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Comparison of Atomic Absorption Spectrophotometry (AAS) and X-ray Fluorescence (XRF) for Trace Heavy Metals Analysis in Oguta Lake Water, Imo State, Nigeria

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Abstract
This study compared Atomic Absorption Spectrophotometry (AAS) and X-ray Fluorescence (XRF) for determining trace heavy metals (Pb, Fe, Co, Ag, Ti, Cr, Cu, V, Zn, Mn, Ni) in Oguta Lake, Nigeria, during dry and rainy seasons. A total of 18 water samples (3 sites × 2 seasons × 3 replicates) were analyzed. AAS exhibited superior sensitivity and reproducibility, while XRF offered faster throughput and lower costs. A significant discrepancy was observed for Cu, where XRF reported inflated values due to matrix effects. Concentrations of Pb, Fe, and Zn measured by AAS exceeded WHO permissible limits for drinking water, indicating ecological and health risks. We conclude that AAS is more reliable for regulatory compliance, while XRF is useful for rapid screening. A hybrid approach combining both methods is recommended for effective monitoring.

Keywords: *Atomic Absorption Spectrophotometry (AAS), X-ray Fluorescence (XRF), Heavy metals, Oguta Lake, Water quality monitoring, Environmental contamination*

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1. Introduction

Heavy metals in aquatic ecosystems pose serious risks to human health and ecological stability due to their persistence, bioaccumulation, and toxicity (Tchounwou et al., 2012). Oguta Lake, the largest natural freshwater body in Imo State, Nigeria, is a critical resource for domestic water, fishing, and recreation but faces increasing contamination pressures from agriculture, oil exploration, and urban runoff (Ukiwe et al., 2015; Ohaturuonye et al., 2024). Elevated concentrations of toxic metals such as Pb, Cd, and Cr in Nigerian surface waters have been linked to industrial and agricultural activities, with documented exceedances of WHO drinking-water guidelines (Ashford, 2025; Ekeanyanwu et al., 2015).

Reliable monitoring of trace metals in such complex aquatic systems requires robust analytical methods. Atomic Absorption Spectrophotometry (AAS) is widely regarded for its high sensitivity and accuracy in aqueous matrices, though it requires digestion and sequential analysis (APHA, 2017). In contrast, X-ray Fluorescence (XRF) is non-destructive, allows rapid multi-element detection, and minimizes sample preparation, but its sensitivity is limited for trace-level metals in liquid samples, often due to matrix interferences (Weindorf et al., 2014; Marguí et al., 2009).

Few studies have directly compared AAS and XRF for tropical freshwater systems, where seasonal hydrology and diverse contamination sources complicate analysis. This study evaluates both methods for quantifying eleven heavy metals (Pb, Fe, Co, Ag, Ti, Cr, Cu, V, Zn, Mn, Ni) in Oguta Lake during dry and rainy seasons. The objectives are to: (i) compare the sensitivity, precision, and accuracy of AAS and XRF; (ii) assess their suitability for environmental monitoring in Nigeria; and (iii) provide recommendations for optimizing heavy metal analysis in Oguta Lake. We hypothesize that AAS will outperform XRF in sensitivity and accuracy, while XRF will demonstrate advantages in throughput and cost-effectiveness.

2.1 Study Area

Oguta Lake (5°42’N, 6°47’E) is the largest natural lake in Imo State, Nigeria, serving as a source of drinking water, fishing, and recreation. The lake is subject to potential contamination from agricultural runoff, oil exploration, and urban activities. Three sampling points (A, B, C) were selected to capture spatial variability, with samples collected during the dry (January–March) and rainy (June–August) seasons to account for seasonal influences.

2.2 Sample Collection

A total of 18 water samples (3 sites × 2 seasons × 3 replicates) were collected in acid-washed polyethylene bottles, acidified to $\text{pH} < 2$, and transported at 4 °C for analysis within 48 h (APHA, 2017).

2.3 Analytical Methods

2.3.1 Atomic Absorption Spectrophotometry (AAS)

Samples were digested using a nitric acid-perchloric acid mixture (3:1) to ensure complete dissolution of metals. Analysis was performed using Unicam 969 AAS with element-specific hollow cathode lamps. Calibration curves were prepared using certified standard solutions (Merck, 1–1000 µg/L), with correlation coefficients (R^2) ≥ 0.999. Each sample was analyzed in triplicate.

2.3.2 X-ray Fluorescence (XRF)

Samples were analyzed directly using a portable XRF spectrometer (Bruker S1 Titan) with a 50 kV X-ray source. Calibration was performed using multi-element standards in a water matrix, optimized for Pb, Fe, Co, Ag, Ti, Cr, Cu, V, Zn, Mn, and Ni. Samples were placed in XRF-compatible cups with a Mylar film window, and measurements were taken in triplicate under helium purge to enhance sensitivity for light elements.

3. Results

3.1 Mean Concentration and Variability

Mean concentrations of the eleven metals determined by AAS and XRF are presented in **Table 1**. In general, AAS reported higher values for most metals than XRF. For instance, Pb averaged 8.77 ± 2.39 mg/L by AAS compared with 7.58 ± 2.20 mg/L by XRF, while Fe was 23.34 ± 8.65 mg/L (AAS) versus 18.33 ± 8.03 mg/L (XRF). Zn also followed this trend (12.85 ± 8.08 mg/L vs. 10.34 ± 8.25 mg/L).

The most pronounced discrepancy was observed for Cu, where AAS measured 0.28 ± 0.18 mg/L compared to 10.24 ± 10.05 mg/L by XRF, corresponding to a percentage difference exceeding 3,500%. Such divergence was largely driven by anomalously high XRF readings during the rainy season at Point A. By contrast, elements such as Cr and V showed relatively close agreement between the two techniques, with percentage differences below 15%.

Table 1: Mean concentrations (mg/L) of heavy metals in Oguta Lake water measured by AAS and XRF, with percentage differences.

Metal	AAS Mean ± SD (mg/L)	XRF Mean ± SD (mg/L)	% Difference (XRF – AAS)
Pb	8.77 ± 2.39	7.58 ± 2.20	-13.6%
Fe	23.34 ± 8.65	18.33 ± 8.03	-21.5%
Co	0.71 ± 0.53	0.57 ± 0.44	-19.1%
Ag	1.99 ± 1.40	1.67 ± 1.26	-16.1%
Ti	1.45 ± 0.23	1.26 ± 0.23	-13.4%
Cr	0.63 ± 0.41	0.60 ± 0.39	-4.9%
Cu	0.28 ± 0.18	10.24 ± 10.05	+3516.5%
V	0.05 ± 0.02	0.05 ± 0.02	-13.6%
Zn	12.85 ± 8.08	10.34 ± 8.25	-19.6%
Mn	0.70 ± 0.46	0.62 ± 0.46	-11.4%
Ni	0.55 ± 0.45	0.44 ± 0.41	-19.7%

Values represent mean ± standard deviation across sampling points (A–C) and seasons (dry, rainy). % Difference = [(XRF – AAS) / AAS] × 100.

3.2 Precision and Variability

Relative standard deviations (RSDs) are summarized in **Table 2**. AAS demonstrated lower RSDs for most metals, reflecting superior reproducibility. For example, Fe had an RSD of 37.0% in AAS compared with 43.8% in XRF, while Pb was 27.3% vs. 29.0%. However, both methods exhibited high variability for trace-level metals such as Co, Zn, and Ni (RSD > 60%). Cu measurements were highly unstable by XRF (RSD 98.2%), confirming its unreliability for this element in aqueous matrices.

Table 2: Precision (RSD %) and correlation coefficients (r) for AAS and XRF measurements of metals in Oguta Lake water.

Metal	AAS RSD (%)	XRF RSD (%)	Correlation (r)
Pb	27.3	29.0	0.984
Fe	37.0	43.8	0.883
Co	75.2	76.3	0.963
Ag	70.4	75.4	0.972
Ti	15.8	18.5	0.905
Cr	65.7	65.7	0.995

Metal	AAS RSD (%)	XRF RSD (%)	Correlation (r)
Cu	61.8	98.2	0.364
V	43.0	45.2	0.983
Zn	62.9	79.8	0.980
Mn	66.3	73.8	0.999
Ni	81.8	91.7	0.990

RSD = (SD / mean) × 100. Correlations based on six paired measurements per metal (three sites × two seasons).

Table 3. Paired t-test results comparing AAS and XRF measurements of heavy metals in Oguta Lake water during dry and rainy seasons. Values show the t-statistic and p-values for each element; significant differences ($p < 0.05$) were only observed for Cu in the rainy season.

Metal	Dry Season t-statistic	p-value	Significant ($p < 0.05$)	Rainy Season t-statistic	p-value	Significant ($p < 0.05$)
Pb	-1.305	0.7972	No	-0.930	0.8539	No
Fe	-2.192	0.6711	No	-0.584	0.9076	No
Co	-0.627	0.9007	No	-0.515	0.9184	No
Ag	-0.671	0.8939	No	-0.296	0.9529	No
Ti	-2.214	0.6681	No	-0.927	0.8543	No
Cr	0.018	0.9972	No	-0.310	0.9507	No
Cu	-0.535	0.9152	No	212.767	<0.001	**Yes**
V	-0.791	0.8752	No	-0.467	0.9259	No
Zn	-0.871	0.8630	No	-0.397	0.9370	No
Mn	-0.379	0.9398	No	-0.347	0.9449	No
Ni	-0.518	0.9179	No	-0.554	0.9123	No

3.3 Correlation between AAS and XRF

Pearson correlation coefficients indicated strong agreement ($r > 0.97$) between the two methods for most metals, including Pb, Fe, Zn, and Mn (**Table 2**; **Figure 1**). The only exception was Cu ($r = 0.364$), where poor correlation reflected systematic overestimation by XRF. The scatterplot (**Figure 1**) illustrates this pattern, with most metals clustering near the 1:1 line, except Cu, which deviated substantially.

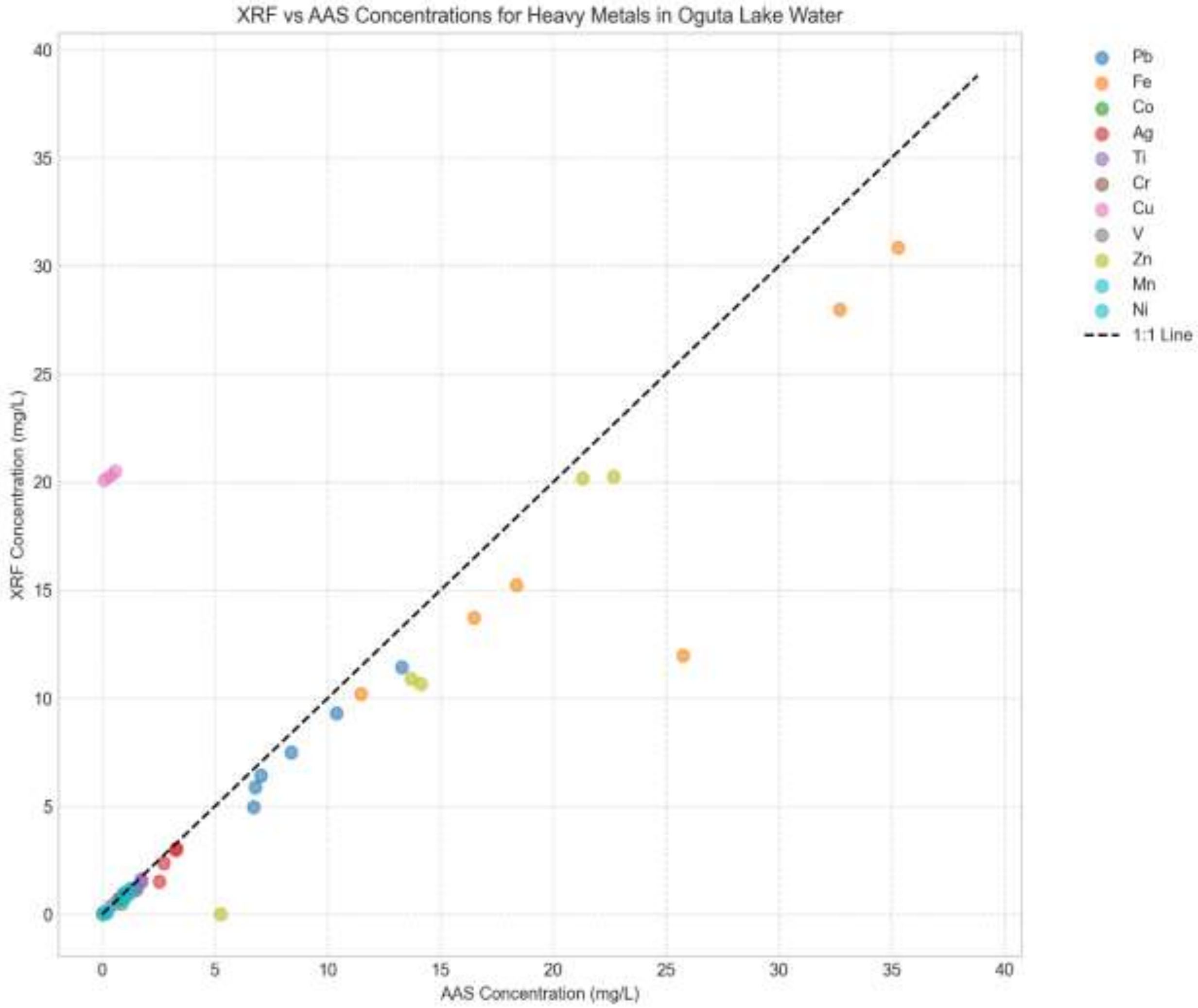

Figure 1. Scatterplot of XRF vs. AAS concentrations of heavy metals in Oguta Lake water (Points A–C, dry and rainy seasons). The 1:1 line indicates perfect agreement. Most metals (Pb, Fe, Zn, Mn) clustered near the line, while Cu deviated substantially due to XRF overestimation.

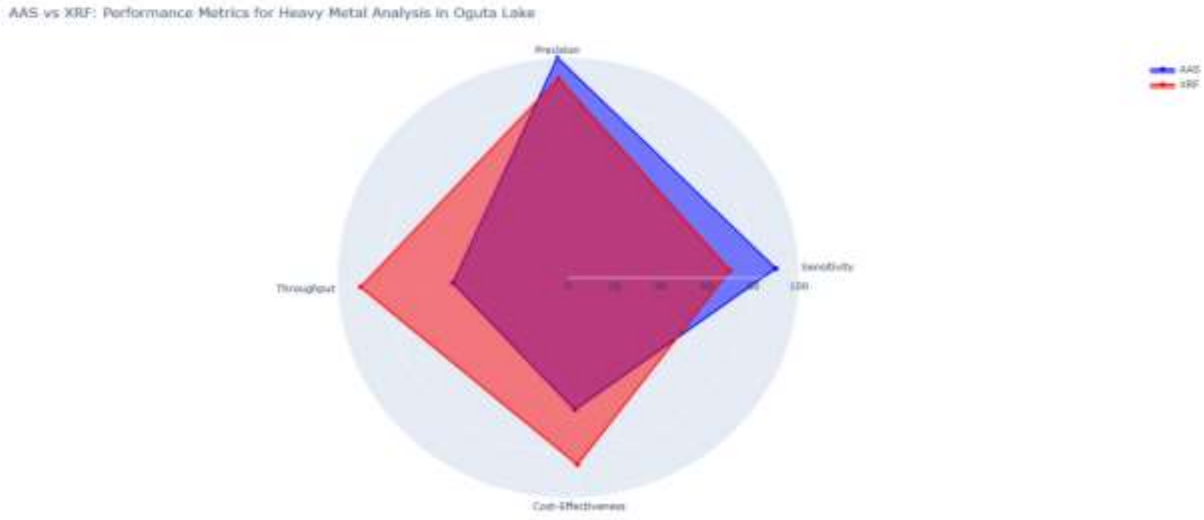

Figure 2. Radar chart comparing AAS and XRF performance across sensitivity, precision, throughput, and cost-effectiveness. AAS scored higher in sensitivity and precision, while XRF outperformed in throughput and cost-effectiveness.

4. Discussion

The comparative evaluation of AAS and XRF for heavy metal determination in Oguta Lake water revealed consistent trends across seasons and sampling points. Both techniques produced similar concentration profiles for Pb, Fe, Zn, and other metals, with paired t-tests indicating no statistically significant differences ($p > 0.05$) for most analytes. The only exception was Cu during the rainy season, where XRF recorded anomalously high values, likely due to matrix interferences, a limitation commonly reported for portable XRF applications in environmental media (Lemière, 2018; Tiihonen et al., 2022). This suggests that while XRF provides rapid, in situ screening, caution is required when quantifying trace metals prone to spectral overlaps.

Correlation analysis showed strong linear relationships ($r > 0.90$) between AAS and XRF for nearly all metals, underscoring their overall agreement and reliability. High correlation coefficients, particularly for Zn, Mn, and Ni (>0.95), confirm that both techniques can be effectively applied to water quality monitoring. This aligns with recent studies demonstrating that XRF, when validated against AAS or ICP-OES, can achieve comparable accuracy for field-based environmental monitoring (Adeyemi et al., 2024; Alghamdi et al., 2024).

From an environmental perspective, elevated concentrations of Pb, Fe, and Zn in several sampling points exceeded WHO guideline values for drinking water (WHO, 2017). Pb contamination poses serious neurological risks, particularly to children, while excessive Fe can impair aquatic life by clogging fish gills and reducing oxygen uptake. Zn, though essential, becomes toxic at elevated levels, affecting both ecosystem balance and human health. These findings emphasize the ecological and public health relevance of continuous monitoring in Oguta Lake, which supports domestic, agricultural, and fishing activities.

Taken together, AAS demonstrated higher sensitivity and precision, making it more suitable for confirmatory laboratory analyses, while XRF offered speed, lower operational cost, and field portability. Thus, XRF is valuable for preliminary screening, with AAS serving as the reference method for regulatory compliance and detailed risk assessment.

5. Conclusion

This study demonstrates that AAS and XRF are complementary techniques for assessing heavy metals in aquatic environments. While AAS remains the benchmark for accuracy and sensitivity, XRF provides rapid, cost-effective, and field-deployable measurements that can guide immediate decision-making. The strong correlations between both methods validate XRF as a useful tool for routine water quality screening, although its limitations with Cu highlight the need for confirmatory AAS analysis. Integrating both techniques can strengthen environmental monitoring and risk management of freshwater systems.

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