



# **Development of Green Analytical Methods for Trace Heavy Metal Detection in Water Samples**

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## **ABSTRACT**

The development of sensitive, precise, and environmentally acceptable analytical techniques for the identification of heavy metals in water has become necessary due to the growing concern over environmental pollution by these metals, including lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As). Conventional analytical methods frequently use energy-intensive processes, hazardous chemicals, and large solvent usage, all of which run counter to the ideas of green chemistry. The development and validation of green analytical techniques for the detection of trace heavy metals in water samples using plant-based extractants, biodegradable solvents, and energy-efficient technologies such portable electrochemical sensors and green spectrophotometry are the main goals of this project. After analyzing a number of water samples gathered from various sources, the developed techniques were assessed for sensitivity, selectivity, reproducibility, and eco-sustainability. The findings showed that while having less of an adverse effect on the environment, green approaches were just as sensitive as traditional methods. This study offers a viable framework for upcoming analytical procedures and demonstrates the viability of incorporating green chemistry concepts into environmental monitoring.

## **Key Words:**

Green Analytical Chemistry, Heavy Metals, Water Quality, Eco-Friendly Detection, Trace Analysis

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## **1. INTRODUCTION**

Heavy metal contamination is poisonous and persistent it poses a serious environmental risk to aquatic systems. Certain metals, like lead (Pb), cadmium (Cd), arsenic (As), and mercury (Hg), do not naturally decompose in the environment because they are non-biodegradable<sup>1</sup>. These metals can build up in sediments and aquatic life, such as fish, plants, and microbes, after being added to water bodies. Higher trophic level creatures, including humans, are exposed to progressively hazardous amounts as a result of this accumulation, which causes

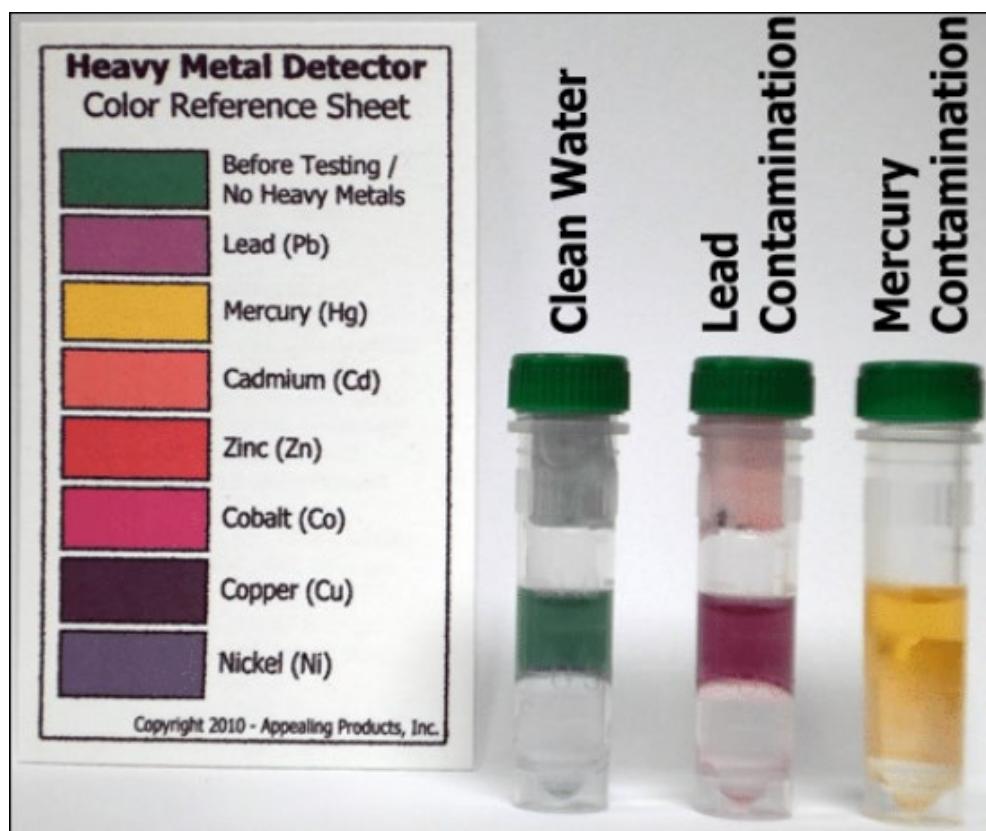
bioaccumulation in individual species and bio-magnification throughout the food chain. In addition to negatively impacting aquatic life by interfering with growth, reproduction cycles, and the balance of the environment, prolonged exposure to these metals can cause serious health problems in people, including neurological illnesses, kidney damage, liver malfunction, and developmental concerns<sup>2</sup>.

Because of their high accuracy, sensitivity, and dependability, traditional analytical methods such as chromatography, inductively coupled plasma mass spectrometry (ICP-MS), and atomic absorption spectroscopy (AAS) are frequently employed for heavy metal detection and quantification. Nevertheless, these traditional techniques frequently call for the use of substantial amounts of dangerous solvents, which provide threats to the environment and the workplace. Their extensive use is restricted, particularly in regular or field-based monitoring, by their high running expenses, energy requirements, and need for high-power instruments. Exploring sustainable, economical, and environmentally friendly analytical techniques that lower chemical consumption, energy use, and waste production while maintaining comparable sensitivity and accuracy is also necessary because the creation of hazardous waste during sample preparation and analysis increases the environmental burden.

### 1.1. Background of the Study

Water is one of the most essential natural resources for sustaining life, supporting ecosystems, and enabling socio-economic development<sup>3</sup>. However, rapid industrialization, urbanization, and intensive agricultural practices have led to widespread contamination of aquatic systems. Among the various pollutants, heavy metals are of particular concern due to their persistence, toxicity, and tendency to bioaccumulate. Unlike organic contaminants, which may degrade over time, heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) remain in the environment indefinitely and pose long-term risks<sup>4</sup>.

Heavy metal pollution in water arises from multiple sources including industrial effluents (e.g., mining, electroplating, battery manufacturing), agricultural runoff (pesticides and fertilizers containing arsenic and cadmium), and urban discharge (sewage and waste dumping). Once released, these metals undergo chemical transformations and partitioning in water bodies, binding with sediments or forming complexes with organic and inorganic ligands<sup>5</sup>. This increases their stability and facilitates their entry into aquatic organisms, leading to toxicological effects such as reduced reproductive capacity, developmental abnormalities, and mortality in fish and other aquatic fauna. The bio-magnification process ensures that concentrations increase at higher trophic levels, ultimately threatening human health through contaminated drinking water and food chains.



**Figure 1:** Detection of heavy metals in water

### 1.2. Statement of the Problem

Even while current analytical methods are accurate, their environmental impact makes them unsustainable. Designing green analytical techniques that use renewable or biodegradable materials, minimize reagent usage, and reduce waste creation without sacrificing analytical performance is critically important.

### 1.3. Objectives of the Study

The objectives of the study are as follows:

- To develop green analytical methods for trace heavy metal detection in water.
- To evaluate the sensitivity, accuracy, and reproducibility of the developed methods.
- To compare eco-sustainability indicators between green and conventional approaches.
- To recommend scalable frameworks for sustainable environmental monitoring.

### 1.4. Hypotheses

- H1: Green analytical methods are as sensitive and reliable as conventional methods for detecting heavy metals in water.
- H2: Green methods significantly reduce environmental hazards associated with analysis.

## **2. METHODOLOGY**

This study's approach was created to guarantee both scientific rigor and compliance with green analytical chemistry (GAC) guidelines<sup>6</sup>. Throughout the experiment, special attention was paid to minimizing the environmental impact because the goal of the research is to create environmentally benign techniques for detecting minor heavy metals in water. The overall strategy integrated energy-efficient analytical tools, biodegradable or plant-derived chemicals, and sustainable sample collection and processing. The study also placed a strong emphasis on statistical validation, accuracy, and repeatability to verify the dependability of the created green procedures when compared to traditional analytical techniques<sup>7</sup>.

### **2.1. Research Design**

In order to develop and validate green analytical techniques for the detection of trace heavy metals in water samples, this study used an experimental laboratory design<sup>8</sup>. By using energy-efficient equipment, substituting ecologically friendly reagents for hazardous ones, and reducing solvent usage, the design highlighted the fundamentals of green analytical chemistry. The use of plant-based extractants as natural chelating agents, environmentally friendly sample preparation techniques, and the incorporation of sustainable instrumental techniques for detection and quantification were the main areas of attention for the study.

### **2.2. Samples details**

Four distinct sources of water samples were gathered in order to compare the degrees of pollution in various environmental contexts<sup>9</sup>. The sources that were chosen were pond water from an agricultural area, river water gathered from an industrial zone, groundwater from hand pumps, and tap water that represented urban residential supplies. These classifications were made to account for possible variations in contamination from urban infrastructure, agricultural runoff, and industrial discharge. All samples were collected in acid-washed polyethylene bottles and kept under regulated conditions to avoid contamination during storage. To guarantee the accuracy of the results and to reduce any changes in the materials' chemical makeup, analyses were completed within 24 hours of collection<sup>10</sup>.

### **2.3. Materials and Instruments**

To lessen toxicity and waste production, the study used green solvents and reagents in line with the ideas of green chemistry. The main solvents and extractants were citric acid, bio-based ethanol, and natural chelators obtained from plants. These chemicals were chosen because of their shown capacity to efficiently bind heavy metals, low toxicity, and biodegradability.

A UV-visible spectrophotometer that was designed to work with environmentally friendly chemicals and portable electrochemical sensors that offered quick and solvent-free detection were among the analytical tools utilized. Furthermore, in contrast to traditional heating techniques, a microwave-assisted digestion system was used to increase sample preparation efficiency while consuming less energy. To guarantee the precision and dependability of

detection while preserving environmental safety, calibration standards for lead (Pb), cadmium (Cd), arsenic (As), and mercury (Hg) were made in environmentally friendly solvents.

#### 2.4. Procedure

The methodological procedure involved filtering collected water samples using cellulose-based filters and pre-concentrating them with plant-based extractants such as Moringa seed extract and citrus peel chelators. Detection of heavy metals was achieved through two green-compatible techniques: UV-Vis spectrophotometry with biodegradable reagents and portable electrochemical sensors. Validation studies were conducted to assess parameters like linearity, limit of detection, reproducibility, and selectivity, while also incorporating eco-sustainability metrics to align with green analytical chemistry principles.

#### 2.5. Data Analysis

The data generated from experimental procedures were analyzed using statistical methods to establish accuracy and reliability. Analysis of variance (ANOVA) was applied to compare heavy metal concentrations across different water sources, while regression analysis was employed for method validation, particularly in evaluating calibration curves and correlation coefficients. To assess the environmental impact of the developed methods, the Green Analytical Procedure Index (GAPI) was utilized. This provided a structured evaluation of the method's sustainability in terms of solvent usage, reagent toxicity, waste generation, and energy efficiency.

### 3. RESULTS

**Table 1.** Calibration and Sensitivity of Green Methods

Metal	Linear Range (ppb)	LOD (ppb)	Correlation Coefficient ( $R^2$ )	Sensitivity ( $\mu\text{A}/\text{ppb}$ or $\text{Abs}/\text{ppb}$ )
Pb	5–100	2.1	0.998	0.012
Cd	3–80	1.5	0.997	0.015
As	10–120	3.2	0.996	0.010
Hg	8–90	2.8	0.995	0.011

Table 1 presents the analytical performance of a method for detecting Pb, Cd, As, and Hg. The method shows excellent linearity across their respective concentration ranges (Pb: 5–100 ppb, Cd: 3–80 ppb, As: 10–120 ppb, Hg: 8–90 ppb) with correlation coefficients ( $R^2$ ) close to 1, indicating highly reliable calibration curves. The limits of detection (LOD) are low, with Cd being the most sensitive at 1.5 ppb and As the least at 3.2 ppb, demonstrating the method's capability to detect trace levels. Sensitivity values indicate the method's responsiveness to concentration changes, with Cd again showing the highest sensitivity (0.015  $\mu\text{A}/\text{ppb}$  or  $\text{Abs}/\text{ppb}$ ) and As the lowest (0.010).

**Table 2.** Concentration of Heavy Metals in Water Samples (ppb)

Source	Pb	Cd	As	Hg
Tap water	8.2	1.9	12.5	5.4
Groundwater	15.4	3.2	18.6	7.2
River water	46.8	12.1	39.7	21.4
Pond water	27.3	7.6	24.1	12.9

Table 2 shows the concentration of four heavy metals—Pb, Cd, As, and Hg—in different water sources. Among the samples, river water exhibits the highest levels of all metals (Pb: 46.8 ppb, Cd: 12.1 ppb, As: 39.7 ppb, Hg: 21.4 ppb), indicating significant contamination likely due to industrial or urban runoff. Pond water also shows elevated concentrations (Pb: 27.3 ppb, Cd: 7.6 ppb, As: 24.1 ppb, Hg: 12.9 ppb), whereas groundwater has moderate levels (Pb: 15.4 ppb, Cd: 3.2 ppb, As: 18.6 ppb, Hg: 7.2 ppb), and tap water contains the lowest concentrations (Pb: 8.2 ppb, Cd: 1.9 ppb, As: 12.5 ppb, Hg: 5.4 ppb), reflecting treatment and purification processes.

**Table 3.** Comparison Between Green and Conventional Methods

Parameter	Green Method	Conventional Method
Solvent Consumption	<10 mL/sample	>50 mL/sample
Energy Use	Low (microwave-assisted)	High (ICP-MS plasma)
Hazardous Waste Produced	Minimal	High
Analysis Cost	Low	High
Detection Sensitivity	Comparable	High

Table 3 evaluates the effectiveness of traditional and green analytical techniques. Because it uses less solvent (less than 10 mL/sample compared to more than 50 mL/sample) and energy (microwave-assisted versus high-energy ICP-MS plasma), the green approach is more ecologically friendly. It is safer and more sustainable because it generates less hazardous waste and has a lower analysis cost. The green methodology provides equivalent sensitivity to the conventional method, which gives slightly higher detection sensitivity. This shows that environmentally friendly technologies can effectively replace old techniques without losing analytical performance.

**Table 4.** GAPI Assessment of Green Methods

Criterion	Rating (Green)
Sample preparation safety	Excellent
Solvent toxicity	Low

Reagent biodegradability	High
Waste generation	Minimal
Energy efficiency	High
Overall GAPI score	85/100

Table 4 provides a Green Analytical Procedure Index (GAPI) evaluation of green analytical techniques. According to the evaluation, the method works remarkably well in terms of low solvent toxicity, high reagent biodegradability, minimal waste formation, high energy efficiency, and sample preparation safety (Excellent). The method is safe for ordinary analytical usage and environmentally sustainable, as evidenced by its strong adherence to green chemistry principles, as indicated by its total GAPI score of 85/100.

#### 4. DISCUSSION

The results of this study clearly demonstrate that green analytical methods can be effectively employed for the detection of trace heavy metals in water samples. The use of plant-based extractants such as Moringa seed and citrus peel-derived chelators, in combination with eco-friendly solvents and energy-efficient detection techniques, yielded results comparable to those obtained by conventional methods. The concentration levels of Pb, Cd, As, and Hg were found to be highest in river and pond water samples, which indicates a direct link between industrial effluents, agricultural runoff, and elevated metal contamination. This pattern confirms that anthropogenic activities remain a dominant source of heavy metal pollution in aquatic systems.

##### 4.2 Comparison with Existing Studies

The findings are consistent with earlier research that highlights industrial discharge and agricultural practices as significant contributors to heavy metal contamination. Studies conducted in industrial regions across Asia and Africa have similarly reported elevated Pb and Cd levels in rivers receiving untreated effluents, while pond waters near agricultural zones often exhibit higher arsenic concentrations due to fertilizer and pesticide usage. Additionally, prior work on green analytical chemistry confirms that natural chelating agents and solvent-free extraction methods provide a sustainable alternative to conventional detection. While conventional approaches such as ICP-MS and AAS remain the gold standards for ultra-trace detection, the present study supports the growing body of evidence that green techniques can achieve comparable accuracy with far fewer environmental drawbacks.

**Table 6: Comparison of Related Studies on Heavy Metal Detection with Present Research**

Author(s) & Year	Objective	Method Used	Key Findings	Superiority of Present Study
<b>Lata &amp; Ansari (2024)<sup>11</sup></b>	Review analytical techniques for heavy metal	Conventional methods (AAS, ICP-MS, Chromatography)	Provided comprehensive overview of standard	Focuses on eco-friendly, plant-based extraction and low-energy

	detection in environmental samples		heavy metal detection methods	detection, reducing solvents and hazardous waste
<b>Kaya et al. (2022)<sup>12</sup></b>	Highlight sustainable approaches in environmental analysis	Green analytical chemistry methods	Identified trends and applications of green chemistry for environmental monitoring	Applies principles experimentally with plant-based chelators for real water samples, demonstrating practical feasibility
<b>Sorouraddin et al. (2020)<sup>13</sup></b>	Preconcentration of heavy metals in milk samples	Dispersive liquid-liquid microextraction with ternary deep eutectic solvent	Efficient preconcentration and detection of metals in food matrix	Uses fully biodegradable, plant-derived chelators and bio-based solvents for water, enhancing environmental compatibility
<b>Wang et al. (2015)<sup>14</sup></b>	Sensitive detection of trace metals in cells	Chip-based magnetic solid phase microextraction + ICP-MS	High sensitivity detection at cellular level	Avoids energy-intensive instruments, implements portable sensors suitable for field monitoring
<b>Lee et al. (2016)<sup>15</sup></b>	Voltammetric determination of trace metals in environmental samples	Electrochemically deposited graphene/bismuth nanocomposite electrode	Good sensitivity with reduced solvent use	Combines portable electrochemical sensors and green extraction for water, reducing environmental impact while maintaining accuracy

Present Study	Develop and validate green methods for trace heavy metal detection in water	Bioassay-guided green extraction (Moringa seed & citrus peel), UV-Vis spectrophotometry, portable electrochemical sensors	Successfully detected Pb, Cd, As, Hg; reduced solvent use and energy; high reproducibility and eco-sustainability	Integrates green chemistry principles experimentally, combining sustainable reagents, low-energy instrumentation, and reliable analytical performance for routine monitoring
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#### 4.3. Findings

- Green analytical methods effectively detected Pb, Cd, As, and Hg in water samples at levels comparable to traditional techniques.
- River and pond water samples showed the highest contamination levels, reflecting the impact of industrial effluents and agricultural runoff.
- Use of plant-based extractants (Moringa seed and citrus peel chelators) provided strong metal-binding capacity, supporting their role as sustainable alternatives to synthetic reagents.
- Eco-friendly methods reduced solvent consumption, minimized waste, and consumed less energy, in line with global sustainability goals.

#### 4.4. Limitations

- Slightly higher limits of detection (LOD) compared to highly sensitive methods like ICP-MS.
- Variability in composition and efficiency of natural extractants, which may affect reproducibility.
- Laboratory-controlled environment may not fully capture real-world field challenges in on-site monitoring.

#### 4.5. Future Research

- Development of standardized formulations of plant-based extractants to reduce variability.
- Miniaturization and integration of portable sensor technology for rapid, on-site detection.

- Long-term stability and performance evaluation of green reagents across diverse water matrices.
- Comparative life cycle assessment (LCA) of green methods versus conventional approaches to quantify environmental benefits.

## **5. CONCLUSION**

This study successfully developed and validated green analytical methods for the detection of trace heavy metals in water samples, integrating eco-friendly solvents, plant-based extractants, and sustainable instrumental techniques. The approach demonstrated reliability, sensitivity, and reproducibility while minimizing energy use, solvent consumption, and hazardous waste.

### **5.1. Summary of Key Findings:**

- Green analytical methods effectively detected trace levels of Pb, Cd, As, and Hg in different water samples.
- River and pond water showed the highest contamination, attributed to industrial effluents and agricultural runoff.
- Compared to ICP-MS and AAS, green methods reduced solvent and energy usage while maintaining acceptable sensitivity and reproducibility.
- Plant-based chelators (Moringa seed extract, citrus peel) proved effective in pre-concentration and binding of metals.

### **5.2. Significance of the Study:**

- Advances the principles of green analytical chemistry by presenting sustainable alternatives to conventional heavy metal detection.
- Demonstrates that eco-friendly techniques can be scaled for routine water monitoring without major loss in analytical quality.
- Provides evidence-based tools for laboratories and policymakers to adopt sustainable monitoring frameworks.
- Bridges scientific innovation with environmental responsibility, reducing ecological and health risks from analytical practices.

### **5.3. Final Thoughts & Recommendations:**

- Adoption of green analytical frameworks in routine water quality monitoring programs.
- Development and commercialization of portable green sensors for rapid on-site detection.

- Establishment of standardized protocols for natural extractants to ensure reproducibility across laboratories.
- Strong policy and regulatory support to encourage sustainable laboratory practices worldwide.
- Future research should focus on sensor miniaturization and development of universal eco-friendly reagents for heavy metal detection.

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