

Comparative Review of Methods for Heavy Metals Analysis by XRF, AAS And PIXE

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ABSTRACT: Heavy metals presences in the environment are often results to health hazard and are also non-biodegradable. Some heavy metals undergo bio-magnification as they move from one trophic level to another in food chain of ecosystem inside living organism. Heavy metals in biotic and abiotic samples are essential in environment studies because of regular evaluations. There are many analytical approaches that are used to measure the concentration of metals in environmental samples such as X – ray Fluorescence (XRF), Atomic Absorption Spectrophotometer (AAS) and Proton Induced X– ray emission (PIXE). This work reviews the methods for analysis of heavy metals by XRF, AAS and PIXE and their usefulness in heavy metal Analysis.

Keywords: Heavy metals, Biotic samples, Abiotic, Bio-magnification, Environment

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I. INTRODUCTION

Heavy metals are naturally occurring elements with high atomic weight and density, which pose serious environmental and health risks when present at elevated concentrations. Unlike organic pollutants, heavy metals are non-biodegradable, tend to persist in the environment, and can undergo bioaccumulation and biomagnification through food chains, leading to toxic effects in humans and ecosystems (García & Báez, 2012). Sources of heavy metals in the environment include mining, industrial processes, agricultural inputs, waste disposal, and natural geochemical weathering (Johansson & Campbell, 1988). Monitoring their presence in environmental matrices such as soil, water, sediments, and biological tissues is crucial for environmental assessment, pollution control, and risk management.

Several analytical techniques have been developed to determine the concentration of heavy metals in environmental and industrial samples. Among the most widely applied are X-ray Fluorescence (XRF), Atomic Absorption Spectrometry (AAS), and Particle-Induced X-ray Emission (PIXE).

XRF is valued for its rapid, non-destructive, and multi-elemental analytical capacity, providing high-resolution elemental data in solid, liquid, and powdered samples (Lowemark *et al.*, 2011; Weltje & Tjallingii, 2008). AAS, in contrast, is widely used for its sensitivity, accuracy, and precision in detecting trace elements, particularly in aqueous and biological samples (Welz, 1998; Bernhard & Michael, 1998). PIXE, though relatively expensive, provides a powerful non-destructive multi-element analysis with high sensitivity and the ability to analyze a wide range of matrices, including solids, powders, and aerosols (Johansson & Campbell, 1988; Garman & Grime, 2005).

Each of these techniques has distinct strengths and limitations. For example, XRF and PIXE are capable of simultaneous multi-elemental analysis but require expensive equipment, while AAS is cost-effective but restricted to single-element determination at a time (Richard & Jack, 1993; Cahill, 1981). Despite the extensive use of these methods, comparative evaluations of their application, accuracy, sensitivity, and cost-effectiveness across diverse environmental samples remain limited in the literature.

Although numerous studies have discussed XRF, AAS, and PIXE independently, there is a lack of integrated comparative reviews that examine the operational principles, strengths, weaknesses, and environmental applications of these techniques. Many researchers focus on the technical aspects of a single method without providing a holistic perspective that allows stakeholders, laboratories, and policymakers to make informed choices about which technique is most suitable for specific analytical contexts (Shefsky, 1995; Young *et al.*, 2016).

Bridging this knowledge gap is critical in guiding appropriate method selection for environmental monitoring and remediation studies.

The aim of this review is to provide a comparative assessment of XRF, AAS, and PIXE techniques in the analysis of heavy metals, highlighting their principles, strengths, limitations, and applications in environmental studies.

This review is significant for environmental scientists, laboratory analysts, and policymakers. By synthesizing knowledge on XRF, AAS, and PIXE, the study provides guidance for selecting the most suitable analytical method based on cost, precision, sensitivity, and sample type. Furthermore, the study contributes to improved environmental monitoring and risk assessment of heavy metal pollution, supporting global efforts toward pollution control, public health protection, and sustainable development.

II. A COMPARATIVE ANALYSIS OF XRF, AAS, AND PIXE FOR HEAVY METAL ANALYSIS

The performance of analytical techniques for heavy metal determination is largely influenced by their sensitivity, selectivity, detection limits, sample preparation requirements, and operational costs. Table 1 provides a comparative summary of the analytical capabilities of X-ray Fluorescence (XRF), Atomic Absorption Spectrometry (AAS), and Particle-Induced X-ray Emission (PIXE) with respect to their sensitivity, selectivity, multi-element capacity, portability, destructive nature, and applicability in different environmental and industrial contexts. The table serves as a practical guide for choosing the most appropriate analytical technique depending on research objectives, sample type, and available resources.

Table 1. Analytical Capabilities of XRF, AAS, and PIXE

Parameter	X-Ray Fluorescence (XRF)	Atomic Absorption Spectrometry (AAS)	Particle-Induced X-Ray Emission (PIXE)
Sensitivity	Moderate; detection limits in ppm range (10–100 ppm) (Lowemark <i>et al.</i> , 2011).	High; sensitive to ppb–ppm levels depending on element (Welz, 1998).	Very high; detection limits in ppb range (Johansson & Campbell, 1988).
Selectivity	Good for most elements but cannot distinguish isotopes or oxidation states (Weltje & Tjallingii, 2008).	Excellent; element-specific hollow cathode lamps ensure high selectivity.	Excellent; high selectivity for wide range of elements (Na to U).
Multi-element capability	Yes; simultaneous analysis of multiple elements (Young <i>et al.</i> , 2016).	No; one element at a time.	Yes; simultaneous detection of many elements in a single spectrum (Garman & Grime, 2005).
Sample state	Solids, powders, liquids (non-destructive).	Requires solution form; sample digestion or ashing often needed.	Solids, powders, liquids, aerosols; largely non-destructive.
Sample preparation	Minimal; grinding/powdering recommended (Margui <i>et al.</i> , 2016).	Extensive; digestion/ashing required (Welz, 1998).	Minimal; often only surface cleaning required.
Accuracy & Precision	High when properly calibrated; influenced by surface roughness and matrix effects.	Very high accuracy and precision with proper standards.	High; less affected by matrix interferences compared to XRF.
Detection limits	ppm levels	ppb–ppm depending on element	ppb levels
Throughput (Speed)	Fast; results within minutes.	Moderate; each element requires separate analysis.	Moderate to fast; multiple elements detected at once.
Cost of Instrumentation	Moderate to high (tens of thousands of USD).	Relatively low to moderate (widely affordable).	Very high (requires accelerator facilities, in millions of USD).
Portability	Portable/handheld models available.	Bench-top, not portable.	Not portable; requires large facilities.
Destructive/Non-destructive	Largely non-destructive.	Destructive (requires dissolution/ashing of samples).	Non-destructive.
Applications	Geology, mining, metallurgy, environmental monitoring, forensics.	Environmental analysis, food, water, biological samples, forensic science.	Environmental monitoring, cultural heritage, biomedical, aerosol analysis.
Best Use Case	Rapid field screening and bulk elemental analysis.	Trace quantification of specific elements in environmental and biological samples.	Sensitive, multi-elemental, non-destructive analysis of diverse sample types.

2.1. Sensitivity and Detection Limits

The sensitivity of the techniques varies significantly. AAS demonstrates high sensitivity with detection limits in the ppb–ppm range, making it suitable for trace element quantification in water, biological, and food samples (Welz, 1998). PIXE surpasses both XRF and AAS in terms of detection sensitivity, with detection limits reaching the ppb level across a wide range of elements (Johansson & Campbell, 1988). Conversely, XRF is moderately sensitive with detection limits typically in the ppm range (Lowemark *et al.*, 2011), which may limit its utility in ultra-trace analysis but makes it highly efficient for bulk elemental characterization.

2.2. Selectivity and Multi-element Capability

AAS is highly selective due to the use of element-specific hollow cathode lamps, but it is limited to single-element analysis at a time, thereby reducing throughput (Welz, 1998). In contrast, XRF and PIXE allow simultaneous multi-element analysis in a single run (Young *et al.*, 2016; Garman & Grime, 2005). This makes them advantageous for studies requiring comprehensive elemental profiling, such as geological exploration and environmental surveys where multiple contaminants may co-exist.

2.3. Sample Requirements and Preparation

Sample preparation is a key determinant in method selection. AAS requires samples in solution form, necessitating digestion or ashing procedures that are time-consuming and destructive to the sample (Welz, 1998). XRF and PIXE, on the other hand, require minimal sample preparation and are largely non-destructive (Margui *et al.*, 2016). This makes XRF and PIXE highly desirable in studies involving rare or valuable samples, such as cultural heritage artifacts, where preservation is critical.

3.4. Accuracy, Precision, and Matrix Effects

AAS generally provides high accuracy and precision due to controlled calibration standards. However, its accuracy may be compromised if matrix interferences are not adequately corrected. XRF offers high accuracy when properly calibrated but is susceptible to errors from surface roughness, grain size, and matrix effects (Weltje & Tjallingii, 2008). PIXE, while also sensitive to matrix effects, is generally less influenced than XRF and provides accurate multi-elemental analysis without extensive corrections (Johansson & Campbell, 1988).

3.5. Instrumentation Cost and Portability

Cost and accessibility are critical factors in method selection. AAS is the least expensive and most widely available technique, making it the preferred choice in resource-limited laboratories. XRF instruments are moderately expensive, but the development of portable and handheld models has made them increasingly popular for field applications (Young *et al.*, 2016). PIXE requires large-scale accelerator facilities, making it prohibitively expensive and less accessible to many laboratories, despite its analytical superiority (Garman & Grime, 2005).

3.6. Destructive vs. Non-destructive Nature

AAS is inherently destructive since it requires digestion of the sample. Conversely, XRF and PIXE are non-destructive, preserving samples for future analysis. This attribute makes XRF and PIXE indispensable in heritage conservation studies, geological core analysis, and forensic investigations where sample integrity is crucial.

3.7. Applications and Best Use Cases

The applicability of each technique is aligned with its strengths. XRF is best suited for rapid field screening and bulk elemental analysis, particularly in geology, mining, and environmental monitoring. AAS is best applied for trace quantification of specific elements in water, food, and biological systems where accuracy and sensitivity are paramount. PIXE excels in sensitive, multi-elemental, non-destructive analysis of diverse sample types, including environmental aerosols, biomedical samples, and cultural heritage materials, though its high cost limits widespread use.

In summary, AAS remains the method of choice for laboratories requiring cost-effective, highly sensitive single-element quantification, whereas XRF is advantageous for rapid, non-destructive, and multi-element field and laboratory analysis. PIXE, while less accessible due to its cost, represents the most powerful option for high-sensitivity, non-destructive, and simultaneous multi-elemental analysis. Thus, the choice of technique depends not only on analytical requirements but also on the balance between cost, sensitivity, and sample preservation needs.

The radar chart shown in Fig. 1 provides a clear visual comparison of three analytical techniques X-ray Fluorescence (XRF), Atomic Absorption Spectrometry (AAS), and Particle-Induced X-ray Emission (PIXE) based on a set of key performance metrics. XRF stands out for its high throughput and portability, making it a good choice for rapid field screenings, while also being largely non-destructive with minimal sample preparation. AAS excels in its selectivity and high accuracy, which are crucial for precise quantification of specific elements, and it is also the most cost-effective option, though it is limited by its single-element analysis and destructive sample preparation. PIXE is the superior technique in terms of sensitivity and multi-element capability, allowing for very high-precision analysis on a wide range of elements without destroying the sample. However, its significant disadvantage is the extremely high cost and lack of portability, as it requires a large accelerator facility.

Overall, the chart demonstrates that XRF is a balanced, practical choice for many applications, AAS is best for targeted, high-accuracy analysis, and PIXE is an extremely powerful but specialized tool due to its cost and infrastructure requirements.

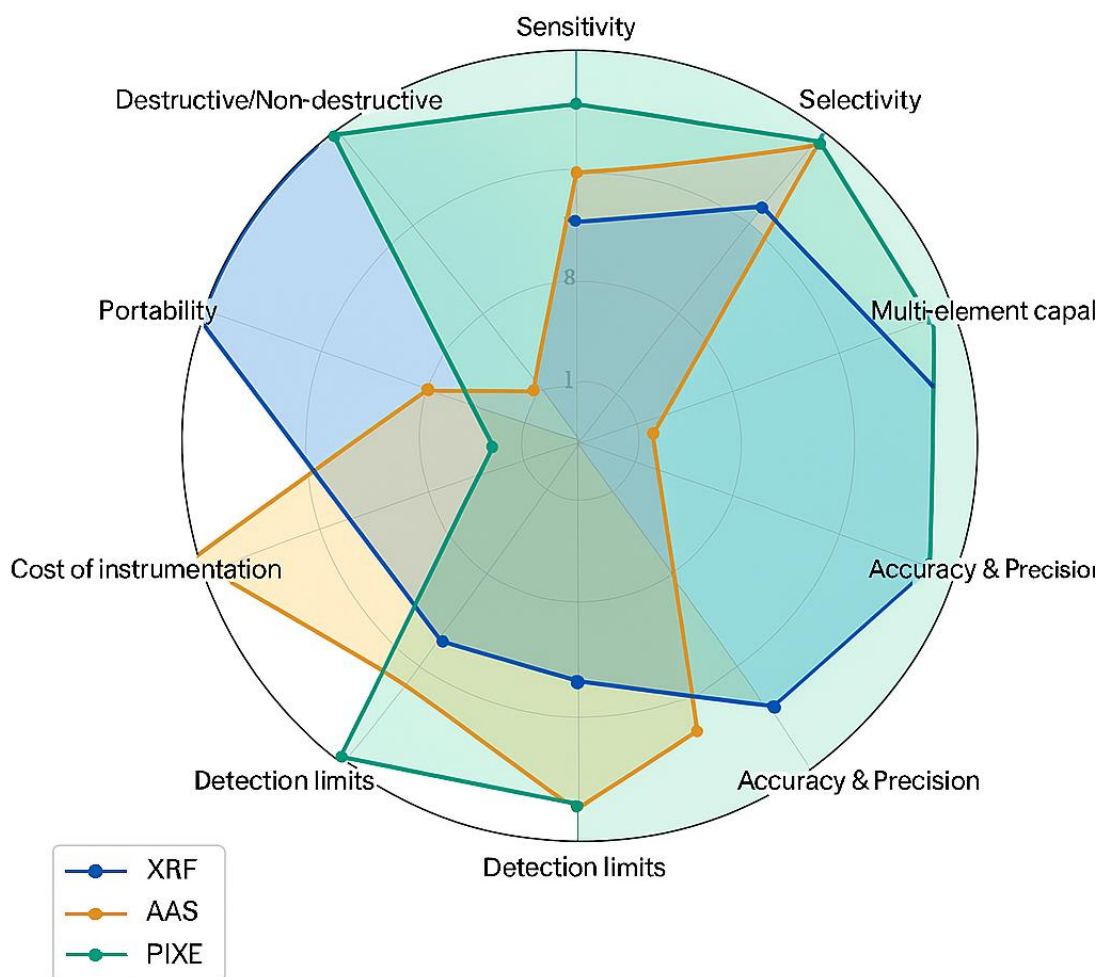


Fig. 1: Graphical analysis of analytical techniques for heavy metal determination

2.0 Theory and Principle of Operation

2.1 X-ray Fluorescence (XRF)

X-ray fluorescence (XRF) is an analytical technique that relies on the excitation of inner-shell electrons by primary X-rays, which causes the emission of secondary element-specific X-rays when electrons from higher shells fill the vacancies. The energy of the emitted photons identifies the element, while the intensity of the signal is proportional to the concentration of the element present in the sample (Beckhoff *et al.*, 2006; West *et al.*, 2015). Matrix effects, including absorption and enhancement, as well as sample geometry, influence the measured line intensities and must be corrected to obtain accurate quantitative results (Weltje & Tjallingii, 2008).

There are two major types of XRF instruments. Wavelength-dispersive XRF (WDXRF) uses a crystal monochromator to diffract secondary X-rays according to Bragg's law, enabling wavelength selection with high resolution and low background noise. This configuration is suitable for laboratory-based analyses requiring high precision and quantitative accuracy (Jenkins, 1999). Energy-dispersive XRF (EDXRF), in contrast, employs solid-state detectors such as silicon drift detectors (SDDs) to directly measure photon energy. Although the spectral resolution of EDXRF is lower than that of WDXRF, it offers simpler hardware, faster operation, and is available in portable and handheld formats, making it useful for rapid field applications (Young *et al.*, 2016).

Quantitative analysis in XRF is based either on empirical calibration using certified reference materials or on fundamental parameter (FP) models that incorporate mass attenuation coefficients, fluorescence yields, and detector efficiencies. Modern applications of FP methods often integrate scatter peak normalization, such as

Compton and Rayleigh scattering, to reduce the influence of matrix heterogeneity in samples like sediments and atmospheric particulates (Tjallingii *et al.*, 2007).

The scope of XRF analysis is broad since the technique is non-destructive, multi-elemental, and effective for detecting elements ranging from sodium ($Z \approx 11$) to uranium. The detection limits in optimized laboratory-based WDXRF systems reach the sub-ppm to low ppm range, while portable EDXRF systems generally have higher detection limits and thus lower sensitivity (Beckhoff *et al.*, 2006; Marguí *et al.*, 2016).

2.2 Atomic Absorption Spectrometry (AAS)

Atomic absorption spectrometry (AAS) is based on the absorption of narrow-band radiation by free atoms in the ground state. The atoms are produced by atomizing the sample in a high-temperature environment such as a flame or a graphite furnace. When the atoms absorb radiation emitted from a narrow-band element-specific light source, typically a hollow cathode lamp (HCL) or an electrodeless discharge lamp (EDL), the decrease in transmitted intensity follows the Beer–Lambert law and is proportional to the analyte concentration (Welz & Sperling, 1999; Skoog *et al.*, 2014).

The two main modes of atomization in AAS are flame atomization and electrothermal atomization. Flame atomic absorption spectrometry (FAAS) employs a flame, often air–acetylene or nitrous oxide–acetylene, to atomize nebulized liquid samples, providing moderate sensitivity and high throughput for routine applications (de Loos-Vollebregt, 2017). Electrothermal atomic absorption spectrometry (ETAAS), also known as graphite furnace AAS (GFAAS), involves introducing microliter volumes of sample into a graphite tube, where sequential drying, charring, and atomization take place. This process significantly enhances sensitivity and lowers detection limits to the ppb range, although the technique is slower compared to FAAS (Lajunen & Perämäki, 2004).

In addition to atomization, the optical system of AAS includes a radiation source, monochromator, and detector. Accurate measurements require correction for background absorption and scattering effects that may arise from matrix interferences. Background correction methods include deuterium lamp (D_2) correction, which compensates for broadband absorption, and Zeeman-effect correction, which distinguishes analyte absorption from background signals, thereby improving analytical accuracy in complex matrices (Hiraide, 2018).

AAS is widely recognized for its high selectivity and sensitivity in trace-level metal analysis, particularly in aqueous and biological matrices after appropriate digestion. The method is cost-effective and well established in routine laboratories. However, its main limitations include its restriction to single-element analysis, relatively low throughput compared to multi-element techniques, and the need for destructive sample preparation, which may result in analyte loss or contamination (Skoog *et al.*, 2014).

2.3 Particle-Induced X-ray Emission (PIXE)

Particle-induced X-ray emission (PIXE) is an ion beam analysis technique in which energetic ions, typically 1–3 MeV protons, interact with the sample through Coulomb forces to eject inner-shell electrons. The resulting electronic transitions produce element-characteristic X-rays, which are collected by detectors for qualitative and quantitative elemental analysis (Johansson *et al.*, 1995; Grime & Dawson, 2015). Because the ionization cross-sections at these energies are high and the bremsstrahlung background is relatively low, PIXE offers excellent sensitivity for trace element detection.

The instrumentation for PIXE usually consists of a small accelerator, such as a Van de Graaff or tandem accelerator, which generates the ion beam. Analyses can be conducted in vacuum chambers or using external beam setups that allow for the study of large, irregular, or delicate objects such as cultural heritage artifacts. Semiconductor detectors, including silicon lithium [Si(Li)] or silicon drift detectors (SDDs), are commonly employed to measure the emitted X-rays. The use of filters, absorbers, and optimized detector geometry improves signal-to-background ratios and enhances measurement precision (IAEA, 2002).

Quantification in PIXE is achieved by comparing measured X-ray line intensities with theoretical yields that account for ionization cross-sections, fluorescence yields, sample absorption, and detector efficiency. Software packages such as GUPIX are widely used to process PIXE spectra and provide reliable quantitative results (Campbell, 1999).

PIXE offers significant analytical advantages as a non-destructive, truly multi-elemental technique capable of detecting elements from sodium to uranium. Its detection limits often reach the sub-ppm range, making it particularly valuable for applications such as environmental monitoring, atmospheric aerosol characterization, biomedical research, and the analysis of cultural heritage materials. Despite these strengths, the requirement for specialized ion-beam facilities limits its accessibility and increases operational costs compared to more conventional techniques (Johansson & Campbell, 1988; Grime & Dawson, 2015).

The flowchart shown in Fig. 2 illustrates the fundamental processes underpinning the operation of three major analytical techniques: X-ray Fluorescence (XRF), Atomic Absorption Spectrometry (AAS), and Particle-Induced X-ray Emission (PIXE). Each pathway begins with the excitation or atomization step, proceeds through

the emission or absorption of characteristic photons, and concludes with detection and quantification. In XRF, primary X-rays ionize core electrons, and the resulting radiative transitions produce element-specific fluorescent photons that are detected using WDXRF or EDXRF systems. In AAS, atomization of a sample in a flame or graphite furnace produces free atoms, which selectively absorb element-specific resonance radiation according to the Beer–Lambert law, with detection achieved via photomultiplier tubes or photodiodes. PIXE, on the other hand, uses a high-energy proton beam to ionize inner shells, generating characteristic X-rays that are recorded with high-resolution detectors such as Si(Li) or SDD. Quantification in each method relies on distinct approaches, including calibration curves, fundamental parameter models, or dedicated computational codes such as GUPIX. The flowchart further emphasizes the analytical scope of each method, with XRF offering rapid, non-destructive multi-elemental analysis; AAS providing high sensitivity and selectivity for trace metals in digested samples; and PIXE excelling in ultra-sensitive, non-destructive multi-elemental characterization across a wide atomic number range.

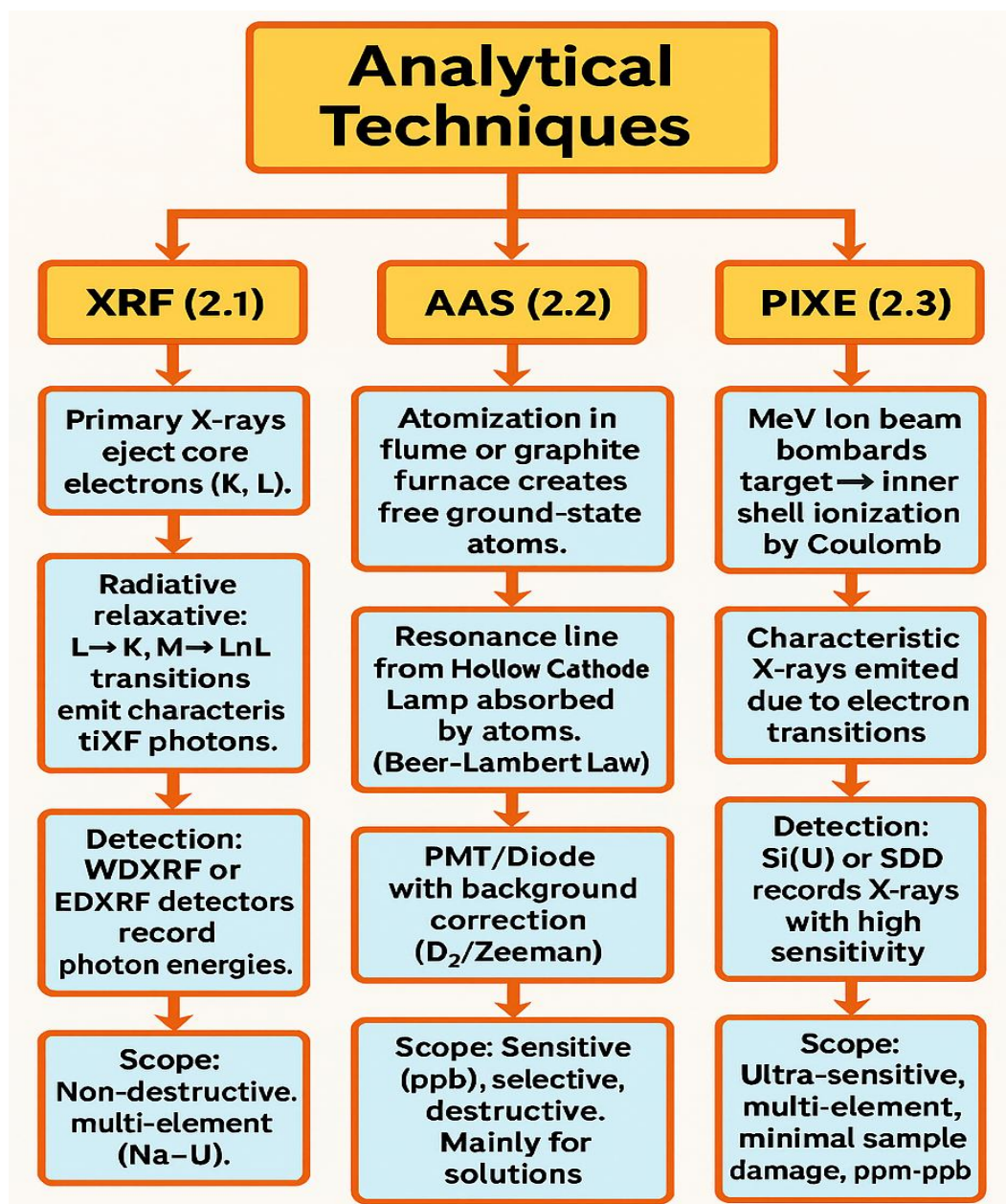


Fig. 2: Flowchart of the Theory and Principle of Operation of XRF, AAS, and PIXE

4.0 Case Studies on Heavy-Metal Analysis by XRF, AAS, and PIXE

4.1 Case Studies in Environmental, Material, and Biological Matrices

X-ray fluorescence (XRF), atomic absorption spectrometry (AAS), and particle-induced X-ray emission (PIXE) have been widely applied to the detection and quantification of heavy metals across environmental, material, and biological matrices. Each technique has distinct advantages that make it suitable for specific applications.

In environmental soil studies, portable XRF (pXRF) has proven particularly useful for rapid in situ mapping of metal contamination. For example, recent work demonstrated that pXRF can effectively identify lead hotspots in urban soils, although matrix effects such as particle size and moisture content necessitate calibration against laboratory reference methods (Jenkins *et al.*, 2025; Ravansari *et al.*, 2020; Schmidt *et al.*, 2024). Similarly, laboratory XRF has been applied to marine and coastal sediments, where pressed pellets and fused beads provide robust multi-elemental profiles (e.g., Fe, Cu, Zn, Pb), facilitating source apportionment and ecological risk assessment (Han *et al.*, 2023; Karthikayini *et al.*, 2023).

AAS continues to be the method of choice for aqueous and biological matrices. Flame and graphite-furnace AAS have been used to measure trace levels of Pb, Cd, Cr, and Ni in drinking and bottled water, highlighting variability among brands and enabling compliance evaluation against international safety guidelines (Mirzaei *et al.*, 2023; Qadir *et al.*, 2018). Similarly, AAS has been employed to investigate plant uptake of metals from contaminated soils. In Ondo State, Nigeria, AAS analysis of dumpsite soils and vegetables revealed high levels of Fe, Cd, Cu, Pb, and Ni, with bioaccumulation factors indicating potential risks to human health through food-chain transfer (Omotayo *et al.*, 2024).

PIXE provides distinct advantages for aerosol and cultural heritage studies. For atmospheric monitoring, time-resolved PIXE applied to streaker samplers enables the characterization of metals such as S, V, Ni, Zn, and Pb at hourly resolution without destructive digestion (Angyal *et al.*, 2024; Nava *et al.*, 2024, 2025). In the cultural heritage sector, external-beam PIXE offers a non-destructive means to analyze pigments and alloys in artefacts, allowing multi-elemental profiling across the Na–U range while minimizing beam damage (Morelle *et al.*, 2005; Harth *et al.*, 2024).

Finally, both AAS and X-ray methods are widely used in the study of nanomaterials. For instance, AAS has been applied to quantify total silver and zinc content in Ag–ZnO nanocomposites and to monitor ionic release relevant to antimicrobial activity (Krüger *et al.*, 2024; “FAAS for silver nanoparticles,” 2023). Complementarily, advanced X-ray approaches such as X-ray standing wave (XSW) analysis provide compositional and interfacial insights into supported nanoparticles, which are critical for catalytic performance (Tiwari *et al.*, 2024).

4.2 Representative Applications

Table 2 summarizes selected case studies highlighting the application of XRF, AAS, and PIXE to heavy-metal analysis across diverse matrices. The table outlines the sample type, analytes, methodological approach, performance outcomes, and key references.

Table 2. Representative applications of XRF, AAS, and PIXE to heavy-metal analysis across matrices.

Technique	Sample/ Matrix	Target Analytes	Method Synopsis	Key Findings / Performance	Reference
XRF (portable)	Urban soils	Pb, Zn, Cu, As	pXRF in situ; calibration vs. ICP	Rapid hotspot mapping; requires calibration	Jenkins <i>et al.</i> , (2025); Ravansari <i>et al.</i> , (2020); Schmidt <i>et al.</i> , (2024)
XRF (lab)	Coastal sediments	Fe, Cu, Zn, Pb	Pressed pellets/fused beads	Multi-elemental trends; source apportionment	Han <i>et al.</i> , (2023); Karthikayini <i>et al.</i> , (2023)
AAS (FAAS/GFAAS)	Bottled water	Pb, Cd, Cr, Ni	Digestion + FAAS/GFAAS	Detection in ppb–ppm; brand variability	Mirzaei <i>et al.</i> , (2023); Qadir <i>et al.</i> , (2018)
AAS (FAAS)	Vegetables/soils	Fe, Cd, Cu, Pb, Ni	Digestion + FAAS	Bioaccumulation; human risk assessment	Omotayo <i>et al.</i> , (2024)
PIXE (filters)	Aerosols	S, V, Ni, Zn, Pb	Proton PIXE, time-resolved	Hourly multi-element profiles	Angyal <i>et al.</i> , (2024); Nava <i>et al.</i> , (2024, 2025)
PIXE (external beam)	Cultural artefacts	Pb, Hg, Cu, Fe	External-beam PIXE	Non-destructive pigment/alloy analysis	Morelle <i>et al.</i> , (2005); Harth <i>et al.</i> , (2024)
AAS (FAAS)	Nanocomposites	Ag, Zn	Digestion + FAAS	Confirms ratios, ion release	Krüger <i>et al.</i> , (2024); “FAAS for silver

X-ray (XSW)	Nanoparticles	Co, Ti	XSW & X-ray methods	Interfacial/ensemble composition	nanoparticles” (2023) Tiwari <i>et al.</i> , (2024)
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The case studies reinforce the complementary roles of XRF, AAS, and PIXE in heavy-metal analysis. XRF, particularly in portable form, is well-suited for rapid, non-destructive screening of solid samples, making it invaluable for field assessments of contaminated soils. Laboratory XRF extends this capability to sediment analysis with robust multi-elemental coverage, provided that matrix corrections are applied.

AAS excels in aqueous and biological matrices, delivering precise trace quantification at relatively low cost. Its application to bottled water and plant tissues underscores its central role in risk assessment and regulatory compliance monitoring, especially where ingestion pathways dominate exposure.

PIXE distinguishes itself through its non-destructive, high-sensitivity, and often time-resolved performance, making it especially advantageous in atmospheric monitoring and cultural heritage research, where sample preservation is paramount.

In materials science, the combined use of AAS for quantitative validation and X-ray methods for structural and interfacial characterization demonstrates the value of integrative approaches to address the complexity of advanced materials such as nanocomposites.

Overall, the evidence indicates that selecting the appropriate technique should be guided by matrix characteristics, sensitivity requirements, and the degree of invasiveness acceptable in the study context. Cross-validation among methods remains best practice, particularly in regulatory and heritage contexts where accuracy and preservation are critical.

V. Conclusion

The findings from this work demonstrate the complementary analytical roles of XRF, AAS, and PIXE in the detection and quantification of heavy metals across environmental, material, and biological matrices. XRF has shown strong potential for rapid, non-destructive multi-elemental analysis, particularly in soil and sediment studies, with portable XRF proving especially useful for in situ hotspot mapping of contaminants such as lead and zinc. AAS remains a robust technique for precise trace-metal determination in aqueous and biological samples, where its sensitivity and selectivity enable detailed assessment of metal uptake in plants and compliance monitoring in drinking water. PIXE has emerged as an advanced technique for non-destructive, highly sensitive, and often time-resolved multi-elemental analysis, with notable applications in atmospheric aerosol characterization and cultural heritage studies. Together, the case studies highlight that the choice of technique is strongly dependent on the sample matrix, required sensitivity, and whether destructive or non-destructive analysis is most appropriate.

In conclusion, the evidence shows that no single technique can be considered universally superior. Instead, XRF, AAS, and PIXE each provide unique strengths that are best leveraged when matched to specific research or monitoring needs. XRF offers efficiency in field and laboratory-based solid analysis, AAS excels in liquid and biological quantification, and PIXE provides unmatched capability in non-destructive, sensitive elemental profiling of delicate or limited samples.

Based on these findings, it is recommended that future studies adopt integrative approaches that combine the complementary strengths of these techniques to achieve more reliable, accurate, and context-specific outcomes. Calibration and cross-validation among methods should be prioritized, particularly in regulatory, environmental, and heritage contexts where precision and sample preservation are essential. Further advancement in instrumentation, data analysis algorithms, and hybrid methodological frameworks will enhance the scope of heavy-metal monitoring and risk assessment, ultimately supporting better-informed decisions in environmental protection, public health, and materials science.

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