it should clarify whether the proposed electrochemical platform is intended for metals and redox-active pharmaceutical residues only, or whether sample pretreatment is included for volatile and weakly electroactive pollutants.

Environmental safety of nanomaterials must also be addressed. The use of nanoparticles, MOFs, COFs, and nanocarbon materials may reduce reagent volume but can introduce secondary contamination if particles leach from the electrode or if used devices are discarded without control. Safe-by-design strategies include immobilizing nanomaterials in stable binders, testing leaching after use, minimizing total modifier mass, using renewable binders, collecting used electrodes as solid laboratory waste, and comparing reusable versus single-use formats with a life-cycle perspective.

Future research should focus on standardized validation protocols for water-sensor studies, interlaboratory comparison of screen-printed electrodes, realistic matrices and unspiked environmental samples, oxygen-tolerant measurement protocols, antifouling/self-cleaning interfaces, open reporting of raw calibration and interference data, integration with portable potentiostats and geospatial mapping, and safe disposal or regeneration of nanomaterial-modified electrodes.

12. Proposed Practical Framework and Supplementary Material

A publishable and transferable method can be developed by applying a staged approach. Stage 1: Analytical Target Profile (ATP) Analyte Matrix Decision concentration Required analysis time (RAT) Acceptable uncertainty Portability need Greenness goal. Stage 2 determines the electrode configuration based on analyte chemistry. Stage 3 applies experimental design optimization to pH, electrolyte, deposition parameters, nanomaterial loading, pulse parameters, oxygen strategy, and sample pretreatment. Stage 4 proves the method at known calibration samples in replicate followed by independent quality control sample testing, testing with real matrices, an interferent panel, and a stability test procedure. Step 5 assesses greenness by at least one accepted indicator and contrasts the approach with prior laboratory methods. Stage 6 assesses field applicability in terms of on-site portable instrument operation with repetitive sample sets. This feasible conceptual system is illustrated in Figure 5. The raw calibration data, blank readings, LOD/LOQ calculation, recovery calculation, representative voltammograms, electrode batch reproducibility, stability data, scoring sheet for greenness, and a brief checklist for field use should be submitted as supplementary material. This type of additional information enhances reproducibility and allows peers to verify the numeric claims of a method.

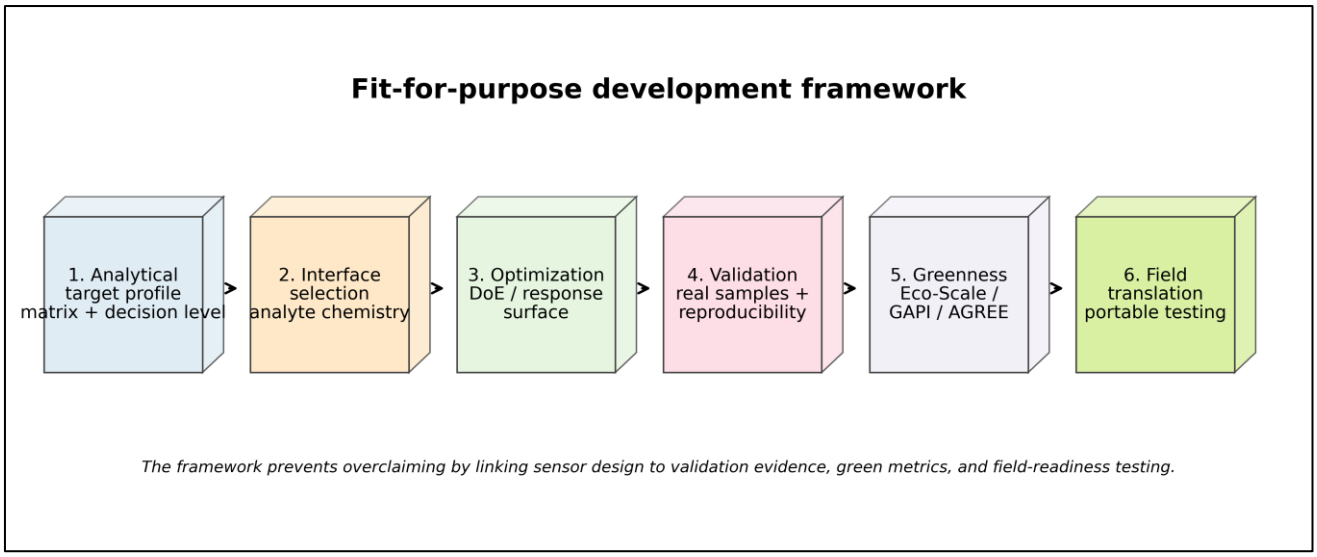

Figure 5 Three-dimensional practical framework for developing a fit-for-purpose environmental electrochemical sensor. The framework connects the analytical target profile, interface selection, optimization, validation, greenness assessment, and field translation.

Table 7 Suggested supplementary material for a publishable sensor manuscript.

Supplementary item	Purpose	Minimum content
Raw calibration data	Allows verification of slope, intercept, residuals, and error bars	Individual replicate signals at each concentration and blank level
LOD / LOQ worksheet	Makes detection-limit claims transparent	Formula, blank SD or low-level SD, slope, n, final calculation
Representative voltammograms	Shows signal shape, baseline, peak separation, and fouling	Blank, standards, real sample, spiked sample, repeated scans
Interference matrix	Supports selectivity claims	Ions, salts, dissolved organic matter, coexisting drugs, concentration ratios
Electrode reproducibility data	Tests independent fabrication variability	At least several independently prepared electrodes or batches
Greenness worksheet	Supports environmental claims	Eco-Scale/GAPI/AGREE input and final score
Reference-method comparison	Supports accuracy in real samples	ICP-MS/AAS for metals or LC-MS/MS/HPLC for pharmaceutical residues when possible

13. Conclusion and Recommendations

Green nanomaterial-based electrochemical sensors represent one of the most promising directions in modern analytical chemistry for water-quality monitoring. Their main value lies in combining nanoscale signal amplification, selective interfacial chemistry, low sample volume, portability, and compatibility with green analytical chemistry. For heavy metals, stripping voltammetry on nanocomposite electrodes provides strong sensitivity and multi-analyte capability. For pharmaceutical residues, nanocarbon, metal oxide, MOF, COF, MIP, and aptamer-based interfaces provide electrocatalysis and molecular recognition. Nevertheless, the field must move from proof-of-concept sensitivity toward validated, reproducible, matrix-tolerant, and sustainable analytical procedures.

Future manuscripts should report raw calibration data, replicate numbers, error bars, residuals, LOD/LOQ formulas, electrode-to-electrode reproducibility, real-matrix recoveries, and greenness metrics. New sensors should be compared with reference techniques such as ICP-MS, AAS, HPLC, or LC-MS/MS whenever possible. Field readiness should not be claimed unless portable instrumentation, storage stability, oxygen/matrix tolerance, and real-sample performance have been demonstrated. Finally, safe-by-design nanomaterials and disposal protocols should be considered part of analytical method quality, not an optional environmental note.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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